

## BASE-CATALYSED SOLVOLYSIS OF *N*-(TRIALKYLSILYL)ANILINES

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### SUMMARY

Rates of solvolysis have been measured for the compounds  $\text{PhNHSiMe}_3$ ,  $\text{PhNHSiEt}_3$ , *m*- $\text{ClC}_6\text{H}_4\text{NHSiEt}_3$ ,  $\text{PhNMeSiEt}_3$ , and  $\text{PhNEtSiEt}_3$  in a mixture of methanol (5 vol) and aqueous potassium hydroxide (2 vol), and for most of these compounds in mixtures of dimethyl sulphoxide (6 vol) and aqueous alkali (1 vol). All the compounds react rapidly with neutral aqueous methanol. For the secondary compounds  $\text{PhNHSiMe}_3$  and  $\text{PhNHSiEt}_3$ , the rates fall when a little alkali is added and the oxonium ion catalysed reaction is suppressed, but then rise as the alkali concentration is increased further, and a base-catalysed reaction takes over. Base catalysis is, however, very much less effective than acid catalysis. There is also a significant "spontaneous" reaction involving catalysis by neutral molecules. For the tertiary compounds  $\text{PhNMeSiEt}_3$  and  $\text{PhNEtSiEt}_3$ , base catalysis is not significant in  $\text{MeOH}/\text{H}_2\text{O}$  but does contribute in  $\text{DMSO}/\text{H}_2\text{O}$ .

There is a very large difference in reactivity between  $\text{PhNHSiMe}_3$  and  $\text{PhNHSiEt}_3$  in the base-catalysed reaction in  $\text{MeOH}/\text{H}_2\text{O}$ , the former being ca.  $2.5 \times 10^4$  times more reactive; this is attributed to unusually severe steric hindrance.

Mechanisms are suggested for the neutral, base-catalysed, and spontaneous reactions.

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### INTRODUCTION

We previously described a study of the acid-catalysed methanolysis of some *N*-(trialkylsilyl)anilines, and found that for  $\text{XC}_6\text{H}_4\text{NHSi-i-Pr}_3$  compounds there appeared to be specific oxonium ion catalysis<sup>1</sup>. The reaction in neutral methanol was, in the absence of contrary evidence, assumed to be due to catalysis by methanol. The methanolysis of the compounds  $\text{PhNHSiMe}_3$ ,  $\text{PhNHSiEt}_3$ ,  $\text{PhNEtSiMe}_3$ ,  $\text{PhNHSi-i-Pr}_3$ ,  $\text{Me}_3\text{SiNEt}_2$ , and  $(\text{Me}_3\text{Si})_2\text{NH}$  were said to be inhibited by base<sup>1</sup>, but we subsequently found that this observation was erroneous as far as  $\text{PhNHSiMe}_3$  and  $\text{PhNHSiEt}_3$  were concerned, while confirming that the reactions of  $\text{PhNEtSiEt}_3$  (which appeared as  $\text{PhNHSiEt}_3$  as a result of an apparent typographical error) and  $\text{Me}_3\text{SiNEt}_2$  were, indeed, strongly inhibited by base<sup>2</sup>. We shall show below that while the rates of solvolysis of  $\text{PhNHSiMe}_3$  and  $\text{PhNHSiEt}_3$  in aqueous methanol

are initially lowered when a little alkali is added to the neutral solution, addition of more alkali causes a base-catalysed process to take over, and the rates increase with increasing base concentration. There is no detectable base-catalysis with the compounds  $\text{PhNMeSiEt}_3$  and  $\text{PhNEtSiEt}_3$  in aqueous methanol, but such catalysis can be observed in aqueous dimethyl sulphoxide (DMSO).

