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# THE INTERACTION OF SILICON WITH POSITIVELY CHARGED CARBON

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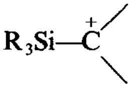
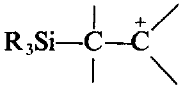
Electron deficient species have long intrigued organic chemists. More than half a century ago, Whitmore developed the chemistry of carbocations here at Northwestern University and later at The Pennsylvania State University. The interaction of positively charged carbon with directly attached substituents that possess $\pi$ or n electrons led to better understanding of the concept of conjugation, as in the familiar carbocations $CH_2{=}CH{-}CH_2^+$, $C_6H_5{-}CH_2^+$, and $CH_3O{-}CH_2^+$. The interaction with more remotely substituted groups, also possessing $\pi$ or n electrons, as in $PhCH_2CH_2^+$ or $Me_2NCH_2CH_2^+$, led to the concepts of neighboring group participation and homoconjugation. In one of his last studies, Whitmore described the remarkable manner in which silyl substituents interact with positive charge on carbon.[1] In basic hydrolyses and ethanolyses, Whitmore and his co-workers found that a silyl group beta to the leaving group enormously enhances the rate of solvolysis, that a gamma silyl group also has an enhancing effect, but that an alpha silyl group actually decreases reactivity in comparison with hydrocarbon models. Sommer, a principal co-worker with Whitmore on this study, went on to become one of the leading silicon chemists of his generation.

The chart below summarizes possible structural relationships between a silicon-containing substituent and positively charged carbon. The silicon atom is distinguished from previously studied substituents in that it possesses neither $\pi$ nor n electrons. Its enormous influence on positive charge must come from other electronic sources. The ability of silicon to influence reactivity at electron-deficient carbon has led to important synthetic applications.[2–5] Study of the phenomenon itself has yielded an enjoyable collaboration of theory, solution-phase experiment and gas-phase experiment. This review endeavors to examine all aspects of this phenomenon from the mechanistic point of


$R_3Si{-}\overset{+}{C}{<}$

The alpha effect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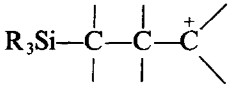
The beta effect


$R_3Si{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{+}{C}{<}$

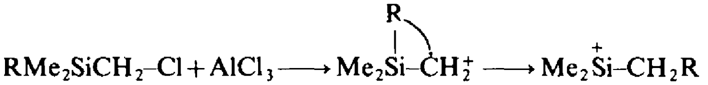
The gamma effect

view. The closely related subject of the interaction of silicon with open-shell carbon[6–8] requires separate treatment and will not be examined herein.

## 1. THE ALPHA EFFECT

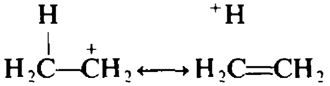
Sommer, Whitmore and co-workers reported in 1946[1,9] that trichloro(1-chloroethyl)silane ($Cl_3SiCHClCH_3$) and trichloro(1-chloropropyl)silane ($Cl_3SiCHClCH_2CH_3$), under conditions of basic hydrolysis, yielded reaction only of the Si–Cl bonds. The alpha C–Cl bonds failed to hydrolyze. In contrast, the beta C–Cl bonds in the analogous 2-chloroethyl and 2-chloropropyl compounds ($Cl_3SiCH_2CH_2Cl$ and $Cl_3SiCH_2CHClCH_3$) reacted rapidly under the same conditions. In basic ethanol, even the 3-chloropropyl compound ($Cl_3SiCH_2CH_2CH_2Cl$) reacted more rapidly than the alpha case. It was concluded that silicon inhibits electrofugal activity at the alpha carbon.

This result seemed contrary to the general understanding of the electronic effect of silicon, which was well known to have a lower electronegativity than carbon and hence be electron donating. For example, Sommer and co-workers[10] compared the acidity of $Me_3SiCH_2CO_2H$ with that of $Me_3CCH_2CO_2H$ and found $Me_3Si$ to be electron donating with respect to $Me_3C$ by a small amount. This observation was attributed to the higher polarizability and lower electronegativity of silicon. Observations of the destabilizing alpha effect, however, persisted. In certain cases, it even appeared that an α-silyl carbocation would rearrange to a silylenium ion (Eqn 1, R = Me, Ar).[11,12] Normal migratory aptitudes to electron deficient carbon were found: *p*-tolyl > phenyl > *p*-chlorophenyl ≫ Me.[11] To avoid a silylenium ion mechanism, however, Eaborn and co-workers suggested a ternary process.



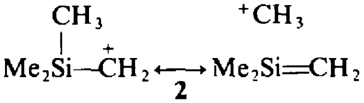
$$RMe_2SiCH_2\text{–}Cl + AlCl_3 \longrightarrow Me_2\overset{R}{\overset{|}{Si}}\text{–}\overset{+}{C}H_2 \longrightarrow Me_2\overset{+}{Si}\text{–}CH_2R \qquad (1)$$

In 1971, in separate pieces of work, Eaborn,[13] Cartledge[14] and their co-workers suggested similar explanations for the destabilizing alpha effect. Cartledge and Jones[14] found that $Me_3C(CH_3)_2C$—Br reacted 38 000 times faster than $Me_3Si(CH_3)_2C$—Br in 60% aqueous ethanol at 25°C. Eaborn and co-workers compared the series $Me_3SiCH_2Cl$, $(Me_3Si)_2CHCl$ and $(Me_3Si)_3CCl$. In stark contrast to the hydrocarbon series (ethyl, 2-propyl, *tert*-butyl), the three silyl substrates had the same rates (within a factor of four) in basic ethanol. In the carbon series, the increased rate on substitution is attributed to C—H hyperconjugation (1), of a type we will call $H^+/C{=}C$ to indicate that σ–π delocalization leads to positive charge on hydrogen and carbon–carbon double bonding. The absence of a rate increase on silyl substitution was consequently attributed to the poor ability of the Si–C bond to hyperconjugate (**2**, $C^+/Si{=}C$ hyperconjugation). The right-hand resonance structure of **2** requires double bonding between silicon and carbon, which is well known to be weak. Cartledge and Jones explained their data in the same way. Thus, when hyperconjugation leads to silicon–carbon multiple bonding, silicon is much less electron donating than carbon.



