THE MECHANISMS OF SOLVOLYSIS OF ORGANOSILICON COMPOUNDS CONTAINING BONDS FROM SILICON TO OXYGEN, NITROGEN, AND CARBON

Bjarne Bøe

Department of Chemistry, University of Bergen, N-5014
Bergen-Universitetet (Norway).

(Received July 17th, 1975)

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MECHANISMS OF SOLVOLYSIS OF ORGANOSILICON COMPOUNDS.

1. INTRODUCTION

The reactions considered in this review may be summarised as in (1):

$$R'OH + R_3Si\text{-}Y \rightarrow R_3Si\text{-}OR' + HY \quad (R'=H,\ \text{alkyl},\ Y=OR,\ NR_2,\ CR_3) \qquad (1)$$

The general characteristics of acid and base catalysed solvolyses of Si-OC were established several years ago [44], and may be extended to Si-N and Si-C substrates:

(i) Acid-catalysis involves prior protonation of the

Si-Y substrate followed by attack of R'OH, and

(ii) base-catalysis involves attack of RO^- (or R'OH + B) and loss of Y^-. In either case a penta-coordinate intermediate may be involved. In acid catalysis a small excess of positive charge on silicon is likely in the transition state, while in base catalysis a rather larger negative charge is expected. Furthermore, with acid catalysis the ease of protonation of the Si-Y will be of great importance, while with base catalysis the leaving ability of Y will be very important.

In the following chapters it is shown how these simple ideas may be refined and quantified to provide a more definite picture of the solvolyses.

In the analysis of substituent effects on rates, use is made of the Hammett equation (2):

$$\lg k = \lg k_0 + \rho \cdot \sigma \tag{2}$$

In such an analysis, the type of σ-constants used in the correlation, and the sign and magnitude of the ρ-value are of mechanistic significance. It has been shown that σ^0-constants are to be preferred to σ-constants in Hammett correlations involving substituted phenyl groups attached to silicon [84, 103]. The applicability of the σ^0-constants demonstrates that there is no additional $d_\pi-p_\pi$ bonding between the silicon atom and the aryl group in the transition state, and that only the inductive effect of the aryl group is kinetically significant.

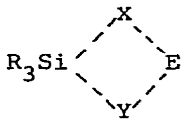
For carbon compounds most ρ-values fall between -4 and +4 for reactions in solution, but may be more negative for electrophilic aromatic substitution [111]. Reaction mechanisms for organosilicon compounds may be written in analogy with well-established mechanisms for carbon compounds only if it can be shown that ρ-values are on the same scale for the two classes of compounds. Examination of the literature reveals that ρ-values reported for rates of organosilicon compounds fall in the same range as for carbon compounds [112] (Tables 2, 3, 7, 8, 11, 12). However, organosilicon reactions analogous to those defining the extreme ρ-values for carbon compounds involving formal charges on the reaction centre are not known. Independent evidence is not available that the silicon atom will tolerate positive or negative charges in the transition state to the same extent as C, O, or N atoms. The possibility cannot be ruled out that further experimental work will result in a broadening of the ρ-scale for organosilicon relative to carbon compounds. In the absence of such results, however, it is assumed that organosilicon reaction centres furnish ρ-values on the scale known in organic chemistry, and the reaction constants are regarded as measures of charge development at silicon in the transition state [64, 123].

As a second-row element, silicon has available 3d-orbitals which may be used for bonding, extending the covalency to five or six. Stable penta- and hexa-coordinate organosilicon species are known [44, 92, 112], and 3d-bonding has been used to rationalise results for both ground state and excited state silicon for a wide variety of data.

Hexa-coordinate silicon complexes represent the maximum coordination number for silicon. Although such complexes have been proposed in solvent induced racemisation of chlorosilanes [40], reaction mechanisms for solvolysis reactions are generally thought to involve no complexes higher than penta-coordinate.

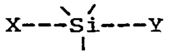
Reaction mechanisms may be written involving expanded octet intermediates and classified according to Sommer [112]:

S_Ni-Si. This mechanism involves simultaneous nucleophilic attack at Si and electrophilic attack at Y resulting in a cyclic transition state and is commonly assumed for reactions leading to retention of configuration:



1

S_N2-Si. This is similar to the S_N2 mechanism of organic chemistry and involves simultaneous bond-formation and -breakage, and inversion of configuration:

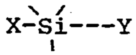


$X{-}{-}{-}Si{-}{-}{-}Y$

2

Retention could, however, also result from equatorial attack in this mechanism [44].

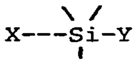
S_N2^*-Si. The formation of a penta-coordinate complex in a fast step is involved, and this mechanism gives rise to the highest possible ρ_Y values. For base catalysed reactions ρ_{Si} values greater than zero result:



$X{-}Si{-}{-}{-}Y$

3

S_n2^{**}-Si. This mechanism involves rate-determining formation of a penta-coordinate complex. Minimum values of ρ_V are obtained, i.e. for base catalysed reactions $\rho_Y > 0$ only as a result of inductive transfer of negative charge from the silicon atom, and in acid catalysed reactions $\rho_Y < 0$ and attains its minimum value due to a formal positive charge on Y.



$$X{-}{-}{-}\overset{\diagdown\ \diagup}{\underset{|}{Si}}{-}Y$$

4

For the mechanisms involving addition complexes, the stereochemical outcome may be inversion, retention or racemisation if pseudo-rotations of the complexes are involved.

Penta-coordinate silicon complexes have been commonly assumed in many discussions of the solvolysis of R_3SiY. Such complexes have, however, never been physically detected as intermediates, and their existence is based on circumstantial evidence only.

In this situation the addition-elimination mechanism must compete with the synchronous mechanism as a reasonable model for the solvolysis, and it is of great interest to investigate further the consequences of the two mechanisms to try to decide between them.

The reactions studied conform to eqn. (1). In Chapters two to four Si-OC, Si-N and Si-C compounds are discussed. The literature of the last ten years up to the end of 1974 is comprehensively reviewed, and some of the more important earlier studies are included. Papers dealing with the mechanistic aspects of the cleavage are discussed, while purely synthetic work is not included.

In Chapter five a general mechanism is proposed, based on a discussion of the evidence presented in Chapters two to four.

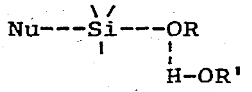
Some of the main results of studies on the solvolysis of R_3SiY have been reviewed recently by Prince [96].

2. MECHANISMS OF SILICON-OXYGEN CLEAVAGE.

The Si-OC bond is fairly reactive in both acid and base catalysed solvolyses, as compared to analogous carbon compounds, and it is always the silicon-oxygen bond rather than the carbon-oxygen bond that is cleaved in this system. Formation of Si-OC by silylation of hydroxyl groups is a very general reaction with applications in analytical chemistry and in organic synthesis, but the reaction mechanisms of Si-OC cleavages have been less well studied. It is shown below that the solvolyses follow S_Ni-Si and S_N2-Si mechanisms, the latter not necessarily strictly synchronous.

Stereochemistry. For solvolysis reactions, the rate equation cannot give information about molecularity, and the uni- or bi-molecularity of reactions has to be decided by non-kinetic methods.

Stereochemical inversion of silicon-oxygen compounds is the result of the S_N2-Si mechanism, according to the S_N2-Si stereochemistry rule [113, 120]. In the transition state for inversion reactions there is electrophilic assistance from the solvent R'OH:

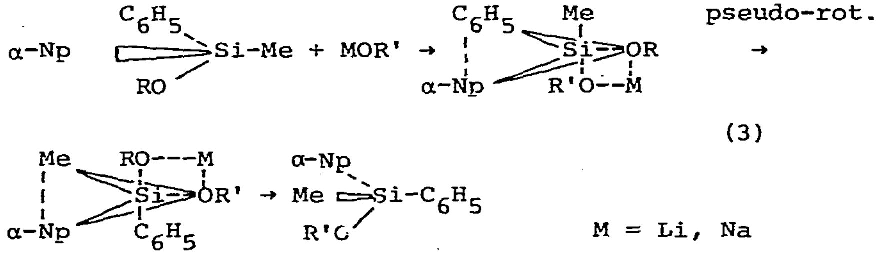


$$\mathrm{Nu{-}{-}{-}\overset{\diagdown\,\diagup}{\underset{|}{Si}}{-}{-}{-}\underset{\underset{\displaystyle H{-}OR'}{\vdots}}{OR}}$$

5

In addition, electrophilic stabilisation of the charge in the transition state of the inversion mechanism is favoured by solvents having large dielectric constants [119].

In less polar solvents the mechanism changes from S_N2-Si to S_Ni-Si. The S_Ni-Si retention mechanism may be written involving penta-coordinate complexes which undergo pseudo-rotation to permit apical exit of OR [117].



(3)

M = Li, Na

It is, however, not necessary to include M in the transition state, and the retention may be explained by a non-cyclic S_N2^{**}-Si mechanism involving rate determining formation of a penta-coordinate complex which subsequently undergoes pseudo-rotation.

A general procedure for rationalising inversion or retention of configuration in reactions involving pseudo-rotating bipyramidal complexes has been described [82].

Activation parameters. The most significant results of the studies concerning the effect of temperature on rates are the highly negative activation entropies in both acidic, basic, and neutral solutions (Table 5). These values seem to be inconsistent with a unimolecular mechanism and are also more negative than entropies usually found for bimolecular substitution reactions of organic compounds [102].

The order of reaction with respect to solvent molecules is quite similar for organosilicon and analogous organic reactions, and it seems likely that specific factors operate for silicon (in Si-OC) to give the highly negative activation entropies [33]. The presence of two electronegative atoms close to the silicon atom in the transition state favours octet expansion, and the silicon atom may extend its covalency by forming new σ- and d_π-p_π bonds. The transition state for silicon is thus more complex than for carbon, and this may be an explanation of the low activation entropies. However, the results for Si-N and Si-C show that the low activation entropies are not general for silicon (see below).

Solvent effects. The faster rates of cleavage of phenoxysilanes in dioxan/water than in ethanol/water [2, 59] or isopropanol/water [33] probably result from poorer solvation of the initial state in dioxan/water. These results conform to the electrostatic model of solvent effects [60].

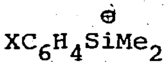
Acid catalysed reactions. The acid catalysed solvolyses conform to the general scheme (4):

$$R_3Si\text{-}OR' + BH \rightleftharpoons R_3Si\text{-}\overset{+}{O}HR' + B^- \qquad (4a)$$

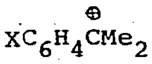
$$R_3Si\text{-}\overset{+}{O}HR' \rightarrow \text{products} \qquad (4b)$$

It is assumed that the proton is attached to the oxygen atom, and in strongly acidic solution this proton can be observed by NMR [88].

Electron donating groups increase the rates of the acid catalysed reactions, whether they are attached to the leaving group or to the silicon atom (Tables 2 and 3). For those reactions which are shown to be catalysed by acid, series 6, 8, and 9 in Table 2, small negative ρ-values are calculated for substrates having substituents in the aryl group attached to silicon, indicating that the silicon atom is slightly more positive in the transition state than in the reactant state. This gives support to a bimolecular mechanism rather than a dissociative one. In further support of a bimolecular mechanism it was found that σ^{o} constants gave significantly better correlation coefficients than σ^{+} (and σ) constants in the Hammett equation [123]. It was argued by Vencl [123] that σ^{+} constants ought to be used for reactions involving siliconium ions 6 due to the similarity with the carbonium ion intermediate 7 for the S_N1 hydrolysis of carbinyl chlorides, defining the σ^{+} scale.


