

Unimolecular Solvolysis of Some Organosilicon Perchlorates and Iodides

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Kinetic studies have been made of the solvolysis (mainly the methanolysis) of the highly sterically hindered compounds $\text{TsiSiMe}_2\text{OCIO}_3$ [$\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$], $(\text{Me}_3\text{Si})_2(\text{Ph}_2\text{MeSi})\text{CSiMe}_2\text{OCIO}_3$, TsiSiHPhX ($\text{X} = \text{I}, \text{Br}, \text{ONO}_2$), and TsiSiHMeI . The rate of methanolysis of $\text{TsiSiMe}_2\text{OCIO}_3$ is increased by only ca. 20% upon addition of 0.1M-NaOMe, and further additions of base have smaller effects. Additions of LiCl or LiNO_3 cause even smaller rate increases, but in the presence of LiNO_3 substantial amounts of $\text{TsiSiMe}_2\text{ONO}_2$ are formed, the amounts being greater than would correspond to the rate increases. Water has a very large accelerating effect, and even with only 1 vol % of water present the product is very predominantly $\text{TsiSiMe}_2\text{OH}$. The solvolysis is slower in EtOH and Pr^iOH , and occurs only very slowly, if at all, in $\text{CF}_3\text{CH}_2\text{OH}$. The methanolysis of $(\text{Me}_3\text{Si})_2(\text{Ph}_2\text{MeSi})\text{CSiMe}_2\text{OCIO}_3$ is slower than that of $\text{TsiSiMe}_2\text{OCIO}_3$. The methanolysis of TsiSiHPhI and TsiSiHMeI are also accelerated only to a small extent by NaOMe. The above results are interpreted in terms of an $\text{S}_{\text{N}}1$ mechanism involving anchimerically assisted ionization of the $\text{Si}-\text{OCIO}_3$ or $\text{Si}-\text{I}$ bond to give a methyl-bridged cation with unusual solvation requirements. In contrast, the methanolyses of TsiSiHPhX ($\text{X} = \text{Br}$ or ONO_2) are markedly accelerated by base, and it seems that, at least in the presence of base, attack by the nucleophile is involved in the rate-determining step in these cases.

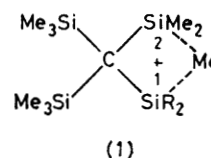
THERE is a long history of attempts to detect siliconium ions \dagger either present in equilibrium with their precursors or as reaction intermediates.¹⁻⁶ It has been clearly shown that organosilicon halides and related species do not dissociate in solution under conditions in which the corresponding organic substrates would readily give carbonium ions, and interpretations of the characteristics of several reactions in terms of the intermediacy of siliconium ions have not stood up to detailed analysis, so that a recent review could state categorically, 'Currently R_3Si^+ siliconium ions are not believed to be intermediates in any reaction in solution'.⁵ (It is possible that they are involved in the reactions of certain organosilicon hydrides with triphenylmethyl hexafluoroantimonate in CH_2Cl_2 , but there were features which gave rise to doubt.⁶)

It was pointed out some time ago that lack of evidence for rate-determining ionizations of organosilicon halides and similar species might be attributable to (a) the relative unimportance of conjugative stabilizing effects which would involve $(p \rightarrow p)_\pi$ double bonding to silicon (so that, for example an α -Ph group would not stabilize a siliconium ion in the way it does a carbonium ion), and (b) the normally very great reactivity of silicon halides and related species in bimolecular, $\text{S}_{\text{N}}2$, processes, which means that $\text{S}_{\text{N}}1$ processes have no chance to operate; it followed that if the alternative mechanism could be suppressed, the silicon compounds might react by an ionization mechanism.¹ The obvious way to suppress the bimolecular reaction is by steric hindrance, and we shall show below that this approach has allowed observation of an ionization mechanism, although the cations involved appear to be somewhat complex species.

We have previously shown that the reactions with electrophiles of the silicon compounds of the type

\dagger By siliconium ions we mean three-co-ordinate silicon cations such as R_3Si^+ , which are also sometimes referred to as silicenium ions following the (unnecessary) use by some authors of the term carbenium ions for R_3C^+ species.

