# Dalton Perspectives

## Do $R_3Si^+$ Ions exist in Solution?

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The proximity of silicon to carbon in the same group of the Periodic Table has led to many comparative studies of the chemistry of the two elements, and although there are similarities between them there are also many differences. For example, it was only relatively recently that compounds containing multiple bonds to silicon were prepared and the properties of long-chain polysilanes investigated [see refs. 1(*a*) and (1*b*) for recent reviews of these topics]. A third potential parallel that has been sought between the two elements for many years involves the possible existence of $R_3Si^+$ ions in salts or as intermediates in reactions, analogous to the well studied $R_3C^+$ ions in organic chemistry.

The respective electronegativities of carbon and silicon are 1.8 and 2.5 (Pauling scale) which would suggest that formation of $R_3Si^+$ ions by heterolytic cleavage of $Si^{\delta+}$–$X^{\delta-}$ bonds (X = C, halogen, *etc.*) should be easier than the corresponding formation of analogous $R_3C^+$ species. This is indeed the case in the gas phase where $R_3Si^+$ ions are abundant in mass spectra and the appearance potentials for $R_3Si^+$ are lower than for $R_3C^+$ ions. The question of formation of $R_3Si^+$ species in solution has, however, been a subject of much debate and remains probably the most controversial subject in organosilicon chemistry.

Early attempts to generate $R_3Si^+$ species concentrated on methods of preparation and identification that had been successful in organic chemistry. For example, much work has been carried out to determine whether $Ph_3SiX$ compounds (X = halogen or OH) will give conducting solutions in suitable solvents such as pyridine or liquid $SO_2$ similar to those found for $Ph_3CX$ analogues. Attempts to use 'super-acid' media such as $FSO_3H$–$SbF_5$–$SO_2$ to prepare $R_3Si^+$ cations have also been made and numerous reactions in which $R_3Si^+$ ions might be expected as intermediates have been investigated. These many unsuccessful attempts and the possible reasons for the reluctance of silicon to form $R_3Si^+$ ions in solution have been reviewed and discussed.[2,3] This article will concentrate on evidence presented in the last 5 years both for and against ionization of silyl perchlorates in solution together with experimental observations and results of calculations which suggest that in some circumstances the formation of $R_3Si^+$ species as short-lived intermediates in solution provides the best interpretation of the available information.

The naming of $R_3Si^+$ species has also been the subject of some discussion, the names siliconium, silicenium, silylenium, silyl cation and silico cation having all been used. The current recommendation from IUPAC[4] is for use of the term silylium, and although this has not yet been commonly adopted it will be used here since all of the other names mentioned suffer from some ambiguity.

### Salts

Perhaps the greatest controversy in organosilicon chemistry in recent years has centred around the work of Lambert and his group who have presented results that they attribute to ionization of simple silyl perchlorates such as $(Pr^iS)_3SiOClO_3$ and $Ph_3SiOClO_3$ in solvents such as $CH_2Cl_2$ and sulfolane (tetrahydrothiophene 1,1-dioxide), to give $R_3Si^+$ and $ClO_4^-$ ions. The first question a newcomer to this type of chemistry is likely to ask is 'Why hasn't the ionzation of such simple compounds been discovered before?' In the case of the sulfur-containing compounds the answer is probably that nobody has previously looked for it, but for $Ph_3SiOClO_3$ and $Me_3SiOClO_3$ the answer is more complicated.

Early attempts to demonstrate an ionic nature for $Ph_3SiOClO_3$ by chemical trapping experiments suggested that the compound was in fact a covalent ester.[5] Lambert and Sun[6] also concluded on the basis of NMR spectroscopy and conductance measurements that $Ph_3SiOClO_3$ (and several other silyl perchlorates) had a covalent structure or formed a tight ion pair, and that free silylium ions were not present in solutions of such compounds. Unfortunately, they did not report the concentration of the perchlorate solutions used for the conductance studies, and these may well have been above the very low concentrations at which $Ph_3SiOClO_3$ has more recently been reported to give conducting solutions.[7] The solid-state structure of $Ph_3SiOClO_3$ has clearly been shown to be covalent by X-ray crystallography, although this cannot be used to argue in favour of a covalent structure in solution.[8]

Lambert's work relies on the generation of silyl perchlorates by the reaction between an $R_3SiH$ compound and trityl perchlorate and investigation of the resulting solutions by various techniques to try and detect ionic species. The preparative method, which is based on the work of Corey,[9] avoids the presence of halide ions. The reaction proceeds in solvents such as $CH_2Cl_2$ or sulfolane according to equation (1) (R = Me, Ph, EtS or $Pr^iS$).

