Relative Stabilities of Trimethylsilyl and *tert*-Butyl Cations Determined by Ion Cyclotron Resonance Mass Spectrometry

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A series of chloride- and hydride-exchange reactions involving the trimethylsilyl cation have been investigated in the gas phase using pulsed ion cyclotron resonance mass spectrometry. Estimates of 154 ± 14 kcal/mol (644 ± 59 kJ/mol) for the heat of formation of the trimethylsilyl cation and a lower limit of −40 ± 2 kcal/mol (−167 ± 8 kJ/mol) for the heat of formation of trimethylsilane have been obtained. With hydride as the reference base the trimethylsilyl cation is established to be 10–20 kcal/mol (42–84 kJ/mol) more stable than the *tert*-butyl cation. Results of a limited laser photodissociation experiment involving two different $C_3H_9SiCl^+$ ions, as well as a new chloride-transfer reaction which forms the trimethylsilylenium ion, are reported. Implications of these gas-phase results for the possible existence of silylenium ions in solution are discussed.

Introduction

After several decades of intensive investigation the search for examples of stable trivalent organosilane derivatives continues unabated. Recently, evidence purporting to establish the transitory existence of >C=Si<, >Si=Si<, —N=Si<, and O=Si< intermediates in both solution and the gas phase has been published.[2,3] In sharp contrast the silylenium ions,[4,5] R_3Si^+, have thus far eluded detection in solution, although their existence in the gas phase seems well established by the mass spectral studies of Lampe,[6] among others.[7] The qualitative conclusion from this work is that trivalent silyl cations are energetically similar to the corresponding trivalent carbocations, a finding which is consistent with the relative electronegativities of silicon and carbon. Of course the more electropositive character of silicon should be partly offset by a more favorable hyperconjugative effect in the carbocation case.[8] Thus for the pair of cations $(CH_3)_3Si^+$ and $(CH_3)_3C^+$ it would be difficult to predict (a priori) which would have the greater thermodynamic stability.

Recognizing the central role played by the *tert*-butyl cation in carbon chemistry, considerable effort has been expended in the determination of its heat of formation ($\Delta H_f°$). Table I provides a chronological listing of the better $\Delta H_f°$ values for this ion reported since 1959. Companion values for the heat of formation of $(CH_3)_3Si^+$ re-

Table I. Chronological Listing of Selected ΔH_f Values for *tert*-Butyl Cation $[(CH_3)_3C^+]$

year	$\Delta H_f°$/kcal/mol	ref
1959	176	a
1963	177.9 ± 2.6	a
1970	166.6 ± 2.1	a
1972	169.1 ± 2.1	a
1976	168.2	a
1979	162.9 ± 1.2	b
1979	162.1 ± 0.8	c
1980	168 ?	d

a Taken from: Lias, S. G. In 'Kinetics of Ion-Molecule Reactions'; Ausloos, P., Ed.; NATO Advanced Study Institute; Plenum Press: New York, 1979; Vol. B40, p 241. Original references may be found therein. *b* Reference 21. *c* McLoughlin, R. G.; Traeger, J. J. *Am. Chem. Soc.* 1979, *101*, 5791. *d* Ausloos, P., private communication.

Table II. Chronological Listing of Selected ΔH_f Values for the Trimethylsilyl Cation $[(CH_3)_3Si^+]$

year	$\Delta H_f°$/kcal/mol	ref
1961	166	a
1962	146	b
1965	140 ± 4	c
1970	171 ± 2	d
1971	176 ± 3	e
1975	160.4	f
1977	154.8	g

a Hobrock, B. G.; Kiser, R. W. *J. Phys. Chem* 1961, *65*, 2186. *b* Hobrock, B. G.; Kiser, R. W. *Ibid.* 1962, *66*, 155. *c* Reference 6a. *d* Reference 6b. *e* Reference 20. *f* Reference 7b. *g* Reference 19.

ported since 1961 are included in Table II for comparison. Both ions show a general trend, at least in the last 10 years, toward lower values of $\Delta H_f°$ as a result of improved experimental techniques and refined thermochemical values employed in the calculations. Prior to 1970 experimental determination of the heat of formation for the trimethylsilyl cation gave values lower than those for the carbon analogue $(CH_3)_3C^+$; however, precipitous jumps of 5–7 kcal/mol in reported $\Delta H_f°$ values for each of these ions in recent years make reliable prediction of their relative stabilities quite uncertain even today.

