The Silylium Ion Problem, R_3Si^+. Bridging Organic and Inorganic Chemistry

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Received May 27, 1997

The well-established existence and mechanistic importance of the carbenium ion (R_3C^+) in organic chemistry[1] has inspired a long search for its elusive silicon counterpart, the silylium ion (R_3Si^+). However, silicon is not carbon. Rather, its chemistry is a unique organic and inorganic blend. Establishing the correct blend has been the cause of much controversy over several decades, and the debate surrounding the existence of silylium ions is one of the more interesting and colorful accounts of how chemists and their ideas interact.[2−15] In the past year, this has culminated in the synthesis of a species closely approaching a trialkylsilylium ion, $i\text{-Pr}_3Si^{\delta+}(CB_{11}H_6Cl_6)^{\delta-}$,[16] and the first believable example of a triarylsilylium ion, Mes_3Si^+ (Mes = mesityl).[17] These milestones have been reached because we now better understand the ways in which silicon is not carbon.

To recount the long and checkered history of all attempts to identify the silylium ion in condensed media is outside the scope this Account.[18,19] Suffice to say, the nucleophilicity of solvents and anions was seriously underestimated, and the concepts which worked to stabilize carbenium ions, chiefly $2p_\pi$ conjugative or hyperconjugative effects, did not translate well to silicon.

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While the *tert*-butyl cation is readily stabilized in superacid media and can be isolated as $[Me_3C^+][Sb_2F_{11}^-]$,[20] the corresponding silyl chemistry leads to species having covalent bonds to oxy or fluoro anions.[21] Adding to the frustration was the knowledge that R_3Si^+ should be *more* stable than R_3C^+, not less. Silicon is the more electropositive element and should better sustain a positive charge. Indeed, this has been amply proven in the gas phase by mass spectrometry[22] and is well supported by theory.[14,23]

R_3Si^+ versus R_3C^+

The distinction between carbon and silicon boils down to two fundamental differences: electronegativity and size.[24,25]

The greater electropositivity of silicon (Pauling electronegativity 1.8 vs 2.5 for carbon) confers $Si^{\delta+}-C^{\delta-}$ ionicity on the silicon−carbon bonds in R_3Si^+ and localizes the positive charge at silicon. This is what creates the extraordinarily high avidity of three-coordinate silicon cations for electron density.[26]

The location of silicon in the third period means that its size is significantly larger than that of carbon. Its tendency toward higher coordination numbers (so-called hypervalent compounds) is therefore much greater. Si−C bonds are typically ca. 25% longer than equivalent C−C bonds,[27] and this leads to a substantial diminishment of π bonding opportunities. Silicon is therefore less able to delocalize positive charge via π-conjugative effects with aryl or heteroatom substituents.[23] The same applies to hyperconjugative stabilization.

The Problem of Anions and Solvents

The revived controversy over the existence of silylium ions in condensed media has its origins in the work of Lambert and co-workers who interpreted the conductivity of silyl perchlorates in polar solvents (acetonitrile, sulfolane, and chlorocarbons) in terms of ionization to $R_3Si^+ClO_4^-$.[28,29] Prakash, Olah, and co-workers[30] recognized that this was inconsistent with earlier work showing silyl perchlorates
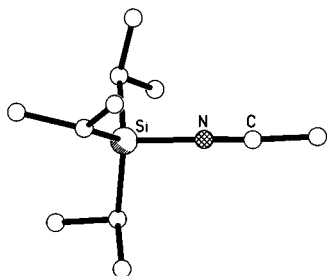
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FIGURE 1. X-ray structure of the *i*-Pr₃Si(NCCH₃)⁺ cation.[32]

FIGURE 2. X-ray structure of the Et₃Si(toluene)⁺ cation.[2,39]

were covalent species and demonstrated coordination of perchlorate via ³⁷Cl NMR line broadening. They also pointed out that proof of existence of a silylium ion required the observation of a significantly downfield shifted ²⁹Si NMR signal. No such signal was observable, and they suggested that the conductivity data might be explained by hydrolysis to perchloric acid, arising from incompletely dried solvents. This certainly contributed to the problem,[12] but repeated conductivity measurements are not entirely consistent with this explanation.[31]