## RESULTS AND DISCUSSION

### Reactions in $\text{H}_2\text{O}/\text{MeOH}$

We first measured the rates of solvolysis of the compounds  $\text{PhNHSiMe}_3$ ,  $\text{PhNHSiEt}_3$ ,  $m\text{-ClC}_6\text{H}_4\text{NHSiEt}_3$ ,  $\text{PhNMeSiEt}_3$  and  $\text{PhNEtSiEt}_3$  in a mixture of methanol (5 vol) and aqueous potassium hydroxide (2 vol). The results are listed in Table 1, which shows the wave-lengths,  $\lambda$ , used for following the progress of the

TABLE 1

SOLVOLYSIS OF  $\text{PhNXSiR}_3$  COMPOUNDS IN MIXTURES OF METHANOL (5 vol) AND AQUEOUS POTASSIUM HYDROXIDE (2 vol)

Compound	$\lambda$ (nm)	[KOH] <sup>a</sup> (M)	$10^3k$ , 31.0° (min <sup>-1</sup> )	$10^3k$ , 50.0° (min <sup>-1</sup> )
PhNHSiEt <sub>3</sub>	260	5.0	86	415
		3.6		305
		2.5		220
		0.50		69
		0.375		60
		0.25		56
		0.125		72
		0.050		113
		0.025		187
PhNHSiMe <sub>3</sub>	245	0.010	ca. $2 \times 10^4$	
		0.005	$2.8 \times 10^3$	
		0.00375	$2.2 \times 10^3$	
		0.0025	$4.1 \times 10^3$	
		0.0010	Very fast <sup>b</sup>	
PhNMeSiEt <sub>3</sub>	255	10.0		6.7
		5.0		8.9
		1.00		35.5
		0.50		57.5
		0.25		100
		0.05	173	280
PhNEtSiEt <sub>3</sub>	260	5.0		8.0
		0.50		59
		0.050	237	350
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> NEtSiEt <sub>3</sub>	250	5.0	280	
		1.0	62	
		0.50	34	
		0.050	ca. 6	
		0.0050	25	
PhNHSi- <i>i</i> -Pr <sub>3</sub>	250	0.10	≪ 1	
		0.00	ca. 35	

<sup>a</sup> Concn. of the aqueous alkali. <sup>b</sup> Too fast to measure.

reaction, and the observed first-order rate constants,  $k$ . The results for  $\text{PhNHSiMe}_3$  are only approximate, since (a) the reactions were too fast for accurate study by the method used, and (b), at the very low concentrations involved the alkali concentration in the reaction mixture may not accurately reflect that in the aqueous alkali. The uncertainty in the rate constants does not affect any conclusions drawn below, and the results clearly show that the behaviour of  $\text{PhNHSiMe}_3$  is analogous to that of  $\text{PhNHSiEt}_3$ .

The compounds  $\text{PhNHSiMe}_3$ ,  $\text{PhNHSiEt}_3$ ,  $m\text{-ClC}_6\text{H}_4\text{NHSiEt}_3$ ,  $\text{PhNMeSiEt}_3$  and  $\text{PhNEtSiMe}_3$  all reacted much too rapidly for measurement in 5/2 MeOH/ $\text{H}_2\text{O}$  containing no alkali. Addition of a little alkali lowered the rate in all cases. With the tertiary compounds  $\text{PhNMeSiEt}_3$  and  $\text{PhNEtSiEt}_3$ , addition of further alkali caused the rate to fall to a small, effectively constant value, but in the case of the secondary compounds,  $\text{PhNHSiMe}_3$ ,  $\text{PhNHSiEt}_3$ , and  $m\text{-ClC}_6\text{H}_4\text{NHSiEt}_3$  it caused a rise in rate, the rate thus passing through a minimum in the region of 0.025–0.25  $M$

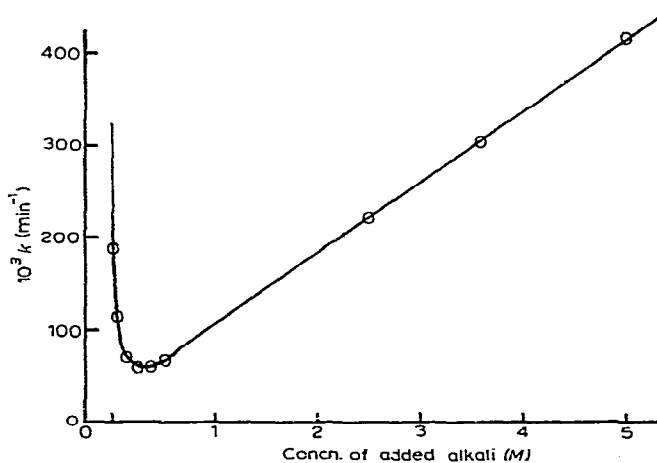


Fig. 1. Plot of rate constant against (added) alkali concentration for cleavage of  $\text{PhNHSiEt}_3$  in MeOH/ $\text{H}_2\text{O}$  at  $50^\circ$ .