Several groups have recently published studies involving the trimethylsilyl cation. Reactions of the ion have been observed in tri- and tetramethylsilane,[6c] it has been used as a reagent ion in chemical ionization mass spectrometry,[9]

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(2) For a brief review of silicon analogues of olefins and ketones prior to 1975 see: Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* 1975, *8*, 18.

(3) Silaethenes: (a) Wiberg, N.; Preiner, G. *Angew, Chem., Int. Ed. Engl.* 1977, *16*, 328. (b) Chapman, O. L.; Chang, C. C.; Kolc, J.; Jung, M. E.; Lowe, J. A.; Barton, T. J.; Tumey, M. L. *J. Am. Chem. Soc.* 1976, *98*, 7846. (c) Brook, A. G.; Harris, J. W.; Lennon, J.; Sheikh, M. E. *Ibid.* 1979, *101*, 83. Disilenes: Wulff, W. D.; Goure, W. F.; Barton, T. J. *Ibid.* 1978, *100*, 6236 and references cited therein. Silanones: (d) Soysa, H. S. D.; Okinoshima, H.; Weber, W. P. *J. Organomet. Chem.* 1977, *133*, C17. (e) Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* 1977, *99*, 6447. Silimines: Wiberg, N.; Preiner, G. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 362.

(4) Although the tricoordinated organosilicon cation R_3Si^+ has been referred to as siliconium ion, or lately a silicenium ion, the silylenium ion terminology recommended by Barton[5] is preferred.

(5) Barton, T. J.; Hovland, A. K.; Tully, C. R. *J. Am. Chem. Soc.* 1976, *98*, 5695.

(6) (a) Hess, G. G.; Lampe, F. W.; Sommer, L. H. *J. Am. Chem. Soc.* 1965, *87*, 5327. (b) Potzinger, P.; Lampe, F. W. *J. Phys. Chem.* 1970, *74*, 719. (c) Potzinger, P.; Lampe, F. W. *Ibid.* 1971, *75*, 13.

(7) (a) Weber, W. P.; Felix, R. A.; Willard, A. K. *Tetrahedron Lett.* 1970, 907 and references cited therein. (b) Potzinger, P.; Ritter, A.; Krause, J. *Z. Naturforsch., A* 1975, *30A*, 347. (c) Krause, J. R.; Potzinger, P. *Int. J. Mass Spectrom. Ion Phys.* 1975, *18*, 303.

(8) Apeloig, Y.; Schleyer, P. v. R. *Tetrahedron Lett.* 1977, 4647.

(9) Odiorne, T. J.; Harvey, D. J.; Vouros, P. *J. Phys. Chem.* 1972, *76*, 3217.

Table III. Chloride- and Hydride-Transfer Reactions Involving the Trimethylsilyl Cation

reaction	thermochemical conclusions
A. Chloride Transfer	
1. $(CH_3)_2SiCl^+ + (CH_3)_3SiCl \rightarrow (CH_3)_3Si^+ + (CH_3)_2SiCl_2$	
2. $i\text{-}C_3H_7Cl + (CH_3)_3Si^+ \rightarrow (CH_3)_3SiCl + i\text{-}C_3H_7^+$	$\Delta H_f°((CH_3)_3Si^+) \geq 142 \pm 4$ kcal/mol
3. $C_2H_5^+ + (CH_3)_3SiCl \rightarrow C_2H_5Cl + (CH_3)_3Si^+$	$\Delta H_f°((CH_3)_3Si^+) \leq 166 \pm 3$ kcal/mol
4. $(CH_3)_3Si^+ + s\text{-}C_4H_9Cl \rightarrow s\text{-}C_4H_9^+ + (CH_3)_3SiCl$	$\Delta H_f°((CH_3)_3Si^+) \geq 136 \pm 5$ kcal/mol
B. Hydride Transfer	
1. $(CH_3)_3Si^+ + (CH_3)_3CH \nleftrightarrow (CH_3)_3C^+ + (CH_3)_3SiH$	
2. $(CH_3)_3C^+ + (CH_3)_3SiH \rightarrow (CH_3)_3CH + (CH_3)_3Si^+$	$\Delta H_f°(CH_3)_3SiH > -40 \pm 2$ kcal/mol