$$\overset{H}{\overset{|}{H_2C}}\text{—}\overset{+}{C}H_2 \longleftrightarrow \overset{^+H}{H_2C{=}CH_2}$$

**1**



$$\overset{CH_3}{\overset{|}{Me_2Si}}\text{—}\overset{+}{C}H_2 \longleftrightarrow \overset{^+CH_3}{Me_2Si{=}CH_2}$$

**2**

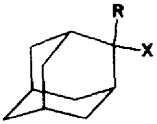
Earlier attempts by Brook and Pannell[12] to observe stable α-silylcarbocations in superacid media were moderately successful, and Olah and co-workers obtained very clean spectra of $Ph_2\overset{+}{C}$—$SiMe_3$, the alpha carbon of which resonated at δ 259.[15] Another type of electronic effect was suggested in a study of the ultraviolet/visible spectrum of silyl ketones of the type $Me_3Si(C{=}O)Ar$.[16]

The distinct yellow color of such ketones was attributed to inductive raising of the non-bonding oxygen orbital and the excited $\pi$ carbonyl orbital.

The alpha effect of silicon is complicated by the fact that in some situations silicon enhances reactivity at an alpha carbon, in contrast to all the above cases. As early as 1946, it was reported that $Me_3SiCH_2Br$ reacts 2600 times more rapidly than $Me_3CCH_2Br$ in basic ethanol.[17] These exceptions to the normal alpha effect appear to occur primarily in neopentyl-type situations. Stang, Apeloig, Schiavelli and their co-workers clarified this aspect of the problem in 1982.[18] They found that $Me_3SiCH_2X$ (X = triflate or tosylate) ethanolyzed without rearrangement, whereas the analogous carbon system (neopentyl) gave almost entirely rearrangement. Their calculations indicated that $Me_3SiCH_2^+$, if formed, should have undergone a neopentyl-type rearrangement to the silylenium ion. They concluded that the free carbocation had not formed. Their solvent studies confirmed that the silicon case appeared to ethanolyze by a nucleophilic mechanism ($k_s$), whereas the carbon case had considerable $k_\Delta$ character (neighboring group participation). The Grunwald–Winstein $m$-value (slope of the plot of log $k$ of the reaction against ionizing power $Y$) was 0.34 for Si and 0.49 for C for the triflates and 0.23 for Si and 0.58 for C for the tosylates. These extremely low values of $m$ for Si are consistent with a bimolecular mechanism. Higher values (close to 1.0) are characteristic of free carbocations (the $k_c$ mechanism).

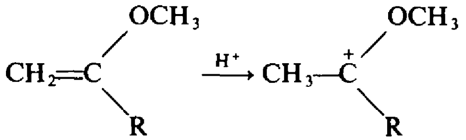
In the relatively nucleophilic solvent 60% ethanol, the silicon substrate ($Me_3SiCH_2X$) reacted much more rapidly than the carbon substrate ($Me_3CCH_2X$): by a factor of 957 for the triflate or 1830 for the tosylate. This reversal of the normal rate-retarding alpha effect of silicon is attributed to an enhanced ability of the silicon substrate to undergo the $S_N2$ ($k_s$) reaction with solvent. In the poorly nucleophilic solvent 97% trifluoroethanol, in which the $S_N2$ reaction is quenched in favor of the $S_N1$ reaction ($k_c$), the usual alpha effect is observed: the silicon substrate is slower than the carbon substrate, by about a factor of two for the triflate. Calculations by the authors indicated that silicon is a better $\sigma$ acceptor than carbon and therefore better stabilizes the negatively charged $S_N2$ transition. Moreover, the longer bonds to silicon should alleviate the steric effects that inhibit the $S_N2$ reaction in neopentyl systems. The classical alpha-destabilizing effect of silicon is observed in $S_N1$ reactions, whereas an alpha-stabilizing effect is observed for $S_N2$ reactions. Understanding any specific case therefore requires measurement of rates as a function of solvent to determine whether the reaction is unimolecular or bimolecular.

In order to minimize the $k_s$ ($S_N2$) component, Apeloig and Stanger continued this study with examination of tertiary 2-silyladamantyl systems (3).[19] The R = $CH_3$ system was 2.18 times as fast as the R = $Me_3Si$ system in 80% acetone, but 0.93 as fast in 97% trifluoroethanol. Such a low solvent effect contrasts with the above neopentyl results and confirms that the reaction is $k_c$ ($S_N1$) in 3 for both R = $CH_3$ and R = $Me_3Si$, because the adamantyl structure inhibits the backside attack. When R = H, the rate is about $10^{-8}$ that of either tertiary system. Despite the similarity of rates for carbon and silicon in 3, there is a considerable alpha effect of the traditional type, because of large ground state differences, which were assessed theoretically. The authors concluded that $CH_3$ stabilizes the cation by about 6–8 kcal $mol^{-1}$ more than does $Me_3Si$, which in turn stabilizes the cation about 12–14 kcal $mol^{-1}$ than H. Product studies[20] later indicated that the $\alpha$-silyl carbocation formed from 3 (R = $Me_3Si$) rearranges to the silylenium ion under solvolytic conditions. This report constituted the first documented case of a solvolytically generated silylenium ion.



3

Soderquist and Hassner[21] reported a novel method for generating $\alpha$-silyl carbocations, by protonation of alkenes (Eqn 2).

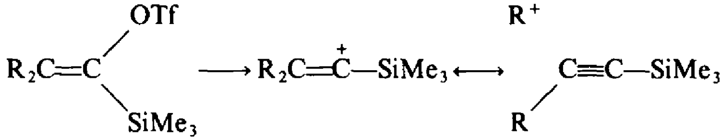


$$CH_2{=}C\begin{matrix}OCH_3\\ \\ R\end{matrix} \xrightarrow{H^+} CH_3{-}\overset{+}{C}\begin{matrix}OCH_3\\ \\ R\end{matrix} \qquad (2)$$

They found by deuterolysis that the silyl system ($R = Me_3Si$) reacted 1.8 times faster than the parent ($R = H$), but that carbon ($R = Me_3C$) reacted 100 times faster than the parent.