$$R_3SiH + Ph_3C^+ClO_4^- \longrightarrow R_3Si^+ClO_4^- \text{ or } R_3SiOClO_3 + Ph_3CH \quad (1)$$

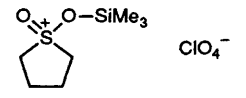
The main techniques used to investigate the structures of the silyl perchlorates in solution have been conductance measurements, molecular weight determinations and multinuclear NMR spectroscopy. Lambert *et al.*[7] reported that dilute solutions (*e.g.* 0.01 mol $dm^{-3}$) of the perchlorates, particularly in sulfolane, are conducting, that molecular weight determinations indicate that two-particle (*i.e.* ionic) species are formed, and that the $^{35}Cl$ NMR spectrum indicates that the $ClO_4^-$ ion is present in solution. Olah and his group[10] have argued that these results are not due to ionization of the silyl perchlorates but to hydrolysis of the perchlorates by residual water in 'dry' solvents to give perchloric acid, as shown in equation (2). A closer examination of the data derived from each of the techniques used is given below.

$$R_3SiOClO_3 + H_2O \longrightarrow R_3SiOH + HClO_4 \xrightarrow{R_3SiOClO_3} R_3SiOSiR_3 + HClO_4 \quad (2)$$

*Conductance Measurements.*—Perhaps the most obvious means of discovering whether a compound is ionized in solution is to measure the conductance of the solution. Lambert has carried out numerous conductance measurements mainly in dichloromethane, sulfolane and acetonitrile. At a concentration of 0.01 mol dm$^{-3}$, $Me_3SiOClO_3$, $PhMe_2SiOClO_3$, and $Ph_3SiOClO_3$ were all found to give conducting solutions in sulfolane and acetonitrile but not in $CH_2Cl_2$,[7] while $(Pr^iS)_3SiOClO_3$ gave conducting solutions in $CH_2Cl_2$.[11] For comparison the conductivity of $Me_3SiN_3$ in $CH_2Cl_2$, MeCN and sulfolane was found to be negligible, and that of $Me_3SiOSO_2CF_3$ was found to be very low in $CH_2Cl_2$ but high in sulfolane and MeCN. However, the triflate $Me_3SiOSO_2CF_3$ and MeCN have been reported[12] to react rapidly in the presence of $Et_3N$ to give $(Me_3Si)_3CCN$, $(Me_3Si)_2C{=}C{=}NSiMe_3$, and, presumably, 3 equivalents of $CF_3SO_3H$ (which would probably form the salt $[Et_3NH]^+[CF_3SO_3]^-$ with $Et_3N$), and so the silyl triflate should be recovered from the conducting solutions in order to discover whether a reaction has occurred. It is possible that the conductivity of the $Me_3SiOSO_2CF_3$ solution in sulfolane is also due to a similarly silylated product. Olah and co-workers[8,10] have argued that the conductance of such dilute solutions of silyl perchlorates arises not from ionization of the compounds but from the $HClO_4$ formed by hydrolysis of such compounds by residual water in the 'dry' solvents used. Lambert has countered this argument for the case of $CH_2Cl_2$ solutions by carrying out a control experiment in which the conductivity of $CH_2Cl_2$ to which a 70% aqueous solution of $HClO_4$ had been added was found to be negligible.[13] This experiment does not, however, seem to reproduce closely the anhydrous and low-concentration conditions under which $HClO_4$ would be present if formed by hydrolysis of the silyl perchlorate and so may not be used as a sound basis for arguing against $HClO_4$ being the conducting species in the silyl perchlorate solutions.