$XC_6H_4\overset{\oplus}{Si}Me_2$

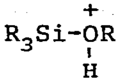
6


$XC_6H_4\overset{\oplus}{C}Me_2$

7

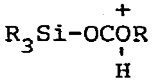
Much of the classical work done to establish the S_N1 mechanism in organic chemistry has been parallelled for organosilicon substrates [40]. Several workers have sought to collect evidence in favour of the siliconium ion hypothesis in dynamic systems. However, the results of stereochemical [29], isotopic exchange [118], and product[18,28] studies , and of spectroscopic experiments [88, 95], have all failed to demonstrate the existence of the siliconium ion in solution. It has been possible, however, to generate siliconium ions in the gas phase and to study their reactions in the mass spectrometer [87, 117].

Few studies have been made on the kinetic effect of substituents in the leaving group (see Table 3). Electron donating substituents increase the basicity of the leaving group [42, 75, 81], and stabilise the protonated intermediates 8 and 9 [94].



$R_3Si-\overset{+}{\underset{H}{O}}R$

8



$R_3Si-OC\overset{+}{\underset{H}{O}}R$

9

The transition state for the slow step of the solvolysis will have a somewhat similar charge distribution, and for a given reaction series negative ρ-values are calculated (in dilute acid) [1, 2, 22]. Comparing different leaving groups, it is expected that the rates increase with the basicity of the leaving group so that the most basic substrates react fastest. This is observed: the benzyloxysilanes 10 react much faster than the phenoxysilanes 11 under comparable conditions [2, 22] (Table 3).

$(XC_6H_4)Me_2Si-OCH_2C_6H_4X'$

10

$(XC_6H_4)Me_2Si-OC_6H_4X'$

11

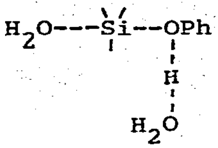
Assuming a normal transmission factor of 0.4 for the

$-CH_2$ group [89] (note, however, that factors reported in the literature are all based on positive ρ-values) it is seen that more positive charge is localised on the oxygen of <u>10</u> than of <u>11</u> in the transition state, while there is a similar excess of positive charge on silicon in the two transition states. This suggests a more reactant-like transition state for <u>10</u> than for <u>11</u>.

It has been stated that acyloxysilanes generally react faster than alkoxysilanes [11, 112]. This may be true for the base catalysed and spontaneous reactions, but no studies have been reported which would permit this generalisation to include acid catalysed reactions. According to the present hypothesis that the rates increase with the basicity of the leaving group, one would expect the acyloxysilanes to react more slowly than the benzyloxysilanes and phenoxysilanes in the range of acid concentration where the reactions are acid catalysed.

Increasing size of the alkyl groups attached to the silicon atom decreases the rates (Table 4). This is opposite from that expected on the basis of the polar effects discussed above, and may be reasonably associated with steric hindrance to the nucleophilic attack of R'OH at the silicon atom. The steric effects observed on replacing methyl groups with bulkier alkyl groups are in general agreement with the effects observed in nucleophilic displacements on carbon [57].

In the hydrolysis of Bu_3SiOPh in aqueous dioxan two molecules of water are involved in the transition state, one may act as nucleophile and the other as base [33].



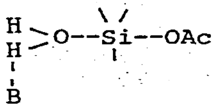
$$H_2O\text{---}\overset{\backslash\,/}{\underset{|}{Si}}\text{--}\underset{\underset{H_2O}{\vdots}}{\underset{H}{\underset{\vdots}{OPh}}}$$

12

In this reaction, the proton is transferred in the rate determining step, and the abnormally small isotope effects may be caused by D_2O being a weaker nucleophile and base than H_2O [33]. However, the use of k_H/k_D as an index of degree of proton transfer in the transition state has been criticised [56], and this criterion must be used with caution.

Base catalysed reactions. The catalytic added base may function as a classical base or as a nucleophile. The methanolysis of triarylphenoxysilane is general base catalysed, nucleophilic catalysis being excluded [107]. For hydrolysis of trialkylphenoxysilanes nucleophilic as well as general base catalysis is operating, giving rise to a Brønsted β coefficient > 1 [59]. The ethanolysis of aryldimethylphenoxysilane is general base catalysed, but nucleophilic catalysis cannot be excluded [20]. One mole of the base is present per mole of the activated complex, and for general base catalysis the proton transfer is part of the rate determining process. The value of the Brønsted β coefficient = 0.7 in the methanolysis may indicate that the proton is close to the catalysing base in the activated complex [107].

Catalysis by KOAc in the hydrolysis of trialkylsilylacetates is more effective at low than at high water concentrations in the water/dioxan medium, and this is said to be due to the increased base strength of the medium at higher water concentrations, water molecules acting more efficiently as the base B in the transition state 13 [97]:



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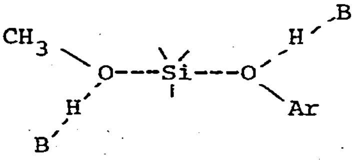
However, a simpler explanation is that the rate determining step involves HO^- + SiOAc. Then HO^- is more active at higher dioxan concentrations because of poorer solvation of the ion.

The change from second order dependence on base at low base concentration to first order at higher concentration in the hydrolysis of aryloxysilanes in acetonitrile/water is said to indicate a step-wise nature of this reaction [121].

$$HO^- + Ph_3SiOAr \rightleftharpoons Ph_3\overset{-}{Si}OAr(OH) \rightarrow \text{products} \qquad (5)$$

However, reexamination of the reaction has shown it to be first order in alkali over a wider range of concentrations as used originally, and the new results are therefore evidence against the step-wise mechanism [47].

The acid-base catalysed methanolysis of aryloxysilanes may be explained by assuming a S_N2-Si mechanism [121]:



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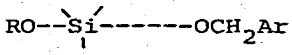
The small ρ-value measured for substituted phenyl groups attached to silicon indicates that there is a similar degree of bond-formation and -cleavage to silicon in the transition state [20]. Generally, higher ρ-values are observed (Table 2) indicating that bond formation is the more important.

The compounds in series 7 and 10 in Table 2 indicate that ρ-values are dependent on the leaving group, and probably also on the strength of the catalysing base [21], and ρ-values for substituents both at phenyl bonded to silicon and in the leaving group are quite different in the two series:

Substrate		$Ar'Me_2SiOCH_2Ar$	$Ar'Me_2SiOAr$
ρ-value	subst. in Ar'	1.5	0.2
ρ-value	subst. in Ar	1.1	1.2

A transmission factor $Z_{CH_2} = 0.9$ may be calculated for R_3SiOCH_2Ar and R_3SiOAr. This is very different from the accepted value of 0.4[89], and indicates differences in polarity of the transition states for the two substrates. The ρ-values 1.5 and 0.2 suggest that the bond to the nucleophile is formed to a greater extent in R_3SiOCH_2Ar, and that the silicon atom carries a partial excess of negative charge. Some of this charge is inductively transferred to the oxygen atom resulting in a ρ-value smaller than 1.5. The calculated value is 2.8 (assuming a transmission factor $Z_{CH_2} = 0.4$) and must therefore be caused by considerable stretching of the Si-O bond in the transition state.

Inversion of configuration of R_3SiOMe [7] is consistent with either S_N2-Si or two-step mechanisms. Assuming that R_3SiOCH_2Ar and R_3SiOMe react by the same mechanism, it seems reasonable to expect the mechanism to be S_N2-Si involving a product-like transition state [22]:



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The R_3SiOAr is assumed to hydrolyse by a strictly synchronous mechanism. The differences may be connected with the poorer leaving ability of OCH_2Ar relative to OAr. In view of the results presented by Humffray and Ryan [59] for hydrolysis in dioxan/water (Table 3), the ρ-value 1.2 for substituents in Ar of R_3SiOAr probably indicates significant stretching of the Si-O bond. The high positive ρ-value, and the use of σ^--constants in the correlations indicate that a substantial negative charge is placed on the oxygen atom in the transition state [59].

The reactivity increases with the stabilisation of negative charge in the leaving group, silyl-acetates and -phenoxides reacting faster than the benzyloxysilanes. In the base catalysed alcoholysis of $Ph_3SiOCOR$, eqn. (6) is followed over a range of pK_a (in water) of approximately five units (lg k of about three units), with $\alpha = 0.7$ [105].

$$\lg k = \alpha \lg K_a + C \qquad (6)$$

A correlation covering a much wider range of different leaving groups is obtained from the close similarities in the magnitudes of ρ_Y and τ_{Ar} values:

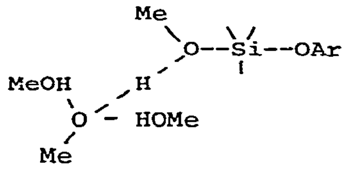
Y	ρ_Y	τ_{Ar}
$OCOCH_3$	1.2	-1.37
OAr	1.7	-1.71
OCH_2Ar	2.8	-3.31

The values $\tau_{Ar} = \lg k - \lg k_o$ are defined for different leaving groups in aromatic nucleophilic substitution reactions [89], and are formally similar to σ-values. These values express the capacity of the leaving group to stabilise negative charge in this type of reaction, and the analogy suggests that the two-step mechanism is a possible model for Si-OC substrates.

The rate decreases observed on substituting bulkier alkyl groups for methyl attached to silicon are much too great to be caused by polar effects alone, and steric effects must be involved (Table 4).

The much higher ρ-values in dioxan/water [59] than in ethanol/water [2] and ethanol [20] may be the result of less charge dispersal by hydrogen bonding in the less protic solvent, placing more charge on the oxygen atom.

From rate studies in mixed MeOH-MeOD solvent it is concluded that the catalytic methoxide ion is solvated by two molecules of methanol [83]:



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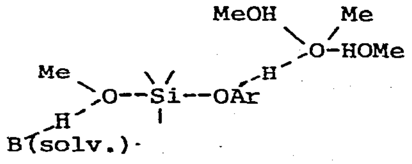
The reaction is concerted, exhibiting simultaneous acid-base catalysis [121], and the methanol molecule giving electrophilic assistance to the leaving group will be solvated as well:



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This solvation will be more important for an advanced degree of proton transfer from the methanol to the leaving group, because of the negative charge developing in the methanol molecule.

Reactions in neutral solvents show ρ-values of similar sign and magnitude as the base catalysed reactions (Tables 2 and 3). The spontaneous rate constant for cleavage of phenoxysilanes in aqueous dioxan increases as the substituents become more electron-withdrawing[59]. The neutral reactions are therefore probably in fact base catalysed, while the spontaneous reactions involve attack of OH^- generated by autoprotolysis of water.

3. MECHANISMS OF SILICON-NITROGEN CLEAVAGE.

Compounds containing the Si-N bond have found wide application in analytical organic chemistry. Silyl derivatives of amines, amino acids, amides and ureas have been used extensively for the gas chromatographic analysis of these compounds [69,92].

The Si-N bond is readily cleaved by various reagents, i.e. water, alcohols, phenols, carboxylic acids, mineral acids, and mercaptans [11,70].

The few studies concerning the mechanisms of the cleavage have centred on the hydrolysis and alcoholysis of silylamines. This cleavage is catalysed by both acid and base, acid catalysis being the more efficient with basic substrates. Both kinetic and non-kinetic methods of studying mechanisms have been employed and the results are reviewed below.

Kinetic data of silylamides are difficult to interpret because of the possibility of amide-imidate tautomerism [69,130], and mechanistic studies of their solvolysis have not yet been reported.

Acid catalysed reactions. The observed stereochemical inversion of silicon-nitrogen compounds (Table 6) is consistent with one-step mechanisms, or two-step mechanisms involving penta-covalent silicon intermediates, as in eqn. (7):

$$R_3Si^*NR'_2 + Y \rightleftharpoons R_3SiNR'_2Y \rightarrow R_3Si^*Y + NR'_2 \qquad (7)$$

It should be mentioned that whereas inversion always results from a bimolecular mechanism at carbon, bimolecular substitution at silicon may give inversion or retention. This is usually ascribed to the different availability of the d-orbitals for the elements carbon and silicon [52].