The correct explanation for the conductivity of silyl perchlorates in polar media became clear from the experimental work of Reed,[32] Kira and Sakurai,[33] and Boudjouk[34] and theory by Cremer.[35] It lies in the ability of donor solvents to coordinate to silicon according to eq 1. The crystallographic characterization of a salt of the

$$R_3Si(OClO_3) + solvent \rightarrow R_3Si(solvent)^+ClO_4^- \quad (1)$$
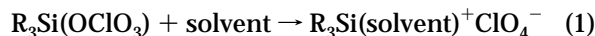
i-Pr₃Si(NCCH₃)⁺ cation[32] (see Figure 1) shows, for example, that acetonitrile can bind strongly and specifically to a silylium ion. The Si–N bond length of 1.82(2) Å is consistent with a dative bond of moderate strength, and the pyramidalization of the trialkylsilyl moiety is substantial (average C–Si–C = 115.6°). O-donor atom solvents such as ethers[36] and sulfolane presumably bind in a similar manner. The detection of these solvent-coordinated species by NMR spectroscopy was masked by the similarity of their ²⁹Si chemical shifts to those of their neutral, perchlorate-coordinated counterparts (30–40 ppm). It is possible that *five*-coordinate silicon cations (siliconium ions)[37] may exist in certain good donor solvents. In chlorocarbon solvents, however, the conductivity of silyl perchlorates is so much lower than in acetonitrile or sulfolane[31] it should be dismissed as evidence for ionization to R₃Si(chlorocarbon)⁺, particularly since silylium ion-like species actually react with chlorocarbon solvents at room temperature via chlorine atom abstraction.[3,16,36]

While the specific coordination of a solvent molecule in R₃Si(solvent)⁺ was not easily anticipated by approaching silylium ion chemistry from the viewpoint of carbocation chemistry, it is a natural consequence of the inorganic character of silicon. Coordinated solvent molecules, even alkanes,[38] are well-recognized ligands in the chemistry of transition and main group metallic elements. In retrospect, the characterization of solvents such as acetonitrile as "nonnucleophilic", a tenable assumption at some level for describing nucleophilic substitution in organic chemistry, was very misleading in silicon chemistry.
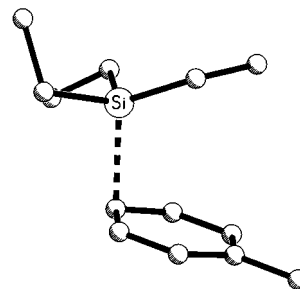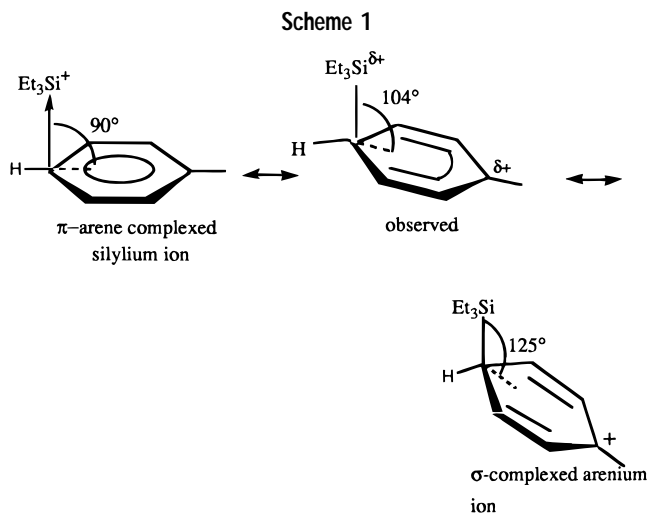
Structure of Et₃Si(toluene)⁺. σ or π Complex?

The problem of solvent nucleophilicity reappeared in an unexpected guise in 1993 when Lambert and co-workers reported the crystal structure of the Et₃Si(toluene)⁺ cation as a perfluorinated tetraphenylborate salt (see Figure 2).[2,39] The intentional omission of a bond between silicon and toluene in the figure of the original publication (see dashed bond in Figure 2) and the comment that "covalent bonding was weak or absent" (implying a species very close to a free silylium ion) once again made Lambert's work the focus of reinterpretation. The spirited polemic on the nature of this silylated arene tended to obscure the novelty of its structure and that of a closely related Cl(arene)⁺ structure reported at about the same time by Kochi.[40]

The structure of the Et₃Si(toluene)⁺ cation was considered exceptional because of the long Si–C bond (2.18 Å), about 0.3 Å longer than a typical Si–C σ bond. Reed pointed out that 2.18 Å was not unreasonable for a bond with π character and that the pyramidalization of the silicon atom substituents (average C–Si–C = 114° to the ethyl groups) was indicative of a substantial covalent interaction.[3] Pauling applied his bond order equation to the structure and concluded that the 2.18 Å length corresponded to a bond of order 0.35.[4] He further approximated the positive charge transfer from Et₃Si⁺ to toluene as 33%. Ab initio calculations by Schleyer, Apeloig, and Siehl,[8] by Olah,[5] and by Cremer[9] reproduced the structure with reasonable accuracy and also concluded there was substantial Si–toluene covalent bonding, and substantial transfer of positive charge to the arene. They also argued that the huge difference between the IGLO calculated ²⁹Si chemical shift of Me₃Si⁺ at ca. 350 ppm and the measured shift of Et₃Si(toluene)⁺ at 82 ppm meant that it was very far from being a free silylium ion. We return to the interpretation of chemical shifts later in this Account.

