The Methanolysis of the Highly Sterically Hindered Organosilicon Compounds $(Me_3Si)_3CSiMe_2X$ with X = OSO_2CF_3, OCN or $OClO_3$. A Mechanistic Enigma

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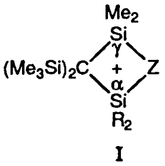
Rates of solvolysis have been determined for the compounds $(Me_3Si)_3CSiMe_2X$ with X = OSO_2CF_3, **3**, or OCN, **6**, $(Me_3Si)_3CSiMe(OMe)OSO_2CF_3$, **5**, and $(Me_3Si)_2C(SiMePh_2)(SiMe_2OSO_2CF_3)$, **4**, in MeOH alone or containing water or NaOMe. The methanolyses of the trifluoromethanesulfonates and the cyanate [like those of the perchlorate $(Me_3Si)_3CSiMe_2OClO_3$, **2**, and iodide $(Me_3Si)_3CSiMe_2I$ previously studied] are only slightly accelerated by the presence of NaOMe (which, however, promotes isomerization of the cyanate to the isocyanate). The rate and course of the reaction are remarkably sensitive to the presence of water; thus the cyanate **6** in the presence of only 0.05% v/v of water gives exclusively the hydroxide $(Me_3Si)_3CSiMe_2OH$, as do the perchlorate **2** and trifluoromethanesulfonate **3** in the presence of 1% of water, and addition of 1% of water increases the rate of disappearance of the substrate by factors of 6.0, 4.8 and 6.2, for **2**, **6** and **3**, respectively. The plot of the rate constant against the water concentration is linear for **3**, but curved for **6**, though tending towards linearity at the higher water concentrations. The approximate relative reactivities of the compounds $(Me_3Si)_3CSiMe_2X$ towards MeOH at 35 °C are (X=) $OClO_3$, 3.0; OSO_3CF_3, 1.0; OCN, 1.0; I, 10^{-3}. The results (and those previously observed for $Bu^t{}_3SiOSO_2CF_3$ and $Bu^t{}_3SiI$) are considered to rule out a mechanism involving a cationic intermediate [including the S_N2(intermediate) mechanism], but also appear to be inconsistent with bimolecular nucleophilic substitution *via* either a five- or six-coordinate transition state. No satisfactory mechanism can be suggested, but some of the observations can be tentatively rationalized in terms of preassociation of water with the substrate or an intermediate.

The rate of methanolysis of the iodide $(Me_3Si)_3CSiMeFI$ has been shown to be very little affected by the presence of base; the estimated relative reactivities of this iodide, $(Me_3Si)_3CSiMe_2I$, and $(Me_3Si)_3CSiMeHI$ towards MeOH at 60 °C are 1, 10^{-2} and 10^4, respectively.

We observed some years ago that iodides of the type $(Me_3Si)_3CSiR_2I$ react with various electrophiles, such as Ag^I salts, Hg^{II} salts, CF_3CO_2H, and ICl, to give the rearranged products $(Me_3Si)_2C(SiR_2Me)(SiMe_2Y)$, either exclusively (R = Ph) or (R = Et) along with the unrearranged products $(Me_3Si)_3CSiR_2Y$.[1,2] (For a review of the nucleophilic substitution reactions of such highly sterically hindered species see ref. 3.) It is thought that methyl-bridged cations of type **I** with Z = Me are initially formed and are then attacked by the nucleophile Y^- at either the α- or γ-Si centre, attack at the least sterically hindered centre usually (though not always[4,5]) being favoured. If one of the Me groups in the $(Me_3Si)_3C$ ligand (the 'trisyl' ligand, subsequently denoted by Tsi) is replaced by a group better able to bridge in the intermediate cation (and thus able to provide greater anchimeric assistance to the departure of I^-), *e.g.* Ph[6] or $CH{=}CH_2$,[7] then the reactions with the electrophiles are faster, so that *e.g.* $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2I)$ reacts readily with the weakly nucleophilic and relatively strongly electrophilic alcohol CF_3CH_2OH, whereas $(Me_3Si)_3CSiMe_2I$, **1** reacts only very slowly if at all.[6]



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Knowing of these reactions involving cationic intermediates, when we found that the methanolyses of the perchlorate $TsiSiMe_2OClO_3$, **2**, and the iodide TsiSiPhHI were not significantly accelerated by the addition of NaOMe [in contrast to those of the corresponding bromide TsiSiPhHBr and nitrate $TsiSiPhH(ONO_2)$], we suggested (using reasoning long established for solvolysis of alkyl halides) that in these methanolyses, and by implication that of **1**, the rate-determining step was the formation of the methyl-bridged cation of type **I** with Z = Me. The cation would then react rapidly with the solvent to give the methoxide.[8] This attribution of an S_N1 mechanism to the methanolysis was later abandoned when it was found that $TsiSiEt_2I$ gave exclusively the unrearranged $TsiSiEt_2OMe$, whereas *ca.* 50% of the rearranged $(Me_3Si)_3C(SiMeEt_2)(SiMe_2OMe)$ would have been expected for reaction *via* the bridged ion **I**, R = Et.[9] (Likewise hydrolysis of $TsiSiEt_2I$ and $TsiSiPh_2I$ gave only unrearranged products).[9,10] For a time we tentatively favoured an S_N2(intermediate) mechanism.[9] In this mechanism solvent is nucleophilically involved in the rate-determining transition state although there is much cationic character at the functional centre; such a process was judged to operate in, for example, the solvolyses of *tert*-butyl halides, which are also not accelerated by base.[11,12] This mechanism in turn was abandoned when we found that in methanolysis of the iodides $TsiSi(C_6H_4Y)HI$ electron-withdrawal by Y increased the rate, whereas the opposite would be expected for a mechanism involving development of positive charge at the functional silicon centre.[13] Thus in solvolysis of highly sterically hindered species of the types under consideration, in addition to reactions by a seemingly straightforward S_N2 process (*e.g.* for methanolysis of TsiSiPhHX, where X = Br of ONO_2 [8]) or by the well-established S_N1 process [*e.g.* for the solvolysis of $TsiSiMe_2I$, **1**, in CF_3CO_2H[1] of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2I)$ in CF_3CH_2OH,[6] and of $(Me_3Si)_2C(SiMe_2C_6H_4OMe\text{-}p)(SiMe_2I)$ in MeOH[6]], there appeared in methanolysis to be a