and it is a major product ion in methane chemical ionization of tetramethylsilane, the process presumably involving CH_3^- transfer.[10] Bowie and co-workers have reported[11] on the reactions of the trimethylsilyl cation with alcohols, ketones, carboxylic acids, and esters. No thermochemical data were derived in any of the above referenced studies. Hehre and co-workers[12] used the $(CH_3)_3Si^+$ ion in ion cyclotron resonance proton-transfer experiments which determined the heat of formation of 1,1-dimethylsilaethylene. They employed the 1975 value given in Table II of 160.4 kcal/mol for $\Delta H_f°[(CH_3)_3Si^+]$ in their calculations. A recent paper by Lampe and co-workers[13a] reporting reactions of methyl cations with methylsilanes contains in its Figure 1 a prediction that hydride transfer from $(CH_3)_3SiH$ to $(CH_3)_3C^+$ should be ca. 21 kcal/mol exothermic. However, an earlier study[6a] from the same laboratory had estimated that the reaction was 8 kcal/mol exothermic.[13b]

Because of the thermochemical uncertainties still surrounding $(CH_3)_3C^+$ and $(CH_3)_3Si^+$, we have employed ion cyclotron resonance mass spectrometric techniques to study directly the relative stability of the trimethylsilyl cation compared to that of several alkyl cations including the *tert*-butyl ion. Both chloride- and hydride-transfer reactions between these ions were investigated. We report here the results of this study which include an upper and lower limit to the heat of formation value for the $(CH_3)_3Si^+$ ion and the first direct evaluation of the relative stabilities of the $(CH_3)_3M^+$ ions (M = Si or C). A chloride-transfer reaction between $(CH_3)_3SiCl$ and $(CH_3)_2SiCl^+$ which generates the trimethylsilyl cation is also reported, as are results of a qualitative laser photodissociation experiment involving $C_3H_9SiCl^+$ ions from two different neutral precursors.

Experimental Section

All ICR experiments were carried out on a pulsed ICR mass spectrometer constructed at the University of Florida. Descriptions of the pulsed ICR technique in general[14] and our application of it[15] have been published. Double-resonance experiments were performed by setting the frequency of a radio frequency oscillator (ω_2) equal to that calculated for a suspected parent ion in some ion–molecule reaction. The oscillation level and the duration of the ω_2 pulse were set so that the ion in question would absorb sufficient energy (thus increasing its cyclotron radius) to cause it to strike the upper or lower plate of the ICR cell, thus completely removing it from the cell. Since there was no indication that any of the reactions studied was near equilibrium, if a substantial

Table IV. Thermochemical Values Used To Establish Conclusions in Table III

	species	$\Delta H_f°$/kcal/mol	ref
A. ions	$C_2H_5^+$	219.2 ± 1.1	a
	$i\text{-}C_3H_7^+$	187.3 ± 1.1	a
	$s\text{-}C_4H_9^+$	176.7 ± 2.9	b
	$t\text{-}C_4H_9^+$	162.9 ± 1.2	a
	$(CH_3)_3Si^+$	154.8	c
B. neutrals	C_2H_5Cl	-26.1 ± 0.4	d
	$i\text{-}C_3H_7Cl$	-33.6 ± 1.0	d
	$s\text{-}C_4H_9Cl$	-38.6 ± 2.0	d
	$(CH_3)_3SiCl$	-79.4	e
	$(CH_3)_3CH$	-32.15	f

[a] Reference 21. [b] Lias, S., Ausloos, P. *J. Am. Chem. Soc.*, in press. [c] Reference 19. [d] Cox, J. D.; Pilcher, G. 'Thermochemistry of Organic and Organometallic Compounds'; Academic Press: New York, 1970. [e] Quane, D. *J. Phys. Chem.* 1971, *75*, 2480. [f] Rossini, F. D.; Pitzer, K. S.; Arnett, R. L.; Braun, R. M.; Pimentel, G. C., 'Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds'; American Petroleum Institute Research, Project 44, Pittsburgh, 1953; Table 1 p, Paraffins C_1 to C_5, p 466.

decrease in the product of an ion–molecule reaction was observed when a particular reactant ion was ejected, this was taken as indication that the reaction in question was exoergic.

