SOLVOLYSIS REACTIONS

OF

ALKOXY SILICON COMPOUNDS

A Thesis
presented for the degree of
Doctor of Philosophy in the Faculty of Science
of the
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by
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All the experimental work herein described has been carried out by the author in the laboratories of the Department of Chemistry, University of Leicester between October 1958 and the present date.

The work has not been presented, and is not being concurrently presented for any other degree.

October 1961

B. Martini
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SUMMARY

The methods of preparation and the mechanisms of the replacement reactions of triphenylsilyl alkoxides are reviewed, with particular reference to substitution at silicon generally.

A radiochemical technique has been used to make a kinetic study of the solvolysis reactions of triphenylsilyl alkoxides. The compounds were prepared with the alkoxy group labelled with tritium. The rates of replacement of the alkoxy group, and thus the rates of solvolysis, were determined by withdrawing aliquots at intervals from the reaction mixtures, extracting the silicon compounds and measuring the radioactivity with a liquid photostimillation counter.

The hydrolysis of triphenylsilyl methoxides and isopropoxides in acetone/water and the methanolysis of the methoxides, a symmetrical exchange reaction, have been studied, with acidic and basic catalysts and in the absence of catalyst. Satisfactory results were obtained except in two cases, the base catalysed hydrolysis of the methoxides and the acid catalysed methanolysis of triphenylsilyl methoxide, which were greatly affected by impurities.
The results show that in the absence of a catalyst the compounds undergo solvolysis only very slowly, but there is a rapid reaction in the presence of very small quantities of acid or base. In general, acid is a more effective catalyst than base.

The relative rates of reaction of the trisubstituted triphenylsilyl alkoxides do not satisfy the Hammett relationship, but the results show there is a tendency for the electron supplying substituents to retard the reaction in all cases. Mechanisms, involving $S_N2$ attack on silicon in the rate determining step are proposed for the reactions.
INTRODUCTION

I Silicon Alkoxides

(i) Preparative Methods

A wide variety of preparative methods are known for silicon alkoxides, generally involving the corresponding alcohol and a compound with a silicon functional group. These methods have recently been reviewed extensively, so only an outline will be included here of the most common and general methods.

The most common method of preparation is from the reaction of the readily available chlorides with alcohols:

$$R_3SiCl + R'OH = R_3SiOR' + HCl.$$  

This equilibrium may be displaced to the right by removal of the hydrogen chloride, by boiling for example, or adding a base such as pyridine or ammonia. This method is improved by using an alkali metal alkoxide as the reacting species, either as a solution in the parent alcohol or as a slurry in an inert solvent such as toluene or ether.

The silicon chlorides however are very susceptible to hydrolysis. This makes them very difficult to obtain pure, and great care and precautions are
essential in their use. Because of this alkoxides prepared from chlorides are often quite impure initially, containing silanols and siloxanes particularly.

Preparations of silicon alkoxides using the corresponding fluorides or silazanes as intermediates are good laboratory methods. These compounds are relatively stable and may be obtained quite pure by the usual techniques.

Silicon fluorides react rapidly with an equivalent amount of sodium alkoxide in the parent alcohol to give the silicon alkoxide in good yield:

$$R_3SiF + NaOR' = R_3SiOR' + NaF.$$  

Silazanes are readily prepared by passing ammonia into the corresponding silicon chloride:

$$2R_3SiCl + 3NH_3 \rightarrow (R_3Si)_2NH + 2NH_4Cl.$$  

The silazanes may then be used to prepare the alkoxides in good yield by refluxing with alcohol in the presence of acid:

$$\{R_3Si\}_2NH + 2R'OH + H^+ = 2R_3SiOOR' + NH_4^+.$$  

Another convenient method of preparation involves replacement of alkoxy groups by a hydrocarbon residue. By using the appropriate organometallic reagent and reaction conditions the desired number of alkoxy groups may be left attached to silicon. For example:
$\text{C}_6\text{H}_5\text{Cl} + \text{Mg} + (\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2 \underset{\text{reflux}}{\rightarrow} (\text{CH}_3)_2\text{C}_6\text{H}_5\text{SiOC}_2\text{H}_5 + \text{MgClOC}_2\text{H}_5.$

Silicon alkoxides may also be prepared from the corresponding hydrides and an alcohol, using a base catalyst. The silane may be reacted with alcohol and piperidine, or with alcohol containing dissolved sodium:

$$\text{R}_3\text{SiH} + \text{R'}\text{OH} \underset{\text{OR'}}{\rightarrow} \text{R}_3\text{SiOR'} + \text{H}_2.$$

Other methods include equilibration of silanols and siloxanes with alcohols containing acid or base catalysts; and the addition of ketones to silanes under the influence of ultra-violet light.

(ii) Mechanisms of Reaction.

Replacement of an alkoxy group attached to silicon involves fission of the silicon-oxygen bond, the carbon-oxygen bond remaining intact. This was demonstrated by a study of the products of the hydrolysis of ethyl orthosilicate with $\text{H}_2\text{O}.$ Furthermore, a silicon alkoxide which was asymmetric at the carbon attached to oxygen, dimethyldi-d-2-butoxysilane was prepared from dimethyldichlorosilane and optically active d-2-butanol. When the dibutoxide was hydrolysed with very dilute acid, d-2-butanol was produced which had a specific rotation
similar to that of the starting material.

\[
(\text{CH}_3)_2\text{SiCl}_2 + 3\text{C}_4\text{H}_9\text{OH} = (\text{CH}_3)_2\text{Si(OC}_4\text{H}_9)_2 + 2\text{HCl}
\]

\(\left[\alpha\right]_D^{20} + 11^\circ\)

\[
(\text{CH}_3)_2\text{Si(OC}_4\text{H}_9)_2 + 2\text{H}_2\text{O} \xrightarrow{\text{H}^+} (\text{CH}_3)_2\text{Si(OH)}_2 + 2\text{C}_4\text{H}_9\text{OH}
\]

\(\left[\alpha\right]_D^{20} + 12^\circ\)

This implies that the carbon-oxygen bond had been preserved throughout so that the replacement involved silicon-oxygen fission.

During a study of the condensation of trimethylsilanol in methanol with acid and base catalysts^1^2

\[2(\text{CH}_3)_3\text{SiOH} \xrightarrow{\text{catalyst}} (\text{CH}_3)_3\text{SiOSi(CH}_3)_3 + \text{H}_2\text{O}\]

the rate determining step of the reaction was found to be:

\[(\text{CH}_3)_3\text{SiOCH}_3 + (\text{CH}_3)_3\text{SiOH} \xrightarrow{\text{catalyst}} (\text{CH}_3)_3\text{SiOSi(CH}_3)_3\]

\[+ \text{CH}_3\text{OH}\]

The rate of reaction being studied was that of the substitution of an alkoxy group attached to silicon by a trimethylsiloxy group. The trimethylsilyl methoxide had been formed in a preliminary fast equilibrium:

\[(\text{CH}_3)_3\text{SiOH} + \text{CH}_3\text{OH} \xrightarrow{\text{catalyst}} (\text{CH}_3)_3\text{SiOCH}_3 + \text{H}_2\text{O}\]

The mechanism of the reaction was deduced consid-
ering analogous replacements at carbon. The acid catalysed reaction was thought to involve protonation of the alkoxyl oxygen in a fast equilibrium step, followed by attack of the trimethylsilanol on silicon in the rate determining step:

\[
\text{(CH}_3\text{)}_3\text{SiO}^+ + \text{H}_2\text{SiOCH}_3 \rightarrow (\text{CH}_3\text{)}_3\text{SiOSi(CH}_3\text{)}_3 + \text{CH}_3\text{OH}^+
\]

General base catalysis had been observed for the base catalysed condensation. This suggested that the attacking species was the silanolate ion, produced previously in a fast equilibrium step.

\[
(\text{CH}_3\text{)}_3\text{SiO}^- + \text{H}_2\text{SiOCH}_3 \rightarrow (\text{CH}_3\text{)}_3\text{SiOSi(CH}_3\text{)}_3 + \text{CH}_3\text{OH}^-
\]

Similar conclusions had in fact been published much earlier\textsuperscript{13} from a kinetic study of the hydrolysis of ethyl orthosilicate. Aqueous ethanol had been used as the reaction medium, and the rate was followed by measuring changes in the water content of the mixture by Karl Fischer titration.

\[
\begin{align*}
(a) & \quad \text{Si(OC}_2\text{H}_5\text{)}_4 + 4\text{H}_2\text{O} \overset{\text{H}^+}{\rightarrow} \text{Si(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH} \\
(b) & \quad n\text{Si(OH)}_4 \rightarrow n\text{SiO}_2 + 2n\text{H}_2\text{O}
\end{align*}
\]

However the authors neglected to account for the reaction of the silanol with Karl Fischer reagent, so that the results do require reinterpretation.\textsuperscript{12} However
the dehydration step (b) is very fast, so that the concentration of Si(OH)₄ in the mixture is never very high. This suggests that the errors may be quite small and their conclusions qualitatively correct.

These preliminary studies have already established that nucleophilic attack on silicon is involved in the replacement of an alkoxy group attached to silicon. This was in fact a necessary conclusion from the observation that the reaction involved silicon-oxygen fission. The reactions have also been shown to be second order substitution and to be strongly catalysed by acid or alkali, the rates of reaction in neutral solution being very low.

Akerman" examined the hydrolysis of various trialkylsilyl phenoxides in aqueous ethanol at 25°C, the reaction being followed by the change in ultraviolet absorption. The rate of reaction in all cases was found to be first order in silicon compound and in acid or base catalyst.

\[ R_3SiOC_6H_5 + H_2O \xrightarrow{H^+} R_3SiOH + C_6H_5OH \]

Again the rate is exceedingly low in neutral solution, the first order rate constant of the hydrolysis of trimethylsilyl phenoxide being approximately \(10^{-5}\) seconds⁻¹ at the neutral point of a sodium
phosphate buffer solution.

For base catalysed hydrolysis, electron releasing substituents on the phenoxy group strongly inhibited the reaction ($\xi = 1.74$). This indicates that at the transition state of the rate determining step the reaction centre is more negative than in the ground state. Since the reaction is first order in silicon phenoxide and base, and silicon-oxygen fission can be assumed to be occurring, this reaffirms that nucleophilic attack by base on silicon is the rate determining step. This is in accordance with the proposed $S_{N}2$ mechanism:

$$\text{RO}^- + \text{Et}_3\text{SiOPh} \rightarrow \text{RO}^-\cdot\text{Et}_3\text{Si}^\cdot\text{Ph} \rightarrow \text{ROSiEt}_3 + \text{OPh}^-$$

The acid catalysed hydrolysis is also facilitated by electron supply to the reaction centre, but the effect of any substituent is much smaller ($\xi = -0.53$) than in the base catalysed reaction. The mechanism proposed for this reaction involves a fast proton transfer to oxygen followed by a slow nucleophilic attack on silicon;

$$\begin{align*}
(a) & \quad \text{ROH}^+ + \text{Et}_3\text{SiOPh} \rightarrow \text{ROH} + \text{Et}_3\text{Si}^\text{Ph}^+ \\
(b) & \quad \text{Et}_3\text{Si}^\text{Ph}^+ + \text{ROH} \rightarrow \text{Et}_3\text{Si}^\text{OR} + \text{PhOH} \\
(c) & \quad \text{Et}_3\text{Si}^\text{OR} + \text{ROH} \rightarrow \text{Et}_3\text{SiOR} + \text{ROH}^+
\end{align*}$$

but it is pointed out that the observed substituent
effect also supports a mechanism in which step (a) is rate determining and step (b) is fast.

It was also shown that there is considerable steric resistance to replacement of phenoxy groups at silicon. With trialkylsilyl phenoxides the rates of acid and base catalysed hydrolysis show a marked reduction as the size of the alkyl groups increase (Table 1). This is due in part to the polar effect of alkyl groups, which show an increasing +I effect with increase in size, thus inhibiting nucleophilic attack on silicon by increasing the electron density on silicon. But the steric effect of the groups may be illustrated by referring to the compounds triethylsilyl phenoxide and dimethyl-"butylsilyl phenoxide. These compounds are isomeric, and because they possess equal numbers of alpha and beta carbons, their inductive effects are similar. But for acid catalysed hydrolysis the ratio of their rates is 219:000591.

Table 1. Rate Constants of the Acid ($k_a$) and Base ($k_b$) Catalysed Hydrolysis of $R_3SiOCeHs$.

<table>
<thead>
<tr>
<th>R₃</th>
<th>Me₃</th>
<th>Et₃</th>
<th>Pr₃</th>
<th>Bu₃</th>
<th>Am₃</th>
<th>Me₂t-Bu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_a$(moles⁻¹·secs⁻¹)</td>
<td>10.4</td>
<td>219</td>
<td>115</td>
<td>081</td>
<td>060</td>
<td>000591</td>
</tr>
<tr>
<td>$k_b$(moles⁻¹·secs⁻¹)</td>
<td>ca.330</td>
<td>2.05</td>
<td>.66</td>
<td>.41</td>
<td>.30</td>
<td>.0172</td>
</tr>
</tbody>
</table>
and 2.05:0172 for base catalysis. The low rate of
the t-butyl compound may be attributed almost entirely
to steric resistance to the attack of the nucleophile.

There appears to have been no comparison of the
rates of hydrolysis of a series such as $R_3SiOR^'$,
where OR' is MeO, EtO, PrO, PrO etc., which would
provide steric resistance from the alkoxy group. But
a qualitative study indicated that the relative
reactivities of alkoxy groups to methylmagnesium
chloride decreases in the following order: $^8$ EtO > PrO >
BuO > BuO > PrO > BuO > t-BuO. This effect may be
attributed mainly to steric hindrance to attack on
silicon, but it is perhaps due in part to increasing
electron supply to silicon through the above series.

Work to date on the hydrolysis of alkoxides and
phenoxides gives a great deal of information on the
mechanism of the replacement of the ether linkage to
silicon.

The reaction involves a second order nucleophilic
attack on silicon in both the acid and base catalysed
reactions. The uncatalysed reactions are very slow,
indicating that attack by such poor nucleophiles as
$H_2O$, $C_2H_5OH$ or $(CH_3)_3SiOH$ on silicon is an energetically
unfavourable process. But in the presence of
base, powerful nucleophiles are formed which react readily. The presence of acids in the reaction mixture facilitates the reaction by forming the conjugate acids of the alkoxides in an equilibrium reaction:

$$R_3SiOR' + H^+ \rightarrow R_3SiOH'$$

The increase in electronegativity of the oxygen atom in passing from Si-OR' to Si-OH' must reduce the electron density on silicon considerably, for it is then susceptible to attack by such reagents as H$_2$O and (CH$_3$)$_3$SiOH.

