

Free and Associated Trimethylsilyl Cation in Solution

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The trimethylsilyl cation (Me_3Si^+) has been prepared as an ion pair with perchlorate in CH_2Cl_2 or as the nonspecifically solvated ion in dilute sulpholane by hydride abstraction from trimethylsilane.

Trimethylsilyl attached to a good leaving group such as trifluoromethanesulphonate (triflate) has become an effective synthetic tool, primarily as a protecting group and as a catalyst. The free trimethylsilyl cation (Me_3Si^+), which is the silyl analogue of the t-butyl cation Me_3C^+ , has heretofore not

been generated in solution.¹ Trimethylsilyl is an example of a silylenium ion, previously known only as the sulphur-stabilized species tris(isopropylthio)silyl, $(\text{Pr}^i\text{S})_3\text{Si}^+$, and as the triphenyl species, Ph_3Si^+ .^{2,3} We report herein that the trimethylsilyl cation may be prepared as the ion pair with

perchlorate in polar solvents of low dielectric constant such as dichloromethane or 1,2-dichloroethane, and as the free ion in dilute solutions of non-nucleophilic solvents of high dielectric constant such as acetonitrile or sulpholane. This species gives the sharp ^{35}Cl resonance expected for an ionic perchlorate.



The trimethylsilyl cation is generated by reaction of trimethylsilane with 1 equiv. of trityl perchlorate, equation (1). The ^1H and ^{13}C spectra of the reaction products are extremely clean, indicating that only a single material is formed in solution. In dichloromethane, the molar conductance (Λ) is $0.65 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, indicative of a poorly ionic species (trityl perchlorate has a conductance of 43.5 under the same conditions). A plot of log molar conductance vs. the log concentration, however, is linear with a negative slope. An increase in molar conductance as concentration decreases is indicative of the presence of ion pairs, since lower concentrations favour dissociation. The molar conductance of $\text{Me}_3\text{SiClO}_4$ is $10.7 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in sulpholane and 175.9 in acetonitrile, the value in sulpholane being low because of its high viscosity. The much higher dielectric constants of these two solvents thus result in conversion of the ion pair into free ions. Hydrolytic titrations were carried out in both CH_2Cl_2 and sulpholane. The results confirmed that little or no hydrolysis has occurred in the original solutions.

Molecular weights were measured cryoscopically in sulpholane. The observed value of 169.8 is only 1.8% different from the theoretical value of 173.0, when two particles are assumed. Assumption of one particle, which would be the case if the material were covalent, yields an observed molecular weight of 84.9, 50.9% different from the theoretical value of 173.0. Assumption of three particles, as in a dimer in which methyl groups are bridged between two silicon ions (a doubly positively charged species requiring two perchlorate anions), gives a value of 253.8, 26.7% different from the theoretical value of 346.0. A two-particle dimer such as $(\text{Me}_3\text{SiO})_2\text{ClO}_2^+ \text{ClO}_4^-$ has a theoretical molecular weight 104% larger than that observed. Thus the molecular weight measurements are in good agreement with the two-particle, monomeric model of an ionic silyl cation in sulpholane. The molecular weight of trimethylsilyl triflate, in contrast, was found to correspond to the one-particle, covalent form under the same conditions. These results are in accord with the earlier observations that perchlorate is a poorer nucleophile towards silicon than is triflate.⁴

In dilute solutions ($<0.005 \text{ M}$) in sulpholane or acetonitrile, the ^{35}Cl spectrum of trimethylsilyl perchlorate contains a single sharp peak ($w_{1/2}$ 15–20 Hz) at δ 4.6 (p.p.m. downfield from the external standard HClO_4 in D_2O), corresponding to ionic, tetrahedral perchlorate ion. The lower symmetry of a covalent perchlorate would result in an extremely broad peak. As the concentration is increased, the peak broadens and disappears (the $w_{1/2}$ ca. 300 Hz at 0.01 M and 1400 Hz at 0.1 M). Thus the ionic form is in equilibrium with an ion pair or covalent form at higher concentrations.

Previous workers^{5,6} have found the ^{29}Si resonance of trimethylsilyl perchlorate at about δ 45. We confirmed this observation at concentrations above 0.2 M. At these concentrations, the ^{35}Cl spectra also clearly indicated that trimethylsilyl and perchlorate were associated. As the concentration is lowered, the peak at δ 45 quickly disappears as if undergoing an exchange process. The extremely low receptivity of ^{29}Si prevented the observation of slow exchange resonances at lower concentrations.⁷

Molecular weight measurements are not sensitive to solvent complexation. We examined the question as to whether a molecule of solvent provides the fourth co-ordination site on silicon by means of n.m.r. experiments. Although ^{13}C chemical shifts of the methyl carbons were nearly insensitive to the solvent for the solvents discussed herein, we felt that ^{15}N chemical shifts of complexing agents would provide a more definitive answer. The ^{15}N chemical shift of acetonitrile was measured for a solution of equimolar amounts of $\text{Me}_3\text{SiClO}_4$ and MeCN in dichloromethane, and compared to that of pure acetonitrile. Complexation of acetonitrile with a Lewis acid would cause an upfield shift of about 100 p.p.m.⁸ Because acetonitrile is a much stronger donor than dichloromethane, any complexation should be detected. The chemical shift of free acetonitrile was measured to be δ 244.2 p.p.m. from ammonia, and that of acetonitrile in the presence of $\text{Me}_3\text{SiClO}_4$ was 244.3 p.p.m. This result indicates that essentially no complexation is occurring. In contrast, the same experiment with pyridine yielded values of δ 314.0 p.p.m. for pure pyridine and δ 218.9 p.p.m. for pyridine in the presence of $\text{Me}_3\text{SiClO}_4$. The latter value is consistent with fully complexed pyridine, $\text{Me}_3\text{Si-pyr}^+\text{ClO}_4^-$. Thus acetonitrile fails to complex with the silyl cation, but pyridine complexes fully. These results are in accord with the known relative nucleophilicities of these two materials.

The solution of trimethylsilyl perchlorate in acetonitrile provides an excellent source of highly electrophilic silicon. Reaction of $\text{Me}_3\text{SiClO}_4$ (in the presence of the by-product Ph_3CH) with an equimolar amount of sodium cyanide at room temperature gave a quantitative isolated yield of trimethylsilyl cyanide. This procedure for preparing Me_3SiCN is simpler and of much higher yield than the best current literature method, which requires an elevated temperature.⁹

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