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Table 1 Rate constant and product data for reactions of the trifluoromethanesulfonates **3** and **4** at 35 °C in MeOH, alone or containing additives

Substrate	Additive[a]	Method[b]	Product(s)[c]	$k/10^{-5}$ s^{-1}[d]	k_{rel}[e]
3	None	A	**8**	23	1.0
	NaOMe, 0.05		**8**	35	1.5
	NaOMe, 0.10		**8**	36	1.6
	NaOMe, 0.20		**8**	37	1.7
	NaOMe, 0.50		**8** (90), **11** (10)	48	2.1
	LiNo$_3$, 0.23		**8** (70), **10** (30)	40	1.7
	LiNO$_3$, 0.91		**8** (45), **10** (55)	50	2.2
	H_2O, 1.00%		**9**	110	4.8
3	None	B	**8**	24	1.0
	H_2O, 0.025%		**8** (65), **9** (35)	25	1.04
	H_2O, 0.050%		**8** (62), **9** (38)	27	1.1
	H_2O, 0.100%		**8** (57), **9** (43)	30	1.25
	H_2O, 0.20		**8** (46), **9** (54)	35.5	1.5
	H_2O, 0.40		**8** (30), **9** (70)	47	2.0
	H_2O, 0.60		**8** (10), **9** (90)	60	2.5
4	None	A	**12**	20	1.0
	MeONa, 0.10		**12**	29	1.5
	MeONa, 0.20		**12**	30	1.5
	MeONa, 0.50		**12** (90), A[f] (10)	42	2.1
	LiNO$_3$, 0.23		**12** (70), **14** (30)	39	2.0
	LiNO$_3$, 0.91		**12** (40), **14** (60)	54	2.7
	H_2O, 1.00%		**13**	100	5.0

[a] Concentrations of salts are in mol dm^{-3}. Concentrations of water are in vol %. [b] See Experimental section. [c] Numbers in parentheses indicate percentages. [d] First-order rate constant for disappearance of substrate. [e] Rate constant relative to that in MeOH alone. [f] Fragmentation product, probably $(Me_3Si)_2CH(SiMePh_2)$.

puzzling third type of process which seemed not to involve a cationic intermediate but was not accelerated by methoxide ion.

It seemed significant that the unusual behaviour was observed only for the best leaving groups studied, *viz.* ClO_4^- and I^-, and to provide further relevant information, and also simply to gain knowledge of the leaving group abilities of perchlorate, trifluoromethanesulfonate, cyanate and iodide ion we decided to examine the methanolysis and hydrolysis of compounds **2**–**7**.

$TsiSiMe_2X$	$(Me_3Si)_2C(SiMePh_2)(SiMe_2X)$
1 X = I	**4** X = OSO_2CF_3
2 X = $OClO_3$	**12** X = OMe
3 X = OSO_2CF_3	**13** X = OH
6 X = OCN	**14** X = ONO_2
8 X = OMe	
9 X = OH	
10 X = ONO_2	

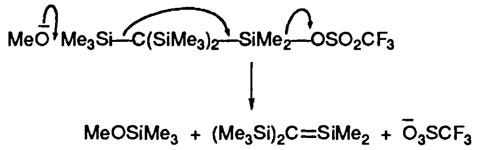
$TsiSiMe(OMe)(OSO_2CF_3)$
5

TsiSiMeFI
7

$(Me_3Si)_2CH(SiMe_2OMe)$
11

Results

The rates of disappearance of the trifluoromethanesulfonate **3** in MeOH, alone or containing NaOMe, were determined by ^1H NMR spectroscopy. The results are shown in Table 1. It will be seen that there is an increase in rate by *ca.* 50% on introduction of 0.050 mol dm^{-3} base, but little further increase on going to 0.20 mol dm^{-3} base. (Similar behaviour was previously observed for the iodide TsiSiPhHI and the perchlorate **2**, but for those the initial increase in rate was somewhat smaller, *e.g.* by *ca.* 20% on addition of 0.10 mol dm^{-3} base).[8] In the presence of 0.50 mol dm^{-3} base *ca.* 10% of the trifluoromethanesulfonate was converted into the methoxide $(Me_3Si)_2CH(SiMe_2OMe)$, **11**, which is presumably formed by the elimination–addition sequence depicted in eqn. (1) (*cf.* ref. 14).



(1a)

$$(MeSi)_2C{=}SiMe_2 + MeOH \longrightarrow (Me_3Si)_2CHSiMe_2OMe \qquad (1b)$$

In the presence of 0.23 and 0.91 mol dm^{-3} LiNO$_3$, the rate of disappearance of **3** was increased by 70 and 120%, respectively, and the nitrate $TsiSiMe_2ONO_2$, **10**, formed *ca.* 30 and 55% of the products. Comparable behaviour was observed for the perchlorate **2**, the presence of 0.24, 0.47 and 0.91 mol dm^{-3} LiNO$_3$ increasing the rate by 39, 96 and 130%, respectively, and leading to formation of *ca.* 30, 50 and 83% of the nitrate, **10**.[8]

Since the addition of a little water had been found to have a marked effect on the methanolysis of the perchlorate **2** (*e.g.*, 1% of water increased the rate six-fold and diverted the reaction wholly to formation of the hydroxide, **9**), we next examined the effect of such addition in the case of the trifluoromethanesulfonate **3**. (The reaction was monitored by determining at intervals the ratio of the height of the signals from the SiMe$_2$ protons in **3** to that of the combined heights of the corresponding signals from $TsiSiMe_2OMe$ and $TsiSiMe_2OH$. The relative amounts of these products were determined by GLC analysis when reaction was complete). The values of the observed rate constants for disappearance of **3** are shown in Table 1.

