Rate-determining Ionization in Methanolysis of an Organosilicon Halide

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Summary Methanolysis of $(Me_3Si)_3CSiPhHI$ is not significantly accelerated by NaOMe, and so is thought to involve rate-determining ionization of the iodide.

Ever since mechanistic studies of organosilicon reactions began, the absence of evidence for S_N1 solvolysis of organosilicon halides has attracted much interest. We recently found that the perchlorate $(Me_3Si)_3CSiMe_2OClO_3$ undergoes unimolecular solvolysis in methanol,[1] and we have now shown that the methanolysis of the iodide $(Me_3Si)_3CSiPhHI$, (1), (see equation 1) probably involves rate-determining ionization.

$$(Me_3Si)_3CSiPhHI + MeOH \rightarrow (Me_3Si)_3CSiPhHOMe \quad (1)$$
$$(1) \qquad\qquad\qquad\qquad (2)$$

The iodide (1) was previously shown to be much more reactive towards methanol than the related species $(Me_3Si)_3CSiPh_2I$ or $(Me_3Si)_3CSiMe_2I$, and it was assumed that the presence of a hydrogen atom at the functional silicon centre allowed nucleophilic attack by the solvent which was sterically inhibited when two organic groups were there.[2] To our surprise, however, spectrophotometric rate studies have revealed that addition of sodium methoxide causes only a small rate increase in the rate of methanolysis of (1), indicating that the nucleophile is not involved in the rate-determining step.

Table. Observed pseudo-first-order rate constants in methanolysis of $(Me_3Si)_3CSiPhHX$ compounds.[a]

X	T/°C	Salt	[Salt]/M	$10^5 k$/s^{-1}
		None		48
		NaOMe	0·10	57
		NaOMe	0·27	60
		NaOMe	0·50	75
		LiCl	0·11	52
		LiCl	0·22	53
I	27	LiCl	0·55	69
		LiClO$_4$	0·10	49
		LiClO$_4$	0·20	53
		LiClO$_4$	0·50	63
		NaI	0·005	48
		NaI	0·008	43
		NaI	0·010	46
		NaI	0·017	50
		None		11·8
Br	42	NaOMe	0·10	107
		NaOMe	0·21	220
		None		58
NO$_3$	27	NaOMe	0·02	490
		NaOMe	0·10	2500

[a] The concentration of the organosilane was *ca.* 1 × 10^{-3} M. A wavelength of 276 nm was used to monitor the reaction.

It will be seen from the Table that, while the presence of 0·1 M NaOMe causes an 18% increase in rate, subsequent increases in the base concentration to 0·5 M have only

much the same influence as additions of LiCl or LiClO$_4$, which can be attributed to salt effects, and it can reasonably be concluded that the rate-determining step in the methanolysis does not involve nucleophilic attack at silicon, and thus that it is an ionization. [The initial increase in rate upon addition of a little NaOMe may perhaps arise from trapping by the base of the small proportion of the originally formed ion pair which might otherwise return to the substrate, as suggested for the solvolysis of $(Me_3Si)_3$-$CSiMe_2OClO_3$.] Addition of a little NaI seemed to bring about a small fall in the rate, which would be expected for a common-ion effect in an S_N1 process (as observed with the perchlorate),[1] but the observed variations may be within the limits of experimental uncertainty.

In contrast, the methanolyses of the corresponding nitrate, $(Me_3Si)_3CSiPhH(NO_3)$ (which reacts a little faster than the iodide), and bromide, $(Me_3Si)_3CSiHPhBr$, are markedly accelerated by NaOMe, the effect being especially large for the nitrate, and the rate increases are roughly proportional to the base concentration. (The large excess of base over organosilane gives rise to pseudo-first-order kinetics.) It is clear that the reactions with NaOMe are S_N2 processes, and it is likely that the methanolyses in MeOH alone are also wholly or in part S_N2 processes. The bulk of the iodide ligand may be a factor in the relative resistance of (1) to nucleophilic attack.

While the results for (1) represent, as we believe, the first evidence for a rate-determining ionization of a silicon halide in solvolysis, we cannot claim that they offer evidence for formation of a simple siliconium (silicenium) ion, since the intermediate ion may well be a bridged species (3),

(3)

analogous to those we suggested to account for the rearrangements observed in reactions of $(Me_3Si)_3CSiR_2I$ compounds with electrophiles.[3] The product from (1) is the unrearranged (2), which would be consistent with the intermediacy of the simple ion $(Me_3Si)_3CSiPhH^+$, but it would follow from our previous proposals that nucleophilic attack on (3) would take place preferentially at the less hindered Si(1) rather than the more hindered Si(2) centre.[3]

Finally we note that, contrary to expectation based on consideration of probable electronic effects and the influence of release of steric strain, (1) must undergo ionization in

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MeOH much more readily than the iodides $(Me_3Si)_3CSiR_2I$ (R = Ph or Me). This may be because the presence of a hydrogen atom permits more effective solvation of the forming cation.

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