$(\text{Me}_3\text{Si})_3\text{CSiR}_2\text{X}$ ($\text{X} = \text{H}$ or I), which contain the very bulky group $(\text{Me}_3\text{Si})_3\text{C}$, can be most satisfactorily interpreted in terms of formation of a bridged cation of the type (1); e.g. the formation of the rearranged products $(\text{Me}_3\text{Si})_2(\text{Ph}_2\text{MeSi})\text{CSiMe}_2\text{Y}$ ($\text{Y} = \text{OMe}$ and NO_3) from



the reaction between $(\text{Me}_3\text{Si})_3\text{CSiPh}_2\text{X}$ and silver nitrate in methanol can be attributed to attack of the nucleophiles MeOH and NO_3^- at the less hindered $\text{Si}(2)$ rather than the more hindered $\text{Si}(1)$ centre in the bridged ion (1; $\text{R} = \text{Ph}$).⁷ It was also shown that the solvolysis of the iodides $(\text{Me}_3\text{Si})_3\text{CSiRR}'\text{I}$ (R and $\text{R}' = \text{Me}$ or Et) in anhydrous trifluoroacetic acid is not catalysed by sodium trifluoroacetate, and so appears to be a unimolecular process, and that a mixture of rearranged and unrearranged trifluoroacetates $(\text{Me}_3\text{Si})_2(\text{RR}'\text{MeSi})\text{CSiMe}_2\text{O}_2\text{CCF}_3$ and $(\text{Me}_3\text{Si})_3\text{CSiRR}'\text{O}_2\text{CCF}_3$ is obtained for $\text{R} = \text{R}' = \text{Et}$ and $\text{R} = \text{Et}$, $\text{R}' = \text{Me}$, suggesting that bridged ions of type (1) are again involved. \ddagger

We have now studied the methanolysis of more reactive compounds containing the tris(trimethylsilyl)methyl group (which we refer to as the 'trisyl' group and symbolize by Tsi) and show below that the kinetic features of the reaction provide strong evidence for an $\text{S}_{\text{N}}1$ mechanism. Preliminary accounts of some of the results have appeared.^{8,9}

\ddagger Professor P. v. R. Schleyer and Dr. A. J. Kos, in a personal communication, have informed us that MNDO calculations on a cation of type (1) with hydrogen atoms in place of all the Me and R groups except the bridging methyl, show it to have virtually the same energy as the corresponding open cation. In our view, the large steric effects in the trisyl derivatives would favour the bridged ion (1) over the open species.

RESULTS AND DISCUSSION

In order to enhance the probability of observing a rate-determining ionization we looked first at a compound containing the highly active perchlorate leaving group, *viz.* TsiSiMe₂OCIO₃. We found that, in contrast to the other TsiSiMe₂X species we have examined (*e.g.* X = F, Cl, Br, I, NO₃, OAc), the perchlorate reacts readily with methanol to give the corresponding methoxide, TsiSiMe₂OMe. We also found that the progress of the reaction in methanol alone or containing inert salts or water could be conveniently monitored by u.v. spectroscopy at 209 nm, at which the perchlorate absorbs while the methoxide does not. This method cannot, however, be used in the presence of sodium methoxide because this gives rise to interfering absorption by the medium, and it is necessary to monitor the disappearance of the signal in the ¹H n.m.r. spectrum from the (Me₃Si)₃C group of the substrate. In a few test runs the rate constants determined in methanol alone by the two methods agreed within 5%.

The observed first-order rate constants under various conditions are listed in Table 1. It will be seen that

TABLE 1
First-order rate constants for solvolysis of
TsiSiMe₂OCIO₃ in MeOH

<i>T</i> /°C	Salt	[Salt]/M	10 ⁵ <i>k</i> /s ⁻¹
30 °	None		51
	LiCl	0.10	61
		0.20	64
		0.31	67
		1.00	75
	NaClO ₄	0.050	50
		0.10	53
		0.68	58
			74
35 °	None		90
	NaOMe	0.10	95
		0.45	102
		1.00	102
	LiNO ₃	0.24 °	71
		0.47 °	100
		0.91 °	117

* Reaction monitored by u.v. spectroscopy (at 209 nm).

^b Reaction monitored by ¹H n.m.r. spectroscopy; *ca.* 1.5 vol % CCl₄ was present. ^c The nitrate TsiSiMe₂ONO₂ formed 35, 50, and 83%, respectively, of the products in the 0.24, 0.47, and 0.91M salt solutions.

while the rate constant is higher by 22% in the presence of 0.1M-NaOMe, further increase in the base concentration has only a small effect, comparable with that of LiCl. The latter salt, while raising the rate, does not affect the product, whereas addition of LiNO₃ not only raises the rate to a rather similar extent but also leads to production of the nitrate TsiSiMe₂ONO₂, in a proportion which increases roughly in line with the increase in the salt concentration.