The other unexpected structural feature of Et₃Si-(toluene)⁺ was the orientation of the silicon atom with respect to the arene ring. It was not quite like the σ-bonded arenium ions known in organic chemistry as Wheland intermediates. Nor was it like the π arene complexes seen, for example, in Ag(arene)⁺ chemistry. It was something in between. This is illustrated in Scheme 1. A π complex, such as Ag(benzene)⁺,[41] has the electrophile positioned above the sp² carbon atom(s) of an essentially unperturbed arene ring and the positive charge is predominantly on the electrophile. A σ complex, such

Scheme 1

π–arene complexed
silylium ion

observed

σ-complexed arenium
ion

FIGURE 3. Very weakly coordinating 7,8,9,10,11,12-hexahalo car-borane anions, $CB_{11}H_6X_6^-$ (H not shown).

as $Me_7C_6^+$,[42] has an sp³ carbon atom at the point of attachment of the electrophile and a marked alternation of C–C bond lengths indicating substantial loss of aromaticity, and the positive charge is predominantly on the arene. These geometric features lead naturally to the 90° and 125° angles shown in Scheme 1 for a π and σ complex, respectively.

Reed argued that with an $E^+–C–C_{para}$ angle of 104°, $Et_3Si(toluene)^+$ was best viewed as a hybrid structure somewhere between an idealized π-complexed silyl cation and a σ-bonded arenium ion.[3,7] Lambert concurred.[6] Olah,[5] Schleyer et al.,[8] and Cremer[9] argued more classically that $Et_3Si(toluene)^+$ was a σ complex. Partly this was based on the desire to emphasize that it was not a free silylium ion, and calculations certainly showed considerable transfer of positive charge to toluene. However, some charge transfer is expected for both a π and a σ complex, albeit more in the latter. What was missing in the arguments in favor of a σ complex were objective criteria for the designation. Since π versus σ is a designation of orientation with respect to an sp² versus an sp³ carbon atom, the angular criterion of Scheme 1 has obvious merit. The observed $E^+–C–C_{para}$ angle in $Et_3Si(toluene)^+$ is approaching midway between a π and a σ complex, suggesting a true admixture. Unfortunately, theory at the HF/6-31G* level for $Me_3Si(toluene)^+$ calculated this angle about 8° too large (and the Si–C bond 0.04 Å too short), leading theorists to give artifactual weight to its σ character. Now that experimental data are becoming available on $E(arene)^+$ species, it should become easier to accept that something previously believed to be black and white can have shades of gray.[43]

It has been argued that $Et_3Si(toluene)^+$ is a σ complex from product distribution in its gas-phase decomposition[44] and from solution reactivity.[5] In other words, it is a σ complex because it reacts as though it is a σ complex. This is a potentially misleading argument because the kinetic reaction pathway may reflect a minor resonance contribution to the overall ground-state structure.

The double-headed arrow used in scheme 1 is typically used to connect resonance structures with less atom movement than those shown in the scheme. In *The*
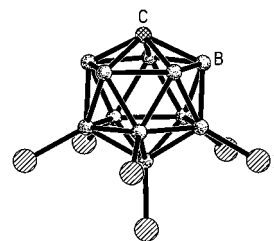
Nature of the Chemical Bond, Pauling specifies that contributing valence bond structures must have "about the same equilibrium configuration of the nuclei".[45] To accommodate a continuum of gradually changing structure, a more liberal interpretation has become necessary. In terms of building bridges between inorganic and organic chemistry we note that the σ/π admixture of Scheme 1 has a close conceptual relationship to Si hyperconjugation.

Solving the Silylium Ion Problem

From the preceding discussion, it will be clear that (a) the choice of counterion Y^- and (b) the role of solvent nucleophilicity are two of the most important considerations in attempting to synthesize a truly ionic, three-coordinate silicon cation in $R_3Si^+Y^-$. The other considerations are (c) the optimal choice of substituent R to delocalize positive charge and sterically hinder access to the Si center, (d) having a viable synthetic route, and (e) having valid criteria for assessing success (X-ray structure, ²⁹Si NMR). These are discussed in turn.