For the one series of qualitative photodissociation experiments carried out, a pulsed dye laser was used to irradiate $C_3H_9SiCl^+$ ions from two different C_3H_9SiCl species 50 ms after ion formation. Experimental methodology was quite similar to that reported in our previous photodissociation studies.[16]

Chlorotrimethylsilane (PCR Research Chemicals, Inc.), $s\text{-}C_4H_9Cl$, and $i\text{-}C_3H_7Cl$ (both Chem. Services) were obtained commercially and purified by fractional distillation. Methane, isobutane, 2,2-dimethylpropane (all from Matheson), and $t\text{-}C_4H_9Cl$ (Chem. Services) were used directly as obtained commercially after freeze–pump–thaw purification on the ICR mass spectrometer inlet vacuum system. Routine mass spectrometric analysis using the ICR mass spectrometer revealed no detectable impurities. (Chloromethyl)dimethylsilane, $ClCH_2(CH_3)_2SiH$,[17] was prepared by lithium aluminum hydride reduction of (chloromethyl)dimethylchlorosilane (Petrarch Systems, Inc.) in diglyme. The distilled product was further purified by freeze–pump–thaw cycles on the ICR mass spectrometer inlet vacuum system.

Results

A. Chloride- and Hydride-Transfer Experiments.

Table III gives the chloride- and hydride-transfer reactions involving the trimethylsilyl cation, $(CH_3)_3SiCl$, $(CH_3)_3SiH$, and various alkyl halides and alkyl ions which were studied in this work. All observed reactions were confirmed by ion cyclotron double-resonance ejection, as detailed in the Experimental Section. Thermochemical values used to obtain the "thermochemical conclusions" in Table III are given in Table IV. Uncertainties in the "thermochemical conclusions" in Table III were obtained by propagation

(10) Klevan, L.; Munson, B. *Int. J. Mass Spectrom. Ion Phys.* 1974, *13*, 261.

(11) (a) Blair, I. A.; Phillipou, G.; Bowie, J. H. *Aust. J. Chem.* 1979, *32*, 59. (b) Blair, I. A.; Bowie, J. H. *Ibid.* 1979, *32*, 1389.

(12) Pietro, W. J.; Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* 1979, *101*, 7126.

(13) (a) Goodloe, G. W.; Austin, E. R.; Lampe, F. W. *J. Am. Chem. Soc.* 1979, *101*, 3472. (b) The lower number has apparently been reconfirmed in a recent study employing a tandem mass spectrometer; see: Goodloe, G. W.; Lampe, F. W. *J. Am. Chem. Soc.* 1979, *101*, 6028.

(14) McIver, R. T., Jr. *Rev. Sci. Instrum.* 1978, *49*, 111.

(15) Dugan, R. J.; Morgenthaler, L. N.; Daubach, R. O.; Eyler, J. R. *Rev. Sci. Instrum.* 1979, *50*, 691.

(16) (a) Eyler, J. R. *J. Am. Chem. Soc.* 1976, *98*, 6831. (b) Morgenthaler, L. N.; Eyler, J. R. *J. Chem. Phys.* 1979, *71*, 1486. (c) *Ibid.*, in press.

(17) Seyferth, D.; Rochow, E. G. *J. Am. Chem. Soc.* 1955, *77*, 907; Kaesz, H. D.; Stone, F. G. A. *J. Chem. Soc.* 1957, 1433.

of the uncertainties in Table IV, with an assumed error of ±3 kcal/mol for $\Delta H_f°[(CH_3)_3SiCl]$, even though none was specifically given in the original reference.

Because $C_2H_5^+$ in C_2H_5Cl is highly reactive with the parent neutral, the $C_2H_5^+$ used in reaction A.3 in Table III was obtained in an excess of methane (ca. 9×10^{-6} torr of CH_4, 5×10^{-7} torr of $(CH_3)_3SiCl$) by the ion–molecule reaction $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$. Neopentane (2,2-dimethylpropane) was used to generate the *tert*-butyl cations in reaction B.2 of Table III, because much higher intensities of these ions could be obtained than with 2-methylpropane.