Proton NMR studies have been carried out to determine the concentration of water present in $CH_2Cl_2$ and sulfolane by measuring the amount of $Me_3SiOSiMe_3$ formed by hydrolysis in $Me_3SiOClO_3$ solutions.[7] For 0.01 mol dm$^{-3}$ solutions about 9% of the silyl perchlorate is hydrolysed in $CH_2Cl_2$ and 'up to 50% of a 0.01 mol dm$^{-3}$ solution would be hydrolysed' for the case of sulfolane.[7] Clearly hydrolysis is a problem at these concentrations, particularly in sulfolane, and despite Lambert's experiment with $CH_2Cl_2$–70% aqueous $HClO_4$ it seems quite possible that the conductivity measured is that of $HClO_4$ and not ionized $Me_3SiOClO_3$. The water concentrations found in sulfolane for $Me_3SiOClO_3$ concentrations of 0.0070, 0.0080 and 0.050 mol dm$^{-3}$ are reported as 0.0020, 0.0019 and 0.0034 mol dm$^{-3}$.[7] No explanation was advanced for the fact that the water concentration varied so much just by adding different amounts of $Me_3SiOClO_3$ to the solvent, but since there was no account of how the $Ph_3CClO_4$ and $Me_3SiH$ used were purified and dried, differing amounts of water may well be added to the solvent when the silyl perchlorate solutions are made up. The concentration of water in the MeCN used has not been reported and so the degree of hydrolysis is not known in this solvent.

*Molecular-weight Determinations.*—Molecular weights have been determined for silyl perchlorates $R_3SiOClO_3$ (R = $Pr^iS$, Me or Ph) and $PhMe_2SiOClO_3$ in sulfolane by the depression of freezing point method. This technique uses a calculation that requires an assignment of the number $\nu$ of particles present in the solute, *i.e.* $\nu = 1$ for a covalent perchlorate and $\nu = 2$ for an ionic species. In the case of 0.33 mol dm$^{-3}$ $(Pr^iS)_3SiOClO_3$ the molecular-weight calculation indicated an ionic system with an error of 6.8%, whereas a similar calculation for a covalent compound would have given a 46.7% error.[13] The ionic species could also in principle have been the silyl ether **1**, which would give a 6.9% error, but this was ruled out by the $^1H$ NMR data.[13] Again isolation and identification of the silicon-containing product would be useful.



**1**

For $Ph_3SiOClO_3$[13] and $Me_3SiOClO_3$ and $PhMe_2SiOClO_3$[7] in sulfolane the ionic model calculations give errors of 6, 1.8 and 3.1% respectively, again supporting the ionic, two-particle structure; it is not clear from the reports exactly what were the molarities of the solutions used. For comparison with these results, analogous solutions of azides and triflates such as $Me_3SiN_3$ and $Ph_3SiOSO_2CF_3$ were also studied, and gave experimental data close to those expected for single-particle, covalent species. A complication in the measurements involving the silyl perchlorates is that an equivalent of $Ph_3CH$ is always present in solution with the silicon compound. In an attempt to model this situation the molecular weights of $Ph_3CH$, $Ph_3CClO_4$, and a 1:1 mixture of $Ph_3CH$ and $Ph_3CClO_4$ were also calculated. As expected $Ph_3CH$ was found to be a single-particle covalent species and $Ph_3CClO_4$ a two-particle ionic species. Surprisingly the mixture of $Ph_3CH$ and $Ph_3CClO_4$, which would seem to be a three-particle system, gave only a 7.1% error for a two-particle calculation of the molecular weights of $Ph_3COClO_3$.[13]

The molecular-weight determination experiments are subject to the same criticisms as the conductivity measurements, namely that the data are obtained for partially hydrolysed mixtures. In solutions of the silyl perchlorates in sulfolane between 0.02 and 0.05 mol dm$^{-3}$ the percentage hydrolysis is about 10–20% (assuming a water concentration of 0.0024 mol dm$^{-3}$). This means that in the solution on which a molecular-weight determination is being carried out not only is the silyl perchlorate present but also an equivalent of $Ph_3CH$ and 5–10% of $Me_3SiOSiMe_3$ and 10–20% of $HClO_4$. The matter is further complicated by Lambert's proposal that there is an equilibrium between the covalent and the ionic species and at the concentrations used for the molecular-weight determinations only about 45–65% of free ions are likely to be present.[14] It seems remarkable that for such mixtures accurate data supporting an ionic model for the silyl perchlorate could be obtained, but it also seems surprising that so many results of such apparent accuracy could be obtained by chance. More model studies using mixtures of known composition and molecular weight are necessary to see if this method can be used with confidence in this system.