Counterion Y^-. There is no such thing as a truly noncoordinating anion. At present, the two candidates for the *least* coordinating anion[46,47] are the perfluorinated tetraphenylborate ion, $F_{20}–BPh_4^-$, and the hexahalo carboranes, $CB_{11}H_6X_6^-$ (X = Cl, Br, I; see Figure 3). Their low nucleophilicity derives mainly from their large size and from their buried and delocalized charge. The Lewis basicity of the lone pairs on the halogen atoms is minimal.

The silylium ion is a fierce electrophile, making chemical stability of the counterion a very important factor. The inertness of $F_{20}–BPh_4^-$ and the hexahalo carborane anions toward degradation is notable in this regard. For comparison, the 3,5-bis(trifluoromethyl)tetraphenylborate ion, $BAr^F_4^-$, is unstable with respect to fluoride ion abstraction in the presence of incipient silylium ions[36] and all anions which are themselves Lewis acid/base adducts (BF_4^-, SbF_6^-, $B(OTeF_5)_4^-$, $B(OSO_3CF_3)_4^-$, $Sb(OTeF_6)_6^-$ etc.) are susceptible to fluoride or oxyanion abstraction by R_3Si^+.

Solvent. There is no such thing as a truly nonnucleophilic solvent even though in organic chemistry a distinction is often made between certifiably active nucleophiles and the more generalized effect of donor solvents. From the earlier discussion regarding $R_3Si(solvent)^+$ it should be clear that even solvents of the basicity of benzene are problematic unless, of course, steric effects can be used to prevent their specific binding to silicon. Neighboring
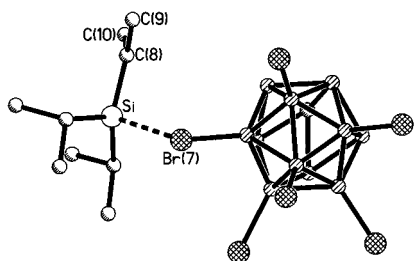
FIGURE 4. X-ray structure of *i*-Pr$_3$Si(CB$_{11}$H$_6$Br$_6$). Hyperconjugative stabilization of the developing positive charge on silicon is indicated by the short Si—C(8) bond and the near planarity of C(8) with respect to its bonds to C(9), C(10), and Si (sum of bond angles 359.5°).[3,50]
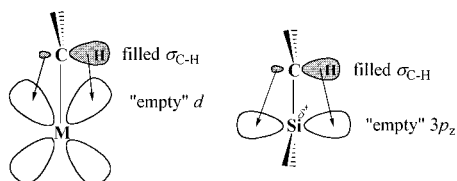

FIGURE 5. Conceptual analogy between C—H bond hyperconjugation and the α-agostic effect of transition-metal chemistry. Shading is used to represent a filled orbital (not the sign of the wave function).

groups such as alkenes can play a role similar to that of a donor solvent.[48,49]

Choice of Substituent R. The two important factors in the choice of substituent R are steric bulk to promote cation/anion separation and electron-donating ability to stabilize positive charge.
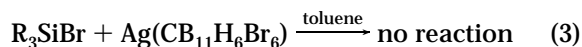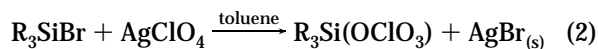
Despite their bulk and inductive capabilities, three *tert*-butyl groups in *t*-Bu$_3$Si$^{\delta+}$Y$^{\delta-}$ type species are insufficient to promote full ionization, even with the least coordinating anions presently available.[50] Surprisingly, isopropyl substituents are somewhat superior to *tert*-butyl substituents in conferring ionic character on the Si—Y bond. This has been traced to C—H bond hyperconjugative stabilization in the R$_3$Si$^{\delta+}$ moiety. One of the *i*-Pr groups in *i*-Pr$_3$Si-(CB$_{11}$H$_6$Br$_6$) has a particularly short Si—C bond, and its isopropyl carbon atom appears nearly trigonal planar (see Figure 4).[50] Apparently, the donation of C—H bond electron density into the developing empty 3p$_z$ orbital on silicon is somewhat more favorable than C—C bond density; i.e., C—H bond hyperconjugation is somewhat favored over C—C bond hyperconjugation. This is consistent with electronegativity considerations. In terms of building bridges between organic and inorganic chemistry, there is a direct conceptual analogy between hyperconjugation and the α-agostic effect of organo-transition-metal chemistry.[50] This is shown in Figure 5. It is clear from the Si—C—C angles in X-ray structures of a variety of trialkyl R$_3$Si$^{\delta+}$Y$^{\delta-}$ species[50] that both C—H and C—C bond hyperconjugation help delocalize positive charge on silicon, albeit less effectively than in carbenium ions.