B. Photodissociation Studies. $C_3H_9SiCl^+$ ions formed from $(CH_3)_3SiCl$ and $ClCH_2(CH_3)_2SiH$ were irradiated by light of wavelength 540 nm from a flashlamp-pumped dye laser 50 ms after the beginning of their formation by electron-impact ionization. Significant photodisapperance of the parent ions formed in $(CH_3)_3SiCl$ was seen. This is presumably due to the process $(CH_3)_3SiCl^+ + h\nu \rightarrow (CH_3)_3Si^+ + Cl\cdot$, which can be calculated[18] to be only 33 kcal/mol endothermic. Since photons of wavelength 540 nm have an energy of 53 kcal/mol, more than sufficient photon energy is present to induce this dissociation. No effect was seen at the same wavelength when the $C_3H_9SiCl^+$ ion was formed from $ClCH_2(CH_3)_2SiH$ indicating that ionization occurred without internal rearrangement to $(CH_3)_3SiCl^+$. Of perhaps more importance these experiments are supportive of the heretofore assumed structure of the ion derived by loss of $Cl\cdot$ from $(CH_3)_3SiCl^+$.

Discussion

From the chloride-transfer bracketing experiments given in Table III, an estimate of the heat of formation of the trimethylsilyl cation, $\Delta H_f°[(CH_3)_3Si^+] = 154 \pm 14$ kcal/mol (644 ± 59 kJ/mol), can be obtained. This agrees quite well with the most recent value of 154.8 kcal/mol obtained by Murphy and Beauchamp;[19] the value of 160.4 kcal/mol given by Potzinger, Ritter, and Krause[7b] is also contained within our (rather large) limits of error. However, the earlier values of 171 ± 2 kcal/mol reported by Potzinger and Lampe[6b] and the 176 ± 3 kcal/mol average of a number of previous workers' values reported by Gaidis, Briggs, and Shannon[20] do not agree with our results.

In addition to providing direct confirmation of the greater stability of $(CH_3)_3Si^+$ relative to $(CH_3)_3C^+$, at least with respect to hydride transfer, reactions B.1 and B.2 in Table III also permit calculation of $\Delta H_f°[(CH_3)_3SiH]$. Because our hydride-transfer results are consistent with the most recent $\Delta H_f°$ values for $(CH_3)_3Si^+$ and $(CH_3)_3C^+$ obtained by photoionization methods,[19,21] we use those values to obtain a lower limit for $\Delta H_f°[(CH_3)_3SiH]$ of -40 ± 2 kcal/mol (-167 ± 8 kJ/mol). This value permits no decision to be made between values of -18.1 ± 5 kcal/mol given by Potzinger and Lampe,[6b] -29.6 kcal/mol given by Potzinger, Ritter, and Krause[7b] and -42 kcal/mol[6a] but is at variance with the earlier value of -60 kcal/mol.[22]

The thermochemical conclusions drawn from reaction A.4 in Table III assume that the s-$C_4H_9^+$ ion formed from chloride transfer to the trimethylsilyl cation does not rearrange to the more stable t-C_4H_9 ion or that if it does, the energy of rearrangement does not influence the overall thermochemistry of the reaction. If this were not the case, the lower limit derived for $\Delta H_f°[Si(CH_3)_3^+]$ from reaction A.4 would be approximately 15 kcal/mol lower. This is not an important point, however, since reaction A.2 in Table III is actually used to obtain a lower limit for $\Delta H_f°[Si(CH_3)_3^+]$. In this case, the i-$C_3H_7^+$ formed is known to be the most stable form of the ion.[23]

Since reactions B.1 and B.2 in Table III are appropriately considered as direct hydride-transfer reactions,[7c,13] the relative stabilities of ions $[(CH_3)_3M]^+$ (M = C or Si) with H^- as the reference base are given by their calculated heterolytic bond dissociation energies (hydride affinities) $D[R_3M^+ - H^-]$ where

$$D[R_3M^+ - H^-] = \Delta H_f°[R_3M^+] + \Delta H_f°[H^-] - \Delta H_f°[R_3MH]$$