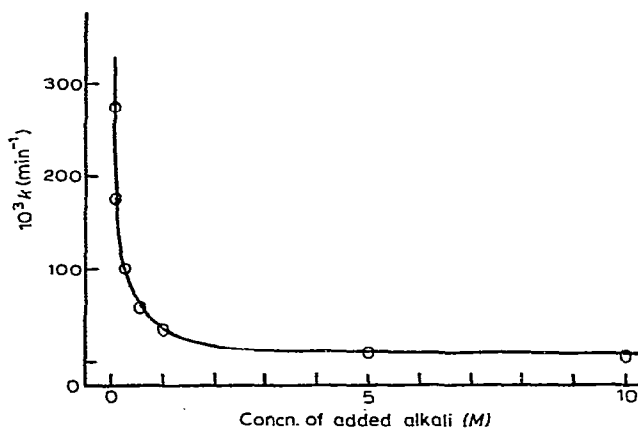


Fig. 2. Plot of rate constant against (added) alkali concentration for cleavage of  $\text{PhNMeSiEt}_3$  in MeOH/ $\text{H}_2\text{O}$  at  $50^\circ$ .

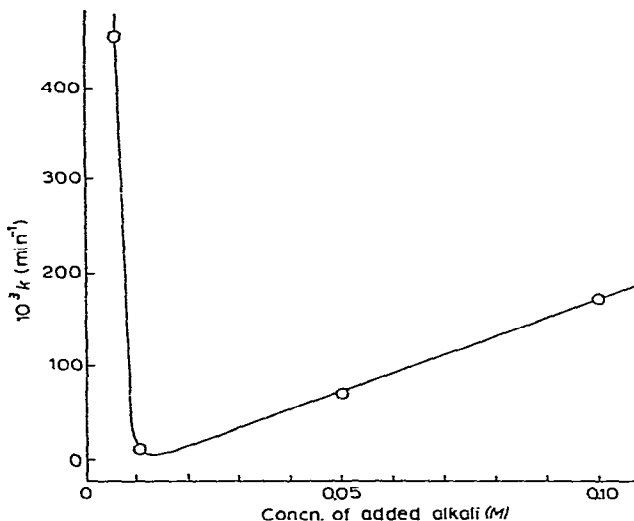


Fig. 3. Plot of rate constant against (added) alkali concentration for cleavage of  $\text{PhNEtSiEt}_3$  in DMSO/ $\text{H}_2\text{O}$  at  $50^\circ$ .

(added) alkali; the two types of behaviour are illustrated in Figs. 1 and 2. It is clear that with the secondary compounds there is a base-catalysed solvolysis, but the catalysis by base is much less effective than that by acid; the linearity of the plot for the base-catalysed region indicates that salt effects associated with the alkali concentration are remarkably small for the base-catalysed process, as they are in the somewhat analogous base cleavage of benzyltrimethylsilanes<sup>3</sup>. The low reactivity of the tertiary compounds  $\text{PhNMeSiEt}_3$  and  $\text{PhNEtSiEt}_3$  towards base can be attributed partly to the electron-releasing effect of the *N*-alkyl group, which inhibits the development of negative charge on the nitrogen atom, and partly to steric hindrance, which appears to be very substantial in these reactions, as pointed out below.

If, for simplicity, we treat the mixed medium as consisting of the MOH species and its derivatives (instead of a mixture of  $\text{H}_2\text{O}$  and MeOH and their derivatives), the observed rate constant,  $k$ , is given by eqn. (1), in which  $k_0$  refers to the "spontaneous" rate, attributable to catalysis by MOH molecules<sup>4</sup>, and  $k_A$  and  $k_B$  are the acid and base catalytic constants, respectively. The relationship can be re-expressed as in eqn. (2), in which  $K_s$  is the autoprotolysis constant. From the two approximately linear portions of the curve in Fig. 1 (and neglecting any salt effects), approxi-