A wide variety of experiments now agree that an $\alpha$-silyl group provides less stabilization than an $\alpha$-carbon group for a carbocation, because double-bond/no-bond resonance (hyperconjugation) is more effective when the double bond is C=C than when it is C=Si (**1** and **2**). The difference in ability to stabilize is 6–8 kcal $mol^{-1}$. The $\alpha$-silyl group is still, however, considerably more stabilizing than only a hydrogen atom. In any individual case, it is necessary to determine that the reaction indeed involves generation of positive charge on carbon, as an $\alpha$-silyl group appears to stabilize an $S_N2$ displacement.

The situation is somewhat different when the positive charge is on trigonal carbon, as in Eqn 3.[22,23] The low $m$ value (0.28) for $R = H$ suggested an $E_2$ reaction, but $m = 0.46$ for $R = Me$ indicated more $S_N1$ character. The silyl substrates depicted in Eqn 3, however, reacted more rapidly than the analogous $\alpha$-methyl substrates, in contrast to the usual alpha effect. The vinylic ion of Eqn 3 is stabilized primarily by hyperconjugation involving the *cis* group across the double bond ($C^+/C{\equiv}C$ hyperconjugation). Thus there is no demand for hyperconjugation from the $\alpha$-silyl group, which can supply better stabilization through induction than can an $\alpha$-methyl group. Again, both alpha silicon and carbon are much more stabilizing than an alpha hydrogen.



$$R_2C{=}C\begin{matrix}OTf\\ \\ SiMe_3\end{matrix} \longrightarrow R_2C{=}\overset{+}{C}{-}SiMe_3 \longleftrightarrow \begin{matrix}R^+\\ C{\equiv}C{-}SiMe_3\\ R\end{matrix} \qquad (3)$$

Theoretical studies have been particularly useful in understanding the alpha effect. Early *ab initio* studies[24–26] provided approximate measures of the relative stabilizing abilities of silicon, carbon and hydrogen. The first higher level study, a double zeta calculation with polarization functions, found that $H_3Si$ was 14.3 kcal $mol^{-1}$ less stabilizing than $CH_3$ in the isodesmic reaction $H_3SiCH_2^+ + CH_3CH_3 \rightarrow CH_3CH_2^+ + H_3SiCH_3$.[27] As already mentioned, calculations played a key role in the studies by Apeloig, Stang, *et al.*, particularly in sorting out ground state contributions[18,19] and in assessing the relative stabilities of the $\alpha$-silylcarbenium ion and the silylenium ions.[28]

The highest level calculations have been carried out by Jorgensen and co-workers.[29] The use of polarization functions and electron correlation at the MP3/6-31G* level appear to be of particular importance in silicon systems and in those involving bridging groups. For the isodesmic reaction $XCH_2^+ + CH_4 \rightarrow XCH_3 + CH_3^+$, this research group found that $X = CH_3$ provided 34 kcal $mol^{-1}$ more stabilization than $X = H$; and $X = SiH_3$ was 17.8 kcal $mol^{-1}$ more stabilizing than $X = H$. The superior hyperconjugative ability of methyl ($H^+/C{=}C$) (see **1**) is responsible for its higher stabilization. The superiority of $SiH_3$ over H may be due to induction by silicon and some $H^+/Si{=}C$ hyperconjugation (analogous to **2**, with $SiH_3$ in place of $SiMe_3$).

These authors also studied the vinyl system through the isodesmic reaction $CH_2{=}CX^+ + CH_2{=}CH_2 \rightarrow CH_2{=}CHX + CH_2{=}CH^+$. They found that $CH_3$ and $SiH_3$ respectively were 27 and 24 kcal $mol^{-1}$ more stabilizing than H. Thus the alpha effect of silicon is comparable to that of carbon in this context. As recognized by Stang and Apeloig,[22,23] the vinyl cation already enjoys C–H (or C–C) in-plane hyperconjugation ($H^+/C{\equiv}C$ or $C^+/C{\equiv}C$) across the double bond (Eqn 3), so that electron demand from the alpha group X is lower than for the saturated cases. Also, the fact that the vinyl cation is sp-hybridized enhances sensitivity to induction. Theory concludes that silicon and carbon stabilize vinylic cations to comparable extents and that specific cases may result in greater stabilization by one or the other.

## 2. THE BETA EFFECT

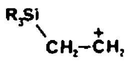
Credit for discovery of the dramatic beta effect of silicon has been given to Ushakov and Itenberg, whose publication occurred in 1937.[30] During the ensuing 50 years, the interaction of silicon with positive charge on a beta carbon has become a major subject for mechanistic, synthetic,[2–5] and theoretical studies. The kinetic magnitude of the effect (at least $10^{12}$ in solution and higher in the gas phase) exceeds almost all other neighboring group effects. Exceptions are silicon's larger congeners, germanium and tin, which exhibit even larger kinetic effects.[31]

In 1946, Sommer, Whitmore and co-workers reported the high reactivity of $\beta$-chlorosilyl systems, in comparison with $\alpha$ and $\gamma$ systems.[1,9,32] By extrusion of $R_3Si$ and the leaving group, this reaction leads to very efficient elimination (Eqn 4). There are numerous mechanisms that can lead

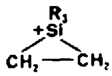
$$R_3Si{-}CH_2CH_2{-}X \longrightarrow CH_2{=}CH_2 + R_3Si{-}X \tag{4}$$

to this result: (1) rate-determining Si–C cleavage to a silylenium ion and a carbanion, followed by loss of $X^-$ (an $E_1cb$ mechanism). This mechanism was originally favored by Sommer but later discarded; (2) a concerted syn elimination of $R_3Si{-}X$. This mechanism is implicated in the thermal or gas-phase variants. It was briefly favored by Eaborn[11] for the solution reaction but also was discarded; (3) rate-determining attack of solvent or added base on silicon (E2-like); (4) rate-determining attack by solvent or added base on the C–X bond ($k_s$ or $S_N2$); (5) rate-determining cleavage of the C–X bond to form a carbocation ($k_c$ or E1).