Using the known[24] value $\Delta H_f°[H^-] = 34.7$ kcal/mol together with the appropriate values in Table IV affords $D[(CH_3)_3C^+ - H^-] = 230$ kcal/mol.[21] The analogous calculation for the silylenium ion is complicated by the uncertainty in the value for $\Delta H_f°[(CH_3)_3SiH]$ as discussed above; however, if the currently acceptable values of -18.1[6b] and -29.6[7b] kcal/mol are used, values of 208 and 219 kcal/mol are obtained for $D[(CH_3)_3Si^+ - H^-]$. Thus we conclude that $(CH_3)_3Si^+$ is 10–20 kcal/mol more stable than $(CH_3)_3C^+$ when hydride is the reference base. In contrast Murphy and Beauchamp[19] have recently established the ion stability order $(CH_3)_3Si^+ < (CH_3)_2FC^+ < (CH_3)_3C^+$ for F^- as the reference base. As these authors correctly point out "... the differences in heterolytic bond dissociation energies reflect directly differences in C–F and Si–F homolytic bond dissociation energies".[19] For the $(CH_3)_3Si^+$ ion the calculated fluoride affinity is 37.5 kcal/mol higher than for the analogous carbenium ion which may explain Olah's failure to detect unambiguously the former ion from treatment of $(CH_3)_3SiF$ with SbF_5 in SO_2ClF at -50 to -80 °C.[25]

Reference to the Olah work in superacid media prompts us to reopen, hesitatingly, the still unresolved question of the possible existence of silylenium ions in solution. Without detailing the claims and counterclaims it is generally recognized that there is no firm evidence for existence of R_3Si^+ ions in solution.[26] Despite this and the well-known tendency of silicon toward coordinative expansion there does not appear to be any logical reason to exclude $[Si^{III}]^+$ ions from possible existence in solution. Indeed if one were to ignore counterion solvation and nucleophilicity for the moment, then two limiting cases for the solvation (eq 1) of gaseous R_3Si^+ can be recognized depending on the nucleophilicity of the solvent (S)

$$R_3Si^+(g) + 2S \xrightarrow{S} [R_3Si\cdot S_2]^+(s) \qquad (1)$$

For solvents of reasonable nucleophilicity such as R_3N,

(18) Calculated by using $\Delta H_f°[(CH_3)_3SiCl^+] = 151$ kcal/mol,[7b] $\Delta H_f°[(CH_3)_3Si^+] = 155$ kcal/mol,[19] and $\Delta H_f°[Cl\cdot] = 29$ kcal/mol (from Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H. NBS Tech. Note (U. S.) 1968 No. 270–3. The alternative loss of $CH_3\cdot$ from $(CH_3)_3SiCl^+$ is clearly a more endothermic process based on the higher heats of formation of $CH_3\cdot$ (34 kcal/mol) and $(CH_3)_2SiCl^+$ (qualitative estimate from reaction A.1 in Table III).

(19) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 2085.

(20) Gaidis, J. M.; Briggs, P. R.; Shannon, T. W. *J. Phys. Chem.* **1971**, *75*, 974.

(21) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067.

(22) Tannebaum, S. *J. Am. Chem. Soc.* **1954**, *76*, 1027.

(23) All thermochemical conclusions assume that highly excited ions were not involved in the reactions studied, although no specific proof that this was indeed the case can be given. In view of the relatively large error limits quoted, presence of ca. 5–7 kcal/mol excess energy would not affect the conclusions drawn here.

(24) JANAF Thermochemical Tables. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1971**, *NSRDS-NBS 37*.

(25) Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 4942.

(26) For earlier reviews of this subject see: (a) Curriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1. (b) O'Brien, D. H.; Hairston, T. J. *Organomet. Rev. A* **1971**, *7*, 95.