*NMR Studies.*—Of the six possible NMR-active nuclei that could easily be studied in silyl perchlorates ($^1H$, $^{13}C$, $^{17}O$, $^{29}Si$ and $^{35/37}Cl$) all except $^{17}O$ have been used. An extensive table of $^1H$ and $^{13}C$ chemical shifts for solutions of $Me_3SiOClO_3$, $MePh_2SiOClO_3$ and $Me_2PhSiOClO_3$ in sulfolane containing 10% of $CD_2Cl_2$ has been presented[7] as well as $^{13}C$ data for $Ph_3SiOClO_3$ in $CD_2Cl_2$.[13] None of the data proves the existence of silylium ions in solution although the data for $Ph_3SiOClO_3$ when compared with those for $Ph_3CClO_4$ may be seen as consistent with an ionic system. The $^1H$ and $^{13}C$ chemical shift data for $Me_3SiOClO_3$, $MePh_2SiOClO_3$ and $Me_2PhSiOClO_3$ change by a stepwise but small amount of *ca.* 0.1 and 0.2 ppm for $^1H$ and $^{13}C$ nuclei respectively, on going from solutions of concentration 0.27 to 0.009 mol dm$^{-3}$ for $^1H$ and to 0.01 mol dm$^{-3}$ for $^{13}C$.[7] Again, such chemical shift changes may be due to increasing concentrations of an ionic species on dilution, but they could also readily be attributed to dilution effects.

More useful nuclei for investigating these systems are $^{29}Si$ and $^{35/37}Cl$. The $^{29}Si$ chemical shifts for $Me_3Si^+$ and $Ph_3Si^+$ have been predicted, by use of correlations with carbon analogues, to be $\delta$ 250 ± 25 and 125 ± 25 respectively.[15] Chemical shifts using the individual gauge for different local-

**Table 1** Free-ion content and percentage of hydrolysis in sulfolane solutions of silyl perchlorates

| Concentration/ mol dm$^{-3}$ | % Free ion from $^{35}$Cl NMR studies[a] | % Hydrolysis[b] |
|---|---|---|
| $Me_3SiOClO_3$ | | |
| 0.584 | $20 \pm 5$ | 0.5–1 |
| 0.036 | $52 \pm 12$ | 10.5–19 |
| 0.011 8 | $77 \pm 10$ | 32–58 |
| 0.004 7 | $98 \pm 1$ | 81–145 |
| $Ph_3SiOClO_3$ | | |
| 0.029 2 | $51 \pm 17$ | 13–23 |
| 0.009 6 | $74 \pm 11$ | 39.5–71 |
| 0.004 90 | $98 \pm 1$ | 77.5–139 |

[a] Values are taken from ref. 14. [b] Calculated using Lambert's formula[7] $100(2b)/a$ (not $1002b/a$) where $a$ is the concentration of the silyl perchlorate and $b$ is the water concentration as measured by $^1$H NMR spectroscopy. The range given is for the extreme values of 0.0019 and 0.0034 mol dm$^{-3}$ water found in the sulfolane used.[7]

ized orbitals (IGLO) method give excellent agreement with experimentally determined chemical shifts for a range of neutral silyl derivatives (including $Me_3SiOClO_3$) and the silyl anion $H_3Si^-$, and give a calculated value of δ 355.7 for $Me_3Si^+$.[16] It is difficult to observe $^{29}$Si NMR signals for dilute solutions due to the relatively low sensitivity of the $^{29}$Si nucleus, and Lambert *et al.*[17] were unable to record a $^{29}$Si spectrum of $Ph_3SiOClO_3$. However, a 0.76 mol dm$^{-3}$ solution of $Ph_3SiOClO_3$ in $CH_2Cl_2$–MeCN (prepared by addition of $AgClO_4$ to $Ph_3SiCl$) gave a shift of δ 3.0 and a $CH_2Cl_2$ solution, apparently of *ca.* 0.25 mol dm$^{-3}$ concentration, of $Ph_3SiOClO_3$ prepared from $Ph_3SiH$ and $Ph_3CClO_4$ gave a weak $^{29}$Si signal also at about δ 3.[8] This is the chemical shift expected for a covalent species, and in line with this the $^{29}$Si NMR chemical shift for solid $Ph_3SiOClO_3$, which was shown by X-ray crystallography to be covalent, is δ 1.4, indicating that the solution and solid-state structures are the same.[8]

Unfortunately, in these solvents conductivity measurements have also indicated covalency for $Ph_3SiOClO_3$[7] and so these NMR spectroscopic experiments provide no useful data on systems that are reported to contain ionic species. No useful $^{29}$Si NMR data have been obtained for $(Pr^iS)_3SiOClO_3$.[12] Lambert *et al.*[7] reported the $^{29}$Si NMR chemical shift for $Me_3SiOClO_3$ to be δ 44.0 in $CH_2Cl_2$ and 46.5 in sulfolane (concentrations not reported). A shift of 'about δ 47' for $Me_3SiOClO_3$ was also said not to change down to about 0.1 mol dm$^{-3}$, but the solvent in which these spectra were recorded was not reported.[7] It should, however, be possible to obtain $^{29}$Si NMR data on dilute solutions by using samples containing silicon enriched in $^{29}$Si and by using pulse sequences such as insensitive nuclei enhanced by polarization transfer (INEPT) to overcome the problems of the low abundance and long relaxation times of the $^{29}$Si nucleus.