Although there may be occasional exceptions, the preponderance of evidence today favors the carbocation mechanism (5) in polar solution. The major point still in need of clarification is whether the interaction of silicon occurs purely by hyperconjugation without significant movement in the transition state (vertical participation, **4**) or by internal neighboring group participation to form a three-membered ring siliconium ion (non-vertical participation, to form **5**, in which pentavalency of silicon is permitted by its d orbitals). In addition, the simple inductive effect of electropositive silicon may assist in stabilizing beta positive charge. Thus we need to describe the evidence that specified which bond making or breaking events are rate determining and how silicon influences these events.



**4**



**5**

The first modern mechanistic study of the reaction was carried out by Sommer and Baughman in 1961.[33] They examined the solvolysis of $Me_3SiCH_2CH_2Cl$ in aqueous ethanol and formic acid. From the rate as a function of solvent they calculated the $m$ value to be 1.02 on the *tert*-butyl chloride scale, a typical $k_c$ value. By observing that the rate was dependent on the ionizing power of solvent rather than on the nucleophilicity, they were able to reject the syn elimination ((2), which would show little or no solvent effect) and the solvent or base attacks ((3) and (4), whose primary dependence would be on solvent nucleophilicity). In their words, 'strong participation of electron-release from silicon in the rate-controlling transition state [occurs] without simultaneous nucleophilic attack by the solvent at the silicon atom.' In their published paper the authors favored the $E_1cb$ variant (1), although in his dissertation Baughman also described the $E_1$ ($k_c$) mechanism (5).[34] Eaborn and co-workers described the shortcomings of the $E_1cb$ mechanism and suggested that

C–X bond breaking is rate determining, but with a polar transition state in the simultaneous syn elimination of X and $R_3Si$.[11]

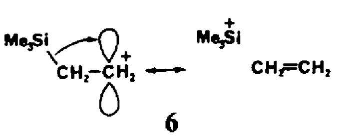
The nature of the transition state also may be explored by variation of the substituent on silicon. In unpublished work described in his book,[35] Sommer reported kinetic studies for solvolysis of a wide variety of structures of the type $R'R_2SiCH_2CH_2X$, with X = Cl or OH, and R or R′ = Me, Et, iPr, and Ar. The Hammett $\rho$ value for ethanolysis of $ArMe_2SiCH_2CH_2Cl$ was found to be $-2.15$ and for acidic hydrolysis of $ArMe_2SiCH_2CH_2OH$ $-1.85$. The Taft $E_s$ was small and negative. Vencl *et al.*[36] carried out similar experiments with $ArMe_2CH_2CH_2Cl$. The Hammett $\rho$ varied from $-1.2$ in 95% ethanol to $-2.3$ in 80% ethanol. Some curvature was found at low water content. These relatively large negative values of $\rho$ indicate a significant build-up of positive charge on the aryl groups and hence on silicon in the transition state. Although these results are formally consistent with the $E_1cb$ (silylenium ion) mechanism (1), they are equally consistent with the $E_1$ transition state (5) leading to intermediates **4** or **5**. Vencl *et al.* noted that there may be a nucleophilic component to the mechanism when solvent nucleophilicity increases.

The stereochemistry of the reaction was finally elucidated by Jarvie and co-workers.[37,38] Solvolysis of *erythro*-$Me_3SiCHBrCHBrCH_3$ led predominantly to *cis*-1-bromopropene. This result is possible only when the nucleofuge Br and the electrofuge $Me_3Si$ are antiperiplanar to each other (180° Si–C–C–Br dihedral angle). The synperiplanar (0°) or gauche (60°) arrangements would have led to the *trans* isomer. This observation ruled out the syn elimination mechanism (2), as had the previously described solvent effects. Although the results are consistent with a concerted E2 mechanism (simultaneous antiperiplanar departure of Br and $Me_3Si$), the solvent effects require the E1 mechanism with rate-determining C–Br cleavage. Jarvie *et al.* favored the cyclic siliconium intermediate (**5**, but with *cis* methyl and bromo groups), and a strong kinetic assist from the inductive effect of silicon. They did observe a small amount of the *trans* propene, from 0.3% when the solvent $Y$ value was $-2.03$ to 15% when the $Y$ value was 2.05. They suggested that the open cation $Me_3SiCHBrCHCH_3^+$ was in equilibrium with the cyclic form. The results, however, do not require the cyclic form. If $Si^+/C{=}C$ hyperconjugative stabilization of the cation in **4** serves to discourage C–C bond rotation, the antiperiplanar geometry would also be maintained.

Stereochemistry was also examined by Hudrlik and Peterson.[39] They found that *threo*-$(Me_3Si)PrCH{-}CHPrBr$ gave over 90% *cis*-4-octene under hydrolytic conditions, as expected for the antiperiplanar stereochemistry.

Jarvie *et al.*[40] studied secondary deuterium isotope effects on the rates of $Me_3SiCH_2CD_2Br$, $Me_3SiCHDCH_2Br$, and $(CD_3)_2MeSiCH_2CH_2Br$, and concluded that C—Br cleavage was rate determining, 'possibly assisted by the beta silicon.' They also found that treatment of $Me_3SiCH_2CD_2OH$ with $PBr_3$ gave equal amounts of $Me_3SiCH_2CD_2Br$ and $Me_3SiCD_2CH_2Br$, i.e. the deuterium had been scrambled. Similar results were obtained by Eaborn and co-workers.[41] They recognized that the scrambling process is consistent with either the symmetrical siliconium ion **5** or the open carbocation **4**, provided that the open cation undergoes a rapid 1,2 shift of the $Me_3Si$ group ($Me_3Si{-}CH_2CD_2^+ \rightleftharpoons {}^+CH_2CD_2{-}SiMe_3$). Detailed analysis of the $\sigma_p^+$ constants led Eaborn *et al.* to favor the cyclic siliconium ion.