The results are strongly indicative of a rate-determining ionization of the perchlorate, presumably to give a bridged cation of type (1). This ion is not trapped by chloride ion, but is by nitrate ion, as would be expected from the fact that the nitrate TsiSiMe₂ONO₂ is produced alongside the methoxide TsiSiMe₂OMe when the iodide TsiSiMe₂I is treated with AgNO₃ in MeOH.⁷ (The

formation of nitrate product in the solvolysis of TsiSiMe₂-OCIO₃ in the presence of LiNO₃ cannot be due to direct attack of NO₃⁻ on the perchlorate, since even with 0.9M-LiNO₃ only *ca.* 40% of the rate constant is attributable to the effect of the salt, whereas 83% of the product is nitrate.)

The inability of chloride ion to trap the cationic intermediate deserves comment, since chloride ion is a good nucleophile towards carbon, and competes effectively with the water or alcohol solvent for capture of carbonium ions.^{10,11} The difference is to be associated with the very high affinity of silicon for oxygen, which is further manifested in the ability of nitrate ion to combine with the silico-cation. It should be pointed out, however, that some TsiSiMe₂Y (Y = Cl or Br) is formed in the reaction of TsiSiMe₂I with HgY₂ in acetic acid, but this may not arise from trapping of a free silico-cation by free halide ion.⁷

Added NaClO₄ has a much smaller effect on the rate, and it is possible that the rate-enhancing salt effect is countered by a rate-lowering common-ion effect arising from some re-capture of the cation by ClO₄⁻.

The effect of added NaOMe is somewhat unusual. A 22% rate enhancement by 0.1M-salt is in the range observed for the effect of a variety of salts in S_N1 solvolysis of organic halides, but for those reactions lyate ion normally has a negligible or a small rate-reducing effect, which has been attributed to the special interaction between the lyate ion and the solvent.¹⁰ Beyond noting that if the influence of 0.1M-NaOMe on the reaction of TsiSiMe₂OCIO₃ arose from a general salt effect, similar in type but greater than that observed for other salts, then further increase in the base concentration should give a correspondingly greater increase in rate, contrary to observation, we defer detailed consideration of this feature to a later part of this Discussion. It is evident, however, that the observed effects are inconsistent with a mechanism involving nucleophilic attack of the methoxide ion on the initial perchlorate.

The effects of changing the solvent were then investigated, with the results shown in Table 2. Change from MeOH to EtOH reduced the rate by about a factor of three, and the further change from EtOH to PrOH by about a factor of two. Addition of only 1% of water to the MeOH, however, causes a six-fold increase in rate, and the increments in the rate constants on going from 1 to 2 to 10% H₂O are almost exactly proportional to the water concentration. The effect of the water is much larger than that, attributable to the increase in the ionizing power of the medium, on the S_N1 reactions of alkyl halides, and the rate increase on going to 10%

* We hope to carry out a more detailed study of salt effects on this type of reaction, including a check on our earlier report that a small amount of NaClO₄ seemingly caused a small rate decrease,⁸ as possibly did a small amount of NaI in the solvolysis of TsiSiHPhI.⁹ We note that while significant external return of ClO₄⁻ to the cation seems possible in the light of the capture of the cation by NO₃⁻, such return of I⁻ seems highly unlikely in view of the failure of Cl⁻ to trap the cation.

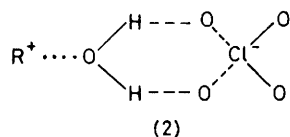
H₂O would correspond with a value of 2.8 for *m* in the Grunwald–Winstein relationship.¹² Moreover, the product is very predominantly (>95%) the hydroxide TsiSiMe₂OH even when only 1% of water is present, and

TABLE 2
First-order rate constants for solvolysis for
TsiSiRR'X in mixed media^a

R	R'	X	Medium	<i>T</i> /°C	10 ⁵ <i>k</i> /s ⁻¹
Me	Me	ClO ₄	EtOH	30	15.6
			Pr ⁱ OH	30	7.0
			MeOH	27.5	48
			1 vol % H ₂ O in MeOH	27.5	290
			2 vol % H ₂ O in MeOH	27.5	520
			10 vol % H ₂ O in MeOH	27.5	2 510
			3.3 vol % H ₂ O in MeOH	27	76
Ph	H	I	10 vol % H ₂ O in MeOH	27	133
Me	H	I	20 vol % MeOH in CF ₃ CH ₂ OH	35	143 ^b
			CF ₃ CH ₂ OH	35	145 ^b
			+ 0.057M-NaOMe		
			20 vol % MeOH in CF ₃ CH ₂ OH	35	148 ^b