The observation of specific acid catalysis is explained by assuming the protonation equilibrium in the general scheme (8) to be over to the left and to be rapidly established, compared to the rate determining step (8b):

$$R_3Si\text{-}NR'_2 + BH \rightleftharpoons R_3Si\text{-}NH^+R'_2 + B^- \qquad (8a)$$

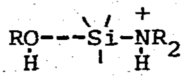
$$R_3Si\text{-}NH^+R'_2 \rightarrow \text{products} \qquad (8b)$$

The cleavage of silylanilines was found to correspond to this scheme [9].

The ρ-values of −1 for substituents in the aryl group

(Table 7) indicate electron-deficient silicon in the transition state.

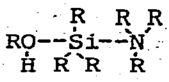
The reaction is facilitated by electron-donating substituents in the nitrogen-containing group as a result of positive charge on the nitrogen atom. The low ρ-value of −2.5 (Table 8) indicates that the Si-N bond has been stretched to only a small extent in the rate determining step giving rise to a reactant-like transition state, as in 18:


$\underset{H}{RO}\text{---}\overset{\diagdown\,\diagup}{\underset{|}{Si}}\text{-}\overset{+}{\underset{H}{N}}R_2$

18

In this structure some of the positive charge on nitrogen will be inductively transferred to the silicon atom. Given the transition state 18 it may be deduced that the substituents exert their polar effects mainly on the protonation step (8a) in the mechanism above. For silylanilines ρ-values of about −4.5 and +2 for (8a) and (8b) respectively are suggested [9]. As a corrolary to this it is found that the most basic substrates react fastest [21,23].

Bulky groups at silicon slow down the rate and this is attributed to steric hindrance of nucleophilic attack at silicon [9]. Replacement of a hydrogen atom on nitrogen by an alkyl group increases the steric hindrance due to interaction between the groups on silicon and nitrogen as the bonds are rehybridised in the transition state [9].


$\underset{H}{RO}\text{--}\overset{R}{\underset{R\ \ R}{Si}}\text{--}\overset{R\ R}{\underset{R}{N}}$

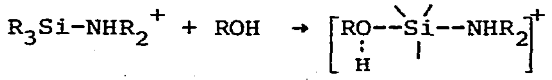
19

Since the Si-N bond is only slightly stretched it is conceivable that these steric effects can have a considerable magnitude.

The calculated activation energies and entropies consist of sums of terms corresponding to step (8a) and (8b), e.g. for the activation enthalpy:

$$\Delta H^{\ddagger} = \Delta H\ (8a) + \Delta H^{\ddagger}\ (8b) \qquad (9)$$

If it is assumed first that the magnitude of ΔH (8a) is much greater than $\Delta H^{\ddagger}$ (8b), the higher activation enthalpy for the silylpyrroles may be explained by loss of aromatic character on protonation of the pyrrolic nitrogen (the resonance energy for pyrrole is 21 kcal/mole) [128]. If on the other hand (8b) determines the activation enthalpy it is step (10) which must be discussed:

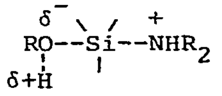


$$R_3Si{-}NHR_2^{\ +} + ROH \rightarrow \left[\underset{\underset{H}{\vdots}}{RO}{-}{-}\underset{|}{\overset{\diagdown\ \diagup}{Si}}{-}{-}NHR_2\right]^+ \qquad (10)$$

Of the reactants, the protonated silylpyrrole has the highest energy (again as a result of loss of aromatic character), and since it is difficult to see why the corresponding transition state should be destablished relative to the transition state for the alcoholysis of the silylanilines, the lowest activation enthalpy is expected for the silylpyrroles. Since the opposite is found it is concluded that the protonation step (8a) determines the activation enthalpies.

The activation entropy is only dependent on the partition functions and therefore on changes in number and kind of degrees of freedom, on converting the reactants to the transition state. For silylpyrroles and silylanilines reacting in the gas phase small differences in degrees of freedom are expected. In solutions, the lower activation entropy for the silylanilines may be best explained by better solvation around the more basic aniline nitrogen atom causing an increased orientation of solvent molecules. The difference in activation entropies of about 50 e.u. indicates that solvent effects are very important.

The positive salt effect found in the methanolysis of silylanilines indicates a transition state more polar than the species which preceded it [60]. This points to a transition state 20 in which the Si-N bond is only slightly broken, and where as a result of the nucleophilic attack, the alcohol molecule has become more polar:



$$\underset{\delta+\text{H}}{\overset{\delta^-}{\text{RO}}}\text{--}\underset{|}{\overset{\backslash\ /}{\text{Si}}}\text{--}\overset{+}{\text{NHR}_2}$$

20

This conclusion regarding the Si-N bond in the transition state is essentially the same as was reached by applying the Hammett equation to substituents in the leaving group.

For solvent isotope effects in water, k_H/k_D-values greater than one indicate either rate determining proton transfer, or a bimolecular mechanism involving deuterium exchange in a pre-rate determining step [109]. In one study of methanolysis of silylanilines, the k_H/k_D-value of 1.3 [9] is in the normal range for hydrolysis of various organic substrates [78].

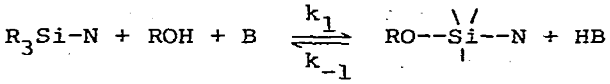
Spontaneous reactions. The spontaneous solvolysis involving neutral solvent molecules show characteristics resembling those for the acid catalysed reactions. Polar effects of substituents, and activation parameters, are of similar sign and magnitude for the two types of reaction [9,23]. The kinetic scheme (8) applies to solvolysis of silylanilines in ethanol containing sodium acetate, demonstrating the importance of the protonation step. The spontaneous reaction involves the two-step sequence (11) [23]:

$$R_3Si{-}NR_2 + ROH \rightleftharpoons R_3Si{-}NHR_2^{+} + RO^{-} \qquad (11a)$$

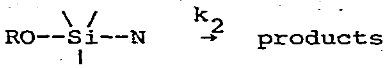
$$R_3Si{-}NHR_2^{+} + RO^{-} \rightarrow R_3Si{-}OR + NHR_2 \qquad (11b)$$

Base catalysed reactions. The kinetic analysis follows the general scheme (12). Since the solvolyses are experimentally found to be first-order in added base B, two possibilities exist [13]:

1. (12a) is fast, corresponding to specific base catalysis.
2. (12a) is slow, corresponding to general base catalysis, in which case either $k_1 << k_{-1}$ or $k_1 \simeq k_{-1}$.



$$R_3Si{-}N + ROH + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RO{-}{-}\underset{|}{\overset{\backslash\;/}{Si}}{-}{-}N + HB \qquad (12a)$$



$$RO{-}{-}\underset{|}{\overset{\backslash\;/}{Si}}{-}{-}N \overset{k_2}{\rightarrow} \text{products} \qquad (12b)$$

General base catalysis was observed in one case [21], but other studies designed to decide between general and specific catalysis have not yet been carried out. Scheme (12) also includes nucleophilic in addition to base catalysis, and at present it is difficult to predict the type of catalysis in specific cases.

Electron-attracting substituents in the aryl group attached to silicon increase the rates. This indicates that the silicon atom is electron-rich in the transition state, and the high ρ-values (1.7-2.6) to be the result of π-bond interaction between the silicon 3d-orbitals and the nucleophile [21]. Thus in the transition state the Si-O bond is formed to a greater extent than the Si-N bond is broken, and two-step mechanisms cannot be excluded [5,21]:

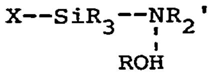
$$R'OH + B + R_3SiNR'R'' \rightleftharpoons R'O\bar{S}iR_3NR'R'' + BH^+ \quad (13a)$$

$$R'O\bar{S}iR_3NR'R'' + BH^+ \rightarrow R'OSiR_3 + NHR'R'' + B \quad (13b)$$

In mechanism (13) the silicon atom is becoming electron-rich in the transition state, and some of this charge will be inductively transferred to the nitrogen atom, giving rise to positive ρ-values. In general, which of the steps (13a) or (13b) is rate determining depends on the relative leaving group abilities of $^-NR'R''$ and OR^-, and for the poor leaving group $NHPh^-$ the breakdown of the complex probably is rate determining. The basicity of pyrrole is comparable to the basicity of ROH, and for the silylpyrroles the transition state will be closer to the penta-coordinated silicon intermediate whose formation or breakdown is rate determining. The ρ-values 2.6 for silylpyrroles and 1.7 for silylanilines are consistent with this (Table 7).

The alternative S_N2-Si mechanism implies a product--like transition state, and is the preferred mechanism, (see Chapter 5).

Reaction constants are in the range 1.4-1.6 for substituents in the nitrogen-containing part of the molecule [5,10]. This suggests that negative charge develops at the nitrogen atom in the transition state, and for groups that can withdraw electrons by a conjugative effect, σ^--constants are needed [5]. The small charge on nitrogen (relative to the charge on carbon in Si-C cleavages [10]) is a result of electrophilic attack by the solvent on the nitrogen atom in the transition state <u>21a</u> [5,10]:



$$\mathrm{X{-}{-}SiR_3{-}{-}\underset{\underset{ROH}{\vdots}}{N}R_2'}$$

(X = RO--HB, RO, or B) (B = general base)

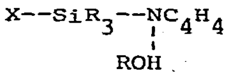
<u>21a</u>

The basicity of the leaving group determines the relative rate,and silylpyrroles react much faster than silylanilines [21,23], in accord with the general rule that weak bases are good leaving groups.

The marked steric hindrance on replacing methyl by bulkier alkyl groups linked to silicon in the base catalysed cleavage of trialkylsilylanilines [5,10] is taken as evidence for a transition state <u>21</u> involving interactions between the nucleophile and the silicon atom [5].

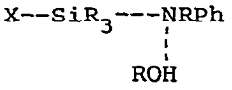
The much faster rates of cleavage of silylanilines in DMSO/aq.KOH than in MeOH/aq.KOH is attributed to the increased reactivity of the base anions, and also to reduced steric interaction as a result of reduced importance of synchronous proton transfer to the nitrogen atom [10]. Bimolecular reactions between anions and uncharged species are generally faster in aprotic/protic than in protic/protic solvent mixtures, and this is ascribed to the less efficient solvation of reactant anions in the former [90].

The electrophilic attack by solvent on the nitrogen atom in the transition state may be a factor in determining the relative activation enthalpies for silylpyrroles and silylanilines. Proton transfer will be more complete towards the less basic pyrrole nitrogen, since the transition state represents an energy maximum on the reaction pathway [79]. By the same argument, the Si-N bond in the silylpyrrole will be stronger than the Si-N(aniline) bond. The least basic substrate will therefore involve less negative charge on nitrogen in the transition state, and consequently have the lowest activation enthalpy.



$\mathrm{X{-}{-}SiR_3{-}{-}\underset{\underset{ROH}{\vdots}}{N}C_4H_4}$

21b



$\mathrm{X{-}{-}SiR_3{-}{-}{-}\underset{\underset{ROH}{\vdots}}{N}RPh}$

21c

4. MECHANISMS OF SILICON-CARBON CLEAVAGE.

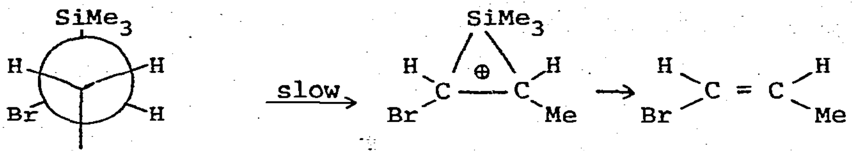
Several reviews have appeared on the chemistry of the silicon-carbon bond [11,12,32,36,37,46,80], and in this Chapter the emphasis is on recent developments. This bond is relatively resistant towards heterolytic cleavage, requiring in most instances vigorous conditions for reaction to occur. The Si-C(alkyl) and Si-C(aryl) bonds are cleaved by strong nucleophiles, the reactivity increasing with the stabilisation of negative charge in the leaving group [24,25,45]. Strong acids and other electrophiles cleave the silicon-alkyl bond. Silicon-aryl bonds are readily cleaved by electrophiles, and the splitting of R_3Si groups from aryl substrates constitutes a convenient way of studying electrophilic aromatic substitution [45,80,86].