Organic chemists are familiar with the necessity that non-vertical ring closure to form a three-membered ring such as **5** requires an antiperiplanar stereochemistry between the internal nucleophile and the leaving group. They are also comfortable with kinetic enhancement from the $\beta$-silyl group in forming the three-membered ring **5**, by analogy with neighboring group participation and elimination reactions that lead to epoxides, halonium ions, and related species. The rate enhancement and stereospecificity, however, may be equally well explained in terms of vertical stabilization in the open cation **4**. The highly polarizable and electron-donating C–Si bond is particularly able to stabilize the carbocation through $Si^+/C{=}C$ hyperconjugation, as depicted in **6**. Rapid 1,2 shifts of $Me_3Si$ may occur in **4** without disrupting hyperconjugation, as required by the deuterium scrambling experiments. Hyperconjugation of this type ($Si^+/C{=}C$) is especially strong not only because of the

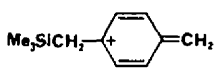


**6**

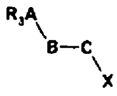
high polarizability of the C–Si bond but also because positive charge is ultimately placed on Si, which is better suited to accept positive charge than either H or C ($H^+/C{=}C$ or $C^+/C{=}C$ hyperconjugation; see **1**).

The high ability of metalloids such as silicon to hyperconjugate was suggested as early as 1948.[42] The distinction between hyperconjugative stabilization by beta silicon and destabilization by alpha silicon should be appreciated. Hyperconjugation of an $\alpha$-silyl carbocation leads to the unstable Si=C double bond and positive charge on carbon (**2**, $C^+/Si{=}C$), whereas hyperconjugation of a $\beta$-silyl carbocation leads to the C=C double bond and positive charge on silicon (**6**, $Si^+/C{=}C$). The latter situation is clearly stabilizing, even more so than normal hyperconjugation in hydrocarbon carbocations (**1**, $H^+/C{=}C$ or $C^+/C{=}C$ (not shown)). The strong beta effect of silicon in fact justifies the term *hyper*conjugation, as pointed out by Traylor, since originally this type of overlap was considered to be superior to $\pi$ conjugation. In order to have maximum hyperconjugation during the solvolysis of $\beta$-silyl systems, the silyl and leaving groups should have bonds parallel to the C–C connector, as provided by the antiperiplanar stereochemistry. Thus, intermediate **4** is as able as **5** to explain the observed stereochemistry and kinetic acceleration. This situation was fully appreciated by workers in the 1960s.[41,43]

Hyperconjugation involving silicon and other atoms was studied extensively by Traylor and coworkers around 1970.[44–47] They described the same two modes of stabilization of positive charge by substituents. Vertical stabilization involves no change in geometry or atom–atom distances as the transition state is approached. Direct conjugation ($CH_3\ddot{O}{-}CH_2^+ \leftrightarrow CH_3\overset{+}{O}{=}CH_2$) and hyperconjugation (**1**) are two primary examples of vertical stabilization. Non-vertical stabilization involves significant changes in geometry or atom–atom distances as the transition state is approached. Neighboring group participation or internal nucleophilic displacement is thus an example of non-vertical stabilization, since significant geometry alteration occurs. In the present context, hyperconjugative stabilization in **4** is vertical and siliconium ion **5** formation is non-vertical. Traylor *et al.* showed that silicon is capable of considerable vertical stabilization because $\sigma_p^+$ of $Me_3SiCH_2$ fell on the linear correlation with the charge transfer band of $Me_3SiCH_2Ph$ with tetracyanoethylene.[45] The latter phenomenon is electronic and must be vertical, and the former phenomenon involves beta stabilization of positive charge in **7**.



**7**



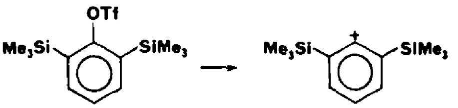
**8**

Vertical stabilization is in general optimized in system **8** (X is the leaving group and C will carry the positive charge) by low electronegativity of A, inductive donation by R, no competing R–A conjugation, low bending and stretching force constants of A–B, a strong B=C double bond, planarity of the ABCX unit, and an antiperiplanar arrangement of ABCX. The synperiplanar arrangement (0°) also is favorable, but less so than antiperiplanar. The orthogonal arrangement, in which the A–B bond cannot hyperconjugate with developing positive charge, is unfavorable.[46] Traylor's analysis of vertical stabilization involving tin, using ionization potentials as a measure of vertical stabilization, indicated that $Me_3SnCH_2CH_2^+$ should be more stable than $Ph_3C^+$ (although its tendency to expel the electrofuge rapidly is not considered).[47] Pitt[48] refined the theory of hyperconjugation for Group IV elements, and Basindale[49] provided updated NMR evidence for these interactions.

These arguments strongly support the hyperconjugative mode (**4**, **6**) for the interaction of silicon with beta positive charge. Eaborn, however, concluded that vertical stabilization is insufficient to explain the kinetic enhancement. Because $\sigma_p^+$ of $Me_3SiCH_2$ ($-0.54$) is less than twice the value for methyl ($2\times(-0.31) = -0.62$), then $Me_3SiCH_2CH_2Cl$ should solvolyze more slowly than $Me_2CHCl$, whereas the former actually reacts $10^5$ more rapidly than the latter and is even slightly faster than $(CH_3)_3C$—Cl.[41] They attributed the extra kinetic enhancement to non-vertical stabilization leading to the cyclic siliconium ion **5**. This analysis of $\sigma_p^+$, however, does not take into consideration the transition state differences between the defining reaction for $\sigma_p^+$ and the reaction of $Me_3SiCH_2CH_2Cl$. These studies therefore did not lead to a definitive resolution of the question of vertical versus non-vertical stabilization.