The most striking feature of the results is that addition of as little as 0.025% of water results in formation of 35% of the hydroxide,* water thus apparently being *ca.* 950 times as

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* Throughout this paper the water concentration is expressed in percentage by volume.

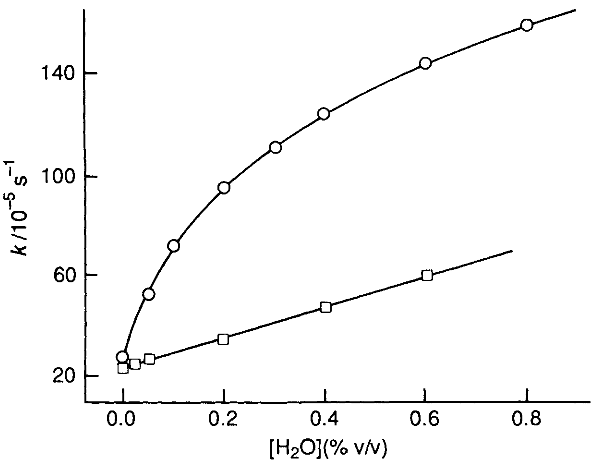

Fig. 1 Plots of observed first-order rate constants at 35 °C against the concentration (in vol%) of water for $TsiSiMe_2OSO_2CF_3$, **3** (□) and $TsiSiMe_2OCN$, **6** (○)

Table 2 First-order rate constants k for the disappearance of $TsiSiMe(OMe)(OSO_2CF_3)$, **5**, and TsiSiMeFI, **7**, at 60.0 °C in methanol alone or containing additives[a]

Substrate	Additive	$k/10^{-5}\ s^{-1}$	k_{rel}[b]
5	None	5.0	1.0
	NaOMe, 0.050	7.7	1.5
	NaOMe, 0.10	7.7	1.5
	NaOMe, 0.30	7.8	1.6
	NaOMe, 0.50	10.0	2.0
	H_2O, 1%	17.2	3.4
7	None	11.0	1.0
	NaOMe, 0.050	12.0	1.1
	NaOMe, 0.10	12.0	1.1

[a] The products were the corresponding methoxides $TsiSiMe(OMe)_2$ and TsiSiMeF(OMe), except for **5** in the presence of water, when it was exclusively TsiSiMe(OMe)(OH). [b] Rate relative to that in MeOH alone.

Table 3 Observed first-order rate constants k for disappearance of the cyanate **6** at 35.0 °C in MeOH alone or with added water[a]

Added H_2O (%)	$k/10^{-5}\ s^{-1}$	k_{rel}[b]
0.00	28	1.0
0.05	52	1.85
0.10	72	2.6
0.20	96	3.4
0.30	112	4.0
0.40	125	4.5
0.60	145	5.2
0.80	160	5.7

[a] With no added water a *ca.* 90/10 mixture of the methoxide **8** and hydroxide **9** was formed. In other cases only **9** was formed. [b] Rate constant relative to that without added water.

effective as methanol on a molar basis in determining the product, but this is probably an overestimate because results for the cyanate described later indicate that the 'dried' methanol probably contained some water; however, even if the water concentration in that methanol was as high as 0.02%, which is unlikely, the selectivity factor would still be *ca.* 530. The apparent selectivity factors at the higher concentrations of added water (with neglect of water initially present, the effect of which would be unimportant above 0.1% of added water) are: 0.05%, 540; 0.10, 440; 0.20, 260; 0.40, 220; 0.60, 670. (The last of these values probably reflects inaccuracy in measurement of the hydroxide/methoxide product ratio for low percentages of either component). A plot of the observed rate constant against the concentration of water is linear (see Fig. 1); *i.e.*, after the initial rate increase on addition of 0.025% of H_2O the observed rate constant shows a first-order dependence on the water concentration. The rate constant for the reaction of the perchlorate **2** also showed a linear dependence on the water concentration for the three concentrations, 1.0, 2.0 and 3.0% used; addition of 1% of water apparently caused a 4.8-fold increase in rate for **3**, compared with one of 6.0 for **2** at 27.5 °C[8] (but we note that extrapolation of the linear rate *versus* %-water plot for **3**, based on data obtained some time later by a different method, indicates a 25% lower rate increase).

The results for the related trifluoromethanesulfonate **4** are also shown in Table 1. This compound was a little less reactive than **3**, but otherwise its behaviour was remarkably similar. The methoxy derivative **5** (which gave the expected product $TsiSiMe(OMe)_2$ [except in the presence of 1% of water when TsiSiMe(OMe)(OH) was exclusively formed] was markedly less reactive and was examined at 60.0 °C (Table 2); if the rate is assumed to increase by a factor of 2–2.5 for a 10 °C rise in temperature then **5** is *ca.* 25–45 times less reactive than **3**. The effects of added NaOMe are very similar to those for **3** and **4**, but the increase in rate on addition of 1% of H_2O, by a factor of 3.4, was apparently rather smaller (the temperature difference possibly playing some part in this).