Mechanistic studies have been reported on the acid catalysed solvolysis of Si-alkyl compounds [38,43,122,123], and in particular on the alkaline solvolysis of these compounds [24,34,45,49,100,119]. More recently, kinetic studies of base catalysed solvolysis of Si-aryl bonds have been performed [6,8,16,24,25,26,41,65,66].

Acid catalysed reactions. The stereospecific anti-elimination of Me_3SiBr in the solvolysis of (erythro-1,2-dibromopropyl)trimethylsilane rules out siliconium ion mechanisms [112] and four-centre mechanisms [12], and suggests an E2 mechanism or mechanisms involving carbonium ions [28,62].

$$\lg (k/k_o) = mY \qquad (14)$$

The E2 mechanism is, however, not in accord with the large charge separation in the transition state (reflected in the m-values close to one in the Grunwald-Winstein equation 14 [112,122]), and a mechanism involving the slow formation of a silicon-bridged ion 22 is proposed:

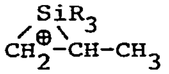


22

(15)

This mechanism is supported by more recent results by Eaborn and co-workers who obtained evidence for the migration of the trimethylsilyl group in solvolysis of $Me_3SiCH_2CD_2Br$ to give $Me_3SiCD_2CH_2Br$ along with elimination products [38], and by the small ρ-values [122,123] (Table 11). A parallel reaction path, involving the classical carbonium ion has to be admitted, however, in order to explain the presence of a small amount of syn-elimination [62].

It is also suggested that the very rapid acid catalysed cleavage of allyl-silicon bonds is associated with formation of a non-classical ion 23 [38]:



$\overset{\oplus\;SiR_3}{CH_2-CH}-CH_3$

23

Rho-values in the range -4 to -5 are found for reactions involving carbonium ions, and for the classical carbonium ions corresponding to 22 and 23 the ≡Si-CHR- group would lower this to -0.8 to -1. The ρ-values observed for 2-chloro- and 2-hydroxy-alkylarylsilanes are much lower [122,123], and suggest interactions between the silicon atom and the carbonium ion centre, in support of the cyclic transition states 22 and 23.

The stereospecificity decreases with increasing Y-values of the solvent as a result of increased stability of the classical carbonium ion in the parallel reaction path [62].

Substitution of deuterium adjacent to silicon has virtually no effect on the rate of solvolysis of 2-halogenoalkylsilanes and indicates that little Si-C bond breaking has occurred at the transition state [63]. Deuterium at the carbon atom carrying the halogen atom produces an isotope effect $k_H/k_D = 1.10$, and this is consistent with cleavage of the carbon-halogen bond in the rate determining step [63].

The reaction mechanisms of 2-halogenoalkylsilanes have been extended to 2-hydroxyalkylsilanes [63,123].

Base catalysed reactions. The Si-C(alkyl) bond is cleaved in base catalysed solvolyses if electron attracting groups or atoms are attached to the carbon atom, i.e. for the following types of compounds: Si-alkynyl [48,49,51,72,119], Si-allyl [100,101], Si-C-Ar [4,14,15,24], Si-C-hal [34,35], and acylsilanes and β-silylketones [18,71]. The cleavages of Si-alkynyl and Si-benzyl bonds have been reviewed [45].

The cleavage of $(XC_6H_4)_3SiC{\equiv}CPh$ is associated with a substantial excess of negative charge on the silicon atom in the transition state, which indicates that the bond to the nucleophile is formed to a large extent [49].

The effect on rate of substituents in the cleaved group indicates that the Si-C(alkynyl) bond is stretched in the transition state, placing a negative charge on the carbon atom [49]. The very marked increase in rate as n increases in the cleavage of $Et_3Si(C{\equiv}C)_nR$ points to a significant amount of bond breaking in the transition state [51]. These results, and also the observed inversion of configuration [119] are in accord with either the S_N2-Si or the S_N2^*-Si mechanisms:

$$HO^- + R_3SiC{\equiv}CR' \rightarrow [HO{-}{-}{-}SiR_3{-}{-}{-}C{\equiv}CR']^- \rightarrow HOSiR_3 + {}^-C{\equiv}CR' \quad (16)$$

$$HO^- + R_3SiC{\equiv}CR' \xrightarrow{\text{fast}} [HOSiR_3C{\equiv}CR']^- \quad (17)$$

$$[HOSiR_3C{\equiv}CR']^- \xrightarrow{\text{slow}} [HO{-}SiR_3{-}{-}{-}C{\equiv}CR']^- \rightarrow HOSiR_3 + {}^-C{\equiv}CR' \quad (18)$$

Bulky alkyl groups R in $R_3SiC{\equiv}CPh$ slow down the rates because of steric hindrance to solvation of the intermediate carbanion [49]. In addition to the insulating effect of the triple bond, solvation of the anion is also partly responsible for the relatively small ρ-values [49].

In the cleavage of $R_3SiCH_2CH{=}CHPh$ in strongly basic media one mole of base is present in the transition state [101]:

$$R'O^- + R_3SiCH_2CH{=}CHPh \rightarrow [R'O{-}{-}R_3Si{-}{-}CH_2CH{=}Ph]^- \rightarrow$$
$$R_3SiOR' + {}^-CH_2CH{=}CHPh \quad (19)$$

The faster cleavages in more aqueous MeOH/H_2O solvent mixtures are the result of the equilibrium (20) being displaced to the left, increasing the concentration of the better nucleophile OH^- [101]:

$$ROH + OH^- \rightleftharpoons RO^- + H_2O \quad (20)$$

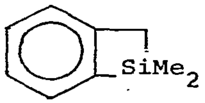
Values of y in the relation (21) indicate that 3-6 molecules of water are involved in the formation of the transition state [100].

$$\lg k_s = y \cdot \lg c_w \quad (c_w = \text{conc. of free water [129]}) \quad (21)$$

The value of k_{H_2O}/k_{D_2O} of 0.5 indicates electrophilic assistance from the solvent to the leaving group synchronous with the Si–C bond-breaking [100,101].

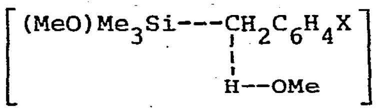
The polar effects in the solvolytic cleavage of the silicon-benzyl bond demonstrate that in this reaction a fairly large excess of negative charge is distributed over both the silicon and carbon atoms in the transition state [14,24] (Tables 11 and 12).

For the compound <u>24</u> the strain is reduced in a transition state in which the Si-benzyl bond is breaking, resulting in a very great increase in reactivity compared with benzyltrimethylsilane [50].



<u>24</u>

A free carbanion is, however, not formed; from recent work on solvent isotope effects it is concluded that proton transfer from the solvent to the carbon atom of the breaking $Si\text{-}CH_2Ar$ bond takes place at the transition state [4].



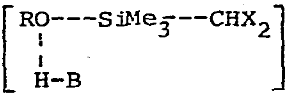
$$\left[(MeO)Me_3Si\text{---}\underset{\substack{\vdots \\ H\text{--}OMe}}{C}H_2C_6H_4X \right]$$

<u>25</u>

The cleavage of α-halo-substituted alkyl groups from silicon displays general base and nucleophilic catalysis

[34,35]. The cleavages depend on the degree of stabilisation of negative charge in the leaving group, and the great rate increases for Me_3SiCHX_2, X = Cl < Br < I suggest a significant amount of Si-C bond weakening in the transition state [34].

$$RO^- + Me_3SiCHX_2 \xrightarrow{ROH,NH_3} [RO{-}{-}H{-}{-}NH_2{-}{-}SiMe_3{-}{-}CHX_2]^- \quad \text{or}$$



$$\left[\begin{array}{l} RO{-}{-}{-}SiMe_3{-}{-}CHX_2 \\ \vdots \\ H{-}B \end{array}\right] \qquad B = NH_3 \text{ or } RO^- \qquad (22)$$

The chemistry of organosilicon ketones has been reviewed [18,71]. For the base catalysed solvolysis of acylsilanes a mechanism involving penta-coordinate silicon intermediates has been proposed [18].

$$RO^- + R_3SiCOR \xrightarrow{ROH} [RO{-}{-}SiR_3{-}{-}COR]^-$$

$$\xrightarrow[\text{displacement}]{\text{rearrangement or}} \text{products} \qquad (23)$$

A comparison of relative rates of cleavage of the Si-C(alkyl) bond by base is given in Table 15, and it is seen that the rates increase with the anion stability, as measured by the pK_a of the conjugate acid. In DMSO/H_2O the relative rates can be accounted for in terms of carbanion stability alone ($\alpha = 1$ in eqn. 6), while in MeOH/H_2O there is less carbanionic character in the transition state.

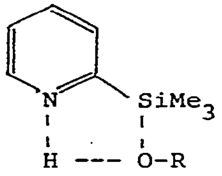
For the Si-C(alkyl) base catalysed cleavages the most reasonable mechanism is S_N2^*-Si involving rate determining breakdown of a penta-coordinate silicon intermediate.

Referring to Table 11 it is seen that this mechanism is characterised by ρ_{Si}-values ≃ 2. Substituents in the cleaved group give rise to maximum ρ-values (see Introduction) and a value of 4.9 is found for the cleavage of benzylsilanes in MeOH/H_2O [14]. In this connection it is interesting to note that a ρ-value of 5 has been measured (in THF) for reactions involving the benzyl carbanion [110].

Cleavage of the Si-C(alkyl) bond in R_3SiR' is associated with rate ratios k_{Me}/k_{Et} (R = Me, Et) of 300-1000 (Table 13), presumably because of steric hindrance to attack by the nucleophile at the silicon atom. Steric hindrance to solvation of the separating carbanion [49] probably does not play an important role, since the rate ratios are relatively constant for different leaving groups.

The very similar ρ-values in the benzofuryl- and benzyl-silicon compounds (Table 11) indicate that the silicon atom carries a similar excess of negative charge in the transition states in the two reaction series. The activation parameters are also quite similar (Table 14) and it is concluded that the nature of the transition state is similar in the two systems [24].

Rho-values measured for substituents in the cleaved group of Si-C(aryl) compounds are highly positive, as a result of a significant amount of Si-C bond breaking in the transition state [8,41]. If the negative charge on the carbon atom can be reduced by the presence of electronegative atoms in the β-position, increased rates of cleavage result. An example of this is found in the faster cleavage of trimethylsilyl-1,3-benzodioxole compared with trimethylsilylveratrol and trimethylsilyl-1,4-benzodioxan [16]. Other more straightforward examples are known. Thus 2-benzofuryl-silicon bonds are cleaved much more readily than aryl-silicon bonds [24], and 2-trimethylsilyl pyridine is cleaved even under neutral conditions [6]. It has been suggested that the high reactivity of the 2-TMS-pyridine and similar systems [65,66] results from the presence of a 5-membered cycle in the transition state [6], and the highly negative activation entropies and relatively low activation enthalpies are consistent with this.



26

Analogous cyclic complexes could be written for the 2-benzofuryltrimethylsilane, but the relatively small absolute activation entropies are not in accord with this. Similar activation entropies are also measured for the polynuclear aromatic compounds [25,26] (Table 14), and it is concluded that the degree of electrophilic assistance from the solvent is relatively small.

5. GENERAL MECHANISM.

In this Chapter the author's conclusions regarding mechanisms are presented, and a general mechanism is proposed.