Olah *et al.*[10] reported that the $^{29}$Si NMR chemical shift of neat $Me_3SiOClO_3$ is δ 47 and that for 0.584, 0.29 and 0.15 mol dm$^{-3}$ solutions in sulfolane the shift remains unaltered clearly indicating covalency over this concentration range. Lambert and Schilf[14] also concluded from $^{35}$Cl data at these three concentrations that there are $20 \pm 5$, $29 \pm 5$ and $35 \pm 7$% respectively, free ions. These results seem to contradict each other, and so the $^{35}$Cl NMR data will be considered in more detail. Both the $^{35}$Cl and $^{37}$Cl nuclei have a spin of $\frac{3}{2}$ and have large quadrupole moments which means that for covalently bonded chlorine the NMR signals are very broad (hundreds or thousands of Hz) while symmetrical, ionic species such as $Cl^-$ and $ClO_4^-$ have much narrower signals. The $^{35}$Cl NMR spectrum for $Me_3SiOClO_3$ has a single chemical shift at δ −28 with a width at half height of 1960 Hz for a 0.584 mol dm$^{-3}$ solution in sulfolane. As the concentration is lowered the chemical shift moves to low field and the linewidth decreases reaching values of δ 4.4 and 24 Hz at 0.0047 mol dm$^{-3}$ concentration.[14] Lambert has interpreted these results as due to a rapid (on the NMR time-scale) equilibrium [equation (3)]

$$R_3SiOClO_3 \rightleftharpoons R_3Si^+ClO_4^- \rightleftharpoons R_3Si^+ + ClO_4^- \quad (3)$$

between an associated (covalent or ion pair) species that would give a broad NMR signal and free ions that would give a narrow $^{35}$Cl NMR signal. At higher dilution the equilibria in equation (3) would lie to the right. The percentage of free ions was calculated from the chemical shifts and linewidths for both $Me_3SiOClO_3$ and $Ph_3SiOClO_3$. About 50% ionization was judged to have occurred for both compounds at approximately 0.03 mol dm$^{-3}$ concentration, and both compounds were considered to be essentially completely ionized below about 0.005 mol dm$^{-3}$.[14] It seems strange that two compounds as electronically and sterically different as $Me_3SiOClO_3$ and $Ph_3SiOClO_3$ should ionize to the same extent at approximately the same concentration, whereas if hydrolysis is occurring then both compounds would be expected to react, to the same extent, very rapidly, before NMR spectra could be recorded.

I have calculated the percentage hydrolysis for several of the concentrations at which the $^{35}$Cl NMR data were recorded to try and ascertain whether the amount of free ions present was similar to that expected from $HClO_4$ formed by hydrolysis and the results are presented in Table 1. It is clear that at high dilution there is likely to be sufficient water present to hydrolyse all of the silyl perchlorate present to give $HClO_4$. This relatively large amount of water will have been introduced by the dilution technique of removing a portion of the solution and then adding the same amount of fresh solvent. Thus if the concentration of the silyl perchlorate solution is halved then 50% more water is introduced than was in the original solution. The percentage hydrolysis calculations in Table 1 were carried out using the ideal situation of preparing a single concentration sample with only fresh solvent. The method of dilution used obviously makes the situation worse (assuming rapid reaction between water and the silyl perchlorate) by continually adding more water to the system with the fresh solvent. This could be overcome by making up each concentration sample separately using a single addition of fresh solvent. This does not solve the problem of why the percentage hydrolysis does not match the calculated free-ion concentration at the highest concentration used for each compound. Unfortunately, the concentration of water in the sulfolane used for the $^{35}$Cl NMR experiments was not determined accurately, for example, by recording the $^1$H NMR spectrum of each solution to determine the amount of $Me_3SiOSiMe_3$ present, and so it is possible that more water was present in the initial sample (introduced during manipulations in making up the original sample) than was thought. Olah *et al.*[10,16] also pointed out that if the equilibria in equation (3) are responsible for the observed chlorine NMR spectra then similar trends in chemical shift should be seen in the $^{29}$Si NMR spectra. For $Me_3SiOClO_3$ at concentrations of 0.584, 0.29 and 0.15 mol dm$^{-3}$ in sulfolane the percentage of free ions present was calculated by Lambert to be *ca.* 20, 29 and 35% respectively. Assuming the predicted $^{29}$Si chemical shift for $Me_3Si^+$ to be δ 225 (which is thought to be a lower limit)[10] and that of neat $Me_3SiOClO_3$ to be δ 47, then 20, 29 and 35% free ions would give average chemical shifts of δ 82, 99 and 109 respectively. If the more reliable chemical shift of δ 355.7 calculated by the IGLO method is taken, then the averaged chemical shifts for 20, 29 and 35% free ions are δ 108.7, 136.5 and 155.0.[16] As mentioned above the actual chemical shift over this concentration range does not change, remaining close to that of neat $Me_3SiOClO_3$, *i.e.* δ 47. These results seem clearly to be inconsistent with Lambert's observations but support the conclusion that $Me_3SiOClO_3$ is a covalent species over this concentration range. Olah *et al.*[10] accounted for these results by suggesting that the important equilibrium in the system is as in equation (4) where $ClO_4^-$ formed by hydrolysis of the silyl