$$k = k_0 + k_A \cdot [\text{H}^+] + k_B \cdot [\text{OM}^-] \quad (1)$$

$$k = k_0 + k_A \cdot K_s / [\text{OM}^-] + k_B \cdot [\text{OM}^-] \quad (2)$$

mate values of  $(k_A \cdot K_s)$  and  $k_B$  can be calculated, while extrapolation of the linear portion relating to base catalysis back to zero concentration of added base gives an intercept of value  $k_0$ . For  $\text{PhNHSiEt}_3$ , the values of the coefficients at  $50^\circ$  are as follows:

$$k_0 = 3.0 \times 10^{-2} \text{ min}^{-1}; k_A \cdot K_s \approx 1 \times 10^{-3} \text{ mole}^{-1} \cdot \text{min}^{-1}; k_B = 0.27 \text{ mole}^{-1} \cdot \text{min}^{-1}$$

In order to obtain a rough idea of the magnitude of  $k_A$ , we can assume that  $K_s$  is of comparable magnitude to  $K_w$  for water alone, *i.e.*  $10^{-14}$ , and  $k_A$  then becomes ca.

$10^{11}$ , which implies that  $k_A$  is in the region of  $10^{12}$  times as large as  $k_B$ ; there is, however, a considerable uncertainty in this factor, corresponding to the uncertainty in  $K_s$ .

From the values of the rates with 5.0 *M* (added) alkali at 31° and 50°, after allowing for a small contribution from the spontaneous rate in each case, an *approximate* value of 15.5 kcal/mole can be calculated for the activation energy of the base-catalysed solvolysis of PhNHSiEt<sub>3</sub>; this value is very much larger than the figure of ca. 5 kcal/mole observed for acid catalysed methanolysis of some XC<sub>6</sub>H<sub>4</sub>NHSi-*i*-Pr<sub>3</sub> compounds<sup>1</sup>.

The data for the *m*-ClC<sub>6</sub>H<sub>4</sub>NHSiEt<sub>3</sub> compound are less complete, and refer only to 31°. At this temperature, the value of  $k_B$  is ca. 0.19 mole<sup>-1</sup> · min<sup>-1</sup>, and that of  $k_0$  is ca.  $3 \times 10^{-3}$  min<sup>-1</sup>. The rates of reaction with 5.0 *M* (added) alkali at 31°, after allowance for estimated small contributions from the "spontaneous" process, show that the *m*-chlorophenyl compound is roughly 3.5 times as reactive as the phenyl-compound, corresponding to a rough value of  $\rho$  ca. 1.4. This value is in contrast with the value of 4.9 for the alkali cleavage of XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SiMe<sub>3</sub> compounds in a similar medium at 50°. While it must be remembered that nitrogen will tolerate a given degree of negative charge more readily than the more electropositive carbon, so that less delocalization of charge into the aromatic ring will take place, the smallness of the  $\rho$  value for the anilino-silane solvolysis suggests that relatively little negative charge develops on the nitrogen atom in the transition state of the rate-determining step. A comparable  $\rho$  value of 1.7 was found for base-catalysed solvolysis of XC<sub>6</sub>H<sub>4</sub>OSiEt<sub>3</sub> compounds in aqueous methanol at 25°<sup>5</sup>, but a higher value, in the range 3.24–3.65, was found<sup>12</sup> for this reaction in 60% aqueous dioxane at 30°.

We have previously drawn attention to the analogy between the base cleavage of PhNH–SiMe<sub>3</sub> bond and that of the PhCH<sub>2</sub>–SiMe<sub>3</sub> bond<sup>1</sup>. The latter cleavage, in aqueous methanol at least, is now known to involve electrophilic attack by the solvent at the benzylic carbon atom (*i.e.* proton transfer to carbon) as it separates<sup>6,7</sup>, though a substantial amount of carbanion character is developed at that carbon atom, as revealed by the large value of  $\rho$  for XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SiMe<sub>3</sub> compounds, and by the fact that for X groups, such as *p*-NO<sub>2</sub>, which can withdraw electrons by a conjugative (resonance) effect,  $\sigma^-$  constants have to be used, as would be expected if a lone pair of electrons were developing on the separating carbon atom<sup>3,7-9</sup>. We previously argued that the PhNH–SiMe<sub>3</sub> bond should be more reactive towards base than the PhCH<sub>2</sub>–SiMe<sub>3</sub> bond, since to the extent that negative charge develops on the leaving atom, PhNH<sup>-</sup> should be a better leaving group than PhCl<sub>2</sub><sup>-</sup>, while to the extent that there is assistance from synchronous proton transfer from the solvent to the separating atom, this could be even more favourable for a leaving nitrogen than for a leaving carbon atom<sup>1</sup>; the smallness of the  $\rho$  factor for the cleavage of the XC<sub>6</sub>H<sub>4</sub>NHSiEt<sub>3</sub> compounds is consistent with such synchronous proton transfer to nitrogen. Contrary to the earlier mistaken observation, which puzzled us<sup>1</sup>, the PhNH–SiMe<sub>3</sub> bond is, indeed, much more readily cleaved than the PhCH<sub>2</sub>–SiMe<sub>3</sub> bond by aqueous methanolic alkali at 50°; comparison of results in Table 1 with those in ref. 3 indicates that the reactivity ratio between the two compounds is in the region of 10<sup>9</sup>.