Substituents have been shown to have a large effect on the rate of reaction, by both polar and steric contributions.

It is interesting to examine the mechanisms of reaction of other silicon functional compounds, particularly the halides and hydrides whose mechanisms are well established, and to compare them with silicon alkoxides. Their mechanism of replacement will be seen to be related but modified by the functional group.

The hydrolysis of triphenylsilyl fluoride in 50% aqueous acetone was found to be of moderate rate in neutral solution and uncatalysed by acid; but strong
catalysis by hydroxide ions was observed. In neutral solution the reaction showed first order kinetics in silicon compound, and the rate was depressed by electron releasing substituents on the three phenyl groups.

The mechanism deduced involved $S_{N}2$ attack by water upon silicon:

$$\text{H}_2\text{O} + \text{Ph}_3\text{SiF} \xrightleftharpoons{\text{fast}} \text{H}_2\text{O} + \text{Ph}^+\text{Si}^{-}\text{Ph} \rightarrow \text{H}_2\text{O} - \text{SiPh}_3 + \text{F}^-$$

A pentacovalent silicon intermediate was proposed.

Silicon chlorides in neutral solution are much more reactive than the fluorides, and it was only by the use of sterically hindered compounds that a reaction could be found sufficiently slow for kinetic studies. The rates of hydrolysis, alcoholysis, and chloride exchange of compounds of the type $\text{R}_3\text{SiCl}$, where $\text{R}=1$-napthyl, cyclohexyl, isopropyl, and phenyl, have been measured in various solvents at 25.1. The reactions are first order in silicon compound and only slight catalysis by acid was observed.

A second order nucleophilic attack on silicon was proposed for the mechanism of the reaction:

$$\text{B}^+\text{HOR}^+ + \text{R}_3\text{SiCl} \rightarrow \left[\text{B}^+\text{H}^+\cdots\text{R}^+\cdots\text{Si}^+\cdots\text{Cl}^-\right] + \text{R}^+\text{OSiR}_3 + \text{HB}^+ + \text{Cl}^-$$

transition state.
where B is a Lewis base which must be present to remove the proton. In hydroxylic media such as isopropyl alcohol the base may be a solvent molecule, but in inert solvents such as dioxan and methylethyl ketone it may be chloride ion or nucleophilic reagent (this produces respectively autocatalysis or an order greater than one in nucleophilic reagent).

The solvolysis of silanes is more complex, but is now well understood. The base catalysed reaction has been studied in aqueous piperidine and aqueous ethanol, being followed by the rate of hydrogen evolution.

\[
R_3SiH + H_2O \rightarrow R_3SiOH + H_2. 
\]

The reaction was found to be first order in silane and base, and is retarded by electron release to silicon. A study of isotopic substitution of hydrogen in the silane and the solvent revealed that both the silicon-hydrogen and the solvent-hydrogen bonds were broken in the rate determining step. On the basis of these observations the mechanism, involving a termolecular collision was proposed to be:

\[
\text{OH}^- + R_3SiH + HS \rightarrow \left[ \text{OH} \right] \rightarrow R_3SiOH + H_2 + S^- \\
(\text{HS} = \text{solvent})
\]

By similar methods the mechanism of acid catalysed
hydrolysis in 95% aqueous ethanol containing hydrochloric acid at 34.9°C has been deduced to be:

\[ \text{H}_2\text{O} + \text{R}_3\text{SiH} + \text{HOH}_2 \rightarrow \text{R}_3\text{Si}\cdot\cdot\cdot\text{H}\cdot\cdot\cdot\text{OH}_2 \rightarrow \text{R}_3\text{SiOH}_2 + \text{H}_2 + \text{H}_2\text{O} \]

The necessity of a termolecular collision has been avoided by Eaborn's postulate (ref. 1, p.205) that preliminary fast reversible association of silane and a protonic species may take place to give intermediates in which the hydrogen-hydrogen bond is already partially formed; respectively:

\[ \text{R}_3\text{Si-H}\cdot\cdot\cdot\text{H-S} \text{ and R}_3\text{Si-H}\cdot\cdot\cdot\text{H-OH}_2. \]

The reaction would then be two successive bimolecular reactions, the second being rate determining.

The reactions of halides and hydrides are subject to considerable influence by substituents as are those of alkoxides. Electron supplying substituents have been shown to reduce the rate of hydrolysis of fluorides\(^1\) and hydrides\(^2\,\,3\) so that an increase of electron density on the silicon strongly retards these reactions.

Steric retardation of the reaction of chlorides has been demonstrated\(^4\) by the reaction of tri-isopropylsilyl chloride with alcohols at 0°C. The relative rates are Pr\(^1\)OH 1: EtOH 10\(^3\): MeOH 10\(^4\), and it has
been indicated the rate of reaction of water is very much greater than that of methanol. This effect must be entirely steric in origin, because decreasing reactivity of the alcohol parallels increasing nucleophilicity.

Even the replacement of the small hydrogen atom of silanes has been shown to be retarded by large substituents on the silicon. The rate constants of the hydrolysis of trialkylsilanes in 93.7% aqueous ethanol at 23°C are given in table 2.

Table 2. First Order Rate Constants (sec⁻¹) of the Hydrolysis of Trialkylsilanes in •2N Potassium Hydroxide Solution.

<table>
<thead>
<tr>
<th>Alkyl</th>
<th>Et</th>
<th>Pr</th>
<th>Am</th>
<th>Bu</th>
<th>Bu²</th>
<th>Bu¹</th>
<th>Pr¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁵x k</td>
<td>11.7</td>
<td>4.64</td>
<td>3.15</td>
<td>3.11</td>
<td>0.509</td>
<td>0.426</td>
<td>0.375</td>
</tr>
</tbody>
</table>

The mechanisms of replacement of hydrides and halides are therefore analogous to those of alkoxides, only slight modifications being caused by the leaving groups.

The reactions for example are all of an order of two or more, indeed first order reactions of an organosilicon compound have never been observed and
cations of the type $R_3Si^+$ are quite unknown in solution.

All the reactions which have been discussed above involve nucleophilic attack on silicon, and this is probably true of all replacement reactions at silicon which involve heterolysis of the breaking bond. In many cases the nucleophilic attack on silicon provides the "driving force" of the reaction, the bond to silicon being formed to a greater extent than the bond to the leaving group is broken. Because strong bases, such as hydroxide and alkoxide ions, are good nucleophiles, base catalysis is observed for most replacement reactions at silicon. Only a few reactions, such as the cleavage of some silicon-carbon bonds, are not base catalysed.

By contrast, acid catalysis is much less common, being restricted largely to the reactions of groups which protonate readily at the atom bonded to silicon. These include alkoxydes, silanols and siloxanes, silylamines and silazanes, hydrides and aryl groups.

II Substitution at Silicon.

The possibility of the formation of a pentacovalent silicon intermediate in the replacement reactions
of organosilicon compounds has been the subject of considerable conjecture. An intermediate was postulated in the neutral hydrolysis of silicon fluorides, but it has been pointed out (ref. 1, p. 111) that the only evidence for its existence is that electron supply to silicon retards the reaction. This is equally consistent with a synchronous process involving no intermediate (cf. p. 14 above):

\[
\text{H}_2\text{O} + \text{Ph}_3\text{SiF} \rightarrow [\text{H}_2\text{O} \cdot \cdot \cdot \text{Si} \cdot \cdot \cdot \text{F}] + \text{H}_2\text{O} \cdot \text{SiPh}_3 + \text{F}^-
\]

transition state

Conversely, the solvolysis of silicon chlorides was stated to be a synchronous process which involved no intermediate (p. 14 above). But the evidence supports equally well a mechanism involving an intermediate (ref. 1, p. 181) provided there is only a small energy difference in the two transition states involved.

A pentacovalent silicon intermediate is generally assumed to be formed in a reaction because other silicon compounds are known to complex quite readily by expanding the octet of electrons. However, the large number of known stable or semi-stable complexes in which silicon has a valency of more than four is almost entirely restricted to inorganic compounds in
which the groups attached to silicon are very elec-
tronegative and sterically small. If an organic group
is attached to it, silicon does not readily form a
complex of this type; in fact the only known examples
are chelates of the type \( \text{RSi(Acetylacetonyl)}_2\text{Cl} \) where
\( R \) is methyl or
phenyl.\(^5\) These have
an octahedral struc-
ture (Fig. 1).

If a second
hydrocarbon residue
is introduced to
replace the electro-
negative chlorine, the acetylacetonates cease to
chelate, reverting to the open chain structures
\( \text{R}_2\text{Si(OCCH}_3\text{:CHCOCH}_3\text{)}_2 \), and the silicon reverts to a
valency of four. Consequently hexacovalent and penta-
covalent silicon complexes are quite unknown if more
than one organic group is attached to the silicon.

Further evidence suggesting that a pentacovalent
silicon complex is at least not readily formed is
supplied by a study of the rate of chlorine exchange
of triorganosilyl chlorides\(^9\) in dioxan/nitromethane
at 25.1°.
\[ \text{R}_3\text{SiCl} + (\text{C}_2\text{H}_5)_4\text{N}^{36}\text{Cl} = \text{R}_3\text{Si}^{36}\text{Cl} + (\text{C}_2\text{H}_5)_4\text{NCl} \]

In this reaction the activation energy of the formation of the hypothetical pentacovalent silicon intermediate would be the same as the activation energy of the complete exchange reaction. Therefore if the intermediate forms in a kinetically fast step, as is generally assumed, the reaction should be very fast; but it is measurably slow.

From this evidence it appears that formation of a pentacovalent silicon intermediate during a reaction is not at least a kinetically fast equilibrium step preceding reaction. But this does not preclude the possibility that a high energy intermediate is formed, nucleophilic attack and repulsion of the leaving group being two separate processes (Fig. 2, path T'T''), rather than a continuous whole (path T).

But in the two cases the transition states T, T' and T'' and the intermediate I are not very far removed along
the reaction coordinate, so that their differences in structure will be quite small. Therefore any external influence which may affect the free energy of intermediate I and thus influence the rate of reaction would influence transition state T in an almost identical manner. Consequently the difference in mechanism which the two reaction paths represent is only of minor significance.

Even if the availability of d-orbitals in silicon does not allow for the rapid formation of a complex with the attacking reagent, it certainly facilitates the reaction by allowing hybrid bonds to form in the activated complex which contain 3d components. Indeed the greater reactivity of all silicon compounds to nucleophilic attack compared with their carbon analogues may be attributed to a large extent to the ready availability of 3d orbitals in silicon.

The use of 3d orbitals during the process of reaction of organosilicon compounds has a profound effect on the structure of the activated complex.

As carbon compounds react, for example by an SN2 process, the activated complex of the reaction consists of three planer 2sp2 bonds to the substituents R, and two nucleophiles N sharing a 2p orbital
This implies that the C-N bonds are quite weak, and correspondingly long, and necessarily diametrically opposed about the central carbon.

In a replacement reaction at silicon however, 3d orbitals are readily available for hybridisation; so the high energy complex formed during a reaction may assume the lower energy hybridisation of 3sp³d for example which has a particularly favourable geometry. If this hybridisation does in fact occur, and it is probable that it makes a considerable contribution, the mechanism of substitution at silicon is slightly different to that at carbon. The Si-N bonds (Fig. 4) are of almost unit order and consist of completely independent orbitals; consequently these bonds are shorter and stronger than their analogues in carbon chemistry.

From this it is reasonable to propose that the stabilisation of the complex thus achieved is more in keeping with a complex existing in a...
potential energy trough than on a ridge i.e. the replacement involves an intermediate (Fig. 2, path \( T'IT'' \)) rather than a single transition state (path \( T \)).

The reduced length of the Si-N bonds in the transition state should make the reaction more susceptible to steric retardation to attack. This has often been observed in practice (see above) in the reactions of silicon alkoxides, chlorides, and hydrides.

Since the Si-N bonds are no longer parts of one orbital but independant, there is no longer any quantum mechanical reason that the bonds should be diametrically opposed about the central atom. If the triagonal bipyramidal structure proposed above is in fact true, N-Si-N bond angles of 90° and 120° are equally possible (Fig. 4, interchange R and N). And only if attack is "backside" to the leaving group does the familiar Walden inversion take place, attack at an angle of 90° or 120° ("flank" attack) leading to retention of the configuration of the molecule.

The ease of flank attack at silicon has often been demonstrated. Bridgehead silicon compounds, for which backside attack is impossible, react at least as readily as a corresponding unhindered compound. The second order rate constants \( k_2 \) of the alkaline hyd-
Rolysis of the following silanes in 95% aqueous ethanal at 35° are: 

\[(C_2H_5)_3SiH, 1: \text{HC}_{2}CH_3CH_2SiH, 10: \text{HC}_{2}CH_2SiH, 1000.\]

Attempts to determine the stereochemistry of some substitution reactions at silicon have been made by Sommer and coworkers who studied various reactions of asymmetric methyl-1-napthylphenylsilyl compounds. The absolute configurations of compounds were compared by Fredga's method, which involves determination of differences in phase behaviour of mixtures of different isomorphous compounds. They concluded that some silicon compounds react by inversion and some by retention, the criterion appearing to be the nature of the leaving group. Leaving groups such as -Cl and -OCOC_6H_5 whose conjugate acids have a pK_a less than 5 tend to react by inversion of configuration. Leaving groups whose conjugate acids have a pK_a greater than 10, -H, -OCH_3 and -OH for example, may react by inversion or retention in different circumstances. For example, (+)methyl-1-napthylphenylsilyl chloride reacts with water/ether, lithium aluminium hydride/ether, methanol/pentane/amine, solid potassium hydroxide/xylene and sodium tetrathoxborate/ether
to give the appropriate product with inversion of configuration. Methyl-1-naphthylphenylsilyl methoxide is hydrolysed in alkaline aqueous acetone with inversion, but is reduced to the silane by both lithium aluminium hydride in ether and t-butylmagnesium chloride with retention. It also racemised rapidly with $10^{-3}$ M sodium methoxide in methanol, showing that the reaction involved at least part inversion of configuration.

Experimental work shows that silicon compounds can react quite readily by flank attack, implying that 3d orbitals play a large part in the hybridisation of activated complex. But it is perhaps surprising that such a large number of reactions take place by inversion of configuration if 3sp$^3$d hybridisation is the true bonding of silicon at the transition state.

From purely statistical considerations, all directions of attack being equally probable one would expect predominant retention, with some racemisation.

The cause of predominant inversion could be the partial charges which reside on the attacking and leaving groups at the transition state. Negative charges are particularly pronounced on these groups when the atom adjacent to silicon is very electroneg-
ative, or the conjugate acid of the group is a strong one. It would be expected that mutual repulsion of these charges would cause the transition state to be of lowest energy when the making and breaking bonds are diametrically opposite about silicon, rather than at 90° or 120° to each other. Substitution would then be by inversion of configuration.