Much experimental and theoretical effort has been made over the years to determine if p$_\pi$ conjugative effects can be used to stabilize silylium ions. Experimentally, 2p$_\pi$ heteroatoms such as N or O have so far led to four-coordinate silicon species with Si—N or Si—O bonds.[51,52] The idea that third period heteroatoms such as S might
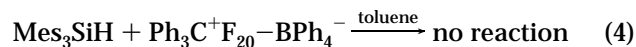
be superior to 2p$_\pi$ heteroatoms in stabilizing an empty 3p$_z$ orbital on silicon has been advanced, but the characterization of species such as the trithiolo (RS)$_3$Si$^+$ ion is presently insufficient to experimentally assess its validity.[53,54] The remarkable efficacy of d$_\pi$ conjugative stabilization of three-coordinate planar silicon with a transition-metal substituent is demonstrated in [Me$_2$SiRu-(Cp*)(PMe$_3$)$_2$]$^+$.[55] One of the major contributing resonance structures to this silylene complex is formally a silylium ion.

The well-known stability of trityl ions, Ar$_3$C$^+$, illustrates how effectively the positive charge on carbon can be delocalized onto phenyl groups via 2p$_\pi$ conjugation. A smaller but nevertheless significant ability of conjugating aryl groups to stabilize a silylium ion is predicted by theory.[56] However, phenyl substituents are unstable under silylium ion forming reaction conditions; the reaction of a trityl carborane salt with Ph$_3$SiH gives a mixture of products, one of which is biphenyl.[57] More recent work has shown that the bulkier and more electron-donating 2,4,6-trimethylphenyl group (mesityl) is the substituent of choice.[17] Other studies of potentially stabilizing groups have involved tris(trimethylsilyl)methyl[13] and ferrocenyl[58,59] substituents. Attempts have also been made to exploit aromatization in silatropylium and related ions.[60-62] Some of these approaches probably deserve a second look now that solvent and anion conditions for silylium ion formation have been better defined.

Synthetic Routes. Electrophilic abstraction of X$^-$ from four-coordinate R$_3$SiX is the typical approach to a silylium ion. Such metathesis reactions are driven either by the insolubility of a halide or oxyanion salt of the electrophile (Ag$^+$, Na$^+$, etc.) or by the formation of a strong covalent bond to the electrophile, e.g., the carbon—hydrogen bond in Ph$_3$CH, from reaction of trityl ion with a silane. These reactions can be limited by both thermodynamic and kinetic factors. For example, while silver halide precipitation drives eq 2 from silver perchlorate, simply switching to a silver salt with a less-coordinating carborane anion (eq 3) leads to no reaction. This rather unexpected result

$$\text{R}_3\text{SiBr} + \text{AgClO}_4 \xrightarrow{\text{toluene}} \text{R}_3\text{Si(OClO}_3) + \text{AgBr}_{(s)} \quad (2)$$

$$\text{R}_3\text{SiBr} + \text{Ag(CB}_{11}\text{H}_6\text{Br}_6) \xrightarrow{\text{toluene}} \text{no reaction} \quad (3)$$

has been observed in a number of other silver salt metathesis reactions and is of thermodynamic, not kinetic origin.[63] Mixing AgBr and *i*-Pr$_3$Si(CB$_{11}$H$_6$Br$_6$) in toluene, the reverse of eq 3, gives *i*-Pr$_3$SiBr in just a few minutes.[57] It shows that a good portion of the driving force for eq 2 is the formation of the Si—O bond to perchlorate. A likely example of a kinetic barrier is the lack of reaction of trityl F$_{20}$—BPh$_4$$^-$ with trimesitylsilane (eq 4).[17] Presumably,

$$\text{Mes}_3\text{SiH} + \text{Ph}_3\text{C}^+\text{F}_{20}\text{—BPh}_4{}^- \xrightarrow{\text{toluene}} \text{no reaction} \quad (4)$$