Comparison of silicon–oxygen, –nitrogen, and –carbon cleavages. The negative charge which develops on Y in the base catalysed cleavages of R_3SiY may be stabilised by resonance and by hydrogen bonding to the solvent. It is seen from Table 16 that ρ_Y-values for OAr and NRAr are lower than for OCH_2Ar by a factor of 0.6 which may be taken to express the stabilising effect of conjugation. If this factor is applied to CH_2Ar a ρ_Y-value free from both types of stabilising effects may be calculated, $\rho_Y = 4.9/0.6 \simeq 8$, and ρ_Y-values for base catalysed solvolyses in protic solvents involving rate determining separation of negative leaving groups may be established (possibly restricted to sp^3 hybridised leaving atoms):

	stabilisation of negative charge	ρ_Y
1)	unstabilised	8
2)	stab. by conjugation	5
3)	stab. by electrophilic assistance from solvent	3
4)	stab. by both 2) and 3)	2

Electrophilic attack from the solvent on a separating carbanion will have to be on the σ-bond joining Si and C, and will be much more difficult than electrophilic attack on a free electron pair of N and O leaving atoms, and electrophilic assistance from the solvent is ignored in calculating the value $\rho_Y = 8$ above.

In the acid catalysed solvolyses the basicity of the leaving group determines the relative rates and the following rate sequence is obtained:

$R_3SiNMePh > R_3SiOCH_2Ph > R_3SiOPh > R_3SiNC_4H_4$. This demonstrates the overriding importance of the protonation step in the reaction sequence.

In the base catalysed reactions it is evident that simple correlations between rates and pK_a similar to those obtained in the $R_3SiOCOR$ reactions (eqn. 6) and for the Si-C(alkyl) series (Table 15) cannot be extended to different leaving atoms. Surprisingly similar rates are found for $R_3Si-NHPh$, -OPh, and $-NC_4H_4$ substrates [10,20,21], while R_3Si-CH_2Ar reacts approximately 10^9 times more slowly [10].

On changing Y in R_3SiY from OR through NR_2 to CR_3 it is found that the activation entropies change from highly negative values for R_3SiOR to normal S_N2 values for R_3SiCR_3. Since the reactivity of R_3SiY is in most cases higher than for analogous carbon compounds, the highly negative activation entropies are coupled with very low activation enthalpies which also become more normal in the direction R_3SiOR, R_3SiNR_2 to R_3SiCR_3.

The transition state. The stereochemistry of the solvolyses of organosilicon compounds is a sensitive function of the medium, substrate, and nucleophile, and crossover from retention to inversion of configuration and *vice versa* has been observed [117,119]. This stereochemical lability must be the result of either

1) the existence of a family of one-step mechanisms having closely similar energies,

or 2) the operation of multi-step mechanisms in which different steps are rate determining depending on the reaction conditions.

In the reaction: $R_3SiY + X \rightarrow$ products, the one-step mechanism involves covalency changes of two bonds to silicon, while addition-elimination mechanisms involve stretching of only one bond to silicon in the transition state.

The transition states are:

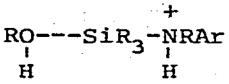
X---SiR_3---Y 2

X-SiR_3----Y 3

X----SiR_3-Y 4

The differential charges on Si and Y are diagnostic of the mechanism and can be estimated by Hammett's ρ-values for substrates carrying substituted phenyl groups attached to Si and Y. The ρ-values for reactions studied under comparable conditions are summarised in Table 16 and are first discussed on the basis of the two-step mechanisms.

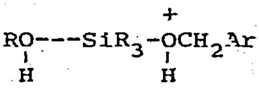
In the transition state of the acid catalysed reaction there is a significant amount of positive charge on Y when Y = NRAr and OCH_2Ar. This means that the Si-Y bond is not stretched in the transition state which therefore is of type 4, and involves rate determining formation of a penta-coordinate complex. For a given ρ_Y-value, a ρ_{Si}-value 0.4 times ρ_Y is measured at the silicon atom:



$$\underset{\mathrm{H}}{\mathrm{RO}}\text{---}\mathrm{SiR_3}\text{-}\overset{+}{\underset{\mathrm{H}}{\mathrm{N}}}\mathrm{RAr}$$

$\rho = -1 \quad -2.5$

27

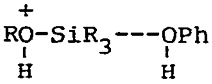


$$\underset{\mathrm{H}}{\mathrm{RO}}\text{---}\mathrm{SiR_3}\text{-}\overset{+}{\underset{\mathrm{H}}{\mathrm{O}}}\mathrm{CH_2Ar}$$

$-0.55 \quad -1.4$

28

For the Si-OPh compounds the ρ_Y-value is -0.5 and this demonstrates that the bond to the leaving group is relatively weak. A transition state 29 involving rate determining breakdown of a penta-coordinate complex thus seems likely.



$$\overset{+}{\underset{\mathrm{H}}{\mathrm{RO}}}\text{-}\mathrm{SiR_3}\text{---}\underset{\mathrm{H}}{\mathrm{O}}\mathrm{Ph}$$

$\rho = -0.6 \quad -0.5$

29

The negative charge on silicon which results from this partial penta-covalent silicon is compensated by the positive charge in the alkoxy group and overall the silicon atom is electron-deficient in the transition state.
The transition states 28 and 29 contain one full bond from Si to a protonated alkoxy group, and the same charge is found on Si in the two reaction series. However, from a discussion of relative stability of positive charge on leaving and entering groups, a transition state similar to 28 cannot be excluded for the phenoxysilanes [20].

The two-step mechanism thus does not seem to provide a satisfactory explanation for the (few) experimental results available for the acid catalysed reaction.

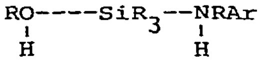
For the base catalysed solvolyses the ρ-values reveal that the leaving groups carry negative charges in the transition states for all reaction series (Table 16). In terms of the two-step mechanism the transition state therefore is of type 3, and involves rate determining breakdown of a penta-coordinate complex.

If the ρ_{Si}-values are measures of the degree of bond formation between Si and Y, the values in Table 16 indicate that the Si-Y bond is strongest for Si-CH_2Ar and weakens in the sequence (Y =) CH_2Ar > NRAr > OCH_2Ar > OAr. As mentioned in Chapter 4, reactions involving the benzyl carbanion are characterised by a ρ-value of +5, and the similar value measured for the solvolysis indicate that the Si-CH_2Ar bond is cleaved to a great extent in the transition state. If the Si-Y bond is in all cases nearly broken it is difficult to see why there should be such a great difference in the ρ_{Si}-values measured for the Si-OAr and Si-OCH_2Ar series. The data in Table 16 thus do not seem to fit a two-step mechanism for the base catalysed solvolyses.

If we wish to formulate a general mechanism for both acid and base catalysed solvolysis of R_3SiY, it is clear that two step mechanisms are unsuitable. We therefore turn our attention to S_N2-Si and S_Ni-Si mechanisms, and it will be seen that in fact all the available evidence can be understood with reference to these mechanisms.

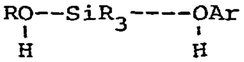
An acceptable S_N2-model for the acid catalysed solvolyses is formulated by allowing the full Si-X or Si-Y bond in the two-step mechanism to weaken slightly, and the result is that the balance between bond-forming and -breaking processes is governed by the principle:

In the transition state of the acid catalysed solvolysis the strongest bond is formed between the silicon atom and the less acidic of the entering and leaving groups.



$$\underset{\substack{|\\ \mathrm{H}}}{\mathrm{RO}}\text{----}\mathrm{SiR_3}\text{--}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{N}}\mathrm{RAr}$$

30



$$\underset{\substack{|\\ \mathrm{H}}}{\mathrm{RO}}\text{--}\mathrm{SiR_3}\text{----}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{O}}\mathrm{Ar}$$

31

The principle applies to groups X and Y that differ considerably in acidity, but for smaller differences other factors dominate, cf results for R_3SiOCH_2Ar.

In the base catalysed solvolyses a mechanism which involves a similar Si-OR bond order for all leaving groups is excluded for the reasons mentioned above in the discussion of the two-step mechanism. From the ρ_{Si}-values the RO-Si bond becomes stronger as the basicity of Y increases.

The leaving groups are of widely different basicities and it is reasonable to assume that this results in different bond orders for bonds to the hard [91] electrophilic SiR_3 centre. The ρ_Y-values are in accord with the assumption that the Si-Y bond is strongest for the less basic leaving group. Relatively small differences in bond orders are involved, however, as implied in the discussion in the first section of this Chapter, and the Si-Y bond is in all cases nearly broken. The structure of the transition state is thus determined by the basicities of the leaving and entering groups:

In the transition state of the base catalysed solvolysis the strongest bond is formed between the silicon atom and the weakest base.

$RO{-}{-}SiR_3{-}{-}{-}{-}CH_2Ar$ $\qquad\qquad$ $RO{-}{-}{-}{-}SiR_3{-}{-}OAr$

<u>32</u> $\qquad\qquad$ <u>33</u>

The principle applies to Si-X and Si-Y bonds in the reactions of a given molecule R_3SiY with X, and may be put in general form as follows: "In the transition state of solvolysis of R_3SiY ($Y = OR, NR_2, CR_3$) the strongest bond is formed between the silicon atom and the weakest acid for acid catalysed reactions, and the weakest base in base catalysed reactions."

As a hard electrophilic centre [91] SiR_3 may be compared with the proton, and a rationale for the principle can be found. If in the base catalysed solvolysis an equilibrium is assumed, we may write:

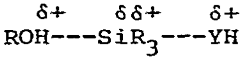
$$R_3SiY + {}^{-}OR \rightleftharpoons R_3SiOR + Y^{-} \qquad (24)$$

The next step is to transform this reaction to an acid-base reaction by substituting H for R_3Si:

$$HY + {}^{-}OR \rightleftharpoons ROH + Y^{-} \qquad (25)$$

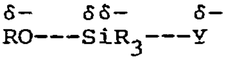
The transition state for reaction (25) bears the greater resemblance to the less stable of the species in the equilibrium [79] , i.e. the strongest bond is formed to the weaker base. By transforming eqn. (25) back to eqn. (24) the principle given above follows.

It is also possible to deduce the principle by applying the Hammond postulate [55] to eqn. (24). The postulate fails, however, in the acid catalysed solvolysis. From the ρ-values in Table 16 it follows that in the transition state of the acid catalysed solvolysis, the central atom is less positive than the entering and leaving groups, and in the base catalysed solvolysis it is less negative:



$\overset{\delta+}{\mathrm{ROH}}\text{---}\overset{\delta\delta+}{\mathrm{SiR_3}}\text{---}\overset{\delta+}{\mathrm{YH}}$

34



$\overset{\delta-}{\mathrm{RO}}\text{---}\overset{\delta\delta-}{\mathrm{SiR_3}}\text{---}\overset{\delta-}{\mathrm{Y}}$

35

The failure of the Hammond postulate may be connected with the fact that although in the acid catalysed reactions, the mechanism is thought to involve nucleophilic attack at silicon by ROH, there is formally a flow of electrons away from the silicon atom in reaching the transition state.

A necessary condition for the operation of the S_Ni-Si mechanism is that the reagent contains nucleophilic and electrophilic sites not completely removed from each other; an example is BuONa in BuOH/C_6H_6 [117]. As the polarity of the protic solvent increases, the concentration of free ion pairs increases, and the S_Ni-Si mechanism becomes less probable. The few examples of retention of configuration in ROH solvent may be explained by flank attack of the nucleophile at silicon in the S_N2-Si mechanism.

Studies directed at distinguishing between general and specific catalysis have revealed that reactions studied until now are of two types: either general base catalysed or specific acid catalysed. There is thus a characteristic difference between acid and base catalysed reactions in that the proton transfer is part of the rate determining step in the base catalysed solvolyses, while acid catalysis involves proton transfer in a fast step preceding the rate determining step. There is, however, no reason to think that general base catalysis is universal for solvolysis of organosilicon compounds. Solvent isotope effects are in accord with general base catalysis for phenoxysilanes [83,108], but for carbon leaving groups k_H/k_D-values less than unity are found [4,101] indicating other types of catalysis.