A key observation in this problem was provided by Davis and Jacocks.[50] In comparison with $Me_3SiCH_2CH_2OH$ (relative rate 1.0), they found that the rate of acid-catalyzed elimination for $Me_3SiCH_2CHMeOH$ was $10^{3.3}$, that for $(Me_3SiCH_2)_2CHOH$ was $10^{5.9}$, and that for $Me_3SiCH_2CMe_2OH$ was $10^{6.8}$. Thus the second silyl group provides an additional six orders of magnitude, about the same as the first silyl group. Because only one silyl group can engage in neighboring group participation, additivity is not expected for non-vertical stabilization. Two silyl groups, however, can both provide vertical stabilization. This observation therefore provided the first strong evidence that hyperconjugation is the primary mode of stabilization. Moreover, the α $CH_3$/H effect is about $10^{3.3}$ for both 2°/1° ($Me_3SiCH_2CHMeOH$ to $Me_3CH_2CH_2OH$) and 3°/2° ($Me_3SiCH_2CMe_2OH$ to $Me_3SiCH_2CHMeOH$), indicative of strong carbocation character in the transition state.

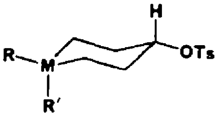
Efforts to observe a β-silylcarbenium ion ($Me_3SiCH_2Ph_2C^+$) by Olah and co-workers were not successful, because of the rapid elimination reaction to form $CH_2{=}CPh_2$.[15] The beta effect was employed successfully to create the first aryl $S_N1$ reaction, Eqn 5.[51] Other examples of the use of the beta effect have appeared.[52,53]



(5)

Although the favored stereochemistry of the reaction of Eqn 4 was proved to be antiperiplanar,[37,39] two important questions had not been answered. What is the full kinetic enhancement when a system is constrained to the antiperiplanar geometry? Is there kinetic enhancement in alternative geometries? Answers to these questions would provide further clarification of the question of vertical versus non-vertical stabilization. Prior to 1977, all systems studied had been acyclic. The systems were free to assume the most favorable conformation in the transition state, but the rate would be diluted by contributions from lower rates in less favorable conformations (Winstein–Holness considerations). The typical rate enhancement, e.g. of $Me_3SiCH_2CH_2X$ versus $CH_3CH_2CH_2X$,[38] was about $10^6$–$10^7$. An alternative method, using electrophilic addition of $R^+$ to $CH_2{=}CH{-}CH_2SiMe_3$ or to $CH_2{=}CH{-}CH_3$ to produce ions stabilized respectively by beta $SiMe_3$ and H, gave a rate ratio of 30 700, or less than that observed in direct solvolysis, presumably due to transition state differences.[54] Replacement of $SiMe_3$ in $CH_2{=}CH{-}CH_2SiMe_3$ by $SiPh_3$ reduced reactivity by a factor of 60, $SiCl_3$ shut down the reaction and Si(hexyl)$_3$ accelerated the reaction by a factor of almost three.[55]

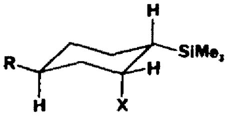
Washburne and Chawla examined the first conformationally constrained system, **9**, in which the silicon atom must be gauche to the leaving group.[56] The silicon system (M = Si) was 3–5 times



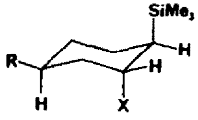
**9**

faster than the carbon system (M = C) for R/R′ = Me/Me, Me/Ph, or Ph/Me. This small acceleration could be attributed to inductive effects. Non-vertical participation is not possible in this system, and vertical participation is vastly reduced. The workers, however, did not provide tests that the silicon and carbon systems reacted by the same mechanism. Six-membered rings are prone to solvolyze by the $k_s$ ($S_N2$) reaction, so without proving that the $k_c$ ($S_N1$) reaction occurred in both cases the comparison of rates may not be apt.

Our group examined conformationally constrained gauche and antiperiplanar systems for the first time (**10**, **11**, X = $O(CO)CF_3$).[57,58] An acyclic silyl system has three conformations (two of which may be equivalent). When R = H in **10** and **11**, one degree of freedom is removed, and each molecule can exist in two chair conformations. When R = *tert*-butyl, two degrees of freedom are removed, and each molecule exists in only one chair conformation. Kinetic comparisons were made with cyclohexyl trifluoroacetate in 97% trifluoroethanol, a solvent of very low nucleophilicity. Solvent studies using the method of Raber and Harris showed that all the systems containing silicon solvolyzed by a $k_c$ mechanism whereas the parent cyclohexyl trifluoroacetate solvolyzed by a $k_s$ mechanism. Thus introduction even of an entirely gauche trimethylsilyl group (**10**) is capable of bringing about a profound change of mechanism, from $k_s$ to $k_c$. Both *cis* compounds (**10**, R = H or *tert*-butyl) solvolyzed about $4 \times 10^4$ times faster than cyclohexyl trifluoroacetate in 97% trifluoroethanol at 25°C. This remarkably high rate for the gauche stereochemistry is inconsistent with a non-vertical mechanism, since internal nucleophilic displacement cannot occur in this geometry, but it is consistent with the vertical (hyperconjugative) mechanism, since weak overlap is possible. The observation also confirms that the unbiased form (**10**, R = H) probably solvolyzes from the conformation shown, rather than from the ring-flipped form with X equatorial, since introduction of the *tert*-butyl group does not alter the rate.



**10**



**11**

The unbiased *trans* form (**11**, R = H) solvolyzes about $10^9$ times faster than cyclohexyl, even though the system exists predominantly in the diequatorial form, which must first flip to the diaxial form before reaction.[58] This value already exceeds all previous measures of the beta effect. Freezing out the final degree of freedom with the *tert*-butyl group in **11** results in a rate $10^{12}$ times faster than cyclohexyl, one of the largest anchimeric accelerations ever observed.[58]