^a U.v. spectroscopy was used for R = R' = Me (λ 209 nm) and R = Ph, R' = H (λ 276 nm), while ¹H n.m.r. spectroscopy was used for R = Me, R' = H. ^b The product was TsiSiHMeOMe.

the results might suggest that water is able to carry out a direct nucleophilic displacement on the TsiSiMe₂OCIO₃. This would appear even more likely in view of the observation (see Experimental section) that reaction of TsiSiMe₂I with AgNO₃ in 4% of H₂O in MeOH produces only a very small amount of the hydroxide TsiSiMe₂OH, indicating that the cation (1; R = Me) does not show a marked preference to react with water rather than methanol. However, such direct nucleophilic displacement by water seems highly improbable in view of the fact that methoxide ion does not carry out such attack, and we suggest that the influence of water arises from special solvating characteristics. First, the small size of the water molecule may enable it to insert more effectively than the methanol molecule to give a solvent separated ion-pair in this highly hindered system, and second, and probably more important, the water can form two hydrogen bonds to the perchlorate ion, as in (2), as it has been suggested to do to the arenesulphonate ion.¹³ It would then be likely that the cation would



react with water to give hydroxide product rather than that replacement of the solvating water by methanol would precede collapse of the ion–solvent complex.

No reaction took place when TsiSiMe₂OCIO₃ was boiled for 24 h with CF₃CH₂OH, an alcohol of relatively high acidity and low nucleophilicity which is exceptionally favourable for S_N1 reactions of, for example, alkyl tosylates (*cf.* the *Y* value of 1.045),^{13–15} but the perchlorate ion is poorly solvated by protic media,¹⁶ and so

the high electrophilicity of CF₃CH₂OH may be of little consequence in solvolysis of TsiSiMe₂OCIO₃.^{*} This cannot be the only relevant factor, however, since, as we shall see below, the iodide TsiSiHMeX is also unreactive towards CF₃CH₂OH, and we return briefly to the question of the solvation requirements in these unusual systems towards the end of this Discussion. It is noteworthy that the iodide TsiSiMe₂I reacts with AgNO₃ in CF₃CH₂OH to give the expected alkoxy-product TsiSiMe₂OCH₂CF₃ along with the nitrate TsiSiMe₂ONO₂, and the proportion of nitrate, *viz.* *ca.* 12%, is comparable with that observed for the corresponding reaction in MeOH,⁷ indicating that in spite of its low nucleophilicity towards carbon CF₃CH₂OH is able to compete with NO₃⁻ for the silico-cation (1), almost as effectively as MeOH.

We next examined the methanolysis of the perchlorate (Me₃Si)₂(Ph₂MeSi)CSiMe₂OCIO₃, which is obtained when TsiSiPh₂I is treated with AgClO₄.¹⁷ The interest in this compound lay in the possibility that a Ph group, which is normally a better bridging group than Me in both R₆Al₂ and carbonium ions, might bridge the Si(1) and Si(2) silicon atoms more effectively than Me in a structure analogous to (1), and thus possibly provide even more anchimeric assistance to the ionization of the Si–OCIO₃ bond. In fact (Me₃Si)₂(Ph₂MeSi)CSiMe₂OCIO₃ was found to react *ca.* 3.5 times as slowly as TsiSiMe₂OCIO₃ (see Experimental section), indicating that Ph bridging is not especially effective, if it occurs at all. No product resulting from migration of a phenyl group was detected. These results can be readily understood when a molecular model is examined, since this shows that there would be severe steric inhibition of bridging by the Ph group. The lower reactivity of the phenyl-containing perchlorate can be attributed to increased steric hindrance to solvation of the forming cation.

We subsequently turned our attention to the iodide TsiSiHPhI, which was observed previously to react quite readily with methanol, in sharp contrast to TsiSiR₂I (R = Ph or Me).¹⁸ The much higher reactivity was interpreted in terms of a considerable reduction in steric hindrance, arising from the presence of the small hydrogen atom at the functional centre, which seemingly permitted the usual direct bimolecular attack by the nucleophile on the substrate. It was thus a surprise to us to find that the rate of the reaction of TsiSiHPhI with methanol to give TsiSiHPhOMe (which can be conveniently monitored, even in the presence of base, by observing the change of the u.v. absorption by the aryl group) is relatively little affected by the presence of NaOMe (see Table 3), so that once again the rate-determining step involves ionization of the organo-silicon substrate. As with TsiSiMe₂OCIO₃, addition of 0.1M-NaOMe causes a *ca.* 20% increase in rate, but further addition of base up to 0.5M has a much smaller effect. Added LiCl and LiClO₄ have small rate-enhancing effects which can be attributed to normal salt

^{*} While we explained the effect of water in terms of electrophilic solvation, as in (2), we were concerned there only with the *relative* effects of water and methanol.

effects. The effect of LiNO_3 was not examined, since if some of the nitrate $\text{TsiSiHPh(ONO}_2\text{)}$ were formed it would then undergo solvolysis somewhat more rapidly than the original iodide (see below).