But the steric properties of the substituents may have some influence on the course of the reaction. The reactions of organosilicon compounds are very susceptible to steric hindrance by the groups attached to silicon, due perhaps to the short 3sp^3d hybrid bonds from the silicon to the five substituents in the transition state. If this is the case it can be seen that compressional B-strain in the transition state will be at a minimum if the three bulkiest groups are disposed mutually at 120° about the silicon. The activation energy of the reaction would then be lowest for a particular direction of attack on silicon, and inversion or retention of configuration may be favoured. Usually the largest groups in a compound with one silicon functional group are the three hydrocarbon residues. A compound of this type would then tend to react with inversion.
The precise mechanism of substitution at silicon, particularly from the stereochemical point of view, is not fully understood. The proportions of inversion and retention of configuration, and hence of backside and flank attack, in a simple replacement reaction have not been measured. In particular, nothing is known of the independent effects of the nature of the nucleophile, leaving group, and the other three substituents on the course of the reaction.
I Measurement of the Rates of Reaction.

The acid and base catalysed solvolysis reactions of triphenylsilyl alkoxides and some trisubstituted triphenylsilyl alkoxides have been studied at 25°. The particular solvolyses concerned were the hydrolyses of methoxides and isopropoxides in acetone/water solvent, and the methanolysis of methoxides, a symmetrical methoxyl exchange reaction.

The rates of reaction have been measured by a radiochemical technique, the triarylsilyl alkoxides being prepared with the alkoxy group labelled with tritium. This is conveniently done by preparing carbon-labelled methyl and isopropyl alcohols from the commercially available tritiated water, and preparing the labelled alkoxides from the corresponding fluorides and the radioactive alcohol. Fluorides were chosen as the intermediates because of the simple preparation of the triarylsilyl fluorides and their relatively high stability to hydrolysis, as discussed above (p. 5), makes them obtainable in a high state of purity.

The solvolysis reaction may then be represented
as follows:

\[ \text{Ar}_3\text{SiOR}^* + \text{ROH} = \text{Ar}_3\text{SiOR} + \text{R}^*\text{OH}. \]

where \( \text{OR}^* \) is a tritium labelled methoxy or isopropoxy group, and \( \text{ROH} \) is methanol or water.

The extent of the reaction at any given time was then determined by taking an aliquot from the reaction mixture and extracting the silicon compounds into toluene solution. A measure of the radioactivity of this solution, obtained by liquid photo-scintillation counting by the technique developed by Eaborn, Matsu- kawa and Taylor, then gave the proportion of unreacted triarylsilyl alkoxide in the reaction mixture. This method is an accurate way of measuring the rate of this type of reaction. There is a large change in the quantity being measured as the reaction progresses, and the magnitude of the radioactivity can be measured at all times to an accuracy of about \( \pm 5\% \).

Even for the hydrolysis reaction the radiochemical method of rate measurement is at least as good as any of the alternatives. Karl Fischer titration has been used to measure the rates of hydrolysis of alkoxides by measuring the rate of removal of water:

\[ \text{Ar}_3\text{SiOR} + \text{H}_2\text{O} = \text{Ar}_3\text{SiOH} + \text{ROH} \]

But this is not accurate if a large excess of water is
present in the reaction mixture, as its change in concentration is then quite small. Furthermore, the Karl Fischer reagent displaces the equilibrium of the above reaction to the left by removing water, so that the reaction mixture could not be titrated directly.

The hydrolysis reaction could also be followed in principle by the change in ultra-violet absorption of the reaction mixture, the method used by Akerman for measuring the rates of hydrolysis of phenoxides.\textsuperscript{14,15}

For the symmetrical exchange reaction of methoxides however, the rates of reaction can only be measured by a radiochemical method.

II Base Catalysed Hydrolysis of Triphenylsilyl Methoxide.

In 10\% water: 90\% acetone containing dissolved sodium hydroxide the rate of hydrolysis of triphenylsilyl methoxide at 25\(^\circ\) was found to be very low even when the solution was saturated with sodium hydroxide; for example, a mixture containing 10\(^{-3}\) moles/litre and having a cloudy appearance due to undissolved sodium hydroxide underwent only about 1\% hydrolysis in 6 hours. However, in 20\% water: 80\% acetone at 25\(^\circ\), the reaction proceeded quite readily
Pig. 5. Run 4, The Hydrolysis of Triphenylsilyl Methoxide with 1·32x10⁻⁴ M. Sodium Hydroxide.

\[
(C_6H_5)_3SiOCH_3 + H_2O \xrightarrow{\text{OH}^-} (C_6H_5)_3SiOH + CH_3OH
\]

in the presence of 10⁻⁴ M. sodium hydroxide:

The product of the reaction was identified by melting point as triphenylsilanol, negligible condensation to hexaphenyldisiloxane having taken place, probably because of the low concentration (~2 gms/litre) of silicon compound.

The apparent order of the reaction in triphenylsilyl methoxide is greater than one. A typical plot
of log D* versus time (mins.), which would be linear for a first order reaction, is shown in fig. 5; and table 3 gives the apparent reductions of first order rate constants throughout the runs. It can be seen

Table 3. The Change in First Order Rate Constant during the Sodium Hydroxide Catalysed Hydrolysis of Triphenylsilyl Methoxide.

\[ k_f = \frac{1}{T} \log \frac{D_0}{D_f}, \Delta k_f\% = \frac{\text{Initial } k_i - k_i}{\text{Initial } k_i} \times 100. \]

<table>
<thead>
<tr>
<th>Run 3</th>
<th>Initial ( k_i ) = 3.57 x 10^{-2} \text{ mins}^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (mins.)</td>
<td>30</td>
</tr>
<tr>
<td>( 10^2 x k_i )</td>
<td>3.02</td>
</tr>
<tr>
<td>( \Delta k_i% )</td>
<td>15.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 4</th>
<th>Initial ( k_i ) = 1.63 x 10^{-2} \text{ mins}^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (mins.)</td>
<td>30</td>
</tr>
<tr>
<td>( 10^2 x k_i )</td>
<td>1.36</td>
</tr>
<tr>
<td>( \Delta k_i% )</td>
<td>16.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 5</th>
<th>Initial ( k_i ) = 1.475 x 10^{-2} \text{ mins}^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (mins.)</td>
<td>30</td>
</tr>
<tr>
<td>( 10^2 x k_i )</td>
<td>1.34</td>
</tr>
<tr>
<td>( \Delta k_i% )</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Footnote* D is the deflection in centimetres of the spot of light on a galvanometer scale. It is proportional to the concentration of unreacted triphenylsilyl methoxide in the reaction mixture at a given time (see Experimental section).
<table>
<thead>
<tr>
<th>Run</th>
<th>Initial $k_i = 1 \cdot 40 \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$ (mins.)</td>
</tr>
<tr>
<td></td>
<td>$10^2 x k_i$</td>
</tr>
<tr>
<td></td>
<td>$\Delta k_i$%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Initial $k_i = 1 \cdot 37 \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$ (mins.)</td>
</tr>
<tr>
<td></td>
<td>$10^2 x k_i$</td>
</tr>
<tr>
<td></td>
<td>$\Delta k_i$%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Initial $k_i = 1 \cdot 60 \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$ (mins.)</td>
</tr>
<tr>
<td></td>
<td>$10^2 x k_i$</td>
</tr>
<tr>
<td></td>
<td>$\Delta k_i$%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Initial $k_i = 1 \cdot 18 \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$ (mins.)</td>
</tr>
<tr>
<td></td>
<td>$10^2 x k_i$</td>
</tr>
<tr>
<td></td>
<td>$\Delta k_i$%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Initial $k_i = 630 \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$ (mins.)</td>
</tr>
<tr>
<td></td>
<td>$10^2 x k_i$</td>
</tr>
<tr>
<td></td>
<td>$\Delta k_i$%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Initial $k_i = 376 \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$ (mins.)</td>
</tr>
<tr>
<td></td>
<td>$10^2 x k_i$</td>
</tr>
<tr>
<td></td>
<td>$\Delta k_i$%</td>
</tr>
</tbody>
</table>
from the graph and the table that the apparent reduction in rate with the progress of the reaction is most pronounced, being as great as 66.8% in one case. A cause of this effect is thought to be the triphenylsilanol formed in the reaction removing hydroxide ion; a similar effect to that observed in the alkaline hydrolysis of triorganosilanes:

\[
(C_6H_5)_3SiOH + OH^- \rightarrow (C_6H_5)_3SiO^- + H_2O
\]

Then as the reaction proceeds the concentration of triphenylsilanol increases, and the concentration of hydroxide ion and thence the rate, decreases. Because the concentrations of silanol and hydroxide ion are similar (ca. 10^-4 moles/litre), the concentration of hydroxide ion is reduced appreciably, causing a pronounced effect.

This effect was investigated by adding triphenylsilanol (0.02 gms/200mls.) to a reaction mixture; it caused the initial rate of reaction to be reduced by 16%. From this reduction in rate it can be deduced (see Experimental section) that the added triphenylsilanol (3.62 x 10^-4 M.) produces an apparent reduction of hydroxide ion concentration of only 7.2 x 10^-6 M. of the total 1.32 x 10^-4 M.. The above equilibrium then removes only a small proportion of the sodium.
hydroxide from the reaction mixture, and in fact an approximate value of $1800 \pm 30000$ can be deduced for the equilibrium constant from this data.

After one half-life of a run, when approximately $0.02 \text{ gms/200mls.}$ of triphenylsilanol has been formed from the $0.04 \text{ gms/200mls.}$ of triphenylsilyl methoxide originally added, reductions in rate vary in different runs from 22% to 78% of the initial rate (Table 4).

Table 4. Initial First Order Rate Constants and Actual First Order Rate Constants at the Half-Life.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^3 x$ Initial $k$, $10^2 x$</td>
<td>3.57</td>
<td>1.63</td>
<td>1.475</td>
<td>1.40</td>
<td>1.60</td>
<td>1.18</td>
<td>0.630</td>
</tr>
<tr>
<td>$10^2 x$ actual $k$, at half-life</td>
<td>2.80</td>
<td>0.906</td>
<td>0.968</td>
<td>0.814</td>
<td>1.10</td>
<td>0.722</td>
<td>0.134</td>
</tr>
<tr>
<td>Reduction %</td>
<td>21.6</td>
<td>44.4</td>
<td>34.4</td>
<td>41.9</td>
<td>31.3</td>
<td>38.8</td>
<td>78.8</td>
</tr>
<tr>
<td>$10^3 x [\text{NaOH}]$</td>
<td>1.76</td>
<td>1.32</td>
<td>1.32</td>
<td>1.32</td>
<td>1.03</td>
<td>1.09</td>
<td>0.816</td>
</tr>
</tbody>
</table>

This is a much greater effect than the 16% reduction in rate observed when conditions at the half-life were simulated by adding triphenylsilanol to the reaction mixture. It indicates that, superimposed upon the reduction in rate due to the triphenylsilanol formed in the reaction, there is another effect of
large and randomly variable magnitude causing the reaction to be retarded as it proceeds. This must be attributed to variable contamination of the reaction mixture during a run by acids, with subsequent neutralisation of the sodium hydroxide catalyst. The effect is more pronounced at lower alkali concentrations, as would be expected.

The first order nature of the reaction in triphenylsilyl methoxide was illustrated by increasing the initial concentration of compound from 0.04 gms/200 mls. to 0.06 and 0.08 gms. Only a small change in the initial rate was observed, a reduction from $1.63 \times 10^{-2}$ min$^{-1}$ to $1.475 \times 10^{-2}$ and $1.40 \times 10^{-2}$ in the pseudo-first order rate constant $k_1$. The reduction of $k_1$ with time is therefore not due to an order of reaction greater than one with respect to the methoxide.

It is unlikely that this reduction of 14% in the initial first order rate constant on increasing the concentration of triphenylsilyl methoxide is caused by contamination of the methoxide by triphenylsilanol, since it has been shown above that the addition of 0.02 gms/200 mls. of silanol only reduces the initial rate by 16%. The reduction more likely represents
the limiting accuracy of determining the rate of reaction. This relatively good reproducibility compared with the large variations in the observed rate constants at the half-life for example, show that the initial first order rate constants are subject to considerably less experimental error than rate constants determined during a run. And although the curvature of the log D versus time plots and the rate of reduction of the rate constants may vary considerably, the initial rate constant is a relatively constant quantity. This value of 14% probably gives a good measure of the experimental error in the measurement of the initial first order rate constants. The curvature of the log D versus time plots is quite pronounced, as can be seen from fig. 5, so the error in drawing the curves and measuring the initial slopes is consequently of the order of 5%.

The dependence of the reaction rate on base concentration was examined by measuring the rate at various concentrations of sodium hydroxide. A graph of the initial pseudo-first order rate constant $k_1$, calculated from the slope at $T = 0$ of the log D versus time plots, plotted against sodium hydroxide concentration is given in fig. 6.
The deviations of the points from the line drawn in fig. 6 are equivalent to experimental errors in the rate constants of up to 200%. But if the experimental error in the measurement of the initial first order rate constant is about 14% as derived above, the deviations of points from the line in fig. 6 represent an error in the sodium hydroxide concentration of up to 15%.

These very large errors in the measurement of
these rate constants are undoubtedly due to the great susceptibility of this reaction system to contaminants. This is very well illustrated by the large and variable reductions of the rate constant which are observed throughout a run, a much greater effect than could be explained by triphenylsilanol neutralising the alkali. This effect must be attributed to carbon dioxide and other acidic components of the laboratory atmosphere entering the reaction mixture whilst aliquots were removed. The possible error of 15% in the sodium hydroxide concentration may also be explained in this manner, being caused by contamination during the preparation of the solvent mixture.

To within the limits of experimental error the reaction may be regarded as being first order in triphenylsilyl methoxide. Presumably the reaction is also of first order in sodium hydroxide, the deviation of the line from the origin in fig. 6 being due to a constant loss of $7.6 \times 10^{-5} \text{M}$. in the base concentration. The rate equation may then be expressed as:

$$\text{Rate} = k_1 [\text{Ph}_3\text{SiOMe}] = k_8 [\text{Ph}_3\text{SiOMe}] [\text{OH}^-]$$

where $k_1$ is the pseudo-first order rate constant, calculated from the initial slope of the log D versus time plots; and $k_8$ is the specific rate constant for
base catalysed hydrolysis. An approximate value of 360 litres. moles-'min.' may be assigned to $k_a$ from the slope of the line in fig. 6.