We next turned to the cyanate **6**. In this case the reactions were carried out in NMR tubes and monitored by ^1H NMR spectroscopy. Again, at the end of the reaction the composition of the product was determined by GLC analysis. The results are shown in Table 3. It was found that even without added water *ca.* 10% of the hydroxide was formed, indicating that at least 0.01% of water must have been present in the MeOH we used, which we had dried by a standard method. With 0.05% of added water only hydroxide could be detected. If we assume that perhaps only 90% of the hydroxide was actually formed (certainly 5% would have escaped detection) and that the actual water concentration was as high as 0.07%, then the selectivity towards reaction with water involves a factor of *ca.* 5700, and this must be a minimum value. In this case the plot of the observed rate constant, k, against the water concentration is curved, tending towards linearity at the higher water concentration (see Fig. 1). Extrapolation points to a *ca.* 6.2-fold rate increase on addition of 1% of water in the case of **6**, compared with factors of 6.2 and *ca.* 4.8 for **2** and **3** respectively.

Both the perchlorate **2** and the trifluoromethanesulfonate **3** had been shown to be unreactive towards CF_3CH_2OH (**3** undergoing no detectable reaction during 24 h under reflux)[10] and we found that the cyanate likewise underwent no reaction with this alcohol during 24 h at room temperature. We also found that it did not react with this alcohol containing 2% of water during 2 h at room temperature. (When the mixture was diluted with an equal volume of MeOH the reaction, giving exclusively the hydroxide, was *ca.* 25, 50 and 100% complete after 1.5, 3 and 18 h, respectively). This result might seem surprising in view of the great sensitivity of the cyanate towards water in MeOH but, at least towards carbocations, on a molar basis water in this medium is only about as nucleophilic as the solvent itself (presumably because of the strong hydrogen bonding to this fairly acidic alcohol),[15] and the overall nucleophilicity of the alcohol is little changed by addition of 3% of water.[16] Therefore no hydrolysis would be expected at the water concentration used if, as appears to be the case, nucleophilic attack at silicon is the greatly dominant feature in the solvolyses.

From the data for **3** and **6** in Tables 1 and 3 and previously published data for the perchlorate **2** ($k = 74 \times 10^{-5}\ s^{-1}$) and the iodide **1** ($k$ = *ca.* 0.02 × 10^{-5} s^{-1} by extrapolation from data at 50 and 61 °C), the relative rates of reaction with methanol at 35 °C can be estimated to be as follows: $TsiSiMe_2OClO_3$, 3.0; $TsiSiMe_2OSO_2CF_3$, 1.0; $TsiSiMe_2OCN$, 1.0; $TsiSiMe_2I$, *ca.* 10^{-3}. (Towards 0.6% H_2O–MeOH, however, the cyanate is 2.7 times as reactive as the trifluoromethanesulfonate. The high leaving group ability of cyanate ion from silicon reflects that from carbon implied by the fact that the isomerization of the primary isocyanate EtOCN proceeds *via* ionization.[17]) The effect of added NaOMe on the rate of solvolysis of **6** was not accurately determined because the base promotes isomerization to the isocyanate $TsiSiMe_2NCO$ (which is very unreactive towards MeOH).[18] However, the first-order rate constant for the overall rate of disappearance of **6** in the presence of 0.10 mol dm^{-3} NaOMe was 130 × 10^{-4} s^{-1} and the products were $TsiMe_2NCO$, $TsiMe_2OMe$ and $TsiMe_2OH$ in *ca.* 7:2:1 ratio, indicating a rough value of k of 40 × 10^{-5} s^{-1} for the solvolysis compared with that of 28 × 10^{-5} s^{-1} for reaction in the absence of base, a percentage increase comparable with that for solvolysis of the trifluoromethanesulfonate.[3]

If the mechanism of solvolysis of **2**, **3**, **4** and **6** is considered in the light of the effects of added water then simple competition between direct displacement of the leaving group by nucleophilic attack by a methanol and that by a water molecule, *via* a pentacoordinate transition state (and possibly a pentacoordinate intermediate), can apparently be ruled out. This is because for such a mechanism the overall rate constant should be the sum of the separate rate constants for the formation of the methoxide and hydroxide. Thus for the perchlorate, for example, if it is assumed that in the presence of 1% of water only 95% of the hydroxide was actually formed, rather than the observed 100%, the rate of hydrolysis would have to be 19 times that of methanolysis and so the overall rate should be 20 times as large as that in MeOH alone, whereas the observed factor is 6. (The actual discrepancy is probably much greater, since it is likely that within the limits of accuracy of the analysis 100% of the hydroxide would be formed with substantially less than 1% of water present, as in the case of the cyanate.) Similarly, if we assume for the cyanate **6** that in MeOH containing no added water, in which *ca.* 10% of the hydroxide was formed, the observed rate constant of 28 × 10^{-5} s^{-1} is made up of *ca.* 25.2 × 10^{-5} for the methanolysis and 2.8 × 10^{-5} s^{-1} for the hydrolysis (as would be the case if there were simple competition between straightforward nucleophilic displacement processes) then at 0.05% added water, on the assumption that only 95% of the product is hydroxide, the rate constant for the hydrolysis would have to be (25.2 × 95/5) × 10^{-5} s^{-1}, *i.e.* 480 × 10^{-5} s^{-1}, and the overall rate constant *ca.* 500 × 10^{-5} s^{-1} compared with the observed 52 × 10^{-5} s^{-1}. (The actual discrepancy is again probably substantially larger). The effect is smaller for the trifluoromethanesulfonate but still evident; thus addition of 0.025% of water, which results in formation of 35% of the hydroxide, should cause a rate increase of *ca.* 54% compared with the observed 6%; after addition of 0.10% of water, when the presence of some water in the 'dried' methanol would have only a small effect, the rate is increased by 75% compared with the calculated 30%.*