A very interesting feature is that addition of water causes a much smaller increase in the rate than it does in the solvolysis of $\text{TsiSiMe}_2\text{OCIO}_3$ (Table 2), and the effects

TABLE 3
First-order rate constants for solvolysis of
 TsiSiHRX in MeOH ^a

R	X	T/°C	Salt	[Salt]/M	$10^4 k/\text{s}^{-1}$
Ph	I	27	None		48
			NaOMe	0.10	57
			NaOMe	0.27	60
			NaOMe	0.50	75
			LiCl	0.11	52
			LiCl	0.22	53
			LiCl	0.55	69
			LiClO_4	0.10	49
			LiClO_4	0.20	53
			LiClO_4	0.50	63
			NaI	0.010	46
Ph	Br	42	NaI	0.017	50
			None		11.8
			NaOMe	0.10	107
Ph	NO_3	27	NaOMe	0.21	220
			None		58
			NaOMe	0.02	490
Me	I	-17	NaOMe	0.10	2 500
			None		61
			NaOMe	0.10	73
			NaOMe	0.20	77

^a The reaction was monitored by u.v. spectrophotometry (at 276 nm) for $\text{R} = \text{Ph}$ and by ^1H n.m.r. spectroscopy for $\text{R} = \text{Me}$.

are, in fact, rather smaller than those in solvolysis of alkyl halides, tosylates, and similar species. (The rate increase on going from MeOH to 10% H_2O in MeOH corresponds to an m value of 0.56.) This result is nicely consistent with the explanation we offered above for the abnormal effect of water in the solvolysis of the perchlorate $\text{TsiSiMe}_2\text{OCIO}_3$, since (a) steric hindrance would be smaller in the presence of one hydride ligand at silicon, and, more important, (b) double hydrogen bonding, such as that in structure (2), could not occur with the iodide ion.

In contrast to those of the iodide, the reactions of bromide TsiSiHPhBr and the nitrate TsiSiHPhONO_2 with MeOH are markedly accelerated by added MeONa , and the rate increase is approximately proportional to the base concentration. The reactions with methoxide ion can thus be most simply regarded as $\text{S}_\text{N}2$ processes, though it is possible that formation of an ion-pair precedes rate-determining attack of the nucleophile. The reactions with methanol alone are not necessarily bimolecular, but are likely to be so, at least in part. (It is noteworthy that the bromide $\text{TsiSiMe}_2\text{Br}$ is very much less reactive than the corresponding iodide in methanolysis promoted by AgNO_3 , a reaction thought to proceed by assisted ionization of the Si-X bonds.⁷) The exceptional tendency of the iodide TsiSiHPhI to react by an $\text{S}_\text{N}1$ mechanism can be attributed to (a) the well known very high leaving group ability of iodine in

cleavage of Si-I bonds (normally manifested in very fast bimolecular reactions), (b) additional steric hindrance by the iodide ligand to attachment of a nucleophile to silicon to give a five-co-ordinate intermediate or transition state, and (c) greater release of steric strain on separation of I^- from the seriously crowded substrate.

Finally, in the light of the results for TsiSiHPhI , we examined the methanolysis of TsiSiHMeI . This was much more reactive, so that the reaction had to be carried out at -17°C , at which it could be conveniently followed by the usual n.m.r. method. The effect of added NaOMe was rather similar to that for $\text{TsiSiMe}_2\text{OCIO}_3$ and TsiSiHPhI , an 0.1M concentration causing a *ca.* 20% increase in rate, and doubling of this concentration having a markedly smaller effect. Once again it seems that the methanolysis involves rate-determining ionization.

Like $\text{TsiSiMe}_2\text{OCIO}_3$, TsiSiHMeI failed to react with $\text{CF}_3\text{CH}_2\text{OH}$. Use of a 20 : 80 v/v $\text{MeOH-CF}_3\text{CH}_2\text{OH}$ mixture gave a convenient rate at 35°C , and the solvolysis in this medium was very little accelerated by the presence of sodium alkoxide (presumably very predominantly $\text{NaOCH}_2\text{CF}_3$). The product in all cases was exclusively TsiSiHMeOMe . (In contrast, reactions of $\text{TsiSiMe}_2\text{I}$ with AgNO_3 in $\text{CF}_3\text{CH}_2\text{OH-MeOH}$ give substantial proportions of $\text{TsiSiMe}_2\text{OCH}_2\text{CF}_3$.¹⁹)

It is noteworthy that the solvolysis of TsiSiHRI ($\text{R} = \text{Ph}$ or Me) gives only unrearranged methoxide TsiSiH-ROMe . This can be readily understood in terms of the intermediacy of bridged ions of type (1), since the nucleophile will attack, to open the bridge, at the least hindered silicon centre, which will be that bearing a hydrogen ligand.