Because of the very great experimental errors in the measurement of the rates of base catalysed hydrolysis of triphenylsilyl methoxide, no further work was done with this system. The rate constants of the tri-substituted compounds were not measured, because the more reactive substituted compounds particularly would be subject to an even larger experimental error.

Instead, a system was sought in which the rate of hydrolysis could be measured more accurately. Triphenylsilyl isopropoxides were chosen because their reduced reactivity would enable a larger concentration of base catalyst to be used in the reaction mixture. This should then reduce the relative effect of contaminants and triphenylsilanol on the base concentration and permit a more accurate evaluation of the rate constants.

III Base Catalysed Hydrolysis of Triarylsilyl Isopropoxides.

The hydrolysis of triarylsilyl isopropoxides was examined in 20% water: 80% acetone solvent at 25°C.
with sodium hydroxide catalyst. The product of the reaction of triphenylsilyl isopropoxide was identified as triphenylsilanol by melting point, no condensation to hexaphenyldisiloxane having taken place even at these higher alkali concentrations. The triphenylsilanol extracted from the reaction mixture was not pure however, its melting point being depressed to 149°-151° (literature value 155°). The impurity was not hexaphenyldisiloxane however, which does not depress the melting point. It was thought that it may be diacetone alcohol, a condensation product of the acetone solvent, or even some higher polymer:

\[
2\text{CH}_3\text{COCH}_3 + \text{OH}^- \rightarrow \text{CH}_3\text{COCH}_2(\text{CH}_3)_2\text{COH}
\]

A marked deterioration of the reaction mixture had been observed when solutions containing higher concentrations of sodium hydroxide had been stored. These solutions, used for the hydrolysis of some of the less reactive trisubstituted compounds, appeared slightly yellow after 36 hours; an effect which may also perhaps be attributed to the condensation of the acetone.

The apparent order of reaction in triphenylsilyl alkoxide was again greater than one during a run. The decrease in pseudo-first order rate constant \( k_1 \),
Fig. 7. Run 38, The Hydrolysis of Triphenylsilyl Isopropoxide with \(2.57 \times 10^{-3}\text{M. Sodium Hydroxide.}\)

with time can be seen from the upward curvature of the log D versus time plot (Fig. 7) and from table 5.

Table 5. The Decrease in First Order Rate Constant \(k_i\) during Run 43.

\[
k_i = \frac{1}{T} \log \frac{D_0}{D_r}, \quad \Delta k_i \% = \frac{\text{Initial } k_i - k_i}{\text{Initial } k_i} \times 100
\]

\[
\text{Initial } k_i = 0.795 \times 10^{-2} \text{ mins}^{-1}
\]

\[
\begin{array}{cccc}
T (\text{mins.}) & 30 & 60 & 90 & 120 \\
10^2 x k_i & 0.784 & 0.772 & 0.737 & 0.739 \\
\Delta k_i \% & 1.1 & 2.9 & 7.3 & 7.0
\end{array}
\]
It can be seen that the effect is very much less than for the triphenylsilyl methoxides above, as would be expected at these higher sodium hydroxide concentrations. This is thought to be due in part, as in the hydrolysis of triphenylsilyl methoxide, to the triphenylsilanol formed in the reaction removing the hydroxide ion catalyst:

\[
(C_6H_5)_3SiOC_3H_7 + H_2O \xrightarrow{\text{OH}^-} (C_6H_5)_3SiOH + C_3H_7OH
\]

\[
(C_6H_5)_3SiOH + OH^- \xrightarrow{K} (C_6H_5)_3SiO^- + H_2O
\]

In support of this postulate, the initial rate of reaction was decreased by 34.3% by adding triphenylsilanol (0.0429 gms/200 mls.) to the reaction mixture, and 35.7% by adding 0.0559 gms/200 mls. From the reduction observed in the initial first order rate constant \( k_i \), it is possible to calculate the apparent loss of sodium hydroxide from the system, and an approximate value of the equilibrium constant \( K \). (Table 6). These values are in agreement with the one calculated.

Table 6. The Effect of Triphenylsilanol on the Rate of Hydrolysis.

<table>
<thead>
<tr>
<th>Conc. of ( \text{Ph}_3\text{SiOH} ) (x 10^4 M)</th>
<th>Run 48</th>
<th>Run 49</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction in Initial ( k_i ) (x 10^2 mins^-1)</td>
<td>0.295</td>
<td>0.307</td>
</tr>
<tr>
<td>Apparent reduction in [OH^-] (x 10^4 M)</td>
<td>6.27</td>
<td>6.53</td>
</tr>
<tr>
<td>( K )</td>
<td>36400</td>
<td>16000</td>
</tr>
<tr>
<td>± 16000</td>
<td>± 9000</td>
<td></td>
</tr>
</tbody>
</table>
above when the large experimental errors are considered.

The curvature of the log D versus time plot may be compared with the increasing concentration of triphenylsilanol. Table 7 gives the concentration of triphenylsilanol in the reaction mixture (calculated from the extent of the reaction) and the reduction in concentration of sodium hydroxide (calculated from the rate of reaction at that time, i.e. from the slope of the log D versus time plot) on two occasions during runs 43 and 38. But it can be seen from these

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (mins)</th>
<th>% Reaction</th>
<th>$[\text{Ph}_3\text{SiOH}]$</th>
<th>$[\text{OH}^-]$</th>
<th>$[\text{OH}^-]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>60</td>
<td>37</td>
<td>$1.17 \times 10^4$ M.</td>
<td>$1.46 \times 10^4$ M.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>59</td>
<td>$1.85 \times 10^4$ M.</td>
<td>$2.23 \times 10^4$ M.</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>60</td>
<td>50</td>
<td>$1.53 \times 10^4$ M.</td>
<td>$2.62 \times 10^4$ M.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>71</td>
<td>$2.25 \times 10^4$ M.</td>
<td>$4.74 \times 10^4$ M.</td>
<td></td>
</tr>
</tbody>
</table>

two specimen runs that the apparent reduction of hydroxide ion concentration during a run is more than can be accounted for by the triphenylsilanol produced in the reaction, even if the triphenylsilanol reacted completely with the sodium hydroxide. This is the same effect as that observed in the hydrolysis of
triphenylsilyl methoxides discussed above, and it must again represent a removal of hydroxide ion from the reaction mixture by other means. This must again be attributed to contamination of the reaction mixture during a run, probably by acidic components of the atmosphere when the reaction vessel was opened to remove an aliquot. It will be observed however that these effects are relatively very much smaller for the hydrolysis of triphenylsilyl isopropoxide than for the methoxide (Fig. 5 and Tables 3 and 4). This is reasonable, since the concentration of sodium hydroxide in this case is about twenty times that in the former, so that contaminants have a relatively smaller effect.

The initial first order rate constants however were quite reproducible, despite the variable reductions in rate constant during the runs. The duplicate runs 43 and 44, and 45, 46 and 47 differed in their initial rate constants by 1.4%. The quoted initial rate constants were calculated from the log D versus time curves by extrapolating to the time of mixing of the components, usually two minutes before the first aliquot was taken out (T = 0).

To discover the dependence of the rate of reaction
on alkali concentration, triphenylsilyl isopropoxide was hydrolysed in solutions of various concentrations of sodium hydroxide and the pseudo-first order rate constants derived from the initial rate were plotted against alkali concentration (Fig. 8). A straight line was obtained passing close to the origin, the distance from the origin being such that the rate appeared to be zero at a base concentration of $10^{-4}$ M. This discrepancy may reflect experimental uncertainty, or it may be due to the several possible contaminants,
as discussed in the previous section. The magnitude of the deviation of the line from the origin is very similar to that in the base catalysed hydrolysis of the methoxide described above, indicating that the nature of the effect is probably the same in both cases. Relatively, the effect is less important in this case because of the higher concentration of sodium hydroxide in the reaction mixture. Within the limits of experimental error however the reaction is of first order in sodium hydroxide.

Then assuming first order kinetics in triphenylsilyl isopropoxide also, the rate equation for the base catalysed hydrolysis of triphenylsilyl isopropoxide may be written:

\[
\text{Rate} = k_1 \left[ \text{Ph}_3\text{SiOPr} \right] = k_8 \left[ \text{Ph}_3\text{SiOPr} \right] [\text{OH}^-]
\]

where \( k_1 \) is the first order rate constant, and \( k_8 \) is the specific rate constant for the base catalysed hydrolysis. The value of \( k_8 \) (4.70 litres.moles\(^{-1}\) mins\(^{-1}\)) can be deduced from the slope of the line from the graph of first order rate constant against sodium hydroxide concentration (Fig. 8). This figure may be compared with the analogous value of 360 obtained from the hydrolysis of triphenylsilyl methoxide under the same conditions, and it is seen that
the methoxide is about 80 times more reactive.

The hydrolysis of nine trisubstituted compounds has been studied in solutions of sodium hydroxide, the concentrations of which were chosen to give a convenient rate of hydrolysis. The specific rate constant, $k_e$, was determined for each compound assuming first order kinetics in silicon isopropoxide and sodium hydroxide (Table 8).

Table 8. The Relative Rates of Base Catalysed Hydrolysis of Triarylsilyl Isopropoxides $(X-C_6H_4)_3SiOC_3H_7$.

<table>
<thead>
<tr>
<th>X</th>
<th>m-Me</th>
<th>p-Me</th>
<th>m-MeO</th>
<th>p-MeO</th>
<th>m-t-Bu</th>
<th>p-t-Bu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_e/k_0$</td>
<td>0.193</td>
<td>1.08</td>
<td>1.20</td>
<td>0.0698</td>
<td>0.0958</td>
<td>0.0736</td>
</tr>
<tr>
<td>log $k_e/k_0$</td>
<td>-0.715</td>
<td>-0.967</td>
<td>0.080</td>
<td>-1.156</td>
<td>-1.019</td>
<td>-1.133</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X</th>
<th>p-Cl</th>
<th>p-Me3Si</th>
<th>p-Me3SiCH2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_e/k_0$</td>
<td>16.25</td>
<td>5.21</td>
<td>0.287</td>
</tr>
<tr>
<td>log $k_e/k_0$</td>
<td>1.211</td>
<td>-2.83</td>
<td>-1.542</td>
</tr>
</tbody>
</table>

The effects of the substituents were compared by the Hammett $\sigma$-rho treatment. The plot of the log relative rate $k_e/k_0$ (where $k_0$ is the specific rate constant $k_0$ for the unsubstituted compound) against $\sigma$ is given in fig. 9.
Fig. 9. Hammett Plot for the Base Catalysed Hydrolysis of Triarylsilyl Isopropoxides.

It is apparent from these results that electron releasing substituents decrease the rate of reaction and electron withdrawing substituents increase it. Although the log relative rates do not plot against the Hammett sigma constant (this is discussed later)
it can be seen that the effect is large, the slope of
the line drawn being \( \psi = 5.70 \). (It should be remem-
bered, however, that three substituents are contrib-
uting to the effect.)

Since electron releasing groups retard the reac-
tion, the silicon atom in the transition step of the
rate determining step must bear a partial negative
charge. Since the reaction is first order in silicon
isopropoxide and in hydroxide ion this is consistent
with a mechanism involving nucleophilic attack by
hydroxide ion upon the silicon atom, as commonly
occurs in the replacement reactions of silicon com-
pounds. The Si-OH bond is always formed to a greater
extent than the Si-OC\(_3\)H\(_7\) bond is broken, leaving a
residual partial negative charge on the silicon.
This is compatible with mechanisms which have been
proposed previously for the replacement of the ether
linkage to silicon, and emphasises again the impor-
tance of nucleophilic attack on silicon in the reac-
tions of organosilicon compounds.

The hydroxide ion is regenerated by a rapid inter-
action of the isopropoxide ion with water. The comp-
lete reaction may be expressed as follows:
The reaction may or may not involve an intermediate.

IV Base Catalysed Methoxyl Exchange of Triarylsilyl Methoxides.

It was assumed that the concentration of methoxide ion required to catalyse the reaction and give a convenient rate would be exceedingly low. Because of this an attempt was made to use the buffering action of sodium acetate as a mild base catalyst:

\[
\text{NaOCOCH}_3 + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{COOH} + \text{Na}^+ + \text{CH}_3\text{O}^-
\]

\[
(C_6H_5)_3\text{SiOCOCH}_3 + \text{CH}_3\text{OH} \rightleftharpoons (C_6H_5)_3\text{SiOH} + \text{CH}_3\text{OH}
\]

A relatively large amount of sodium acetate would then be required which could be obtained anhydrous and pure, and weighed accurately and easily.

The exchange reaction of the methoxy group of triphenylsilyl methoxide was found to proceed readily in methanol at 25°, with 10^{-2} M. sodium acetate catalyst. The reaction was apparently of an order slightly greater than one, the log D versus time plot showing upward curvature and the first order rate constant decreasing with time. The apparent reduction in rate
constant throughout a typical run is illustrated in table 9 for run 99.

Table 9. The Apparent Reduction in First Order Rate Constant During Run 99.

\[
k_i = \frac{1}{T} \log \frac{D_o}{D_r}, \quad \Delta k_i \% = \frac{\text{Initial } k_i - k_i}{\text{Initial } k_i} \times 100
\]

<table>
<thead>
<tr>
<th>T (mins.)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^2 \times k_i) (mins(^{-1}))</td>
<td>3.20</td>
<td>3.00</td>
<td>2.76</td>
<td>2.69</td>
</tr>
<tr>
<td>(\Delta k_i %)</td>
<td>5.7</td>
<td>11.5</td>
<td>18.4</td>
<td>20.6</td>
</tr>
</tbody>
</table>

Initial \(k_i = 3.39 \times 10^{-2}\) mins\(^{-1}\)

This effect must represent a change in the composition of the reaction mixture due to contamination as the reaction proceeds, since a true order of greater than one is unlikely from a mechanistic point of view. The high sensitivity of the reaction to contamination is perhaps surprising in this reaction in view of the buffering action of the sodium acetate catalyst.

The rates of reaction were measured at different concentrations of sodium acetate and plotted on a graph (Fig. 10). The rates show an increase with catalyst concentration, but the scatter of the points shows that the precision of the results is not high. The procedure used for the measurement of the rate of reaction did not permit duplicate runs to be made, but
from the results it seems that the maximum experimental error in the rate constants quoted is of the order of 20%. The relationship between rate and sodium acetate concentration is thus uncertain, but from a consideration of the equilibria involved a linear relationship would not be expected.