The clear implication is that the products are not determined in the rate-limiting step, and so we must briefly consider again the possibility that for the perchlorate **2**, the trifluoromethanesulfonate **3**, and the cyanate **6** this step involves ionization to give a cation (presumably of type **I**), which is then attacked by the nucleophiles present, even though we previously discarded this mechanism for the methanolysis of the iodides TsiSiMe(C_6H_4Y)I, and by implication that of the iodide **I**.[13] We can rule out the generation of 'free', *i.e.*, fully-separated, fully-solvated cations, as in the classical picture of S_N1 reactions of alkyl halides, for the following reasons. (i) Since the cation would be the same in each case, compounds **2**, **3** and **6** should show the same selectivity between water and methanol, which is not the case. Moreover, it would be the same cation as that formed from the iodide **1** and $AgNO_3$ in MeOH, and it is known that in the presence of 4% of water the latter reaction gives the methoxide (75%) and the nitrate (25%), with no detectable (*i.e.* <5%) hydroxide.[8] [This is consistent with the fact that, on a molar basis, in H_2O–MeOH mixtures carbocations react more readily with methanol than with water molecules; *e.g.* reaction of the cation (p-$MeOC_6H_4)_2CH^+$ with 10% H_2O–MeOH gives only 7% of the alcohol (p-$MeOC_6H_4$)CHOH].[19] (ii) Compounds **2**, **3**, **6** are unreactive towards CF_3CH_2OH (and **6**, and probably the others, also towards 2% H_2O–CF_3CH_2OH) whereas ionization should be much faster in this solvent than in MeOH; *e.g.* 2-adamantyl perchlorate undergoes S_N1 solvolysis 113 times as rapidly in CF_3CH_2OH as in MeOH at 0 °C,[20] and for the related p-toluenesulfonate the factor is 520 at 25 °C.[11] (For the reaction of methyl p-toluenesulfonate, by an S_N2 mechanism, the reaction is 140 times as fast in MeOH as in CF_3CH_2OH).[11] (iii) The effect of water on the overall rate (although small in relation to the amount of hydroxide formed, as noted above) seems too large to be simply a medium effect; for example, in the case of the perchlorate **2** addition of 1% of water causes a six-fold increase in the rate, whereas addition of 10% of water is needed to bring about such an increase in the rate of S_N1 solvolysis of 2-adamantyl perchlorate at 0 °C.[20] (iv) If the rate-determining step involved ionization, the trifluoromethanesulfonate **4** would be expected to be markedly more reactive than **3** because of anchimeric assistance by a γ-Ph group to the breaking of the Si–OSO_2CF_3 bond [$(Me_3Si)_2C(SiMePh_2)(SiMe_2I)$ is much more reactive than **1** in solvolysis in CF_3CH_2OH[21]], whereas it is actually somewhat less reactive than **3**. (v) Such a mechanism cannot operate in the case of the iodide **1** since, as mentioned earlier, the methanolysis of $TsiSiEt_2I$ is not accompanied by any rearrangement; however, as we consider later below, it is possible that **1** undergoes solvolysis by a mechanism different from that for the more reactive species **2**, **3** and **6**.†

For alkyl halides and related species a range of mechanisms intermediate between the classical (limiting) S_N1 and S_N2 processes has been suggested but none seems to us to offer a wholly satisfactory interpretation of our results. We can consider, for example, the possibility that the products are determined in a fast nucleophilic attack not on a free cation but on an intimate ion-pair formed in the rate-determining step (*ca.* ref. 22). In this case the ratio of hydroxide to methoxide product would not be the same for all the reactants, but, with this one exception, all the arguments advanced above against reaction through a solvent-separated ion pair apply here also.

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* It may be significant that the rate constants, k_{OMe}, for the methanolysis, given by multiplying the observed overall rate constant by x/100, where x is the percentage of the methoxide in the products, after an initial fall from the value of 25 × 10^{-5} s^{-1} for MeOH alone, remain roughly constant, at values around 17 × 10^{-5} s^{-1} for 0.025–0.4% added water; over this range the corresponding rate constant, k_{OH}, for the hydrolysis rises from *ca.* 9 to *ca.* 33 × 10^{-5} s^{-1}.

† When we favoured an S_N1 mechanism for methanolysis of the perchlorate **2** we attributed the exclusive formation of the hydroxide in the presence of 1% of water to the stability of the solvent-separated ion pair arising from the presence of two hydrogen bonds between a water molecule and the ClO_4^- ion (*cf.* J. M. Harris, *Prog. Phys. Org. Chem.*, 1974, **11**, 89).[8] Such an explanation could, in principle, apply also to the effect of water on the reaction of the trifluoromethanesulfonate **3**, but not to that of cyanate **6**, which is the most sensitive of all to the presence of traces of water, and so would have to be discarded for all three compounds **2**, **3** and **6**.

Since the mechanism for the iodide **1** is not necessarily the same as that for **2**, **3** and **6**, we must consider for the latter compounds the S_N2(intermediate) mechanism that we previously discarded for **1**. In this mechanism a nucleophilically solvated ion-pair intermediate is generated in the rate-determining step and the products are determined by the fate of this intermediate, which can go on to give the same product as that from a direct nucleophilic displacement (with inversion of configuration in the case of alkyl derivatives), or be attacked by other nucleophiles, or undergo other reactions.[11,12] The rate enhancement on addition of water would then be the result within the ion-pair of both better electrophilic solvation of the anion and better nucleophilic solvation of the cation by water than by methanol. In these very crowded systems the smaller size of the water molecule could make it markedly more effective than methanol for the nucleophilic solvation and much more effective as a nucleophile in the subsequent O-Si bond formation. Thus water would substantially enhance the rate and very effectively divert the reaction to formation of hydroxide, but there need be no simple quantitative relation between the rate enhancement and the proportion of hydroxide formed.