Some further points of interest emerge from an overall examination of the results for the several compounds studied. (a) The ease of methanolysis by the $\text{S}_\text{N}1$ mechanism increases in the sequence $\text{TsiSiMe}_2\text{I}$ and $\text{TsiSi-Ph}_2\text{I} \ll \text{TsiSiHPhI} < \text{TsiSiHMeI}$. This is in sharp contrast to the sequences which would be expected by analogy with $\text{S}_\text{N}1$ reactions of alkyl halides, for which replacement of a hydrogen atom on the central carbon by a methyl group normally leads to a substantial rise in reactivity and replacement of a methyl by a phenyl group to a further such rise. The pattern for the silicon compounds can be understood in terms of (i) the much poorer ability of silicon than of carbon to form $p_\pi-p_\pi$ bonds, which means that there will be little, if any, hyperconjugative stabilization of even a simple siliconium ion by an alkyl group,* or conjugative stabilization by a phenyl group, which will thus destabilize the cation by virtue of its inductive effect;† (ii) the relative unimportance of electronic effects of substituents on the Si(1) atom of the bridged ion (1) (and thus of a transition

* Similarly there will be little stabilization by the $(\text{Me}_2\text{Si})_3\text{C}$ group associated with hyperconjugative electron release from the $\text{Me}_2\text{Si-C}$ bonds.

† Larsen and his colleagues have pointed out that evidence of greater stabilization of carbonium ions by phenyl than by methyl groups is confined to the simplest types of such ions, and that destabilization by the inductive effect is more common.²⁰

state on the way to it) arising from the dispersal of the positive charge over this and the Si(2) atom; and (iii) increase in the already severe steric hindrance to solvation of the forming ion pair on replacing a hydride ligand at the functional silicon centre by a methyl, or more especially, a phenyl group. We suspect that this last factor is very important in the special systems we are concerned with.

(b) The trisylsilicon iodides, TsiSiHRI, examined are much more reactive in S_N1 methanolysis than simple secondary alkyl iodides. There is at present no means of assessing the extent to which the ease of ionization depends specifically on the presence of the trisyl group, and is attributable to (i) anchimeric assistance associated with formation of bridged ions of type (1), and (ii) relief of steric strain on separation of the leaving group, these factors outweighing the serious steric interference to solvation. Ordinary silicon iodides, such as Me_3SiI and Me_2HSiI are very much more reactive towards alcohols, and it is impossible to estimate how readily they would react by an S_N1 mechanism if the much faster bimolecular processes were not available.

(c) The main observations remaining to be discussed are the lack of reaction of the examined compounds with $\text{CF}_3\text{CH}_2\text{OH}$ and the unusual effect of added NaOMe in MeOH. We consider these together because we suspect that both features may originate in the special solvation requirements of the transition state for the unusual reactants involved.

We first note that the well developed conventions for interpreting solvent effects on reactions of organic halides, tosylates, *etc.*, are, in fact, only rationalizations of the vast body of empirical data for a range of rather closely related systems. Even for those systems it is clear that the solvation requirements of the transition state depend markedly on the type of carbonium ion generated, being different, for example, for simple alkyl, bridged-alkyl, and vinyl carbonium ions.^{13-15, 21, 22} It is by no means certain that the principles developed for C-X bonds will apply even approximately to analogous reactions involving ionization of other M-X bonds, and certainly it cannot be expected that they will apply satisfactorily to the generation of cations as unusual as those we believe to be formed from TsiSiR₂X and TsiSiHRX compounds.* If the forming ion has the bridged structure of type (1) it is evident that with the positive charge dispersed over the Si(1) and Si(2) centres, nucleophilic solvation specifically at the positive end of the breaking M-X bond will be much less important than is the case for ionization of C-X bonds. Yet it cannot be doubted that considerable solvation of the forming cation is needed if the ionization of the TsiSiR₂-X bond is to take place at all, and thus solvation must involve some less specific interaction between the solvent (more particularly the oxygen lone pairs of the solvent) and part of the periphery of the bridged ion. In such

* The drastic disruption of the solvent structure by the massive hydrocarbon-like substrate molecules could itself give rise to abnormal solvation effects.

nucleophilic solvation $\text{CF}_3\text{CH}_2\text{OH}$ will be much less effective than other alcohols, so that it does not react even with TsiSiHMeI, although it would be expected to be especially effective in solvating the leaving iodide ion. (We should note here that $\text{CF}_3\text{CO}_2\text{H}$ does react with the iodides TsiSiR₂I,⁷ the markedly greater electrophilicity of the medium¹³ seemingly outweighing its low nucleophilicity.)