there is a steric barrier to hydride abstraction. A clever solution to this problem was recently developed by Lambert and Zhao.[17] Remote attack of a strong electro-
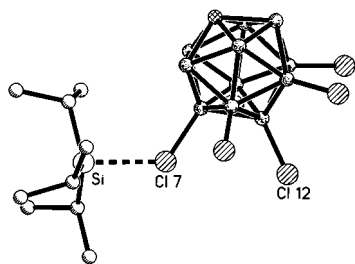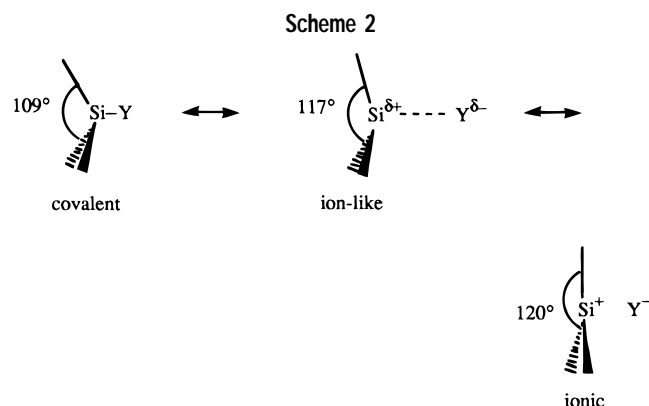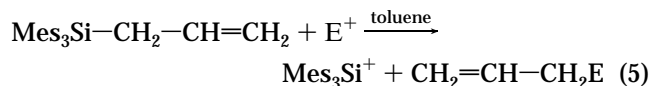
FIGURE 6. X-ray structure of *i*-Pr$_3$Si(CH$_{11}$H$_6$Cl$_6$).[16]

Scheme 2

phile (E$^+$) at the sterically accessible terminus of an allenyl substituent leads to a 1,2-shift of the double bond and cleavage of the Si–C bond three carbon atoms distant (eq 5).

$$\text{Mes}_3\text{Si}-\text{CH}_2-\text{CH}=\text{CH}_2 + \text{E}^+ \xrightarrow{\text{toluene}}$$

$$\text{Mes}_3\text{Si}^+ + \text{CH}_2=\text{CH}-\text{CH}_2\text{E} \quad (5)$$

Assessing Silylium Ion Character by X-ray Structure. In carbon chemistry, the combination of ^{13}C NMR spectroscopy and IGLO calculations leaves little doubt about the structure of most carbocations.[64] The same is not true for silicon. Rather, it is the combination of X-ray crystallography, NMR studies, and theory that has proved crucial for assessing progress toward silylium ion formation.

In carbocation chemistry, there is typically a black and white distinction between covalent species R$_3$CX and carbenium ions R$_3$C$^+$Y$^-$. Silicon is different. Trialkyl species of the type R$_3$SiX lie along a continuum between idealized sp^3 and sp^2 geometries, i.e., an admixture of covalent and ionic. The closest approach to a trialkylsilylium ion is found in *i*-Pr$_3$Si(CB$_{11}$H$_6$Cl$_6$) (see Figure 6).[16] The average C–Si–C bond angle to the substituents (117.3°) is about 75% of the way from tetrahedral to trigonal planar. This, and a number of other structural criteria such as the long Si–Cl bond to the carborane anion (2.23 Å) and the short Si–C bonds to the isopropyl groups (1.85 Å), suggests the development of a high degree of charge separation: *i*-Pr$_3$Si$^{\delta+}$(CB$_{11}$H$_6$Cl$_6$)$^{\delta-}$. It is useful to view this *ion-like* compound as an electronic and structural hybrid of covalent R$_3$SiY and ionic R$_3$Si$^+$Y$^-$ species (see Scheme 2). As explained earlier, the double-headed arrow is used to indicate both a structural and electronic admixture.

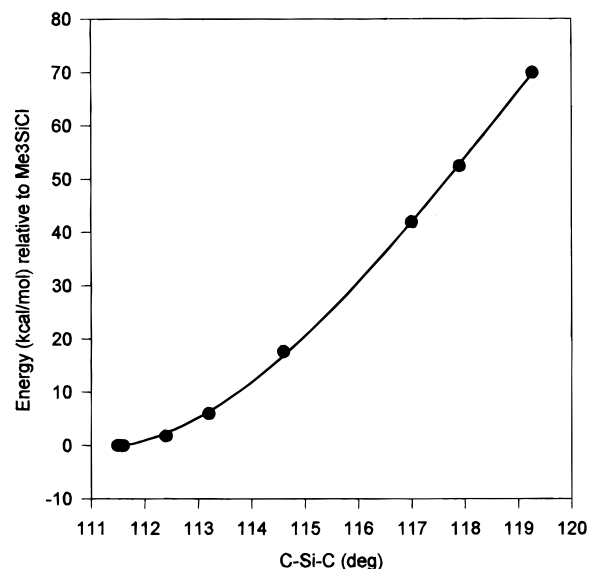Assessing the degree of charge separation in a partially ionized R$_3$Si$^{\delta+}$Y$^{\delta-}$ species is dependent on (a) which