The absence of significant rate enhancement upon addition of NaOMe could perhaps be attributed to the need for desolvation of the methoxide ion before it can participate in the initial nucleophilic interaction, as suggested for solvolysis of alkyl derivatives that are thought to proceed by the S_N2(intermediate) mechanism;[11,12] the bulk of the solvated methoxide or hydroxide ion may make it especially ineffective in approaching the highly hindered reaction centre in compounds **2**–**6**. However, in contrast to alkyl derivatives, *e.g.* Bu^{t}Cl, thought to react by this mechanism, compound **1** and (very readily) compounds **2**, **3** and **6**, undergo seemingly normal bimolecular displacement reactions with strong nucleophiles such as N_3, F and SCN$^-$ in MeOH[23] (and the formation of nitrate products in the reactions of the perchlorate **2** and the trifluoromethanesulfonate **3** and **4** in the presence of $LiNO_3$ is possibly also wholly or mainly by direct displacement). A further difficulty is that the nucleophilically solvated ion pair would be expected to be formed more readily in the case of **4** than of **3** because of anchimeric assistance by the Ph group. We thus conclude that the S_N2-(intermediate) mechanism does not provide an adequate explanation of the behaviour of compounds **2**–**4** and **6** (and certainly not that of the iodide **1**).

Corriu and his colleagues have suggested that some nucleophilic substitutions at silicon involve rapid and reversible attack by one molecule of the nucleophile to give a five-coordinate intermediate, which is then attacked by a second such molecule with displacement of the leaving group *via* a six-coordinate transition state, and perhaps a six-coordinate intermediate.[24] (For a discussion of this mechanism see ref. 3.) Such a mechanism would not account for the fact that the rate of hydrolysis shows first-order dependence on the water concentration and that the rate increase on addition of water in the case of compounds **2**–**6** is not commensurate with the proportion of hydroxide product, but both features would be consistent with a related mechanism in which the second step is fast, with water, mainly for steric reasons, acting as a sufficiently better nucleophile than methanol to give a substantial increase in the rate when present even at very low concentrations, and then being much more effective than methanol in the subsequent product-determining step. However, neither of the mechanisms involving a six-coordinate transition state would offer any obvious explanation of the absence of acceleration by added base, and furthermore six-coordinate species seem especially unlikely for the very crowded compounds under consideration.

The results for the α-methoxy-substituted trifluoromethanesulfonate **5** (Table 2) seem to throw no further light on the mechanism. Inductive electron-withdrawal by the OMe group should facilitate nucleophilic attack at silicon but this could be outweighed by increased steric hindrance. The deactivating effect of the α-methoxy group contrasts greatly with the very large activating effect of the γ-OMe group in solvolysis of the chloride $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$.[25]

The α-F substituted iodide **7** is markedly more reactive than **1** (see Table 3) and markedly less reactive than the related iodide TsiSiMeHI; from data at other temperatures for the latter and **1**, the relative reactivities at 35 °C can be very roughly estimated as $TsiSiMe_2I$, *ca.* 10^{-2}; TsiSiMeFI, 1; TsiSiMeHI, 10^4. The increase in reactivity in this series is probably mainly attributable to the decreasing steric hindrance to nucleophilic attack. The effects of added NaOMe seem to be even smaller for **7** than for the other two iodides and TsiSiPhHI.

We have in the past usually assumed that the perchlorate **2**, the trifluoromethanesulfonate **3**, and the iodides **1**, TsiSiPhHI and TsiSiMeHI undergo methanolyses by the same mechanism because in all cases there is no significant acceleration by sodium methoxide, and it further seemed reasonable to group perchlorates, trifluoromethanesulfonates and iodides together since they contain by far the best leaving groups studied, though iodide is much less powerful in this respect than the other groups. This assumption may not have been justified, however, and there is at least one significant difference between the reactions of the iodides and the other species, namely that the iodide **1** reacts (at 60 °C) only about 2.5 times as rapidly with 5% water in MeOH as in MeOH alone,[26] and TsiSiPhHI only 1.7 times as rapidly with 3.3%, and 2.8 times with 10%, of water present as in MeOH alone.[8] We know that the effects of substituents Y in the methanolysis of the iodides $TsiSiH(C_6H_4Y)I$ are consistent with direct bimolecular nucleophilic displacement, and this applies also to the non-S_N1 component of the (mixed-mechanism) methanolysis and hydrolysis of the iodides $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2I)$, and since anions attack all the above iodides readily the best working hypothesis at present would seem to be that the iodides **1**, TsiSiPhHI, and TsiSiMeFI undergo solvolysis by an S_N2 mechanism, with the anomaly that methoxide is remarkably ineffective as a nucleophile towards these compounds. For $TsiSiMe_2I$ this could plausibly be attributed to a combination of the steric effects arising from the bulk of the iodine atom and that of the solvated methoxide ion, and steric hindrance by the iodide ligand was suggested to be partly responsible for the fact that the highly hindered iodide Bu^t_3SiI is less reactive than the corresponding chloride towards the nucleophiles N_3^-, SCN$^-$ and OCN$^-$ in MeCN and the iodide **1** only six times as reactive as the chloride $TsiSiMe_2Cl$ under similar conditions.[26] It would be surprising, however, for the hindrance to be large enough to inhibit attack of methoxide ion in the case of TsiSiPhHI and TsiSiMeHI, containing the small hydride ligand.

In summary it seems that three mechanistic classes can be distinguished for solvolysis of TsiSiRR′X and related species, as follows.

(*a*) Bimolecular S_N2 substitution (possibly *via* a five-coordinate silicon intermediate) as, for example, in the methanolysis of the compounds TsiSiPhHX with X = Br, ONO_2, O_3SMe, F *etc.*, all of which are substantially accelerated by the presence of NaOMe.[8,27] Methanolysis of the iodides **1** and TsiSiPhHI is also probably of this type, but with the seeming anomaly that NaOMe has little effect on the rate.

(*b*) Substitution involving rate-determining ionization with anchimeric assistance by a γ-Me or other group, to give a bridged cationic intermediate of type **I**, which is then attacked by the solvent. Examples are the solvolysis of iodides TsiSiRR′I in CF_3CO_2H,[1] of $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2I)$ in CF_3CH_2OH,[6] and of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ in MeOH[26] (the increasing anchimeric assistance in this series more than compensating for the decreasing ionizing power of the medium).