If the major mode of interaction is hyperconjugation, a parallel may be drawn between beta stabilization of positive charge by silicon and hydrogen/deuterium secondary kinetic isotope effects. Adaptation of isotope effect mathematics leads to Eqn 6,

$$\log(k_{\mathrm{Si},\theta}/k_{\mathrm{H}}) = \cos^2\theta\,[\log(k^{\mathrm{V}}_{\mathrm{Si,max}}/k^{\mathrm{V}}_{\mathrm{H}})] + \log(k^{\mathrm{I}}_{\mathrm{Si}}/k^{\mathrm{I}}_{\mathrm{H}}) \qquad (6)$$

in which $k_{\mathrm{H}}$ is the rate of the cyclohexyl system, $k_{\mathrm{Si},\theta}$ is the rate of the silicon system with dihedral angle $\theta$ for the Si—C—C—X fragment, V refers to the vertical contribution, and I refers to the inductive contribution. From the rate data for the two *tert*-butyl systems, in which the dihedral angle is 180° or 60°, the $10^{12}$ overall acceleration was partitioned into a $10^{10}$ hyperconjugative component and a $10^2$ inductive component.[58] Similar studies have been carried out on the five-membered rings, *cis*- and *trans*-2-(trimethylsilyl)cyclopentyl trifluoroacetate.[59]

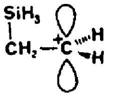
In gas-phase reactions, the absence of solvent can result in a change of mechanism. Davidson and co-workers[60] studied the extrusion of $R_3Si—Cl$ from $R_3SiCH_2CH_2Cl$ and Musker and Larson[61] studied the extrusion of $Me_3Si—OCH_3$ from **10** and **11** (R = H; X = $OCH_3$). Both groups concluded that the reaction took place by a four-centered syn elimination.

Mass spectrometric methods have been employed only recently to study the beta effect. Hajdasz and Squires[62] prepared the ion $R_3SiCH_2CH_2^+$ (with structure either **4** or **5**, R = Me) by the reaction of $Me_3Si^+$ with $CH_2{=}CH_2$ or of $H^+$ with $Me_3SiCH{=}CH_2$. They measured the beta effect to be 39 kcal mol$^{-1}$ by assessing the enthalpic change in the isodesmic reaction $Me_3SiCH_2CH_2^+ + CH_3CH_3 \rightarrow Me_3SiCH{=}CH_2 + CH_3CH_2^+$. The silicon atom stabilizes beta positive charge more than does hydrogen by this amount, provided that there are no large differences for the neutrals.

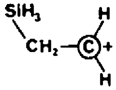
Li and Stone[63] used high pressure mass spectrometry to study the isodesmic reaction $Me_3SiCAB{-}CXY^+ + CHAB{-}CHXY \rightarrow Me_3SiCAB{-}CHXY + CHAB{-}CXY^+$. When all the substituents (A, B, X, Y) were hydrogen, the system was the same as that of Hajdasz and Squires, and the measured value of the beta effect was 48.2 kcal mol$^{-1}$. The difference in the two values of about 10 kcal mol$^{-1}$ was attributed entirely to differences in the chosen heat of formation of $Me_3Si^+$. Since this value is constant for the series, differences between systems are probably measured accurately. For secondary ions (A, X = H; Y = Me; B = H or Me) the beta effect was about 28 kcal mol$^{-1}$. These observations provided the first experimental demonstration that the effect is lower as the carbocation becomes more stable (reduced demand). At least for the unsymmetrical systems ($A \neq X$ or $B \neq Y$), these results require that the ions have the unbridged structures, like **4**, as the energies are determined by the substitution pattern at only the carbocation center, with the beta effect largest for primary and smallest for tertiary. The symmetrical systems (A, B, X, Y = H or Me; A, X = H, B, Y = Me) can also be unbridged, although fortuitous adding of substituent effects in the bridged forms might be possible.

Calculations also refer to the gas phase. The earliest *ab initio* studies, by Eaborn and Murrell,[24] suggested that the bridged form was more stable than the open form by about 0.5 eV. Calculations by Apeloig and co-workers[28] compared $Me_3SiCH_2CH_2^+$ with the isomeric alpha cation and the silylenium ion. They found that the beta ion was not a minimum on the potential surface. Apeloig also reported calculations on the silyl-substituted aryl cation.[64]

The most sophisticated calculations have been carried out by Jorgensen and co-workers.[8,29] For the isodesmic reaction $H_3SiCH_2CH_2^+ + CH_4 \rightarrow H_3SiCH_2CH_3 + CH_3^+$, the cyclic form (**5**, R = H) has the greatest stabilization, 74.4 kcal mol$^{-1}$ at the MP3/6-31G* level. Two unbridged ions were considered: **12**, in which the empty orbital is aligned for overlap with the C–Si bond, and **13**, in which the orbitals are orthogonal and non-overlapping. The aligned structure gave a stabilization energy of 72.0 kcal mol$^{-1}$, and the unaligned structure 42.4 kcal mol$^{-1}$. The increased overlap in the aligned form results in a shorter C–C bond (1.360 Å in **12** versus 1.443 Å in **13**) and a smaller Si–C–C angle (94.3° versus 119.6°). Thus the so-called vertical process involves considerable change in geometry to optimize hyperconjugation. The bridged form (**5**, R = H) is about 2.4 kcal mol$^{-1}$ more stable than the unbridged form (**12**). The beta effect of silicon may be assessed by comparison of the system $H_3Si{-}CH_2CH_2^+$ with $H{-}CH_2CH_2^+$. For the unaligned conformation (**13** and the analogous H–C structure), the silicon system is 8.9 kcal mol$^{-1}$ more stable than the hydrogen system, a measure of the inductive stabilization of silicon. For the aligned conformation (**12** and the analogous H–C structure), the silicon system is 38 kcal mol$^{-1}$ more stable, a measure of contributions from all sources. This value is in excellent agreement with the experimental value of Hajdasz and Squires.[62] The contribution from Si–C hyperconjugation alone would be the difference between these figures, or about 29 kcal mol$^{-1}$.