As discussed above for Si-OC compounds, solvation of the leaving group depends on its basicity. As a result of this the complexity of the transition state is greater for OR and NR_2 than for CR_3 leaving groups resulting in more negative activation entropies in the former cases.

It is evident from the discussion above that at present only a very limited amount of detail is possible in the description of the transition state. One way of increasing our knowledge would be to study the solvent effects on reaction rates, and since many of the reactions discussed here are catalysed by both acid and base giving rise to positive and negative transition states, an extensive background of empirical information should be possible, against which new mechanisms would be tested.

6. EXPERIMENTAL RESULTS

SILICON-OXYGEN CLEAVAGE

Stereochemical investigations, (Table 1). Inversion of configuration was shown to occur in the neutral,.acid- and base-catalysed methanolysis of R_3SiOMe [7]. Both inversion and retention of configuration were found for R_3SiOR' in various alcohol/benzene and alcohol/toluene mixtures containing metal alkoxides [116,117]. Alcoholysis of R_3SiOMe results in retention, inversion or racemisation according to the dielectric constant of the medium [119].

Catalysis. Cleavage of the silicon-oxygen bond is catalysed bv both acid and base [11,44], but reaction is slow in neutral solution [1,22]. First order general base catalysis [20,59,107], and specific acid catalysis [22] have been found. The hydrolysis and alcoholysis of silylacetates are first-order or slightly less in added potassium acetate [104,105]. The solvolysis of alkoxysilanes is first order in hydrogen ion cocentration [1,19,20]. The Si-OC bond in $(RO)_3SiCH_2CH_2X$ is cleaved in base catalysed hydrolysis [54]. The hydrolysis of aryloxytriphenylsilanes is said to be second order in hydroxide ion at low base concentration, and first order at higher concentrations [121]. The second order dependence on base is, however, apparently due to a misinterpretation [47]. Simultaneous acid and base catalysis is observed in the methanolysis of methoxyphenoxymethylphenylsilane [121].

Polar effects. Substituents at the silicon atom. Acid catalysed alcoholysis of silicon-oxygen bonds is relatively insensitive to polar effects, small negative ρ-values being observed [19,20,22] (see Table 2). The rates are thus slightly increased by electron donating substituents. The uncatalysed reaction of p-substituted phenyldiethylsilyl methacrylates in acetone/water was studied conductiometrically [53]. A non-linear Hammett plot was observed and attributed to a change in medium rather than to a change in mechanism. It seems, however, that further work with substituents covering a wider range of σ-values would be necessary to test the hypothesis of a curved Hammett-line. Indeed, by using σ^o constants instead of σ-constants in the Hammett equation a linear plot is obtained, and a ρ-value of approximately -4 may be calculated. Rates for acid catalysed hydrolysis of $R_2Si(OR')_2$ decrease as the electron-withdrawing effect of R (alkyl and aryl) increase [31].

On the other hand, ρ-values measured in the base catalysed cleavage are positive, ranging from about 0 to

+3 [20,22,104,112] (see Table 2). The rates are thus increased by electron attracting substituents, as expected for a process which involves negative charge on silicon.

The additivity rule for substituent constants in the Hammett equation (26) was found to be valid for the alcoholysis of silylacetates [103,104,105].

$$\lg k = \lg k_o + \rho\Sigma\sigma \qquad (26)$$

The rate of alkaline hydrolysis of $Me_{4-n}Si(OEt)_n$ in aqueous dioxan increases with increasing number of ethoxy groups [125]. $Me_2Si(OR)_2$ compounds are more reactive than Me_3SiOR in acid catalysed alcoholysis [19]. In aqueous acidic ethanol an equilibrium is set up between the products ethoxysilane and hexamethyldisiloxane in the solvolysis of trimethyl-tert-butoxysilane [85].

Substituents in the leaving group. Several studies on the effect of substituents in the leaving group have been published, and summarised by Chipperfield [32]. Rates for the solvolytic cleavage of phenoxysilanes have been reported in ethanol/water [1,2], methanol [107,108] and in aqueous dioxan [33,59]. A small negative ρ-value was found for the acid catalysed cleavage, while ρ and ρ^*-values ranging from +1.1 to +3.5 were calculated for the base catalysed reactions (Table 3). Logarithmic rates were correlated with σ for the meta and para substituents [2,108], (eqn. 2), but Humffray and Ryan [59] obtained a better fit for para substituents by using the Yukawa-Tsuno equation [131] in an appropriate form (eqn. 27).

$$\lg k = \lg k_o + \rho(\sigma + r(\sigma^- - \sigma)) \qquad (27)$$

Curved Hammet plots were obtained by Schowen and Latham [108], but the reality of this was challenged by Humffray and Ryan [59] and more experimental data are needed to reach a decision [32]. For a series of silylated benzyl alcohols leaving group ρ-values of -0.54 and +1.1 were obtained for the acid and base catalysed reactions respectively [22]. The effect on rates of substituents in the acetate part of silylacetates is proportional to the strength of the acid formed in the base catalysed alcoholysis [105]. Electron attracting groups in the acetate part also increase rates in the hydrolytic cleavage [106], and in the alcoholysis in dry, neutral isopropanol [77]. The rates of uncatalysed hydrolysis of $Pr_3SiOCOR$ increase linearly as the pK_a of RCOOH decreases [98]. The rates of acid catalysed alcoholysis of $Me_2Si(OR)_2$ compounds are very dependent on the nature of R [19]. When R is a tertiary group the reactivity is much lower than when R is primary or secondary. Within a group of Me_3SiOR compounds, both the position and rate of attainment of equilibrium varied with the nature of R in the uncatalysed methanolysis [58]. The relative rate constants for base catalysed methanolysis of $Me_3SiO(CH_2)_nR$ follow the modified Taft equation (28) [93].

$$\lg(k/k_o) = \rho^*\sigma^* + E_s + \text{const.} \qquad (28)$$

Steric Effects, (Table 4). The effects of alkyl groups R in the hydrolysis of R_3SiOAc compounds have been studied by Prince and Timms [97], and they found the rate order (R=) n-Pr > n-Hex > Ph > i-Pr > c-Hex. For the acid- and base catalysed hydrolysis of R_3SiOPh, Akerman found the rate sequence Me > Et > n-Pr > n-Bu > n-Pentyl [1]. The substitution of a tert-butyl group for a methyl group lowers the catalytic constant by a factor of 10^{-5}, and these low rates were ascribed to the steric effect of the tert-butyl group [2]. Rates also decrease with increasing size of alkyl groups in the acid catalysed alcoholysis of $R_2Si(OCMe_2)_2$ compounds [19]. Steric effects of R on the base catalysed methanolysis of $Me_3SiO(CH_2)_nR$ were described by means of the Taft equation (28) [93].

Solvent Effects. Phenoxysilanes have been cleaved in various solvents, and it seems that both the relative rates and the substituent effects are influenced by the solvent. For base catalysed solvolysis of $Et_3SiOC_6H_4X$ much higher ρ-values were found in dioxan/water [59] than in ethanol/water [2], +3.5 and +1.7 respectively, and the reaction rates were about five times faster in dioxan/water. Smaller rate differences were found for acid catalysed hydrolysis of Bu_3SiOPh in aqueous dioxan, aqueous isopropanol, and aqueous acetonitrile [33]. This reaction is at least second order in water [33]. Rate increases were observed for the alkaline hydrolysis of Ph_3SiOAc as the percentage of water was increased in water/tert--butanol/benzene mixtures [106]. The rates of uncatalysed hydrolysis in water/dioxan mixtures of $R_3SiOCOR'$ also increase with the water content, and linear $lg(H_2O)$ versus lg k_{obs} plots were obtained with formal water orders of 4.4-4.9 [97,98.99]. The uncatalysed hydrolysis of Pr_3SiOAc is faster in aqueous iso-propanol than in aqueous acetone and rates in both solvents increase with increasing water content [99]. Higher concentrations of alcohol in n-propanol/benzene mixtures likewise increased the rates for the base catalysed alcoholysis of Ph_3SiOAc and high orders in alcohol were found [105]. Trimethylbenzoxysilane was found to react instantaneously with water as well as with methanol or ethanol in dioxan, while the reaction was slow in iso-propanol/dioxan [77]. Rates for the acid catalysed solvolysis of 2-sila-dioxolanes are higher in n-propanol than in iso-propanol [19]. In aqueous ethanol the acid catalysed hydrolysis of tetraethoxysilane is more rapid than in aqueous dioxan [126]. This reaction is a very complicated process which consists of a series of consecutive and parallel hydrolyses and condensations. The rate of alcoholysis of trimethylethoxysilane decreases with increasing branching of the reactant alcohol [124].

Temperature Effects. In the few studies on the effect of temperature on reaction rates large negative $\Delta S^{\ddagger}$-values and low activation enthalpies were calculated (Table 5).

Salt Effects. For Bu_3SiOPh in 40% aqueous acidic dioxan at 30° there is a linear relationship between k_a and $[NaClO_4]$, eqn. (29) up to 0.2 M $NaClO_4$ with b = 2.6 $l mol^{-1}$ [33].

$$k_a = k_o(1 + b[NaClO_4]) \quad (29)$$

Isotope Effects. A solvent isotope effect $k_H/k_D = 1.3$ was obtained by Schowen for the general base catalysed methanolysis of aryloxytriphenylsilane [108]. In the methoxide catalysed methanolysis of aryloxytriphenylsilane in CH_3OH/CH_3OD mixtures solvent isotope effects $k_H/k_D = 2\text{-}4$ were nearly cancelled by inverse isotope effects of similar magnitude [83]. Very small solvent isotope effects were found for acid catalysed hydrolysis of Bu_3SiOPh in D_2O/dioxan (H_2O/dioxan) [33].

SILICON-NITROGEN CLEAVAGE

Stereochemical Investigations. Inversion of configuration was found for neutral and acid catalysed hydrolysis [67,68,112,115] and neutral alcoholysis of silylamines [67,68]. (Table 6).

Catalysis. The solvolysis of silylanilines is catalysed by acid, but inhibited by small amounts of base [9]. Base catalysis is noticeable at high base concentration and in mixtures of dipolar aprotic solvents with water [10]. Trimethylsilyldihydropyridine is cleaved rapidly in methanol containing acid or base [39]. With less basic substrates, base catalysis is more efficient than acid catalysis [21]. The Si-N bond is also cleaved spontaneously in a reaction involving neutral solvent molecules [5,9,10,23].

Specific acid catalysis [9], and general base catalysis [21] have been found. The catalysed reactions are of first order in added catalyst for acid catalysed reactions [9,21], and base catalysed reactions [5,10].

Polar Effects. Substituents in the aryl group. Solvolyses of compounds 36 are facilitated by electron-donating substituents X in the acid catalysed and spontaneous reactions, while base catalysed reactions are facilitated by electron-attracting groups in the meta and para-positions.

$(XC_6H_4)R_1R_2Si\text{-}NRR'$ 36

The polar effects are more pronounced in the base catalysed cleavages giving rise to high ρ-values (Table 7).

Substituents in the leaving group. Electron-donating groups increase the rates of the acid catalysed cleavage, and give rise to negative ρ-values, while the opposite is found in the base catalysed cleavages (Table 8).

Steric Effects. In pure methanol the rate sequence $Et_3SiNHPh > Et_3SiNEtPh > i\text{-}Pr_3SiNHPh$ was found [9]. The rate of neutral alcoholysis of $Et_3SiNHPh$ decreased as the alcohol was varied in the sequence methanol, ethanol, iso-propanol [9]. The $Me_3SiNHPh/Et_3SiNHPh$ reactivity ratio is ca. $2.5 \cdot 10^4$ in aqueous methanol containing base [10], while the effect of alkyl groups at the nitrogen atom is much less apparent in methanol/water or DMSO/water containing base [10]. The following reactivity sequence was obtained for base catalysed solvolysis of $R_3SiNHPh$ [5]: $MeEt_2Si > Me_2\text{-}i\text{-}PrSi > Et_3Si > Me_2\text{-}t\text{-}BuSi > i\text{-}Pr_3Si$ (Table 9).