In cases which permit its detection, *e.g.* solvolysis of $TsiSiEt_2I$ in CF_3CO_2H[1] or of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$ in MeOH,[6] some rearranged product is formed by migration of a γ-Me or γ-Ph group. Rates are little affected by the presence of lyate ion. In some cases the mechanism can operate alongside a bimolecular process; *e.g.* in methanolysis and hydrolysis of the iodides $(Me_3Si)_2C(SiMe_2C_6H_4Y)(SiMe_2I)$.[6]

(*c*) An unidentified process, seemingly operating in methanolysis and hydrolysis for the very reactive compounds **2**, **3** and **6** (which are very readily attacked by anions such as N_3^-, F^-, and SCN^- in MeOH).[18,24] The reactions are not significantly accelerated by the addition of base, but markedly accelerated by the addition of a little water, which also diverts the reaction very powerfully towards formation of the hydroxide, to a much greater extent than would be expected from the overall rate increase. The reactions do not involve ionization, but seem not to be straightforward bimolecular nucleophilic substitutions.

There is available a concept that could be used to account for both the marked increase in rate of solvolysis on addition of water and the disproportionate amount of hydroxide formed, namely that of selective solvation of the substrate or an intermediate, often referred to as solvent sorting.[15] Thus water molecules might, because of their small size, aggregate very selectively around the substrate, $TsiSiMe_2X$, presumably mainly by hydrogen bonding to the OSO_2CF_3, $OClO_4$ or OCN group; and not only could the rate be increased substantially by the presence of a little water but furthermore methanol molecules could be virtually denied access to the reaction centre. Moreover, if such preassociation of solvent molecules involved hydrogen bonding, with subsequent nucleophilic attack by one of the pre-bound solvent molecules in a direct substitution of the S_N2 type, then it is conceivable that attack by lyate ions would also be inhibited (though, as we note elsewhere, other anions do readily attack these substrates). Solvent sorting has recently been judged to be relatively unimportant in solvolyses of alkyl halides, arenesulfonates, perchlorates and related species,[15] and we are not enthusiastic about it as an explanation of our results (partly because it can in a sense be regarded only as a restatement rather than a solution of the problem, and furthermore its operation is virtually impossible to prove or disprove), but it does offer a very tentative rationalization of them. Whether or not this explanation is valid, it should not be surprising to find unusual solvation effects in the systems under consideration, in which the hydrogen-bonded solvent structure is disrupted by massive near-spherical, largely hydrocarbon-like, molecules having a polar centre on the shell of the sphere.

$Bu^t_3SiOSO_2CF_3$ Bu^t_3SiI
12 **13**

It should be emphasized that the puzzling features of the solvolysis of highly hindered trifluoromethanesulfonates and iodides of silicon are not specific to compounds containing $(Me_3Si)_3C$ and related ligands, being observed also for the tri-*tert*-butylsilyl compounds **12** and **13**.[26] Thus methanolysis of the trifluoromethanesulfonate **12** (which proceeds at a very similar rate to that of **3**) was found not to be accelerated in the presence of 0.1 or 0.2 mol dm^{-3} base (after an initial somewhat faster reaction in which traces of water present were selectively consumed), and this was the case also for the solvolysis in 1% H_2O–MeOH, which gave exclusively the hydroxide Bu^t_3SiOH and was *ca.* 14 times as fast as that in MeOH alone (compared with a factor of *ca.* 5 for **4**). The reaction of the iodide **13** with MeOH alone was very slow (perhaps about 40 times slower than that of **1**) but was substantially accelerated by addition of 2.0 mol dm^{-3} base; however, in 5% H_2O–MeOH the solvolysis proceeded at much the same rate as that of **1** and was not accelerated by 0.1 mol dm^{-3} base. Remarkably, hydrolysis by 2% water in dimethyl sulfoxide was not accelerated by the presence of 0.1 mol dm^{-3} NaOH, which produces a powerful nucleophilic system in this medium. It is very significant that whereas iodide **12** is (except for the reaction with MeOH alone) rather similar in reactivity to **1** towards nucleophiles (including various salts in MeCN), it is much less reactive towards electrophiles than **1**, which can give the stabilized cation of type **I**.[27]

Finally we suggest that knowledge of the peculiar features of substitutions at highly hindered silicon centres will in the long term increase understanding of mechanisms of substitution at unhindered centres in the way that studies of neopentyl derivatives played a major role in elucidation of mechanisms of substitution of alkyl halides and related compounds. The problems are much greater with silicon compounds, however, not only because the relevant reactions at less hindered centres are normally too fast to be studied by ordinary means but also because the range of possible mechanisms is much greater as a consequence of the availability (along in principle with a simple ionization mechanism of the S_N1 type) of processes involving five- or six-coordinate transition states and/or intermediates, each with several possible stereochemistries.

Experimental

Spectra.—The NMR spectra were recorded on a Perkin-Elmer R32 spectrometer (with solutions in CCl_4 unless otherwise stated) at 90 MHz for ^1H and 84.6 MHz for ^{19}F spectra, with Me_4Si or $CFCl_3$ as internal reference. The ^{19}F shifts are in ppm relative to $CFCl_3$.

Mass spectra were by electron impact at 70 eV. For analysis by GLC or linked GLC–mass spectrometry (GLC–MS) a 2 m column of 3% OV-1 on GasChrom G at 200 °C was used.

Materials.—The preparations of $TsiSiPh_2I$,[28] $TsiSiMe_2I$,[28] $TsiSiMe_2OCN$,[18] TsiSiMeFI,[29] $TsiSiMe(OMe)(OSO_2CF_3)$[29] and TsiSiMe(OMe)I[30] have been described. Silver trifluoromethanesulfonate (Aldrich) was dried for several hours at 110 °C at 1 mmHg with protection from light. Methanol was boiled with, and distilled from, $Mg(OMe)_2$ and stored over 3 Å molecular sieves. The solutions of NaOMe were made by dissolving sodium in methanol and diluting to the required concentration. The CCl_4 and CH_2Cl_2 were refluxed over $CaCl_2$ for 2 h, distilled, and stored over 4 Å molecular sieves.