R_2S, and R_2O, pentacoordinate siliconium ions of the type I are expected and have literature precedence.[26a] On the


I   II
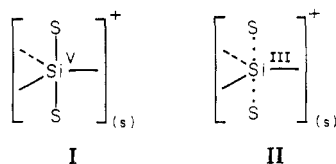
other hand, solvents of limited nucleophilicity such as CH_2Cl_2, benzene, trifluoroethanol, FSO_3H, etc. could well promote trigonal hybridization of silicon to give II or some less idealized version of a solvated $[Si^{III}]^+$ ion. Of course for a given solvent the nucleophilicity of the medium, including counterion, would be the dominant factor determining the lifetime of either ionic species I or II. Given these factors, conditions favoring the formation of silylenium ions II, if only as reactive intermediates, should exist. Tentative and as yet unrefuted evidence supporting this viewpoint has been recently published.[27,28] The most recent of these reports[28] describes a study of the solvolytic behavior of (tris(trimethylsilyl)methyl)dimethylsilyl perchlorate, $(Me_3Si)_3CSiMe_2OClO_3$.[29]

Organosilicon perchlorates offer perhaps the greatest promise as precursors of silylenium ions in solution because of the low nucleophilicity and high solvation energy of the perchlorate ion. Barton and Tully's reinvestigation of the

synthesis and utility of silyl perchlorates as silylating agents[30,31] has stimulated recent interest in these substrates. As a group silyl perchlorates show greatly enhanced reactivity toward hydroxyl groups as compared with the analogous silyl halides.[30] Pertinent to this discussion is the highly hindered silylating agent tri-*tert*-butylsilyl perchlorate, $(t\text{-Bu})_3SiOClO_3$, which reacts almost instantaneously with water in acetonitrile whereas under the same conditions the corresponding iodide, $(t\text{-Bu})_3SiI$, fails to react even at 75 °C.[30] This is a striking result even considering the relative leaving group abilities of iodide and perchlorate and is reminiscent of the reactivity difference between a covalent halocarbon and the corresponding carbenium perchlorate. Although Barton has presented[5] convincing NMR evidence for the essential covalency of $(t\text{-Bu})_3SiOClO_3$ in acetonitrile solution, there is no evidence to preclude kinetically significant generation of the silylenium perchlorate ion pair which reacts according to eq 2 where $k_2 > k_{-1}$ (or $k_2 < k_{-1}$). Eaborn and co-workers[28] have in fact obtained kinetic evidence for just such a pathway (typical S_N1) in the methanolysis of the hindered perchlorate $(Me_3Si)_3CSiMe_2OClO_3$.[29] Further investigation of organosilicon perchlorates and related derivatives is clearly warranted.

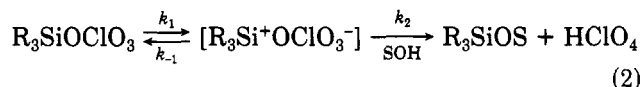(27) Chojnowski, J.; Wilczek, L.; Fortuniate, W. *J. Orgnaomet. Chem.* **1977**, *135*, 13.

(28) Dua, S. S.; Eaborn, C.; Mahmoud, F. M. S. *J. Organomet. Chem.* **1980**, *192*, 293.

(29) Eaborn and co-workers[28] suggest rate-determining ionization of $(Me_3Si)_3CSiMe_2OClO_3$ to give the methyl-bridged ion i (R = Me); however, the available evidence is equally consistent with the trivalent ion ii (R = Me). The previously observed rearrangement of $(Me_3Si)_3CSiR_2X$

i   ii
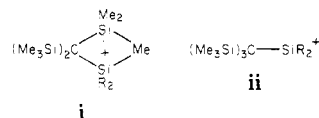
substrates to $(Me_3Si)_2C(SiR_2Me)SiMe_2Y$ by a formal 1,3-methyl shift (see literature citations in ref 28) may be considered analogous to intermolecular methide transfers from silicon in the gas phase. In fact the ease and extent of methide transfer relative to hydride transfer prompted Lampe to suggest that they may have mechanistic significance in the solution chemistry of organosilanes. It is conceivable then that ion ii and its rearranged ion $(Me_3Si)_2C(SiR_2Me)SiMe_2^+$ are interconverted via a transition state similar to i.

$$R_3SiOClO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [R_3Si^+OClO_3^-] \xrightarrow[SOH]{k_2} R_3SiOS + HClO_4$$

$$(2)$$

In conclusion, it appears that the search for silylenium ions in solution will continue, spurred by the evolving gas-phase chemistry of these species and the development of new organosilicon materials of mechanistic utility.

(30) Barton, T. J.; Tully, C. R. *J. Org. Chem.* **1978**, *43*, 3649.

(31) Barton, T. J.; Tully, C. R. *J. Organomet. Chem.* **1979**, *172*, 11.