Solvent Effects. Hydrolysis of $R_3SiNXPh$ compounds is faster in mixtures of aqueous potassium hydroxide with DMSO than in mixtures with methanol [10].

Temperature Effects. Activation entropies ranging from -8 to -63 e.u. and activation enthalpies in the range 2-20 kcal/mole were calculated [9,10,21,23] (Table 10). The silylpyrroles show quite different behaviour from the silylanilines.

Salt Effects. The rate constant for the acid catalysed methanolysis of N-(triisopropylsilyl)aniline was found to increase linearly with the ionic strength of the medium, on addition of lithium perchlorate to the solvent at constant buffer ratio [9].

Isotope Effects. The rate of acid catalysed methanolysis of N-(triisopropylsilyl)aniline was increased by a factor of 1.3 when deuterio-methanol was used in place of methanol [9].

SILICON-CARBON CLEAVAGE

Stereochemical Investigations. Cleavage of α-naphthylphenyl(phenylethynyl)methylsilane by potassium hydroxide in isopropanol results in 70% inversion of configuration [119]. Stereospecific trans-elimination was found in the solvolysis of 1,2-dibromopropyltrimethylsilane [62].

Catalysis. Alkynyl-silicon bonds are readily cleaved in alcohol/water mixtures containing acid or base [45,49,51], and in alcohol containing base [119]. Substituted alkyl groups are cleaved from silicon in acid catalysed solvolysis [38,122,123], and in base catalysed solvolysis [24,34,100] and logarithmic rates are correlated with various acidity functions [100]. Silicon-allyl bonds undergo allylic cleavage in boiling acetic acid with allylic rearrangement [27,43]. Silicon-aryl bonds are cleaved by base in water/DMSO mixtures [16,21,25,26], and by base in aqueous methanolic alkali [24]. The Si-C(aryl) bond in heterocyclic aromatics containing nitrogen adjacent to the C(aryl) atom is cleaved under neutral conditions [6,65,66]. The cleavage of ethynylsilanes in ethanol and methanol is catalysed by alkali halides [72]. A linear dependence of rate on added base is found in the cleavage of the cinnamyl group from silicon [101], and in the general base and nucleophilic catalysed cleavage of α-halo-substituted alkyl groups from silicon [34].

Polar Effects. Substituents in the aryl group. The silicon atom is electron-deficient in the acid catalysed solvolysis and electron-rich in the base catalysed reactions, giving rise to negative and positive reaction constants respectively (Table 11). Curved Hammett plots were obtained for the solvolysis of (2-chloroethyl)aryldimethylsilanes in alcchol/water mixtures with low water content [122]. This curvature may, however, be removed by using σ^{o} constants instead of σ constants in the correlation. The absolute values of the reaction constants are relatively high for both acid and base catalysed reactions.

Different leaving groups. (Table 12). Highly positive ρ-values are found in the base catalysed cleavage of silicon-alkyl and silicon-aryl bonds, and it is necessary to use σ^{-} constants in Hammett-type correlations [8,14]. Rates of cleavage of trimethylsilyl groups from polynuclear aromatic rings increase according to the stabilisation of negative charge in the aryl carbanion [25]. For Si-Ar compounds where the aryl group contains strained ring systems fused to benzene, specially high reactivities are observed in base catalysed solvolysis (so-called Mills-Nixon effect) [16]. For the base catalysed cleavage of α-halo-substituted alkyl groups from silicon, the reactivity increases with increasing stabilisation of negative charge in the leaving group [34]. The rates of base catalysed cleavage of alkynyl-silicon bonds in $Et_3Si(C{\equiv}C)_nR$ increase with n, reaching limiting values for n=8-10 [51].

Steric Effects. (Table 13). Relative rates k_{Me}/k_{Et} for $R_3SiCH(C_6H_4)_2$ and $R_3SiCH_2CH{=}CHPh$ (R = Me, Et) are of the order of 10^3 in the base catalysed solvolysis [15,101].

Relative rates of solvolysis of $R_3SiC{\equiv}CPh$ are in the order: (R=) i-Pr_3 > Et_3 > $MeEt_2$ > Ph_3 > Me_2Et > Me_3 [49]. The Si-C bond in 1,1-dimethyl-2,3-benzo-1-sila-2-cyclobutene is cleaved by base at least 10^{10} times as fast as that of benzyltrimethylsilane [50].

Solvent Effects. Rates of solvolysis of (2-chloroethyl)-aryldimethylsilanes in ethanol/water and in methanol/water mixtures conform to the Grunwald-Winstein equation (14), with m-values ranging from 0.64 to 0.98 [122]. Cleavage of $Me_3SiCH_2CH{=}CHPh$ in aqueous methanol containing base is faster in the more aqueous solvents [101]. The stereospecificity of the solvolysis of 1,2-dibromopropyltrimethylsilane decreases as the ionic strength of the medium increases [62]. The order of reactivity of cinnamyl silanes in ROH/DMSO mixtures by bases RO^- is (RO^-=) OMe < OEt ≃ O-n-Pr ≃ O-i-Bu ≃ O-neopentyl < OH [100].

Temperature Effects. (Table 14). Activation entropies from -4 to -42 calmol^{-1}K^{-1} were calculated and are thus in the normal range for S_N2 reactions.

Salt Effects. A small negative salt effect was observed for the alkaline cleavage of $Me_3SiCH_2CH{=}CHPh$ [101].

Isotope Effects. Values of solvent isotope effects k_{H_2O}/k_{D_2O} are less than unity in the base catalysed solvolysis of cinnamyl silanes in aqueous DMSO [100], and in aqueous methanol [101]. Use of a deuterium labelled substrate in the solvolysis of (2-bromoethyl)-trimethylsilane demonstrated migration of the trimethylsilyl group [38]. Secondary deuterium isotope effects k_H/k_D are in the range 1.00-1.14 in the acid catalysed solvolysis of 2-halogenoalkylsilanes [63]. There is a small decrease in rate of solvolysis of 2-trimethylsilylpyridine on changing the solvent from H_2O to D_2O [6]. The product ratio $XC_6H_4CH_3/XC_6H_4CH_2D$ in the cleavage of $XC_6H_4CH_2SiMe_3$ in MeOH-MeOD containing base is in the range 1.07-1.25, and the solvent isotope effect $k_{ROH}/k_{ROD} = 0.5$ [4].

Table 1. Stereochemistry of solvolysis of Si-OC.

Series	Substrate	Solvent	Added catalyst	Product	Stereochemistry	Ref.
1	R_3SiOMe^*	MeOH	NaAc,NaOMe, benzoic acid	R_3SiOMe	Inversion	7
2	R_3Si^*OPh	n-BuOH/benzene	n-BuOM	R_3Si^*O-n-Bu	Inv. or ret.	117
3	R_3Si^*OMe	"	"	"	(dep. on conc.	116,117
4	R_3Si^*OPh	i-PrOH/benzene	i-PrOM	R_3Si^*O-i-Pr	of ROH)	117
5	R_3Si^*OMe	i-PrOH/MePh	"	"		116,117
6	$R_3Si^*OCH{=}CH_2$	"	i-PrOLi	"	Ret.	30
7	$R_3Si^*OCH{=}CH_2$	i-PrOH	"	"	Inv.	"
8	R_3Si^*OMe	t-BuOH	KOH	R_3Si^*OH	55 % ret.	119
9	R_3Si^*OMe	i-PrOH	"	(after	70 % inv.	"
10	R_3Si^*OMe	t-BuOH/dimethoxyethane	"	hydrolysis)	60 % ret.	"
11	R_3Si^*OMe	EtOH	"	"	(rac.)	"
12	$R_3Si^*OC(R'){=}CHCOR''$	H_2O/THF, MeOH/C_6H_{12}	none	R_3Si^*OH R_3Si^*OMe	Rac. (inv.)	73
13	R_3Si^*OAr	H_2O/THF, MeOH/C_6H_{12}	"	R_3Si^*OH R_3Si^*OMe	Rac.	74
14	R_3Si^*OMe	$C_6H_{11}OH$/MePh	$C_6H_{11}OM$	R_3Si^*O-c-Hex	Ret.	116
15	R_3Si^*OEt	"	"	"	"	"
16	R_3Si^*O-i-Pr	"	"	"	"	"

R_3Si^* = α-naphthylphenylmethylsilyl

Table 2. Solvolytic reactions of $(XC_6H_4)R_1R_2Si\text{-}OR$ and $(XC_6H_4)R_1Si(OR)_2$.

Series	Substrate			Solvent	Added catalyst	Reaction constant	Ref.
	R_1	R_2	R				
1	XC_6H_4	XC_6H_4	$COCH_3$	n-PrOH/C_6H_6	CH_3COOK		105
2	"	"	"	i-PrOH/C_6H_6	"	1.7	103
3	"	"	"	t-BuOH/C_6H_6/H_2O	"	1.9	106
4	Me	Me	"	n-PrOH/C_6H_6	"	1.9	104
5	Et	Et	$COCMe{=}CH_2$	Me_2CO/H_2O	none	-4	53
6	Me	Me	Ph	EtOH	H_2SO_4	-0.57	20
7	"	"	"	"	$BuNH_2/BuNH_3Cl$	0.19	"
8	"	-	CMe_2	n-PrOH	H_2SO_4	-0.41	19
9	"	Me	CH_2Ph	EtOH	$ClCH_2COOH/ClCH_2COONa$	-0.55	22
10	"	"	"	"	EtONa	1.5	"

Table 3. Solvolytic cleavage of Si-OC substrates with substituents in the leaving group.

Series	Substrate	Solvent	Added catalyst	Reaction constant	Ref.
				ρ or ρ^*	
1	$Et_3SiOC_6H_4X$	$EtOH/H_2O$	HCl	-0.53	2
2	"	"	NaOH	1.7	"
3	$Ph_3SiOC_6H_4X$	MeOH	NaAc/HAc	1.2	108
4	"	MeOD	"	1.2	"
5	$Ph_3SiOCOR$	$n\text{-}PrOH/C_6H_6$	Cl_3CCOOK	1.2	105
6	"	$i\text{-}PrOH/C_6H_6$	"	1.2	"
7	$Et_3SiOC_6H_4X$	$dioxan/H_2O$	$BuNH_2/BuNH_3Cl$	3.5	59
8	$Me_2PhSiOCH_2C_6H_4X$	EtOH	$ClCH_2COOH/ClCH_2COONa$	-0.54	22
9	"	"	EtONa	1.1	"
10	$Me_3SiOCOC_6H_4X$	i-PrOH	none	1.6	77
11	$Bu_3SiOC_6H_4X$	$dioxan/H_2O$	$HClO_4$	curved Hammett-line	33
12	$(n\text{-}Pr)_3SiOCOCH_{(3-n)}Me_n$	"	none	-	98
13	$Me_3SiO(CH_2)_nR$	MeOH	$EtNH_2$	4.64 (extended Taft eq.)	93

Table 4. Steric effects of R in the solvolysis of R_3SiOR' and $R_2Si(OR')_2$.