$$R_3SiOClO_3 + H^+Cl^*O_4^- \rightleftharpoons R_3SiOCl^*O_3 + H^+ClO_4^- \quad (4)$$

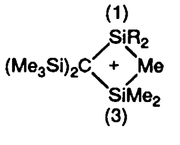
perchlorate exchanges with a covalently bound $ClO_4$ group. As the solutions are made more dilute the amount of water increases so that more hydrolysis occurs, until at <0.005 mol dm$^{-3}$ concentrations of silyl perchlorate virtually all of the compound is hydrolysed and the signal seen is that of $HClO_4$. Lambert has recorded $^{35}Cl$ NMR spectra for 70% aqueous $HClO_4$ in sulfolane at various concentrations but it is probably unwise to try and compare such data with those for $HClO_4$ formed in the relatively anhydrous conditions used in the silyl perchlorate experiments. It would thus seem that the equilibrium in equation (4) resulting from hydrolysis accounts for almost every result from both research groups, and that the presence of free $R_3Si^+$ ions is not required to explain the NMR data.

Several other techniques such as IR and UV/VIS spectroscopy as well as assessment of the degree of any complexation of a solvent molecule to an $R_3Si^+$ ion have been used to investigate silyl perchlorates.[7] There has also recently been an attempt to generate $R_3Si^+$ ions from disilanes by electrochemical methods.[18] None of these experiments provides conclusive evidence for the presence of free silylium ions; space does not permit further discussion of these results.

Eaborn[19] has recently pointed out that the sterically hindered silyl perchlorate $(Me_3Si)_3CSiMe_2OClO_3$ undergoes solvolysis in methanol relatively slowly with a half-life at 27.5 °C of about 24 min and little, if any, solvolysis in $CF_3CH_2OH$. These reactions were carried out using a *ca.* 1 mol dm$^{-3}$ solution for the methanolysis and a 0.052 mol dm$^{-3}$ solution for the trifluoroethanolysis[20] and on the basis of the percentage ionizations calculated for $Me_3SiOClO_3$ solutions of different concentrations from the $^{35}Cl$ NMR studies this trialkylsilyl perchlorate could be expected to be slightly ionized in MeOH and approximately 45% ionized in $CF_3CH_2OH$. {Although it is larger than $Me_3SiOClO_3$ the relief of steric strain on going to a trivalent $[(Me_3Si)_3C]Me_2Si^+$ ion could be expected to aid ionization.} If any ionization were to occur in $(Me_3Si)_3CSiMe_2OClO_3$ (which might be expected in such good ionizing solvents) then reaction of the silylium ion with the solvent would be extremely rapid, and the fact that no such rapid reactions are observed suggests that no silylium ions are present, although there seems no good reason why this silyl perchlorate should not ionize in the way proposed by Lambert for other perchlorates. This observation casts further doubt on Lambert's conclusion that the systems he investigated do indeed contain free $R_3Si^+$ ions.