Since the PhO<sup>-</sup> group should be an even better leaving group than the PhNH<sup>-</sup> group, Me<sub>3</sub>SiOPh would, taking the simplest views of the reactions, be expected to undergo base-catalysed solvolysis even more readily than Me<sub>3</sub>SiNHPh; in fact, the two compounds seem to show rather similar reactivities, the specific rate

constant for solvolysis of  $\text{Me}_3\text{SiOPh}$  in aqueous ethanolic alkali at  $25^\circ$  (*viz.*  $\approx 2000 \text{ mole}^{-1} \cdot \text{min}^{-1}$ )<sup>5</sup> being a little smaller than for base-catalysed solvolysis of  $\text{Me}_3\text{SiNHPPh}$  in aqueous methanolic alkali at  $31^\circ$  (*viz.*  $\approx 7000 \text{ mole}^{-1} \cdot \text{min}^{-1}$ ); an explanation for this can again be found in the assistance provided by synchronous proton transfer to the separating nitrogen atom. In the acid-catalysed solvolysis,  $\text{Me}_3\text{SiNHPPh}$  is much more reactive than  $\text{Me}_3\text{SiOPh}$ <sup>5</sup>, no doubt because the pre-protonation is much easier for the nitrogen atom than for the oxygen atom.

The very large reactivity difference between the compounds  $\text{PhNHSiMe}_3$  and  $\text{PhNHSiEt}_3$  in the base-catalysed solvolysis is worthy of note. With  $0.01 M$  (added) alkali at  $31^\circ$ , the value of  $k$  for the trimethyl compound is ca.  $20 \text{ min}^{-1}$ , and effectively all of the rate appears to be due to the base-catalysed process. This would correspond to a rate of about  $10^4 \text{ min}^{-1}$  with  $5 M$  (added) alkali, compared with a value of about  $0.39 \text{ min}^{-1}$  for the triethyl compound (after allowance for the "spontaneous" reaction). Thus the  $\text{PhNHSiMe}_3/\text{PhNHSiEt}_3$  reactivity ratio is ca.  $2.5 \times 10^4$ . This factor is much too large to be attributed to differences in electronic effects, and must be associated with unusually serious steric hindrance. The factor is in marked contrast to the factor of about 5 for base cleavage of  $\text{Me}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{CO}_2^-p$  and  $\text{Et}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{CO}_2^-p$  in a similar medium<sup>8</sup>, and is much larger than the factor of 160 which applies in solvolysis of  $\text{Me}_3\text{SiOPh}$  and  $\text{Et}_3\text{SiOPh}$  compounds by aqueous ethanolic alkali<sup>5</sup>. It is also markedly larger than the  $\text{Me}_3\text{Si}/\text{Et}_3\text{Si}$  factor of 960 observed for base cleavage of 9-(trialkylsilyl)fluorenes<sup>10</sup>, previously the largest accurately known such factor; a factor of "at least"  $10^3$  is known to apply in base cleavage of  $\text{PhCH}=\text{CHCH}_2\text{SiR}_3$  compounds<sup>11</sup>.