Preparations of $TsiSiMe_2OSO_2CF_3$, **3** *and* $(Me_3Si)_2C(SiMePh_2)(SiMe_2OSO_2CF_3)$, **4**.—(*a*) A mixture of $TsiSiMe_2I$ (1.53 g, 3.7 mmol) and $AgSO_3CF_3$ (1.00 g, 3.9 mmol) in CH_2Cl_2 (25 cm^3) was stirred at room temperature under dry N_2 for 1 h. The solution was filtered under dry nitrogen, the solvent removed under reduced pressure, and the residue sublimed (80 °C at 0.2 mmHg) to give [dimethyl(trifluoromethanesulfonato)silyl]tris(trimethylsilyl)methane, **3** (1.34 g, 85%), m.p. 198 °C (Found: C, 35.8; H, 7.6. $C_{13}H_{33}F_3O_3SSi_4$ requires C, 35.6; H, 7.6%); δ_H 0.33 (27 H, s, $SiMe_3$) and 0.72 (6 H, s, $SiMe_2$); δ_F −77.0.

(*b*) A similar procedure but starting from $TsiSiPh_2I$ (2.0 g), and with recrystallization (twice) from dry pentane in place of sublimation, gave [dimethyl(trifluoromethanesulfonato)silyl](methyldiphenylsilyl)bis(trimethylsilyl)methane, **4** (0.78 g, 38%), m.p. 102 °C (Found: C, 49.4; H, 6.5; $C_{23}H_{37}F_3O_3SSi_4$ requires C, 49.1; H, 6.6%); δ_H 0.31 (18 H, s, $SiMe_3$), 0.61 (6 H, s, $SiMe_2$), 1.01 (3 H, s, SiMe), 7.2–8.0 (10 H, m, ArH); δ_F −76.7; *m/z* 562 (M^+) (low intensity), 547 ($[M - Me]^+$) and 197 ($MePh_2Si^+$).

Kinetic Studies.—Two methods were used for rate measurements, as follows.

Method A. A sample (*ca.* 4–5 mg) of the substrate was dissolved in two micro-drops (*ca.* 4 k mm^3) of $CHCl_3$ (for **3** and **4**) or $CHBr_3$ (for others) in an NMR tube and MeOH (0.5 cm^3), prewarmed to 35 °C in the case of the faster reactions, alone or containing MeONa, $LiNO_3$ or H_2O, was added. The tube was stoppered, shaken briefly, and placed in the probe of the NMR spectrometer, which was kept at the selected temperature (±0.4 °C) and the ^1H NMR spectrum was recorded at intervals. The ratio of the height of an appropriate signal from the substrate [at δ 0.72 ($SiMe_2$ protons) for **3**; 0.31 ($SiMe_3$) for **5** (except for the reactions with $LiNO_3$ present when the peak from the $SiMe_2$ protons at δ 0.61 was used); 0.68 ($SiMe_2$) for **6**; and 0.33 ($SiMe_3$) for **7**] to that from the $CHCl_3$ or $CHBr_3$ was used as the measure of the concentration of the substrate. On completion of the reaction the solution was normally either evaporated under reduced pressure and the residue taken up in CCl_4 or (when MeONa was present) shaken with CCl_4/H_2O, and the ^1H NMR spectrum of the CCl_4 solution recorded and compared with that of authentic samples of $TsiSiMe_2OMe$, $TsiSiMe_2OH$, and (where relevant) $(Me_3Si)_2CHSiMe_2OMe$, **11**. (The identity of the latter was confirmed by GLC–MS.) However in the case of reactions of **5** with $LiNO_3$ present the ratio of nitrate to methoxide product was estimated from the spectrum of the reaction solution by use of the peaks from the $Si\mathit{Me}_2Ph$ protons at δ 1.01 and 0.94 respectively, and for the similar reactions with **3** the ratio was determined from the spectrum of the product mixture extracted into CCl_4, by use of the peaks from the $Si\mathit{Me}_2$ protons in the $TsiSiMe_2ONO_2$ and the OMe protons in $TsiSiMe_2OMe$.

Method B. Methanol (0.5 cm^3) prewarmed to 35 °C, was added to *ca.* 10 mg of the trifluoromethanesulfonate **3** or cyanate **4** dissolved in 3 micro-drops (*ca.* 6 mm^3) of CH_2Cl_2 contained in an NMR tube, and the tube was stoppered, briefly shaken, and placed in the probe of the spectrometer at 35.0 ± 0.4 °C. The ratio of the height of the signal from the Me_3Si protons of the substrate (at δ 0.33 for **3** and δ 0.29 for **4**) to that of the corresponding signal, at δ 0.23, from $TsiSiMe_2OMe$ and/or $TsiSiMe_2OH$, was used as the measure of the substrate/product ratio.

At the end of the reaction the composition of the product mixture was determined by GLC on the assumption that the relative areas of the peaks from the methoxide and hydroxide were proportional to the relative concentrations. Authentic samples of the products were used to establish the retention times, but in selected cases GLC–MS was used to confirm the identities.

In all cases good first-order plots were obtained up to at least 80% completion of the reaction. Observed rate constants are estimated to be accurate to within ±10%.

Acknowledgements

We thank the SERC for support and for the award of a Research Studentship (to D. E. R.), the Royal Society for the award of a 1983 University Research Fellowship (to P. D. L.), the Libyan government for the award of a Postgraduate Scholarship (to Y. Y. El-K.) and Dr. D. A. R. Happer for valuable comments.

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Paper 2/02945F
Received 4*th June* 1992
Accepted 29*th June* 1992