## Reactions thought to involve $R_3Si^+$-Like Intermediates

During the last ten years Eaborn and co-workers have carried out extensive investigations into the chemistry of very bulky organosilicon compounds of the general type $(Me_3Si)_3CSiRR'X$ and $(Me_3Si)_2C(SiMe_2X)(SiRR'X)$ (R or R' = Ph, Et or Me; X = halogen, H, *etc.*).[21] It has been demonstrated that a number of the reactions of such compounds proceed *via* rearrangements involving 1,3 Si to Si migrations of a range of groups apparently in bridged silylium intermediates. For example, the reactions of $(Me_3Si)_3CSiR_2I$ with silver or mercury salts AgY or $HgY_2$ (Y = $MeCO_2$, $CF_3CO_2$, $ClO_4$, *etc.*) in solvents such as $Et_2O$ or $CH_2Cl_2$ give rearranged products $(Me_3Si)_2C(SiMe_2X)(SiPh_2Me)$ exclusively if R is large (*i.e.* phenyl) or a mixture of rearranged and unrearranged products $(Me_3Si)_3CSiR_2X$ if R is smaller, *e.g.* Et. These reactions are thought to be due to the formation of a bridged cationic intermediate **2**. An incoming nucleophile $X^-$ may attack the bridged ion at either Si(1) or Si(3) giving unrearranged or rearranged products respectively.



**2**

If the difference in size between the groups on Si(1) and Si(3) is large, *e.g.* if R = Ph, then attack occurs exclusively at the less-hindered site Si(3) to give rearranged products. If the size difference is less, *e.g.* if R = Et, then some attack occurs at Si(1) and some at Si(3).[22–24] The rearranged products in these reactions are the result of 1,3 migration by a methyl group. In extensions of this work it was discovered that a variety of other groups or atoms, such as Ph,[25] vinyl,[26] OMe,[27,28] and Cl and $N_3$,[29] could also bridge and/or migrate in cations of type **2** in these bulky compounds.

It is of interest that at one time it seemed possible that methanolysis of the compounds $(Me_3Si)_3CSiMe_2X$ (X = $OClO_3$, $OSO_2CF_3$ or I) and $(Me_3Si)_3CSiPhHI$ and $(Me_3Si)_3CSiMeHI$ (which shows puzzling kinetic features) might involve rate-determining formation of a bridged ion, but this is no longer thought to be the case.[30,31] However, solvolysis of $(Me_3Si)_3CSiEt_2I$ [and by implication $(Me_3Si)_3CSiMe_2I$] in $CF_3CO_2H$[22] and solvolyses of $(Me_3Si)_2(XC_6H_4Me_2Si)CSiMe_2I$ (X = *p*-OMe, *p*-Me, H, *p*-Cl or *m*-$CF_3$) species in $CF_3CH_2OH$ (and in some cases MeOH)[25,32] are known to involve rate-determining formation of the bridged cations. It is significant that when such compounds do ionize they give the bridged ions rather than simple $R_3Si^+$ type ions, a further illustration of the reluctance with which the latter species are formed.

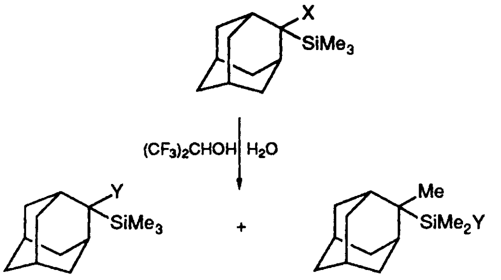
Chojnowski *et al.*[33] have investigated the reaction between various $R_3SiH$ (R = Et, Ph, $Bu^n$, *etc.*) species and trityl salts such as $Ph_3CBF_4$ and $Ph_3CSbF_6$. They concluded on the basis of steric arguments, isotope effects and other data that a single electron-transfer process [equation (5)] involving a cationic

$$R_3SiH + Ph_3C^+ \longrightarrow \underset{\text{charge-transfer complex}}{[R_3SiH^+CPh_3]} \xrightarrow{\text{r.d.s.}} [R_3Si^+HCPh_3] \longrightarrow R_3Si^+ + Ph_3CH \quad (5)$$

silicon species was occurring rather than a synchronous hydride transfer. Chojnowski *et al.* considered that if the reactions involved rate-determining formation of the $R_3Si^+$ ion then changes in the size of the R groups would have little effect. This was indeed found to be the case for R = Me, Et, $Pr^n$, $Bu^n$ and *n*-$C_6H_{13}$, but the fact that $Bu^t_3SiH$ reacted too slowly for its rate to be measured precisely might appear to invalidate their conclusions. However, Apeloig[34] has pointed out that if the attack of $Ph_3C^+$ were sideways on to the Si–H bond there could indeed be considerable steric hindrance to formation of the $R_3Si^+$ ion, and the results would be consistent with such a process. If these reactions do involve formation of $R_3Si^+$ ions then the reactions of $R_3SiH$ compounds with $AgClO_4$ probably also do so, since the only evidence against this was the lowering of the rate of reaction by bulky R groups.[19,35,36]