#### Reaction in $\text{H}_2\text{O}/\text{DMSO}$

Results for cleavages in a mixture of DMSO (6 vol) and aqueous potassium hydroxide (1 vol) are shown in Table 2. As in  $\text{MeOH}/\text{H}_2\text{O}$ , the rate for the compound  $\text{PhNHSiEt}_3$  goes through a minimum with increasing base concentration, but the base is about  $2 \times 10^3$  times more effective in the  $\text{DMSO}/\text{H}_2\text{O}$  medium, as shown by comparison of the rates at  $31^\circ$  for  $\text{PhNHSiEt}_3$  in  $\text{MeOH}/\text{H}_2\text{O}$  containing  $5.0 M$  (added) alkali and in  $\text{DMSO}/\text{H}_2\text{O}$  containing  $0.05 M$  (added) alkali. As expected, in view of the electron-releasing nature of the substituent, the compound *m*- $\text{MeC}_6\text{H}_4\text{NHSiMe}_3$  is a little less reactive than  $\text{PhNHSiMe}_3$ .

The most interesting result in this more basic medium is that a definite base-catalysed reaction is revealed for tertiary compounds  $\text{PhNMeSiEt}_3$  and  $\text{PhNEtSiEt}_3$  (*cf.* Fig. 3). From the rates with  $0.05 M$  (added) alkali, it is seen that the relative reactivities of  $\text{PhNHSiEt}_3$ ,  $\text{PhNMeSiEt}_3$ , and  $\text{PhNEtSiEt}_3$  are roughly 50/5/1 in the base-catalysed process at  $31^\circ$ . The difference between the secondary and tertiary compounds is thus much smaller than in  $\text{MeOH}/\text{H}_2\text{O}$ ; this can reasonably be attributed mainly to the levelling effect resulting from the enhanced reactivity of the base anions in  $\text{DMSO}/\text{H}_2\text{O}$ , but it is possible that at the same time there is less need for assistance by synchronous proton transfer to the separating nitrogen atom, so that there is less steric inhibition in the tertiary systems in this medium. (Proton transfer to the separating carbon atom in base cleavage of C-Si bonds appears to be less important in  $\text{DMSO}/\text{H}_2\text{O}$  than in  $\text{MeOH}/\text{H}_2\text{O}$ <sup>7</sup>). In spite of the enhancement of the base catalysis in  $\text{DMSO}/\text{H}_2\text{O}$ , the results for the compound  $\text{PhNEtSiEt}_3$  indicate that hydroxonium ion catalysis is still of the order of  $10^9$  times as effective as hydroxide ion

TABLE 2

HYDROLYSIS OF  $\text{PhNXSiR}_3$  COMPOUNDS IN MIXTURES OF DMSO (6 vol) AND AQUEOUS POTASSIUM HYDROXIDE (1 vol)

Compound	$\lambda$ (nm)	[KOH] <sup>a</sup>	$10^3 k$ , 31.0° (min <sup>-1</sup> )	$10^3 k$ , 50.0° (min <sup>-1</sup> )
PhNHSiEt <sub>3</sub>	260	0.050	800	
		0.030	300	
		0.010	38	
		0.0050	440	
PhNMeSiEt <sub>3</sub>	315	0.10	170	
		0.050	84	
		0.010	35	95
		0.0050	290	ca. 1500
PhNEtSiEt <sub>3</sub>	310	0.10		170
		0.050	15.6	71
		0.010		12
		0.0050	150	460
<i>m</i> -MeC <sub>6</sub> H <sub>4</sub> NHSiEt <sub>3</sub>	265	0.010	15.7	
		0.050	640	
		0.030	280	
PhNHSi- <i>i</i> -Pr <sub>3</sub>	250	0.10		≤ 1 <sup>b</sup>

<sup>a</sup> Concentration of aqueous alkali. <sup>b</sup> Too slow to measure.

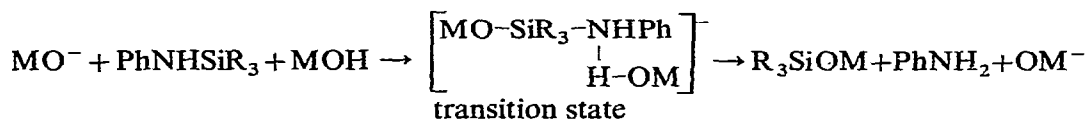
catalysis if an autoprotolysis constant of  $10^{-14}$  is assumed.