FIGURE 7. 6-31G* calculated total energy of Me$_3$Si$^{\delta+}$Cl$^{\delta-}$ versus C–Si–C angle upon gradual ionization.[16]

criterion of ionicity is chosen, (b) how the respective covalent and ionic boundaries are defined, and (c) how the chosen property scales along the continuum. To illustrate this, consider the gradual *in computero* ionization of Me$_3$SiCl into Me$_3$Si$^+$ and Cl$^-$.[16] The calculated total energy as a function of the C–Si–C bond angle is shown in Figure 7. At a bond angle of 117.3°, that of the closest experimental approach to a trialkylsilylium ion in *i*-Pr$_3$Si(CB$_{11}$H$_6$Cl$_6$), Me$_3$Si$^{\delta+}$Cl$^{\delta-}$ is energetically about 60% ionized. Note, however, that the function is decidedly nonlinear and that the boundaries do not coincide with fully covalent or ionic ideals. In particular, even at cation/anion separations corresponding to a generous sum of the Si and Cl ionic radii (3.5 Å), the Me$_3$Si$^+$ cation is still not completely planar. The marked effect of even quite distant electron density on a cationic silicon center is particularly important in the context of ^{29}Si NMR chemical shifts discussed below. Observations such as these remind us that ionicity is a very useful but ultimately rather imprecise concept.

Although a planar, three-coordinate silicon cation has not been achieved with alkyl substituents, success has recently been achieved in solution with bulky aryl groups.[17] The *o*-methyl groups of the mesityl substituents in [Mes$_3$Si$^+$][F$_{20}$–BPh$_4^-$] play an important role in maintaining charge separation and excluding solvent.

Assessing Silylium Ion Character by ^{29}Si NMR. As with ^{13}C shifts in carbocations, a marked downfield ^{29}Si shift is the expected signature of silylium ion formation. The important question is "How far downfield?". The ^{29}Si shift for *i*-Pr$_3$Si(CB$_{11}$H$_6$Cl$_6$), the closest experimental approach to a trialkylsilylium ion, is 115 ppm downfield from TMS.[16] That of the triarylsilylium ion Mes$_3$Si$^+$ is 225 ppm.[17]

The earliest projection for Me$_3$Si$^+$ was in the range 225–275 ppm, based on empirical correlations of ^{29}Si and ^{13}C shifts in isostructural compounds of silicon and carbon.[65] A retreat from this projection occurred with the
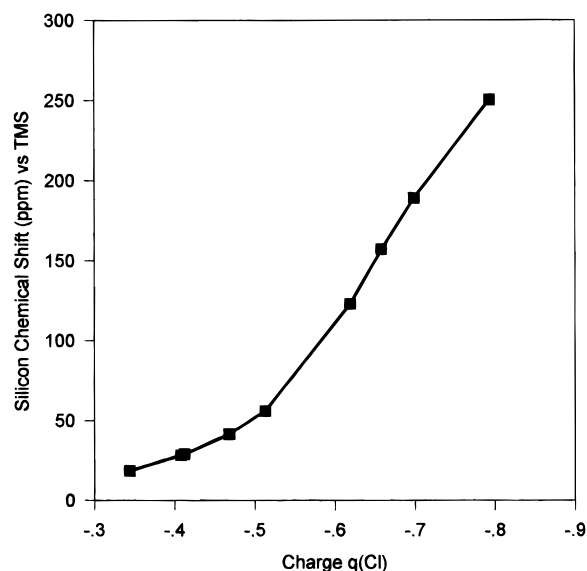
FIGURE 8. GIAO method calculated ^{29}Si chemical shift versus charge as Me_3SiCl is gradually ionized.[16]

introduction of the IGLO method of calculation which suggested a value of 351 ppm.[66] Buoyed by the success of IGLO methods in carbocation chemistry, an engagement ensued where those doing theory chided those doing experiments that they were far away from attaining a free silylium ion.[5,8,9] But how relevant are calculations on R_3Si^+ done in a vacuum to expectations for the condensed phase? What are the appropriate covalent and ionic boundary values, and how do ^{29}Si shifts scale along the $R_3Si^{\delta+}Y^{\delta-}$ continuum?