From these results the exchange reaction appears to

![Graph](image-url)
be most sensitive to slight contamination. In the solvolysis of triphenylsilyl methoxide in methanol with sodium methoxide catalyst, great care was taken to avoid contamination by using an atmosphere of dry nitrogen. This system required a very low concentration of catalyst \(10^{-5} \text{ M.}\) to give a convenient rate of reaction. The plots of log D versus time were straight lines (Fig. 11), the reaction being first

---

**Fig. 11.** Run 106, Methoxyl Exchange of Triphenylsilyl Methoxide with \(12.19 \times 10^{-6} \text{ M.}\) Sodium Methoxide.
order in triphenylsilyl methoxide. These rate studies showed good reproducibility, the differences in first order rate constant $k_i$ of the duplicate runs 109 and 110, and 117, 118 and 119 being less than 1.5%.

A plot of pseudo-first order rate constant against sodium methoxide concentration gave a good straight line passing close to the origin (Fig. 12), showing that to within the limits of experimental error the

Fig. 12. First Order Rate Constants for the Sodium Methoxide Catalysed Exchange of Triphenylsilyl Methoxide.

$10^2 x k_i$ (mins$^{-1}$)

$10^5 x$ Sodium Methoxide Concentration, (moles/litre)
reaction is also first order in methoxide ion. The failure of the line to pass through the origin is possibly due, as in the hydrolysis of methoxides and isopropoxides above, to impurities present in the system. It will be realised that because the base concentration is lower than in the hydrolysis reactions above this effect appears more pronounced, but in absolute terms the deviation from the origin in this case (1.7 x 10^{-5} M.) is less than in any previous case. This is perhaps due to the use of the nitrogen atmosphere, so reducing contamination of the reaction mixture.

Addition to the reaction mixture of greater amounts than could possibly have been introduced accidentally, of water had no effect on the reaction (for example, 0.05% added water was found to produce no detectable change in the rate), showing that contamination by water was not a source of error.

The sodium methoxide catalysed \( \text{exchange} \) of the methoxy group of triphenylsilyl methoxide in methanol is thus first order in silicon methoxide and methoxide ion, and the rate equation may be represented as:

\[
\text{Rate} = k_1 \left[ \text{Ph}_3\text{SiOMe} \right] = k_6 \left[ \text{Ph}_3\text{SiOMe} \right] [\text{MeO}^-]
\]

where \( k_1 \) is the first order rate constant, and \( k_6 \) is
the specific rate constant for the base catalysed exchange. The value of $k_B$ (1190 litres.moles$^{-1}$min$^{-1}$) may be calculated from the slope of the line in fig. 12.

To determine the effect of substituents on the rate, six trisubstituted compounds were prepared and solvolyzed in one of two standard solutions of sodium methoxide in methanol (concentrations 4.06 and 22.0 x 10$^{-6}$ M.). Their relative rates were determined by comparison with that of the unsubstituted compound.

Fig. 13. Hammett Plot for the Base Catalysed Methoxyl Exchange of Triarylsilyl Methoxides.
which was measured in both solutions. Their relative
rates are given in table 10, and the Hammett plot of log
relative rate against $\sigma$ is given in fig. 13.

Table 10. Relative Rates of the Base Catalysed
Exchange of Triarylsilyl Methoxides,
$(X-C_6H_4)_3SiOCH_3$.

<table>
<thead>
<tr>
<th>$X$</th>
<th>$m$-Me</th>
<th>$p$-Me</th>
<th>$m$-MeO</th>
<th>$p$-MeO</th>
<th>$m$-Cl</th>
<th>$p$-Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k/k_0$</td>
<td>0.331</td>
<td>0.287</td>
<td>0.641</td>
<td>0.152</td>
<td>20.6</td>
<td>22.8</td>
</tr>
<tr>
<td>log $k/k_0$</td>
<td>-4.8</td>
<td>-5.9</td>
<td>-1.93</td>
<td>-8.17</td>
<td>1.315</td>
<td>1.358</td>
</tr>
</tbody>
</table>

It can be seen that in general, electron supply to
silicon retards the reaction and electron withdrawl
facilitates it, although the Hammett plot is not a
good straight line (this is discussed below, Section
VIII). Since the reaction is also first order in tri­
phenylsilyl methoxide and in methoxide ion, these
observations are consistent with a mechanism involving
nucleophilic attack by methoxide ion on silicon in the
rate determining step. At the transition state of
this step the bond making process has proceeded to a
greater degree than the bond breaking process, inducing
a partial negative charge on silicon, in an analogous
way to that shown above for the alkaline hydrolysis of
triphenylsilyl isopropoxides.

The mechanism is then a simple, $S_N2$ type, replace-
ment reaction, which may or may not involve an inter-
mediate:

\[ \text{MeO}^- + \text{Ph}_3\text{SiOMe} + \left[ \frac{\text{Si}^\text{OMe}^-}{\text{MeO}^-} \right] \rightarrow \text{MeO} \vdash \text{Si} \vdash \text{OMe}^+ \rightarrow \text{MeOSiPh}_3 + \text{OMe}^+ \]

**V Acid Catalysed Hydrolysis of Triarylsilyl Methoxides**

Triphenylsilyl methoxide was hydrolysed in a solvent mixture of 10% water: 90% acetone with 10^-4 M. hydrochloric acid at 25°C. The reaction was found to be first order in silicon methoxide during a run, perfectly straight plots of log D versus time being obtained. These results showed good reproducibility, the duplicate runs 22 and 23 differing in rate constant by 1.5%. Furthermore, the plot of observed first order rate constant \( k_i \) against acid concentration (Fig. 14) was a straight line passing close to the origin, indicating that the reaction is also first order with respect to acid. The rate equation may then be written

\[(\text{C}_6\text{H}_5)_3\text{SiOCH}_3 + \text{H}_2\text{O} \rightarrow (\text{C}_6\text{H}_5)_3\text{SiOH} + \text{CH}_3\text{OH} \]

Rate = \( k_i \) [Ph\(_3\)SiOMe] = \( k_A \) [Ph\(_3\)SiOMe] [H\(^+\)]

where \( k_i \) is the observed first order rate constant and \( k_A \) is the specific rate constant for acid catalysed hydrolysis. A value of 111 litres.moles\(^{-1}\)mins\(^{-1}\) may be assigned to \( k_A \) from the slope of the line in fig.**
From these results it is not possible to estimate the relative effectiveness of acidic and basic catalysts because of the different media involved. But the rapid increase of the rate of reaction which has been observed on the addition of only $10^{-4}$ M. of acid or alkali catalyst, illustrated by the high specific
rate constants $k_A = 111$ and $k_b = 360$ litres.moles$^{-1}$ mins$^{-1}$ illustrates in turn the very high sensitivity of this reaction to both types of catalyst.

The first order rate constants, $k_1$, for four tri-substituted compounds were determined in an acid concentration calculated to give a convenient rate of reaction. Then the specific rate constant $k_A$ was determined for each individual compound. The results are shown in table 11, and a Hammett plot of log relative rate against $\sigma$ is given in fig. 15.

It can be seen from the results that although

---

Fig. 15. Hammett Plot for the Acid Catalysed Hydrolysis of Triaryl-silyl Methoxides.

\[
\begin{align*}
\log k_A/k_0 & \\
\cdot 1 & \\
-3 & \quad -2 & \quad -1 & \quad 1 & \quad 2 & \quad 3
\end{align*}
\]
Table 11. Relative Rates of Acid Catalysed Hydrolysis of Triarylsilyl Methoxides, \( (X-C_6H_4)_3SiOCH_3 \).  

<table>
<thead>
<tr>
<th>( X )</th>
<th>( p-Cl )</th>
<th>( m-Cl )</th>
<th>( p-Me )</th>
<th>( p-MeO )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_A/k_0 )</td>
<td>1.78</td>
<td>1.25</td>
<td>0.749</td>
<td>0.687</td>
</tr>
<tr>
<td>( \log k_A/k_0 )</td>
<td>0.251</td>
<td>0.097</td>
<td>-0.126</td>
<td>-0.163</td>
</tr>
</tbody>
</table>

there is only poor correlation between log relative rate and the \( \sigma \) constant (this will be examined in section VIII), electron supplying substituents lower the rate of hydrolysis and electron withdrawing substituents raise it. The effect is relatively small however, the three para methoxy substituents, for example, only lowering the rate to 0.687 times that of the unsubstituted compound. The \( \rho \) value of the line drawn on the Hammett plot (Fig. 15) is 0.95, a relatively small value.

Since the reaction is also first order in silicon methoxide and acid; these observations are consistent with a mechanism involving protonation of the oxygen in a fast step, and nucleophilic attack by water upon silicon in the rate determining step.

The observation that electron release to silicon hinders the reaction means that in the transition state of the rate determining step (b) the silicon atom is
more negative than it was in the original ground state (Ph₃SiOMe). Therefore, the reaction may be represented as follows:

(a) \[ \text{Ph₃SiOMe} + \text{H}_3\text{O}^+ \overset{\text{fast}}{\longrightarrow} \text{Ph₃SiOHMe} + \text{H}_2\text{O} \]

(b) \[ \text{H}_2\text{O} + \text{Ph₃SiOHMe} \rightarrow \left[ \text{H}^+ \cdot \text{Si}^+ \cdot \text{O}^\text{Me} \right]^+ + \text{H}_2\text{OSiPh₃} + \text{MeOH} \]

Transition state

(c) \[ \text{Ph₃SiOH₂} + \text{H}_2\text{O} \overset{\text{fast}}{\longrightarrow} \text{Ph₃SiOH} + \text{H}_3\text{O}^+ \]

The silicon must bear a partial positive charge in the protonated intermediate (step a) Ph₃Si+OHMe, induced upon it by the neighbouring positive charge. But this observation suggests that during step (b) the H₃O+···Si bond is formed to a much greater extent than the Si···OHMe bond is broken, so that the partial negative charge induced on silicon by the forming bond more than outweighs the total partial positive charge. The importance of nucleophilic attack in the replacement of groups at silicon is thus very well illustrated.

VI Acid Catalysed Hydrolysis of Triarylsilyl Isopropoxides.

Triphenylsilyl isopropoxide and ten trisubstituted compounds were hydrolysed at 25° in a solvent mixture of 20% water: 80% acetone containing 1.24 x 10⁻³ M hydrochloric acid.
The product of the reaction of triphenylsilyl isopropoxide was identified as triphenylsilanol by its melting point, no condensation to hexaphenyldisiloxane having taken place.

\[
(C_6H_5)_3SiOC_3H_7 + H_2O \xrightarrow{H^+} (C_6H_5)_3SiOH + C_3H_7OH.
\]

The triphenylsilanol was also contaminated less than that obtained in the base catalysed hydrolysis (p. 42). This indicates that condensation of the acetone solvent is much less appreciable with acid catalysis than with base.

The reaction was first order in silicon isopropoxide, perfectly straight plots of log D versus time being obtained. No investigation was carried out of the relationship between rate and acid concentration, but first order kinetics in acid were assumed by analogy with the acid catalysed hydrolysis of triphenylsilyl methoxide described above (p. 60). The rate equation may then be expressed as:

\[
\text{Rate} = k_a [\text{Ph}_3\text{SiOPr}] = k_a \cdot \text{Ph}_3\text{SiOPr} [H^+]\]

where \(k_a\) is the specific rate constant for acid catalysed hydrolysis.

A comparison may now be made of the relative effectiveness of acid and alkali catalysts for this reaction. The specific rate constant for acid catalysed
hydrolysis of triphenylsilyl isopropoxide in this medium at 25° ($k_A = 8.46$ litres.mole$^{-1}$ min$^{-1}$) is almost twice as great as the corresponding figure for base catalysed hydrolysis ($k_B = 4.70$ litres.mole$^{-1}$ min$^{-1}$). This shows that acid is a more effective catalyst than alkali in the hydrolysis of unsubstituted triphenylsilyl isopropoxide in this medium. This may be contrasted with the hydrolysis of trialkylsilyl phenoxides in 51.4% ethanol/water, in which alkali is more effective than acid,$^4$ but this difference may well be attributed to the different medium involved. It is well known that the rates of acid catalysed reactions particularly vary considerably with the water content of mixed aqueous-alcoholic solvents.$^3$

In a neutral solution of triphenylsilyl isopropoxide the hydrolysis was exceedingly slow; only 4.06% of reaction could be detected in 43 days. This illustrates the stability of these compounds to water even when in solution, and emphasises the large effect that small quantities of acid or alkali catalyst have on the rate of hydrolysis.

The relative rates of hydrolysis of the trisubstituted triphenylsilyl isopropoxides in $1.24 \times 10^{-3}$ M. hydrochloric acid are given in table 12; and the Ham-
Table 12. Relative Rates of the Acid Catalysed Hydrolysis of Triarylsilyl Isopropoxides,

\[ (X-C_6H_4)_3SiOC_3H_7 \]

<table>
<thead>
<tr>
<th>X</th>
<th>m-Me</th>
<th>p-Me</th>
<th>m-MeO</th>
<th>p-MeO</th>
<th>m-Cl</th>
<th>p-Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1/k_0 )</td>
<td>0.566</td>
<td>0.742</td>
<td>0.579</td>
<td>0.768</td>
<td>0.794</td>
<td>1.47</td>
</tr>
<tr>
<td>( \log k_1/k_0 )</td>
<td>-2.47</td>
<td>-1.30</td>
<td>-2.33</td>
<td>-1.15</td>
<td>-1.00</td>
<td>-0.168</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X</th>
<th>m-t-Bu</th>
<th>p-t-Bu</th>
<th>p-MeSi</th>
<th>p-MeSiCH (_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1/k_0 )</td>
<td>0.362</td>
<td>0.308</td>
<td>0.232</td>
<td>0.428</td>
</tr>
<tr>
<td>( \log k_1/k_0 )</td>
<td>-1.442</td>
<td>-0.511</td>
<td>-0.636</td>
<td>-0.368</td>
</tr>
</tbody>
</table>

Fig. 16. Hammett Plot for the Acid Catalysed Hydrolysis of Triphenyl-silyl Isopropoxides.
mett plot of log relative rate against \( \sigma \) is given in fig. 16. Although the Hammett plot shows a very wide scatter of the points, it can be seen that there is a tendency for the electron supplying substituents to retard the reaction by a small amount, and the electron withdrawing substituents to accelerate it. This means, as in the acid catalysed hydrolysis of silicon methoxides discussed above, that in the transition state of the rate determining step the reaction centre is more negative than in the original ground state. This is consistent with a mechanism involving nucleophilic attack by water upon silicon in the rate determining step, the partial negative charge being induced upon silicon by the attachment of the oxygen \( \text{H}_2\text{O} \rightarrow \text{Si}^- \). The first order dependence of the rate on acid concentration is then consistent with a fast proton transfer to the oxygen. The overall reaction may then be represented as follows:

\[
\begin{align*}
\text{(a)} & \quad \text{Ph}_3\text{SiOPr} + \text{H}_3\text{O}^+ \overset{\text{fast}}{\longrightarrow} \text{Ph}_3\text{SiOHPr} + \text{H}_2\text{O} \\
\text{(b)} & \quad \text{H}_2\text{O} + \text{Ph}_3\text{SiOHPr} \rightarrow \left[ \begin{array}{c} \text{H}_3\text{O}^+ \rightarrow \text{Si}^- \rightarrow \text{Ph}_3\text{SiOHPr} \\ \text{Ph}_3\text{SiOH}^+ \end{array} \right] + \text{Ph}_3\text{SiOH}_2 + \text{PrOH} \\
\text{(c)} & \quad \text{Ph}_3\text{SiOH}_2 + \text{H}_2\text{O} \overset{\text{fast}}{\longrightarrow} \text{Ph}_3\text{SiOH} + \text{H}_3\text{O}^+
\end{align*}
\]

These observations may be compared with those of Akerman\(^5\) on the acid catalysed hydrolysis of triethyl-
silyl phenoxides in aqueous ethanol at 25°. In this case electron donating substituents were found to facilitate the reaction and electron accepting substituents to hinder it, so the reaction must be facilitated by a high electron density at the silicon. The effect was very small however, the slope of the line on the Hammett plot being $\rho = -53$.