From the rates of reaction of PhNEtSiEt<sub>3</sub> with 0.050 *M* (added) alkali at 31° and 50° an *approximate* value of 15.5 kcal/mole can be calculated for the activation energy,  $E_A$ . This is the same as the value of  $E_A$  for PhNHSiEt<sub>3</sub> in MeOH/H<sub>2</sub>O, and it seems likely that the effect of the higher activity of the base in DMSO/H<sub>2</sub>O, which should lower the value of  $E_A$ , is just balanced by the increase in  $E_A$  brought about by the presence of the ethyl group at the nitrogen atom.

The compound PhNHSi-*i*-Pr<sub>3</sub> reacts too slowly for measurement even in the strongest base used in DMSO/H<sub>2</sub>O, and is at least  $10^4$  times less reactive than PhNHSiEt<sub>3</sub>; the actual factor may be substantially larger.

#### The mechanisms of the base-catalysed, neutral, and "spontaneous" reactions

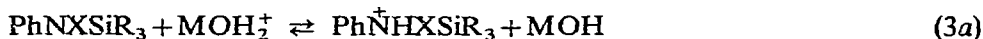
The simplest mechanism consistent with the characteristics of the base-catalysed cleavage is as follows:



There is, of course, no reason to think of this as involving a termolecular collision, since there must be substantial hydrogen bonding between the solvent and the starting amine; indeed, it would be reasonable to regard the hydrogen-bonded species Ph-(R<sub>3</sub>Si)HN-H-OM as the substrate. The process represented is not fully synchronous, in that some excess of negative charge accumulates on the separating nitrogen atom in the transition state.

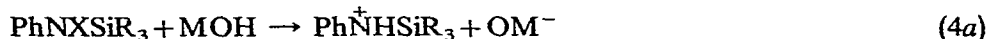
We cannot rule out the possibility that formation of a pentacoordinate complex of the type  $[\text{MOSiR}_3\text{NHPh}]^-$  precedes the cleavage of the Si-N bond.

It is clear that the rapid reactions in neutral MeOH/H<sub>2</sub>O or DMSO/H<sub>2</sub>O are virtually wholly attributable to catalysis by oxonium ions produced by autoprotolysis, the catalysis by water or methanol molecules being negligible by comparison. The mechanism in the neutral solvents is thus most simply represented as in eqns. (3).



We previously<sup>1</sup> wrote the mechanism in neutral solution as (i)  $\text{PhNXSR}_3 + \text{MOH} \rightleftharpoons \text{Ph}\overset{+}{\text{N}}\text{HXSIR}_3 + \text{OM}^-$ ; (ii)  $\text{Ph}\overset{+}{\text{N}}\text{HXSIR}_3 + \text{MOH} \rightarrow \text{PhNHX} + \text{R}_3\text{SiOM} + \text{H}^+$ . This is kinetically equivalent to the scheme of eqn. (3)]. The proton shown as becoming localized in the product  $\text{R}_3\text{SiOMH}^+$  of eqn. (3b) may actually be synchronously transferred to the solvent.

There is also as we have been, a "spontaneous" reaction, involving catalysis by water or methanol molecules. The mechanism of this can be written as in eqn. (4).



The existence of this reaction demonstrates that there can be general acid (and base) catalysis<sup>4</sup>. We were unable to detect such catalysis in methanol containing CH<sub>3</sub>CO-OH/CH<sub>3</sub>COONa mixtures<sup>1</sup>, no doubt because it is masked by the much more powerful oxonium-ion catalysis, or, in other words, because the Brønsted coefficient for this reaction is large<sup>4</sup>.

A noteworthy feature of the "spontaneous" reactions in MeOH/H<sub>2</sub>O is that the rates for PhNMeSiEt<sub>3</sub> and PhNEtSiEt<sub>3</sub>, while very similar to one another, are significantly smaller than that for PhNHSiEt<sub>3</sub>. This was to be expected, since the "spontaneous" reaction has some of the nature of both the acid-catalysed and base-catalysed processes, and in both of these PhNEtSiMe<sub>3</sub> is less reactive than PhNH-SiMe<sub>3</sub>.

#### EXPERIMENTAL

Rates were measured spectrophotometrically as previously described<sup>1</sup>, except that a Unicam SP800 spectrophotometer was used, and the thermostating was accurate to only  $\pm 0.1^\circ$ . These changes increased the uncertainty of even the best rate constants to  $\pm 5\%$ , but this is unimportant for the discussion.

#### ACKNOWLEDGEMENTS

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