We turn now to the effect of added sodium methoxide. We have seen that the *ca.* 20% rate enhancement by 0.1M-base contrasts with the negligible effect very small rate reduction caused by added lyate salts in S_N1 solvolysis of alkyl halides and related species, for which similar concentrations of other salts cause substantial rate increases. The influence of base on the alkyl halide solvolyses has been attributed to a special rate-retarding effect of the lyate ion superimposed upon the usual accelerating general salt effect, the retarding effect arising from the fact that the negative charge on each lyate ion is dispersed throughout the solvent, with this 'distributed proton defect' impairing solvation of the leaving group.¹⁰ If, as we have suggested above, there is a particular requirement for a general nucleophilic solvation on the periphery of the bridged ion of type (1), it follows that the distribution of the negative charge of added methoxide throughout the methanol solvent could lead to enhancement of such solvation in the transition state, with acceleration of the reaction, this effect more than outweighing the poorer electrophilic solvation of the leaving group. It is conceivable, too, that the largest disruption of the solvent structure could be caused by small concentrations of the methoxide ion, with subsequent additions having smaller effects.

There is, however, an alternative explanation of the unusual effect of methoxide ion, as we have tentatively suggested previously.^{8,9} This involves the assumption that in the solvolysis of the TsiSiR₂X species there is some internal return of the leaving ion X⁻ within an ion pair. The methoxide ion, an exceptionally powerful nucleophile towards silicon, might trap this ion pair, to give the normal product, so enhancing the rate. A little NaOMe might serve to trap all the ion pairs, so that further addition of the base would have only a salt effect. The disadvantage of this explanation is that the close similarity of the effects of the NaOMe on the reaction of all three substrates examined which react by an S_N1 mechanism would have to be attributed to a rather unlikely coincidence, since the degree of any internal return within ion pairs would not be expected to be the same for all three reactants. The special effect on solvation of the cation which we have proposed above, arising from change in the structure of the medium, would, in contrast, be relatively independent of the reactant.

We note finally that while we have, we believe, provided the first demonstrations that reactions of Si-X bonds can proceed by rate-determining ionization, we cannot at the same time convincingly claim that we have demonstrated the participation of siliconium ions as

reactions intermediates, since it is a matter for debate (largely semantic in nature) whether the bridged ions of the type (1) can acceptably be described as siliconium ions. It is relevant in this connection to note that the MNDO calculations referred to in a footnote on page 1309 indicate that the positive charge does reside on the bridged silicon atoms, with a substantial negative charge on the bridging methyl group.

EXPERIMENTAL

Starting Materials.—(a) *Organosilicon substrates.* The compounds TsiSiMe₂OCIO₃, (Me₃Si)₂(Ph₂MeSi)C(SiMe₂OCIO₃), and TsiSiHPhI were made as previously described.^{17, 18}

For the preparation of TsiSiHMeI, a solution of ICl (0.37 mmol) in CCl₄ (5 cm³) was added dropwise with swirling to TsiSiMeH₂ (0.36 mmol) in CCl₄ (2 cm³). The solvent was evaporated and the solid residue sublimed to give [*iodo(methyl)silyl*][*tris(trimethylsilyl)methane*, δ (CCl₄) 0.31 (27 H, s), 1.14 (3 H, d), and 4.80 (1 H, q) (Found: C, 33.0; H, 7.6. C₁₁H₃₁ISi₄ requires C, 32.8; H, 7.7%).

(b) *Salts.* Salts, of analytical reagent grade, were carefully dried before use.

(c) *Solvents.* The alcohols were dried by standard methods [Mg(OMe)₂ for MeOH, CaH₂ for EtOH and PrⁱOH, and molecular sieve 4A for CF₃CH₂OH]. The absence of any detectable hydroxide product in the reaction of TsiSiMe₂OCIO₃ with MeOH, EtOH, and PrⁱOH confirmed the absence of appreciable quantities of water.