A further interesting observation by Chojnowski *et al.*[33] which is relevant to Lambert's work is that $(EtS)_3SiH$ reacts much more slowly with $Ph_3CSbF_6$ than does either $Me_3SiH$ or $Ph_3SiH$. These results are in agreement with calculations by Apeloig,[37] who found that Et was better than EtS in stabilizing $R_3Si^+$ ions. This is in contrast to Lambert's report[13] that $(EtS)_3SiOClO_3$ and $(Pr^iS)_3SiOClO_3$ are more extensively ionized than is $Ph_3SiOClO_3$ in $CH_2Cl_2$.

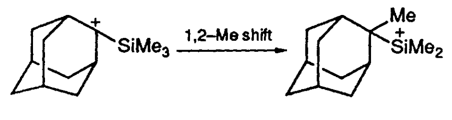
Another example of a reaction in which formation of an $R_3Si^+$ species provides the best interpretation of the results obtained is the solvolysis of adamantyl derivatives **3** in aqueous hexafluoroisopropyl alcohol, shown in equation (6).[38] The



(6)

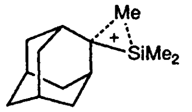
$X = Cl$ or $O_2CC_6H_4NO_2$-*p*
$Y = OH$ or $OCH(CF_3)_2$

mechanism of this reaction seems to involve a 1,2-methyl migration from a α-silyl atom in a carbon-centred cation to give a silylium ion, as shown in reaction (7), both cationic species



(7)

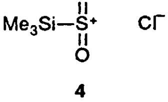
reacting with water and $(CF_3)_2CHOH$. The product ratios are best interpreted as due to the reactions of solvent-separated ion pairs, although the possibility of formation of a bridged species **3** (analogous to **2** above) which could then be attacked by water or $(CF_3)_2CHOH$ at either C or Si cannot be ruled out completely.[19,39]



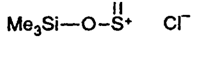
**3**

The rearrangement of the carbon- to the silicon-centred cation in reaction (7) suggests that such a trialkyl-substituted silylium ion is more stable than the carbon-centred ion. Calculations have also indicated this to be the case, with $Me_3CSiMe_2{}^+$ judged to be 40.6 kJ mol$^{-1}$ more stable than $Me_3SiCMe_2{}^+$.[37]

Fairly recently a claim was made for the 'first report of a silico cation' of $[Me_3Si^+(SO_2)]Cl^-$ as an ionic liquid. No convincing evidence was given for the formula proposed, and it is more likely that the species formed is a sulfur-centred cation such as **4** or **5**.[40]


$Me_3Si{-}\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O}{\|}}{S^+}}}\quad Cl^-$

**4**


$Me_3Si{-}O{-}\overset{\displaystyle O}{\overset{\|}{S^+}}\quad Cl^-$

**5**

## Conclusion

It can be seen from the discussion above that despite the considerable work on silyl perchlorates there is no *clear* evidence for their ionization to give $R_3Si^+$ ions in the solvents studied. Indeed it would seem that there is much evidence to suggest that such ions are not present, but that many of the results may best be accounted for by assuming hydrolysis of the perchlorates by residual water in the 'dry' solvents used. As mentioned above more conclusive data might be obtained by use of isotopically enriched $^{29}Si$ samples for NMR studies. Experiments should also be carried out with pure (isolated) silyl perchlorates, preferably with rigorous exclusion of water by use of high-vacuum techniques, in order to see if they give the same results as those obtained by use of the *in situ* method of preparation from $R_3SiH$ and $Ph_3CClO_4$. Although the evidence so far presented is far from conclusive, it remains possible that evidence will be found for ionization of polarized trioganosilanes such as perchlorates or triflates in dilute solution in suitably ionizing solvents.

Simple (as well as bridged) silylium ions are probably involved as intermediates in a few reactions and it is likely that in the next few years more such examples will be discovered.

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