The proposed mechanism of the reaction is analogous to the one proposed above for the methoxides and isopropoxides. The opposing substituent effects which have been observed however are significant. It means that in the rate determining step of the hydrolysis of the phenoxides, the partial negative charge induced upon silicon by the attachment of the water ($H_2O \cdots Si^{6+}$) is insufficient to outweigh the partial positive charge induced upon silicon by protonation of the neighbouring oxygen ($Si^{6+} \cdots OHPh$). Then, even if the $H_2O-Si$ bond is formed to a greater extent than the $Si-OHPh$ bond is broken, as proposed above for the alkoxides, the nett charge on silicon at the transition state is small and positive.

The differences in the reactions of alkoxides and phenoxides are thus quite small. In the former case the substituent effects are also quite small, the lines
drawn in figs. 15 and 16 representing \textit{rho} values of \cdot 95 and \cdot 75 respectively; and three substituents are contributing to this effect. This means that in the transition state of the rate determining step of the hydrolysis of the alkoxides, the silicon does bear a partial negative charge, but only of an extremely small magnitude. It can be seen then that in all these cases the positive charge induced on silicon by the protonation of the oxygen is of about the same magnitude as the negative charge induced by nucleophilic attack upon silicon. The nett charge is then extremely small, and may be positive or negative in different cases.

The fact that the sign of \textit{rho} differs in the two classes of compounds, electron releasing substituents facilitating the hydrolysis of phenoxides and retarding the hydrolysis of alkoxides, is not unexpected. The different positions of the substituents \( X \) in the two classes of compounds, \( X-\text{C}_6\text{H}_4-\text{Si}-0-R \) and \( \text{R-Si-0-C}_6\text{H}_4-X \), must influence differently the electron distribution in the neighbourhood of the silicon and oxygen atoms, and so affect the mode of reaction.
VII Acid Catalysed Methoxyl Exchange of Triphenylsilyl Methoxide.

The rate of exchange of the methoxy group of triphenylsilyl methoxide in methanol at 25° is extremely low without a catalyst. The reaction does not appear to be first order throughout, the log D versus time plots showing downward curvature (Fig. 17), and the pseudo-first order rate constant increasing from an initial value of $1.55 \times 10^{-4}$ mins$^{-1}$ as the reaction progresses (Run 131). It is proposed however that this
effect was due to the absorption of contaminants by the reaction mixture when an aliquot was taken out, even though dry nitrogen was blown in at the time. The contaminant, being acidic or basic, then catalysed the exchange and increased the observed first order rate constant. When the run was duplicated (Run 132) the first aliquot was taken out after 70 hours, the initial value of D being calculated from the concentration. The initial slopes then showed good agreement ($k_1 = 1.51 \times 10^{-4} \text{ mins}^{-1}$ in Run 132), but the increase in first order rate constant with time was very much reduced.

The low rate of exchange of triphenylsilyl methanide in neutral methanol provides further evidence (see p. 20) that complex formation between organosilicon compounds and Lewis bases is not a ready process. In this case co-ordination of methanol to silicon would essentially constitute reaction of the compound:

$$\text{MeOH} + \text{Ph}_3\text{SiOMe} \xrightarrow{\text{slow}} \text{Me}^+\overset{\text{Ph}_3}{\text{H}}\rightarrow\overset{\text{Si}^-\text{OMe}^*}{\text{Si}^-\text{OMe}^*} \quad (a)$$

$$\text{MeOSiPh}_3 + \text{Me}^*\text{OH} \xrightarrow{\text{slow}} \overset{\text{Me}^*\text{OH}}{\text{MeO}}\rightarrow\overset{\text{Si}^-\text{OMe}^*}{\text{Si}^-\text{OMe}^*} \quad (b)$$

since the proton transfer from complex (a) to complex (b) must be a very fast step. But the low rate of exchange observed indicates that complex formation of
this type, if it does occur, must require a substantial activation energy.

This is in good agreement with the low rates of exchange of chloride ion with triphenylsilyl chloride (p. 20), and water with triphenylsilanol. In this latter case, triphenylsilanol dissolved in 90% dioxan/H$_2$O at 25°, no exchange could be detected after 24 hours. This exchange is analogous to the methoxyl exchange, requiring co-ordination of water to silicon and a fast proton transfer:

$$\text{H}_3\text{O}^+ + \text{Ph}_3\text{SiOH} \xrightarrow{\text{slow}} \text{H}_3\text{O}^\text{Si}^+\text{Ph}_3\text{OH} \xrightarrow{\text{fast}} \text{H}_3\text{O}^+\text{Si}^\text{Ph}_3\text{OH}$$

From this evidence it appears that complex formation, or co-ordination to silicon is not at least a kinetically fast step preceding the rate determining step. If pentacovalent silicon intermediates are formed during a reaction process the activation energy of their formation is substantial.

The acid catalysed methoxyl exchange was first examined using benzoic acid catalyst. The advantages of benzoic acid as a catalyst are that it is a weak acid so that it could be used in relatively large, easily measurable quantities, and it is readily obtained
In a high state of purity.

The exchange reaction proceeded readily in methanol at 25° containing 5 x 10^{-3} M. benzoic acid, and the log D versus time plots were straight lines, indicating that the reaction is first order in silicon methoxide.

The rate of reaction was measured at various concentrations of benzoic acid. The plot of the first order rate constant, $k_1$, against benzoic acid concentration (Fig. 18) gave a curve, as would be expected for a weak acid. But the relationship between rate

![Graph showing the relationship between $10^3 x$ Benzoic Acid Concentration (moles/litre) and $10^2 x k_1$ (mins^{-1})](image)

Fig. 18. Benzoic Acid Catalysed Methoxyl Exchange of Triphenylsilyl Methoxide.
and acid concentration is complex, particularly as the undissociated acid may act as a relatively weak proton donor:

\[
\text{Ph}_3\text{SiMe} + \text{MeOH}^+ \xrightleftharpoons{K_1} \text{Ph}_3\text{SiOHMe} + \text{MeOH} \\
\text{Ph}_3\text{SiOMe} + \text{PhCOOH} \xrightleftharpoons{K_2} \text{Ph}_3\text{SiOHMe} + \text{PhCOO}^-
\]

The rate of exchange was also measured using hydrochloric acid catalyst. The reaction had a convenient rate with \(5 \times 10^{-3}\) M. hydrochloric acid present, but the log D versus time plots showed slight upward curvature (Fig. 19), the actual first order rate constant \(k_1\), decreasing about 10-15\% after one half-life.

Fig. 19. Run 135, Hydrochloric Acid Catalysed Methoxyl Exchange of Triphenylsilyl Methoxide.
Table 13 gives the apparent reduction in first order rate constant during a typical run (135); it can be seen that the effect is quite small.

Table 13.

\[ k_I = \frac{1}{T} \log \frac{D_0}{Y}, \quad \Delta k,\% = \frac{\text{Initial } k_I - k_I \times 100}{\text{Initial } k_I} \]

\[
\begin{array}{cccc}
T (\text{mins.}) & 15 & 60 & 151 & 180 \\
10^2 x k_I & 1.45 & 1.35 & 1.25 & 1.24 \\
\Delta k,\% & -0.7 & 6.3 & 15.3 & 15.9 \\
\end{array}
\]

The reduction in rate constant during a run may well be due to contamination of the reaction mixture with water. It is well known that the rate of acid catalysed reactions in alcohols are dependent on the water concentration, and the rate has been observed to decrease very sharply as the water concentration of a water/ethanol mixture was increased from 0 to 5%.

The proton affinity of water is much greater than that of alcohol so that $H_2O^+$ is a relatively poor proton donor, and hence acid catalyst, compared with $MeOH^+$. Thus, when water is added to hydrochloric acid/methanol, the equilibrium

\[
MeOH^+ + H_2O \rightleftharpoons H_3O^+ + MeOH
\]
removes MeOH$_2^+$ from the reaction mixture and the catalytic action decreases.

The apparently first order reactions of the benzoic acid catalysed reaction can probably be explained by the buffering action of the large concentration of benzoic acid. This would practically eliminate any small changes in the methoxonium ion concentration due to contamination.

However, the first order rate constants calculated from the initial slope plotted satisfactorily against

Fig. 20. Hydrochloric Acid Catalysed Methoxy Exchange of Triphenylsilyl Methoxide

$10^2 \times k_1$ (mins$^{-1}$)

$10^6 \times$ Hydrogen Chloride Concentration (molea/litre)
hydrogen chloride concentration to give a straight line (Fig. 20). The deviations of the points from this line indicate a maximum experimental error in the quoted rate constants of %. The deviation of the line from the origin \( (3.2 \times 10^{-6} \text{ M}) \) appears to be relatively large in this case, but in terms of its absolute value it is only a third of the deviation in the acid catalysed hydrolysis of triphenylsilyl methoxide but twice that of the sodium methoxide catalysed methoxyl exchange.

This deviation of the first order rate constant versus catalyst concentration graph from the origin for the acid catalysed reactions appears to be inexplicable. It is unlikely that it represents contamination of the reaction mixture, since contamination of the base catalysed reaction mixture tended to reduce the pH of the solution. In this case of the hydrogen chloride catalysed methoxyl exchange however, it is possible that the effect is due to the methanol solvent being incompletely dried. This could cause a graph of the type shown in fig. 20, although the rate of exchange at the low acid concentrations (below \( 3 \times 10^{-6} \text{ M.} \)) should be appreciable.
If the solvolysis may be regarded, within the limits of experimental error, as first order in both triphenylsilyl methoxide and hydrogen chloride, the rate equation may be written as follows:

\[ \text{Rate} = k_1 [\text{Ph}_3\text{SiOMe}] = k_A [\text{Ph}_3\text{SiOMe}] [H^+] \]

where \( k_1 \) is the pseudo-first order rate constant and \( k_A \) is the specific rate constant for the acid catalysed exchange. A value of 8000 litres.moles\(^{-1}\)mins\(^{-1}\) may be assigned to \( k_A \) from the slope of the line in fig. 20.

A comparison may now be made of the relative effectiveness of acidic and basic catalysts on the rate of exchange of the methoxy group of triphenylsilyl methoxide in methanol solvent. The values of \( k_A \) and the specific rate constant for base catalysed exchange (\( k_B = 1190 \) litres.moles\(^{-1}\)mins\(^{-1}\)) indicate that acid is about six times as effective a catalyst as base in this reaction.

The moderate stability of triphenylsilyl methoxide when dissolved in pure dry methanol and its great reactivity on the addition of small concentrations of acids and bases is very well illustrated by these high catalytic rate constants and the low rate of exchange (\( k_1 = 1.5 \times 10^{-4} \) mins\(^{-1}\)) in neutral methanol.

The rates of exchange of triphenylsilyl methoxide
and four trisubstituted compounds were measured in methanol containing $4.96 \times 10^{-8}$ M. hydrogen chloride, under an atmosphere of dry nitrogen. The results were generally not reproducible in this solvent mixture. This may be attributed to the different experimental procedure which was used for these compounds. In order to react all the compounds at precisely the same acid concentration, a large volume of a standard solution of hydrogen chloride in methanol was prepared. So that the silicon compound could mix rapidly with this solution at the start of each run it was necessary to first dissolve a weighed amount of the compound in a few drops of methanol. This was probably sufficient to introduce a small but variable amount of moisture into the reaction mixture and so affect the rate.

The rates of reaction however did show a tendency to be lower for the compounds with electron releasing substituents, in agreement with the results for the acid catalysed hydrolysis of triarylsilyl alkoxides.

It seems possible that the acid catalysed methoxyl exchange in methanol is too sensitive to contamination to be able to be examined by the method employed. A completely enclosed system, in which the reactants could be mixed and the aliquots taken out without expo-
sure of the reaction mixture to the atmosphere would perhaps eliminate this source of error.

VIII The Effect of Substituents.

It can be seen from figs. 9, 13, 15 and 16 that the log relative rates of the solvolyses which have been studied do not plot against the Hammett $\sigma$ constant to give points lying closely about one line. There is a distinct tendency for the points due to the meta substituents to lie well below a line drawn through the points due to the para substituents. Moreover, this tendency is more pronounced in the acid catalysed reactions (Figs. 15 and 16) than in the base (Figs. 9 and 13), but the differences in the relative rates between different substituted compounds in the acid catalysed reactions are much less than in the base. It is a well known phenomenon that the scatter of points on a Hammett plot is always more pronounced when there is little difference between the relative rates of the different substituted compounds. 

These graphs may be compared with others obtained from the reactions of silicon-functional compounds. Only five investigations have been carried out in which three or more substituted compounds were examined, and
these included few in which meta substituted compounds were used. The Hammett plots for these five reaction series are given in figs. 21 to 25. From these graphs it can be seen that in no case is there good correlation between log relative rate and \( \sigma \). Probably the best plots are obtained from Akerman's on the hydrolysis of triethylsilyl phenoxides (Figs. 22 and 23),

![Graph showing Hammett plots for reaction series with meta substituted compounds](image_url)
Fig. 22.
\[(\text{C}_2\text{H}_5)_3\text{SiOC}_6\text{H}_4\text{X} + \text{H}_2\text{O} + \text{H}^+\]
in ethanol/water at 25°
(Ref. 15)

Fig. 23.
\[(\text{C}_2\text{H}_5)_3\text{SiOC}_6\text{H}_4\text{X} + \text{OR}^-\]
in ethanol/water at 25°
(Ref. 15)
but in this case the substituted phenyl group is not directly attached to silicon and is $\xi$ to the reaction centre. It can be seen that the disposition of points on these graphs, particularly figs. 21, 24 and 25, is similar to that of corresponding points on figs. 9, 13, 15 and 16.