Kinetic Studies.—(a) *By u.v. spectroscopy.* Finely powdered organosilane (3–4 mg) was shaken vigorously for a short time with methanol (3 cm³) pre-heated approximately to the reaction temperature, and containing salt where appropriate. Any residual solid was allowed to settle out, and some of the clear solution was transferred with a Pasteur pipette to the absorption cell contained in a thermostatted holder. Recording of the absorption at the specified wave length (see Tables) was begun.

(b) *By ¹H n.m.r. spectroscopy.* For the reaction of TsiSiMe₂OCIO₃, a sample of the latter (*ca.* 1 mmol) was dissolved in two microdrops of CCl₄ (which formed *ca.* 1.5 vol % of the final solvent) in an n.m.r. tube, and the alcohol (*ca.* 1 cm³), pre-adjusted roughly to the reaction temperature and containing a little CHCl₃ as reference and also MeONa where appropriate, was added. The tube was closed off and briefly shaken, and recording of the ¹H n.m.r. spectrum was begun. The height of the peak (at δ 0.37) from the Me₃Si protons of the substrate relative to that from the CHCl₃ was used as the measure of the concentration of TsiSiMe₂OCIO₃.

An analogous procedure was used for (Me₃Si)₂(Ph₂MeSi)-CSiMe₂OCIO₃; the observed first-order rate constant at 35 °C was $20.8 \times 10^{-5} \text{ s}^{-1}$, and the product was (Me₃Si)₂(Ph₂MeSi)CSiMe₂OMe.

A similar procedure was used for TsiSiHMeI except that the CHCl₃ was omitted and the height of the Me₃Si protons used directly.

In all cases good first-order kinetics were observed up to at least three half-lives, and rate constants were reproducible to within $\pm 5\%$.

Identification of Products.—The identities of the products were established by comparison of their ¹H n.m.r. spectra with those of authentic samples; usually the n.m.r. spectra of the product solutions were used, but in some cases the

product was isolated as a solid and its solution in CCl₄ used. The proportions of TsiSiMe₂ONO₂ in the product mixtures obtained from methanolysis in the presence of nitrate ion were derived by comparing the heights of the signals from the Me₂Si and Me₃Si protons with those of the corresponding signals from TsiSiMe₂OMe; the proportions are probably accurate to within $\pm 10\%$.

Treatment of TsiSiMe₂OCIO₃ with CF₃CH₂OH.—A solution of TsiSiMe₂OCIO₃ (0.1 g) in CF₃CH₂OH (5 cm³) was boiled under reflux for 24 h. The solvent was evaporated off, and the residue shown spectroscopically to be unchanged starting material.

Reaction of TsiSiMe₂OCIO₃ with H₂O in MeOH.—A solution of TsiSiMe₂OCIO₃ (0.1 g) in MeOH (5 cm³) containing 1 vol % of water was kept at 22 °C for 1 h. The solvent was then evaporated off under vacuum, and the ¹H n.m.r. spectrum of the residue was recorded. This showed that the product was TsiSiMe₂OH, and contained no detectable TsiSiMe₂OMe (*i.e.* <5%). An identical result was obtained when 4 vol % H₂O was used.

Reaction of TsiSiMe₂I with AgNO₃ in Aqueous MeOH.—A solution of TsiSiMe₂I (0.10 g, 0.24 mmol) and AgNO₃ (0.30 mmol) in MeOH (5 cm³) containing 4 vol % of H₂O was refluxed for 1 h. (Reaction was probably complete in a much shorter time.) The solid was filtered off, and the filtrate was evaporated to dryness under vacuum. The residue was extracted with hexane, and the hexane solution was filtered and evaporated. The ¹H n.m.r. spectrum of the residue showed that it consisted of TsiSiMe₂OMe and TsiSiMe₂ONO₂ in 75 : 25 ratio, and that no detectable TsiSiMe₂OH (*i.e.* <5%) had been formed.

Reaction of TsiSiMe₂I with AgNO₃ in CF₃CH₂OH.—A solution of TsiSiMe₂I (0.24 mmol) and AgNO₃ (0.27 mmol) in CF₃CH₂OH (5 cm³) was refluxed for 3 h, then evaporated to dryness. The residue was extracted with hexane, and the hexane solution was evaporated. The ¹H n.m.r. spectrum of the residue showed it to be a *ca.* 88 : 12 mixture of TsiSiMe₂OCH₂CF₃ [δ 0.24 (s, 27 H), 0.34 (s, 6 H), and 3.86 (q, 2 H)] and TsiSiMe₂ONO₂ [δ 0.30 (s, 27 H) and 0.63 (s, 6 H)].

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