The problem turned out to lie in the unexpected sensitivity of the ^{29}Si shifts to even the slightest amount of nearby electron density. Calculations which place a solvent molecule at van der Waals distance from the silicon atom in R_3Si^+ lead to upfield shifts of as much as 170 ppm.[56] The 3.08 Å approach of an Ar atom to Me_3-Si^+ reduces the ^{29}Si shift by 62 ppm.[14] The experimental value of 110 ppm for *i*-$Pr_3Si(CB_{11}H_6Br_6)$ is essentially reproduced in the calculated value of 102 ppm for Me_3-Si^+ when methyl bromide is allowed to approach an identical Si−Br distance (2.48 Å).[14] We conclude that the appropriate expectation for the downfield shift of a condensed-phase *i*-Pr_3Si^+ ion is in the range 220−320 ppm, considerably short of the "gas-phase" value of about 340−370 ppm.[16] To get an idea of how the ^{29}Si shift scales along the continuum between TMS and this expectation, we calculated the variation in shift as $Me_3Si^{\delta+}Cl^{\delta-}$ is ionized along the Si−Cl coordinate.[16] Figure 8 shows that chemical shift is a decidedly nonlinear function of developing charge and that the greatest sensitivity is at the largest separations. This suggests that the experimental shift of 115 ppm in *i*-$Pr_3Si(CB_{11}H_6Cl_6)$ is a considerably stronger indicator of silylium ion character than was previously believed.

In comparing triaryl- with trialkylsilylium ions, a smaller downfield shift is expected. In carbocation chemistry, the 335 ppm downfield ^{13}C shift of Me_3C^+ is diminished to 210 ppm in Ph_3C^+ by $2p_\pi$ conjugative effects.[64] A parallel

diminishment for ^{29}Si shifts in silicon chemistry makes the observed value of 225 ppm for Mes_3Si^+ very reasonable, and this has been confirmed by theory.[67]

Reactivity

While ion-like trialkylsilylium species of the type $R_3Si^{\delta+}Y^{\delta-}$ ($Y = CB_{11}H_6X_6^-$ or $F_{20}-BPh_4^-$) are not true silylium ions, they react like silylium ions. The potent electrophilic nature of the silicon center is manifest in a variety of R_3-Si^+ transfer reactions with nucleophiles. They scavenge traces of water from solvents and glassware to give the first examples of water-coordinated silyl cations, i.e., protonated silanols. In the case of *t*-$Bu_3SiOH_2^+CB_{11}H_6$-Br_6^-, the strongly acidic product was isolated and fully characterized by X-ray crystallography, IR, NMR, etc.[68] Silylium ion-like species react with siloxanes to give trisilyloxonium ions which catalyze the polymerization of cyclosiloxanes.[69] They abstract halide from some alkyl halides[36] and even from some aryl halides.[16] They react with alkenes to give β-silyl carbenium ions,[70] and as discussed earlier, they silylate toluene to give R_3Si-(toluene)$^+$. Except in mass spectrometric studies[71] (where the walls of the spectrometer are the perfect noncoordinating anion) the seemingly straightforward deprotonation of this species to give silylated toluene has yet to be achieved in good yield.[72]

Silylium Ions as Intermediates

Much of the discussion of silylium ions has revolved around their possible existence as intermediates in reactions involving the heterolytic cleavage of a bond to silicon.[13,52] Various kinetic data can be interpreted in terms of silylium ion intermediates but only if the nucleophilicity of solvents and anions is ignored. What we have learned from trying to isolate a silylium ion is that they cannot be ignored. Having said this, however, it remains very puzzling that bulky silyl halides can be exceptionally inert to nucleophilic media which instantly ionize the corresponding carbon compounds.[13] With bulky substituents which can physically exclude solvent molecules and anions, it may be possible to demonstrate the intermediacy of silylium ions in substitution reactions, but with the kinds of substituents typically encountered in silicon chemistry, truly three-coordinate species are unlikely on any time scale. Exceptional heteroatom substituent effects can probably promote the formation of three-coordinate entities as intermediates, or even long-lived species, but they will do so only by removal of much of the silylium ion character.

Conclusion

The recent exploration of the silylium ion problem has proved to be illuminating for both silicon and carbon chemistry. The way in which the greater size and electropositivity of silicon differentiates the properties of silylium ions from carbenium ions has been brought into sharp focus such that the concept of a free silylium ion is

less distinct than that of a carbenium ion. Its ionicity is more a matter of degree. The underlying reason for this is the diminished importance of directional covalent bonding. In carbon chemistry, sp³ and sp² hybridized carbon atoms are typically distinct wells on the potential energy surface. A "silicon valley" apparently connects these points in silylium ion chemistry. Less directional, ionic bonding allows an electronic and geometric continuum of structures between covalent and ionic ideals.

The study of the silylium ion has also highlighted the sharp contrasts that can exist between gas-phase and condensed-phase chemistry. Since we are probably not far away from the time when ab initio theory can more routinely take account of the effects of solvents and counterions, more convergent perspectives of theory and experiment can be anticipated soon.

Silicon has proved to be a bridge element for connecting the sometimes divergent concepts and perceptions of organic and inorganic chemistry. Building conceptual bridges which harmonize these differences has been discussed in this Account along with the analysis of the recent advances that have given solution to most aspects of "the silylium ion problem".

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