Hammett plots similar to the ones obtained from the silicon alkoxides are often obtained from the $S_N2$
replacement reactions of benzyl halides and allied compounds in which the seat of reaction is the α atom of the side chain. This is due to resonance interaction between +E para substituents and the forming and breaking bonds. It may be represented as fig. 25 on the molecular orbital model. There is sufficient overlap between the π electron system of benzene and and the 2p orbitals of carbon to permit a drift of
electrons from the lone pair of the oxygen into the making and breaking bonds ($p_n-p_n$ bonding). It may be represented in valence bond terminology by these canonical structures:

\[
\begin{align*}
\text{N} & \quad \text{H}_2 \quad \text{N} \\
\text{C} & \quad \text{N} \\
\text{OCH}_3 & \quad \leftrightarrow \quad \text{N}^- & \quad \text{H}_2 & \quad \text{N}^- \\
\text{N} & \quad \text{C} & \quad \text{N} \\
\end{align*}
\]

This effect, which stabilises the transition state and so facilitates the reaction, is superimposed upon the normal polar effect of the substituent due to its inductive and resonance contributions which are transmitted to the reaction centre through the phenyl-carbon $\sigma$ bond.

Because of the close relationship in structure
between the benzyl halides and the triphenylsilyl alko
oxides, the reaction centre in both cases is α to the
substituted ring, it was thought possible that the
scatter of points on the Hammett plots of the solvolyses
of triphenylsilyl alkoxides was also due to resonance
stabilisation of the transition state. But the modi-
fied Hammett relationships derived by Taft and Yuk
awa in which allowances can be made for changes in
resonance interaction during the course of the reaction,
do not bring the points due to the meta and para sub-
stituents on to one common line.

In the treatment proposed by Taft the inductive and
resonance contributions by a substituent to its sigma
constant are regarded as being separable and additive:

\[ \sigma = \sigma_I + \sigma_R. \]

Values of \( \sigma_I \) and \( \sigma_R \) have been deduced and assigned to
many individual substituents. To attempt to account
for resonance interaction between the para substituents
and the reaction centre, \( \sigma \) values were compounded from
\( (\sigma_I + \sigma_R) \) for the meta substituents and \( (\sigma_I + f\sigma_R) \) for
the para.

Schott and Harzdorf used a treatment of this
nature with their results from the base catalysed hydro-
lysis of para substituted triphenylsilanes in aqueous
ethanol (see Fig. 25) and obtained a good straight line by using a value of $f = 0.75$. But for the solvolysis reactions of triarylsilyl alkoxydes it is not possible to arrive at a scale of $\sigma$ values by adjusting the value of $f$ which will produce a line passing through the points due to both the meta and para substituents.

Yukawa showed that the quantity:

$$\Delta \sigma^+_R = \sigma^+_{\text{Brown and Okamoto}^+} - \sigma$$

is also a measure of the resonance interaction in the transition state, at least for electrophilic substitutions. But from a plot of the type

$$\log \frac{k}{k_0} = q(\sigma + r\Delta \sigma^+_R)$$

it is not possible to obtain a graph in which the points due to both the meta and para substituents lie about one line.

This does indicate that the scatter of points on the Hammett plot is not simply due to excessive resonance contributions of the para substituents with the reaction centre in the transition state, as commonly occurs in reactions which take place at the first atom of a side chain.

It appears from the Hammett plots for the solvolyses of triarylsilyl alkoxydes and for other reactions
of organosilicon compounds that in general the Hammett treatment does not provide good correlation for compounds in which the substituted phenyl group is attached to silicon. (Correlation is not good for the hydrolyses of triethylsilyl phenoxides\(^5\) (Figs. 22 and 23) in which the substituted benzene ring is \(\delta\) to the silicon.) Limited correlation is often found for the unsubstituted and a few select para substituted compounds, but in general this does not extend to the meta substituted compounds.
EXPERIMENTAL

I Measurement of the Rates of Reaction.

All the triphenylsilyl alkoxides prepared were labelled with tritium in the alkoxy group. The extent of the reaction of one of these compounds at a given time could then be determined by the measurement of the radioactivity of an aliquot from the reaction mixture, after it had been suitably treated.

An estimation of the tritium content of a sample was made by liquid photo-scintillation counting, using the apparatus\(^{28}\) whose circuit diagram is represented diagrammatically in fig. 27. An Isotopes Developments Ltd. extra high tension unit, type 532/A supplied 1200 volts to the circuit with a maximum variation of \(\pm 0.05\%\). The current was measured with a critically damped, sensitive, high voltage galvanometer (type Pye and Co. Ltd. 7943) equipped with a lamphouse and scale. The photomultiplier tube was an Electrical and Musical Instruments Ltd. type 6097B, with 11 stages.

To measure the radioactivity of a tritium labelled compound, it was dissolved in 20 mls. of scintillation solution (in this case, toluene containing scintillator (\(\beta\)-terphenyl, 4gms./litre) and wavelength
Fig. 27. Circuit Diagram of the Liquid Pho­
toscintillation Counting Apparatus.
shifter (1,6-diphenylhexatriene, 0.01 gms./litre) and poured into the cell. This is a small, plane-bottomed vessel, silvered and painted externally to reflect the maximum amount of light from the scintillating solution onto the light-sensitive cathode. The cell was placed on top of the photomultiplier tube (on which a few drops of oil had been spread to give good optical transmission) inside the light-tight canister. After five minutes the current was switched on and the current passing, as measured by the deflection in centimetres of the spot of light on the galvanometer scale, was recorded. The process was then repeated without the cell in place to give the Dark Current Deflection of the instrument, due mainly to thermal electrons in the tube. The difference between the first deflection and the dark current then gave a measure of the radioactivity of the sample.

The true proportionality of the relationship between deflection and tritium concentration for the type of compound being studied, was investigated by measuring the nett deflection due to 20 mls. of several solutions of known concentrations of triphenylsilyl tritiomethoxide in scintillation solution (Table 14). The graph of deflection against concentration
Table 14. Deflections due to Triphenylsilyl Triomethoxide in Scintillation Solution.

<table>
<thead>
<tr>
<th>Concentration of Ph$_3$SiOMe (gms./20mls.)</th>
<th>Deflection (cms.)</th>
<th>Dark Current Deflection (cms.)</th>
<th>Nett Deflection (cms.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0075</td>
<td>6.39</td>
<td>2.70</td>
<td>3.69</td>
</tr>
<tr>
<td>0.0195</td>
<td>10.28</td>
<td>2.81</td>
<td>7.47</td>
</tr>
<tr>
<td>0.0390</td>
<td>17.88</td>
<td>2.60</td>
<td>15.28</td>
</tr>
<tr>
<td>0.0584</td>
<td>25.12</td>
<td>2.91</td>
<td>22.21</td>
</tr>
<tr>
<td>0.0682</td>
<td>28.93</td>
<td>3.00</td>
<td>25.93</td>
</tr>
<tr>
<td>0.0779</td>
<td>32.42</td>
<td>2.99</td>
<td>29.43</td>
</tr>
</tbody>
</table>
(Fig. 28) passes through the origin and is perfectly linear up to deflections of 15 cms., after which there is a slight fall-off.

II Preparations.

(i) Triarylsilyl Fluorides

The Grignard reagent was prepared, generally on about a one-third molar scale, by adding the corresponding aryl bromide dissolved in five molar equivalents of ether, to dry magnesium turnings. After the addition the mixture was refluxed for 30 minutes.

\[ \text{ArBr + Mg = ArMgBr} \]

Ether (100 mls.) was added, and silicon tetrafluoride,\(^2\) generated from a mixture of sodium hexafluorosilicate (50 gms.), silica (10 gms.) and concentrated sulphuric acid (125 mls.), was bubbled slowly through the solution. After the gas ceased to be absorbed and two layers had separated, the mixture was refluxed for two hours.

\[ 3\text{ArMgBr + SiF}_4 = \text{Ar}_3\text{SiF} + 3\text{MgBrF} \]

It was poured onto dilute sulphuric acid to hydrolyse the excess Grignard reagent, and the triarylsilyl fluoride was extracted with ether. The ether extract was washed with dilute sulphuric acid, dilute sodium
carbonate solution and several times with water before drying with anhydrous sodium sulphate.

The solvent was distilled off and the crude product was fractionated at reduced pressure using a Vigreux column of about 10 theoretical plates. Solid products were recrystallised from light petroleum. The physical constants of the compounds are listed in Table 15.

The compounds were analysed for fluorine by titration of the hydrofluoric acid liberated from the compound by hydrolysis.

An aqueous/ethanolic solution of sodium hydroxide was standardised by titration with a standard solution of potassium hydrogen phthalate using phenolphthalein indicator.

A weighed amount of silicon fluoride was placed in a conical flask and a known volume of the sodium hydroxide solution was pipetted onto it. The mixture was then heated until the compound dissolved.

$$\text{Ar}_3\text{SiF} + \text{NaOH} = \text{Ar}_3\text{SiOH} + \text{NaF}$$

The remaining sodium hydroxide in the solution was then determined by back titration with the potassium hydrogen phthalate solution. The proportion of fluorine bound to silicon in the compound could then be determined from the results.
### Table 3.5. Physical Constants of Triarylsilyl Fluorides, (X-C₆H₄)₃SiF.

<table>
<thead>
<tr>
<th>X</th>
<th>M. pt.</th>
<th>B. pt.</th>
<th>Yield (%)</th>
<th>Analysis</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>62.5-63.5°</td>
<td>65</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>π-CH₃</td>
<td>109-110.5°</td>
<td>61</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-CH₃</td>
<td>nD°1.5822*</td>
<td>174°/4mm 75</td>
<td>5.93</td>
<td>5.90</td>
<td></td>
</tr>
<tr>
<td>π-CH₃O</td>
<td>74.5-75°</td>
<td>251°/2mm 50</td>
<td>5.16</td>
<td>5.27</td>
<td></td>
</tr>
<tr>
<td>m-CH₃O</td>
<td>81.1-82°</td>
<td>210°/4mm 49</td>
<td>5.16</td>
<td>5.01</td>
<td></td>
</tr>
<tr>
<td>π-Cl</td>
<td>78.7-80.2°</td>
<td>221°/3mm 60</td>
<td>4.98</td>
<td>5.16</td>
<td></td>
</tr>
<tr>
<td>m-Cl</td>
<td>nD°1.6118*</td>
<td>183°/2mm 49</td>
<td>4.98</td>
<td>4.98</td>
<td>3</td>
</tr>
<tr>
<td>π-t-C₆H₄</td>
<td>203-204.5°</td>
<td>210°/1mm 20</td>
<td>4.25</td>
<td>4.23</td>
<td></td>
</tr>
<tr>
<td>m-t-C₆H₄</td>
<td>nD°1.5498*</td>
<td>185°/1mm 42</td>
<td>4.25</td>
<td>4.16</td>
<td>4</td>
</tr>
<tr>
<td>π-(CH₃)₃Si</td>
<td>185.3-186.3°</td>
<td>206°/5mm 3.84</td>
<td>3.67</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>π-(CH₃)₃SiCH₂</td>
<td>124.5-125°</td>
<td>237°/4mm 56</td>
<td>3.54</td>
<td>3.42</td>
<td>5</td>
</tr>
<tr>
<td>π-C₆H₅</td>
<td>225-226°</td>
<td>280°/1mm 3.75</td>
<td>3.69</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

* Liquids, the refractive index is quoted.

**Notes**

1. Triphenylsilyl fluoride was prepared from the commercially available chloride and 40% aqueous hydrofluoric acid¹. Literature value of m.pt. 64°.
3. m-Bromochlorobenzene was prepared from m-chloroaniline by means of a Sandmeyer reaction.
4. m-Bromo-t-butylbenzene was prepared by the series of reactions described by Taylor."
5. p-Chlorophenyltrimethylsilane and p-chlorobenzyltrimethylsilane were prepared by the methods described by Parker. Recrystallised from toluene.

A convenient method of preparation from the aryl chloride when the corresponding bromo-compound is not readily available is the preliminary preparation of the organolithium reagent. This must then be converted into the Grignard reagent, a simple process requiring only the addition of magnesium bromide:

\[
\text{ArCl} + 2\text{Li} = \text{ArLi} + \text{LiCl}
\]

\[
\text{ArLi} + \text{MgBr}_2 = \text{ArMgBr} + \text{LiBr}
\]

before it is reacted with the silicon tetrafluoride, because the triarylsilyl fluoride is the desired product. The reaction between silicon tetrahalides and organolithium reagent produces tetraorganosilanes predominantly:
The tri-m-methyl, p-trimethylsilyl and p-trimethylsilylmethyl substituted triphenylsilyl fluorides were prepared by this method.

The organolithium reagent was prepared by adding an ether solution of the aryl chloride dropwise to a rapidly stirred mixture of small pieces of lithium metal in ether. After the addition the mixture was refluxed for 45 minutes.

Magnesium bromide was prepared by cautiously adding bromine dropwise to an excess of magnesium turnings under ether. After the addition the mixture was refluxed for 10 hours and kept overnight to remove the last traces of bromine.

The organolithium reagent was filtered into a dry flask and the magnesium bromide solution was filtered into it. White lithium bromide was immediately precipitated, and the resulting mixture was refluxed for 45 minutes to complete the reaction.

The resulting Grignard reagent was converted into triphenylsilyl fluoride by passing silicon tetrafluoride into it, as described above.
Tritiated water (5 mls., 1 curie) was shaken for a long period with a saturated solution of benzoic acid (122 gms. = 1 mole.) in ether in a dropping funnel. After equilibration, this solution was run slowly with stirring into an ether solution of diazomethane:7

\[
\begin{align*}
\text{C}_6\text{H}_5\text{COOH} + \text{THO} & \rightarrow \text{C}_6\text{H}_5\text{COOT} + \text{H}_2\text{O} \\
\text{C}_6\text{H}_5\text{COOT} + \text{CH}_2\text{Na} & \rightarrow \text{C}_6\text{H}_5\text{COOCH}_2\text{T} + \text{N}_2 \\
\text{C}_6\text{H}_5\text{COOCH}_2\text{T} + \text{NaOH} & \rightarrow \text{C}_6\text{H}_5\text{COONa} + \text{CH}_2\text{TOH}
\end{align*}
\]

After the addition most of the ether was slowly distilled off and the solution was cooled. A solution of sodium hydroxide (40 gms. = 1 mole.) was then added to hydrolyse the ester.

The solution was then slowly distilled until water started to come over. The distillate was then dried with sodium sulphate, and the supernatant liquid was fractionated from quicklime to separate the ether and methanol.