Series	Substrate	Solvent	Added catalyst		Relative rates					Ref.
1	R_3SiOAc	dioxan/H_2O	none	(R=)	Ph	n-Pr	c-hex	n-hex	i-Pr	
					114	1220	179	1	7.8	97
2	R_3SiOPh	EtOH/H_2O	HCl		Me	Et	n-Pr	n-Bu	n-pentyl	
					173	3.7	2.0	1.3	1	1
3	"	"	NaOH		1100	7.0	2.2	1.4	1	1
4	$R_2Si(OCMe_2)_2$	n-PrOH/C_6H_4	H_2SO_4	(R_2=)	Me_2	Et_2	Pr_2	MePh		
					3.8	1.8	1	1.4		19
5	R_3SiOAc	dioxan/H_2O	none	(R=)	Me	Et	n-Pr	n-Bu	n-hex	
					171	4.5	1	0.53	0.14	99
6	"	i-PrOH	"			2.2	1	0.68		"

Table 5. Activation parameters for Si-OC.

Series	Substrate	Solvent	Added catalyst	ΔS^*	ΔH^*	Ref.
				$(cal mol^{-1} K^{-1})$	$kcal mol^{-1}$	
1	R_3SiOAc	dioxan/H_2O	none	-(36-48)	6-11	97
2	$MeRSi(OCMe_2)_2$	PrOH/C_6H_6	H_2SO_4	-50	4	19
3	"	i-PrOH/C_6H_6	"	-50	10	"
4	$ArMe_2SiOCH_2Ar'$	EtOH	EtONa	-50	6	22
5	"	"	$ClCH_2COOH/ClCH_2COONa$	-46	9	"
6	Bu_3SiOAr	dioxan/H_2O	$HClO_4$	-(31-40)	7-10	33
7	$Pr_3SiOCOCH_{(3-n)}Me_n$	"	none	-(48-59)	5-7	98
8	R_3SiOAc	"	"	-(46-67)	1-6	99
9	"	i-PrOH	"	-(52-54)	4	"

Table 6. Stereochemistry of solvolysis of silylamines.

Series	Substrate	Solvent	Added catalyst	Product	Stereochemistry	Ref.
1	$(+)R_3Si^*Pyr$(a,b)	Et_2O/H_2O	HCl	$(-)R_3Si^*OH$	76% inv.	115
2	$(+)R_3Si^*NH\text{-}i\text{-}Bu$	"	"	"	95% inv.	"
3	$(+)R_3Si^*NH_2$	"	"	$(+)R_3Si^*OH$	96% inv.	"
4	$(-)R_3Si^*NMe_2$	THF/H_2O	none	"	95% inv.	68
5	"	MeOH/cyclohexan	"	$(+)R_3Si^*OMe$	95% inv.	"
6	$(-)R_3Si^*NHMe$	dioxan/H_2O,THF/H_2O	"	$(+)R_3SiOH$	inv.	67
7	"	MeOH in Et_2O,	"	$(+)R_3Si^*OMe$	"	"
8	"	n-BuOH dioxan,	"	$(+)R_3Si^*OBu$	"	"
9	"	cyclohexanol pentan,	"	$(-)R_3Si^*OC_6H_{11}$	"	"
10	"	$PhCH_2OH$ or cyclo-	"	$(+)R_3Si^*OCH_2Ph$	"	"
11	$(+)R_3Si^*NEt_2$	MeOH/cyclohexan hexan	"	$(+)R_3Si^*OMe$	"	"
12	$(+)R_3Si^*NH_2$	"	"	"	"	"

(a) R_3Si^* = α-naphthylphenylmethylsilyl

(b) Pyr = 1-pyrrolidinyl

Table 7. Solvolytic reactions of $(XC_6H_4)R_1R_2Si\text{-}NRR'$.

Series	Substrate			Solvent	Added catalyst	Reaction constant	Ref.
	R_1	R_2	RR'				
1	Me	Me	$-C_4H_4-$	EtOH	H_2SO_4	-0.97	21
2	"	"	"	"	$BuNH_2/BuNH_3Cl$	1.8 (2.6)	"
3	"	"	MePh	"	none (NaAc)	-0.96	23
4	$(XC_6H_4)_2$		HPh	$MeOH/H_2O$	KOH	1.7	5

Table 8. Solvolytic cleavage of Si-N substrates with substituents in the leaving group.

Series	Substrate	Solvent	Added catalyst	Reaction constant	Ref.
1	$XC_6H_4NHSi\text{-}i\text{-}Pr_3$	MeOH	HAc/NaAc	-2.5	9
2	$XC_6H_4NHSiEt_3$	$MeOH/H_2O$	KOH	ca. 1.4	10
3	$XC_6H_4NHSiEt_3$	"	"	1.6	5

Table 9. Steric effects of R in the solvolysis of $R_3SiNR'R''$.

Series	Substrate	Solvent	Added catalyst	Relative rates						Ref.
1	$PhNHSiR_3$	$MeOH/H_2O$	KOH	(R_3=)	Et_3	Et_2Me	Me_2-i-Pr	Me_2-t-Bu	i-Pr_3	5
					1.0	18	8	0.012	0.006	
2	$PhNXSiR_3$	"	"	(X=H,R=)	Me	Et				10
					$2.5\cdot10^4$	1				
3	"	$DMSO/H_2O$	"	(X=Et,R=Me)	(X=Me,R=Et)	(X=H,R=Et)				"
				1	5	50				
4	$PhNXSiR_3$	MeOH	none	$PhNHSiEt_3$ > $PhNEtSiEt_3$ > $PhNHSi$-i-Pr_3						9

Table 10. Activation parameters for Si-N.

Series	Substrate	Solvent	Added catalyst	ΔS^* (calmol^{-1}K^{-1})	ΔH^* (kcalmol^{-1})	Ref.
1	RC_6H_4NHSi-i-Pr_3	MeOH	HAc/NaAc	-54	5	9
2	$PhNHSiEt_3$	$MeOH/H_2O$	KOH	-19	15	10
3	$PhNEtSiEt_3$	$DMSO/H_2O$	"	-23	15	"
4	$(XC_6H_4)Me_2SiNC_4H_4$	EtOH	H_2SO_4	-8	20	21
5	"	"	$BuNH_2/BuNH_3Cl$	-48	8	"
6	$(XC_6H_4)Me_2SiNMePh$	"	NaAc	-63	2	23

Table 11. Solvolytic reactions of $(XC_6H_4)R_1R_2Si\text{-}R$.

Series	Substrate			Solvent	Added catalyst	Reaction constant	Notes	Ref.
	R_1	R_2	R					
1	Me	Me	$-CH_2CH_2$ Cl	$MeOH/H_2O$ $(EtOH/H_2O)$	none	-1.2 (-2.3)	(at higher water conc. in the solv. mixt.)	122
2	"	"	$-CH_2CH_2OH$	$MeOH/H_2O$	H_2SO_4	-1.44 (-1.60)	(at higher temp.)	123
3	"	"	$-CH_2C_6H_4Cl\text{-}p$	"	KOH	1.9		24
4	"	"	C_8H_5O (2-benzofuryl)	$MeOH/H_2O$	"	2.0		"
5	"	"	"	$DMSO/H_2O$	borax	2.1		"
6	$R_1=R_2=XC_6H_4$		$-C{\equiv}CPh$	$MeOH/H_2O$	NaOH	2.2	m-substituents	49

Table 12. Solvolytic cleavage of Si-R substrates containing different R-groups.

Series	Substrate	Solvent	Added catalyst	Reaction constant or relative rates	Ref.
1	$Me_3SiC_6H_4X$	$DMSO/H_2O$	KOH	$\rho = 6.2$ ($\lg k_{rel} = \rho(\sigma + r\Delta^-)$)	8
2	Me_3SiR	$n\text{-}PrOH/H_2O$	NH_3/NH_4Cl	(R=) $CCl_2Me < CHCl_2 < CHBr_2 < CHI_2$	34
3	Me_3SiAr	$DMSO/H_2O$	NaOH	4-TMS-veratrol < 6-TMS-1,4-benzodioxan < 5-TMS-1,3-benzodioxole	16
4	$Me_3SiC_6H_4X$	"	KOH	$\rho = 6.0$	41
5	$Me_3SiCH_2C_6H_4X$	$MeOH/H_2O$	NaOH	$\rho = 4.9$	14
6	Me_3SiAr	$DMSO/H_2O$	KOH	(Ar=) Ph < 1-naphthyl < 2-naphthyl < 9-phenanthryl < 1-pyrenyl	25
7	$R_3SiC{\equiv}CC_6H_4X$	$MeOH/H_2O$	NaOH	$\rho = 1.7$	48
8	R_3SiR	"	"	(R=) benzyl < diphenylmethyl < triphenylmethyl < fluorenyl	15

Table 13. Steric effects of R in the solvolysis of R_3SiR'.

Series	Substrate	Solvent	Added catalyst	Relative rates	Ref.
1	$R_3SiCH_2CH{=}CHPh$	$EtOH/H_2O$	NaOH	$k_{Me}/k_{Et} \simeq 10^3$	101
2	$R_3SiCHPh_2$	$MeOH/H_2O$	"	$k_{Me}/k_{Et} \simeq 440$	15
3	$R_3SiCH(C_6H_4)_2$	"	"	$k_{Me}/k_{Et} \simeq 960$	"
4	$R_3SiC{\equiv}CPh$	"	"	$(R_3{=})$ i-Pr_3 Et_3 $MeEt_2$ Me_2Et Me_3 Ph_3 0.00074 1 7.4 49 277 11.8	49
5	$R_3SiCH_2C_6H_4CO_2$-m^-	"	"	$k_{Me}/k_{Et} \simeq 5$	80

Table 14. Activation parameters for Si-C.

Series	Substrate	Solvent	Added catalyst	ΔS^*	ΔH^*	Ref.
				(calmol^{-1}K^{-1})	(kcalmol^{-1})	
1	$Me_3SiCH_2CH=CHPh$	$DMSO/H_2O$	NaOH	-22	10	100
2	$Me_3SiCH_2CH=CHPh$	i-BuOH/DMSO	NaOBu-i	-23	11	"
3	$Et_3SiCH_2CH=CHPh$	$DMSO/H_2O$	NaOH	-22	13	"
4	$Me_3SiCH_2CH=CHPh$	$EtOH/H_2O$	"	-18	19	101
5	$Me_3SiC_5H_4N$	ROH	"	-(29-42)	13-16	6
6	R_3SiCH_2Ar	$MeOH/H_2O$	KOH	-8	24	24
7	$R_3SiC_8H_5O$	"	"	-8	22-25	"
8	$R_3SiC_8H_5O$	$DMSO/H_2O$	borax	-10	18-20	"
9	$R_3SiCH(C_6H_4)_2$	$MeOH/H_2O$	NaOH	-(12-14)	13-16	15
10	$R_3SiCHHal_2$	$n-PrOH/H_2O$	NH_3/NH_4Cl	-(21-41)	11-13	34
11	Me_3SiAr	$DMSO/H_2O$	KOH	-(2-19)	18-22	25

Table 15. Base catalysed cleavages of Si-C(alkyl) bonds.

Substrate	pK_a (R=H)	rel. rate (R=R_3Si)		Ref.
		(MeOH/H_2O)	(DMSO/H_2O)	
PhC≡CR	21	$2 \cdot 10^7$	-	49
PhCH=CHCH_2R	30	-	10^5	100
PhCH_2R	35	1	1	-
Ph_2CHR	33	$1.4 \cdot 10^3$	-	15
Ph_3CR	31.5	$1.8 \cdot 10^3$	-	"
$(C_6H_4)_2$CHR	22	$1.9 \cdot 10^6$	-	"

Table 16. Rho-values for solvolysis of R_3SiY in protic solvents.

	Y	OAr	OCH_2Ar	NRAr	CH_2Ar
	catalysis				
ρ_Y	acid	-0.5 (Ref. 2)	-1.4 (22)[a]	-2.5 (9)	
	base	1.7 (2)	2.8 (22)[a]	1.6 (5)	4.9 (14)
ρ_{Si}	acid	-0.6 (20)	-0.55 (22)	-1.0 (23)	
	base	0.2 (20)	1.5 (22)	1.7 (5)	1.9 (24)

[a] Transmission factor 0.4 assumed for the methylene group.

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