**12**



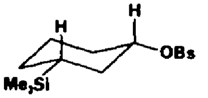
**13**

These calculations were carried out on systems with primary carbons, whereas the conformationally constrained systems in solution experiments (**10**, **11**)[58] of necessity possessed secondary carbons. Moreover, the beta effect is expected to be larger in the gas phase, since solvent would not provide alternative stabilization. Ibrahim and Jorgensen[8] carried out calculations on secondary and tertiary systems in order to be able to make more apt comparisons with experiment and because the relative stability of the bridged and unbridged forms may change. For the same isodesmic reaction ($XR^+ + CH_4 \rightarrow HR^+ + XCH_3$), they found that beta silicon in an unbridged secondary system ($XR^+ = SiH_3CH_2C^+HCH_3$) is 22.1 kcal $mol^{-1}$ more stabilizing than hydrogen ($XR^+ = CH_3C^+HCH_3$) at the MP2/6-31G(d) level, compared with 38 kcal $mol^{-1}$ previously calculated for the primary system. The bridged form is stabilized by only 18.2 kcal $mol^{-1}$, and furthermore is not an energy minimum, in contrast to the primary systems. In the unbridged tertiary system ($XR^+ = SiH_3CH_2C^+(CH_3)_2$), silicon is 15.9 kcal $mol^{-1}$ more stabilizing than H in $(CH_3)_3C^+$. For $SiH_3$ on cyclopropane, the stabilization of the beta positive charge is 17.5 kcal $mol^{-1}$ more than H on the cyclopropyl cation (these structures are not minima, as ring opening to the propenyl cations occurs). The $\beta$-silyl effect of 22 kcal $mol^{-1}$ in $SiH_3CH_2C^+HCH_3$ compares favorably with 18 kcal $mol^{-1}$ observed experimentally by us in **11**.[58] The difference would be larger if the experiment had been with $SiH_3$, as expected for complete charge development and optimal orbital alignment reflected in the calculations.

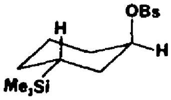
The beta effect of silicon on positive charge is now well understood. Stabilization in optimally aligned secondary systems results in a solvolytic acceleration of about $10^{12}$ or a theoretical stabilization of about 22 kcal $mol^{-1}$ compared with analogous systems containing H in place of Si. Stabilization may occur by hyperconjugation, but the bridged form is not far distant on the energy surface and may be preferred in primary systems. Further experimentation on alternative geometries may still yield new insights into the interaction.

## 3. THE GAMMA EFFECT

The pioneering paper by Sommer and Whitmore[1] recognized in 1946 the possibility that a gamma silicon atom could interact with positive charge. They found that $ClCH_2CH_2CH_2SiCl_3$ was more reactive than the alpha isomer, though less reactive than the beta isomer. It was not for another 40 years, however, that the quantitative and stereochemical study by Shiner and co-workers[65] demonstrated the significance of the gamma effect. Using the relatively constrained six-membered rings **14** and **15**, they found that the *cis* isomer (**14**) reacted about 450 times faster than its unsilylated analogue in 97% trifluoroethanol, but the *trans* isomer (**15**) showed essentially no acceleration.[65]



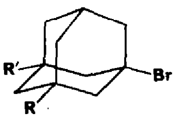
**14**



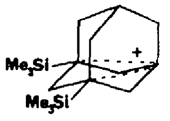
**15**

The small (and inverse) secondary deuterium isotope effect for the beta tetradeuterated analogue of **14** confirmed that the molecule reacted from the diequatorial conformation. In contrast, the *trans* compound **15** and the unsilylated analogues had secondary deuterium isotope effects of 2.5–3.0, as expected for hyperconjugative involvement of beta C—H(D) within the H(D)—C—C—X fragment in the transition state, which requires brosylate to be in the axial position.

The gamma effect appears to require the diequatorial conformation, in which the back lobes of the Si–C bond at the 3 position can interact with the developing p orbital at the 1 position, a so-called percaudal interaction. This type of interaction was confirmed by a theoretical study at the 6–31G level, in which the 1–3 ($\alpha$–$\gamma$) distance was found to be shortened to 1.82 Å in the full carbocation.[66] Shiner and co-workers[67] also studied the open chain, optically active system $Me_3SiCH_2CH_2CHCH_3OBs$, whose rate was 130 times faster than that of the carbon analogue, $Me_3CCH_2CH_2CHCH_3OBs$. The racemic nature of the substitution product requires either that the cation intermediate may be attacked equally from two sides or, as the authors prefer, that participation may occur with equal likelihood from both the W and the sickle conformations, in contrast to the cyclic systems (**14**, **15**).



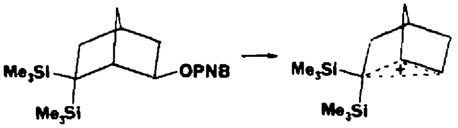
**16**



**17**

The effect of a $\gamma$ trimethysilyl group was examined in the adamantyl framework (**16**) by Grob and co-workers.[68,69] Compared with hydrogen (R, R′ = H), one trimethylsilyl group (R = Me$_3$Si, R′ = H) accelerated ethanolysis by a factor of 8.6 and a second such group (R, R′ = Me$_3$Si) by an additional factor of 3.8, for a total acceleration of 33. In contrast, one or two methyl groups reduced the rate of ethanolysis by factors of 0.7 and 0.5, respectively. These authors referred to this type of interaction between silicon and a $\gamma$ positive charge as homohyperconjugation.

In the norbornyl framework (**18**), a study by Kirmse and Söllenböhmer[70] suggested that intermediate **19** is formed first during trifluoroethanolysis, followed by 6, 2 migration of silicon and Wagner–Meerwein shifts. Unpublished work of T. W. Bentley cited in this study indicated that the bis(trimethylsilyl) system **18** is 30 000 times faster than 2-norbornyl *p*-nitrobenzoate. This large acceleration confirms a major role for silicon that is $\gamma$ to positive charge. The effect of single *exo*- or *endo*-trimethylsilyl groups would be interesting.



**18** **19**

## 4. THE DELTA EFFECT

The effects of silicon regretfully do not extend beyond the gamma position, at least so far as solvolytic accelerations indicate. Fessenden and co-workers[71] studied the *cis*- and *trans*-4-(trimethylsilyl)cyclohexanols) and found that the rates of ethanolysis of the tosylates were, respectively, almost identical to those of the *cis*- and *trans*-4-*tert*-butylcyclohexyl tosylates. Although proper tests have not been carried out, it is likely that all four systems react by the $k_s$ mechanism, and that silicon is not palpably involved.

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