Yield (boiling range 62°-74°, b. pt., 64°),

\[
23.9 \text{ gms.} = 76\%.
\]

Theoretical activity = 20.1 millicuries/gm.

(iii) 1-Tritio-2-propanol.

Oleum (65% SO₃; 35 gms.) was added dropwise to tritiated water (5 mls., 1 curie) containing silver...
sulphate (5 gms.) cooled in an ice bath. This mixture was calculated to give 99% sulphuric acid.

\[ \text{THO} + \text{SO}_3 \rightarrow \text{THSO}_4 \]

\[ (\text{CH}_3)_2\text{CHOH} + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{CH}:\text{CH}_2 + \text{H}_2\text{O} \]

\[ \text{THSO}_4 + \text{CH}_3\text{CH}:\text{CH}_2 \overset{\text{Ag}^+}{\underset{15^\circ}{\rightarrow}} \text{CH}_3\text{CHOSO}_4 + \overset{200^\circ}{\underset{\text{H}_2\text{SO}_4}{\rightarrow}} \text{CH}_3\text{CHOHCH}_2\text{T} \]

Propene was generated by refluxing a mixture of concentrated sulphuric acid (100 mls.), water (50 mls.) and isopropyl alcohol (200 mls.) in a flask containing glass wool. The propene was passed through a soda-lime tower to remove water and sulphur dioxide, and through bubblers immersed in ice containing 5 mls. of concentrated sulphuric acid to cool and dry it. The propene was bubbled through the tritiated sulphuric acid at 15° ± 5° until absorption ceased. The mixture was then poured onto crushed ice (160 gms.) and shaken. It was distilled, the fraction boiling below 95° being collected.

The isopropyl alcohol-water azeotrope was dried with sodium sulphate and decanted off, washing the drying agent with ether. Cuprous chloride (5 gms.) was added to remove mercaptans, excess quicklime to remove water and sulphur dioxide, and xylene chaser. The mixture was fractionated, the fraction boiling from
81°-83° being collected (b. pt. 82.4°).

Yield 22.7 gms. = 92%

Theoretical activity = 21 millicuries/gm.

(iv) Triarylsilyl Tritiomethoxides and 1-Tritio-2-propoxides.

A 200% excess of tritium labelled alcohol was added to the triarylsilyl fluoride (ca. 5 gms.) in a dry 100 mls. flask. A piece of freshly cut sodium (200% excess) was added and the mixture was fused for 8 hours (24 hours in the preparation of the isopropoxides).

\[ 2ROH + 2Na = 2RONa + H_2 \]
\[ Ar_3SiF + RONa = Ar_3SiOR + NaF. \]

Light petroleum was added (benzene if the product was insoluble in petroleum), and after shaking the supernatant liquid was decanted onto acid saturated with salt to minimise emulsification. This mixture was shaken and separated, and the organic layer was washed with dilute sodium bicarbonate solution and several times with water before drying with sodium sulphate.

The solvent was distilled off and the product fractionated at reduced pressure; solid products were then recrystallised to constant melting point from light petroleum.
Table 16. Physical Constants of Triarylsilyl Methoxides, (X-C₆H₄)₃SiOCH₃.

<table>
<thead>
<tr>
<th></th>
<th>M. pt.</th>
<th>B. pt.</th>
<th>Analysis</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc.</td>
<td>Found</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>57-57.5°</td>
<td>197°/4mm</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>m-CH₃</td>
<td>51.7-52.7°</td>
<td>195°/1mm</td>
<td>C 79.46</td>
<td>79.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 7.27</td>
<td>7.31</td>
</tr>
<tr>
<td>m-CH₃</td>
<td>nD²0 1.5877*</td>
<td>160°/1mm</td>
<td>C 79.46</td>
<td>79.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 7.27</td>
<td>7.46</td>
</tr>
<tr>
<td>p-CH₃</td>
<td>78-78.6°</td>
<td>234°/3mm</td>
<td>C 69.44</td>
<td>69.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 6.36</td>
<td>6.62</td>
</tr>
<tr>
<td>m-CH₃</td>
<td>nD²0 1.5929*</td>
<td>191°/1mm</td>
<td>C 69.44</td>
<td>69.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 6.36</td>
<td>6.37</td>
</tr>
<tr>
<td>p-Cl</td>
<td>104.7-105°</td>
<td>204°/2mm</td>
<td>C 57.95</td>
<td>58.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 3.84</td>
<td>3.94</td>
</tr>
<tr>
<td>m-Cl</td>
<td>nD²0 1.6097*</td>
<td>202°/5mm</td>
<td>C 57.95</td>
<td>58.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 3.84</td>
<td>4.12</td>
</tr>
</tbody>
</table>

* Liquids, the refractive index is quoted

Notes

1 Literature value 63.6°-54.5°
2 Literature value 52°-53°

Finally, prior to kinetic measurements being made, liquids and recrystallised solids were gently distilled at low pressure in a microdistillation apparatus. This was found to remove silanols which accumulate, particularly in methoxides, during recrystallisation and storage. The compounds were kept in the ground-glass stoppered
Table 17. Physical Constants of Triarylsilyl Isopropoxides, \((X-C_6H_4)_3SiOCH(CH_3)_3\).

<table>
<thead>
<tr>
<th></th>
<th>M. pt.</th>
<th>B. pt.</th>
<th>Analysis</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>90-90.7°</td>
<td>203°/12mm</td>
<td>C 79.18 78.87</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 6.96 6.82</td>
<td></td>
</tr>
<tr>
<td>p-CH₃</td>
<td>48.8-49.8°</td>
<td>181°/4mm</td>
<td>C 79.95 79.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 7.83 7.96</td>
<td></td>
</tr>
<tr>
<td>m-CH₃</td>
<td>(n^0_2 1.5680^*)</td>
<td>160°/4mm</td>
<td>C 79.95 79.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 7.83 7.91</td>
<td></td>
</tr>
<tr>
<td>p-CH₃O</td>
<td>51.5-52.1°</td>
<td>226°/4mm</td>
<td>C 70.55 70.74</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 6.91 7.08</td>
<td></td>
</tr>
<tr>
<td>m-CH₃O</td>
<td>(n^0_2 1.5760^*)</td>
<td>202°/4mm</td>
<td>C 70.55 70.73</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 6.91 7.20</td>
<td></td>
</tr>
<tr>
<td>p-Cl</td>
<td>108-108.7°</td>
<td>210°/4mm</td>
<td>C 59.78 59.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 4.54 4.46</td>
<td></td>
</tr>
<tr>
<td>m-Cl</td>
<td>60-60.6°</td>
<td>209°/4mm</td>
<td>C 59.78 59.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 4.54 4.51</td>
<td></td>
</tr>
<tr>
<td>p-t-C₄H₉</td>
<td>136-136.5°</td>
<td>224°/5mm</td>
<td>C 81.42 81.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 9.52 9.55</td>
<td></td>
</tr>
<tr>
<td>m-t-C₄H₉</td>
<td>(n^0_2 1.5384^*)</td>
<td>213°/5mm</td>
<td>C 81.42 81.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 9.52 9.55</td>
<td></td>
</tr>
<tr>
<td>p-(CH₃)₃Si</td>
<td>150.4-151.4°</td>
<td>200°/5mm</td>
<td>C 67.33 67.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 8.66 8.45</td>
<td></td>
</tr>
<tr>
<td>m-(CH₃)₃SiCH₂</td>
<td>91.5-92°</td>
<td>255°/4mm</td>
<td>C 68.68 68.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 9.08 9.37</td>
<td></td>
</tr>
</tbody>
</table>

* Liquids, the refractive index is quoted.

Notes

1 Literature values, 88° (ref. 9) and 88-89°(ref.50).

2 Further purified by chromatography on an alumina column, 25x.8 cms.; eluting with light petroleum.
distillation flasks in a desiccator over silica gel, as a protection from atmospheric moisture.

Their physical constants are listed in tables 16 and 17.

Carbon and hydrogen analyses were carried out by Drs. Weiler and Strauss, Oxford.

III Kinetic Measurements.

The reaction vessels used for the kinetic measurements were E-mil standard flasks of 200 mls. capacity, with polythene stoppers. They were cleaned consecutively with alcohol, alcoholic sodium hydroxide solution, alcohol, water, chromic acid and water. They were then filled with water and allowed to stand at least 12 hours before use.

The reactions were carried out at $25^\circ \pm 0.02^\circ$ in a thermostatically controlled water bath. At measured time intervals 25 mls. aliquots of the reaction mixture were pipetted onto 25 mls. of scintillation solution in a 250 mls. separating funnel. Immediately an aqueous phase (150 mls.), the composition of which was adjusted to give subsequent rapid separation of the toluene and water layers, was added and the mixture was shaken to quench the reaction. The toluene layer was then washed.
free of radioactive alcohol and the solvent and cat-
ylant for the reaction; and dried in a 50 mls. conical
flask with anhydrous sodium sulphate.

The resulting solution then contained only the
unreacted radioactive triphenylsilyl alkoxide and the
non-radioactive reaction product dissolved in scint-
illation solution. Consequently, the concentration of

\[
\text{Ar}_3\text{SiOR}^\ast + \text{ROH} = \text{Ar}_3\text{SiOR} + \text{R}^\ast\text{OH}
\]

\[
\text{OR}^\ast = \text{OPr}^\dagger \text{ or } \text{OMe}, \quad \text{ROH} = \text{MeOH} \text{ or } \text{H}_2\text{O}
\]

the unreacted starting material could be determined by
measurement of the radioactivity of the solution.

To do this, 20 mls. of this solution was pipetted
into the cell, and the nett deflection due to its
tritium content was determined as described previously.
This procedure was carried out for all the aliquots,
to give a series of nett deflections for samples taken
at known times.

A correction was then applied to each of these
nett deflections. The reaction mixture was allowed to
react "completely," in practice for at least ten half-
lives, when an aliquot was taken out, treated as des-
cribed above, and its nett deflection determined. The
nett deflection for this sample was then subtracted
from all the others to give a series of corrected
deflections D. This is a small correction which is
thought to be due mainly to background radiation, particularly cosmic rays, passing through the scintillation solution. Its magnitude in most cases is the same as the nett deflection observed for the pure scintillation solution, but it does vary slightly from compound to compound.

Since the reactions were expected to be first order in triphenylsilyl alkoxide, a plot was made of log D versus time. The pseudo-first order rate constant \( k_1 \), at any given time, could then easily be deduced from the slope of the line at that point:

\[ k_1 = -2.303 \times \text{slope} \]

(i) Base Catalysed Hydrolysis of Triphenylsilyl Methoxide.

Acetone solvent for the reaction was prepared by standing May and Baker Ltd. reagent grade over potassium permanganate and anhydrous sodium sulphate for three days. The mixture was then filtered and distilled through a 10 inch Dufton column.

Carbonate free sodium hydroxide solution was prepared by dissolving reagent grade pellets in an equal weight of water. After the solution had cooled it was filtered through sintered glass and diluted with water which had been boiled free of gas and cooled in a
sealed flask.

The sodium hydroxide solution was standardised against dilute hydrochloric acid, which in turn had been standardised with recrystallised analytical reagent grade sodium tetraborate, using methyl red indicator.

The standard sodium hydroxide solution was diluted further as required, and 20 mls. of this diluted solution was pipetted into a clean reaction vessel, which had been washed out several times with purified acetone. It was then made up to 200 mls. with acetone, producing a solution containing 10% water by volume; a similar procedure was used to make up the solutions containing 20% water. The reaction vessel was then left immersed in the constant temperature bath.

To start the reaction, the triphenylsilyl methoxide was weighed out and dissolved in a few drops of acetone. This solution was introduced into the reaction vessel with a dropper, and the components were mixed rapidly by inversion. The first aliquot was taken out immediately.

During the extraction procedure the toluene layers were washed with 150 and 100 mls. of 0.01 N. sulphuric acid, followed by 100, 50, 50, and 25 mls. of water.
The acid prevented emulsification. The samples were then dried with anhydrous sodium sulphate prior to the tritium count being taken.

Given below are the sodium hydroxide concentration, weight of triphenylsilyl methoxide per 200 mls. of solution, time T (mins.), and observed corrected deflection D (cms.) for each run.

Reaction mixture: 10% water:90% acetone.

Run 1

| 1.78 x 10^-4 M | 0.07 gms |
| T | 0 | 240 |
| D | 15.57 | 15.52 |

Run 2

| 1.0 x 10^-3 M (incompletely soluble) | 0.07 gms |
| T | 0 | 360 |
| D | 14.61 | 14.46 |

Reaction mixture: 20% water:80% acetone.

The plots of log D versus time were curves. The quoted first order rate constants k, (mins^-1), were calculated from the slopes of the curves at T = 0 and at the half-life. All observations are given in full in run 3 as an example.
<table>
<thead>
<tr>
<th>Run 3</th>
<th>(1.76 \times 10^{-4}) M</th>
<th>0.04 gms</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0  30  60  90  1440</td>
<td></td>
</tr>
<tr>
<td>Observed deflection</td>
<td>15.97 11.50 9.99 9.40 8.76</td>
<td></td>
</tr>
<tr>
<td>Dark current deflection</td>
<td>7.87 8.17 8.33 8.48 8.66</td>
<td></td>
</tr>
<tr>
<td>Nett deflection</td>
<td>8.10 3.33 1.55 *92 *10</td>
<td></td>
</tr>
<tr>
<td>Corrected defln. (D)</td>
<td>8.00 3.23 1.56 *82</td>
<td></td>
</tr>
<tr>
<td>(\log D)</td>
<td>*903 *509 *193 *086</td>
<td></td>
</tr>
</tbody>
</table>

Initial \(k_1 = 3.57 \times 10^{-2}\) at \(T_\text{a} \), \(k_1 = 2.80 \times 10^{-2}\).

<table>
<thead>
<tr>
<th>Run 4</th>
<th>(1.32 \times 10^{-4}) M</th>
<th>0.04 gms</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0  30  60  90  120</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>8.54 5.68 4.13 3.28 2.61</td>
<td></td>
</tr>
</tbody>
</table>

Initial \(k_1 = 1.63 \times 10^{-2}\), at \(T_\text{a} \), \(k_1 = 9.06 \times 10^{-3}\)

<table>
<thead>
<tr>
<th>Run 5</th>
<th>(1.32 \times 10^{-4}) M</th>
<th>0.06 gms</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0  30  60  150  240</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>12.29 8.24 6.12 2.82 1.73</td>
<td></td>
</tr>
</tbody>
</table>

Initial \(k_1 = 1.475 \times 10^{-2}\), at \(T_\text{a} \), \(k_1 = 9.68 \times 10^{-2}\)

<table>
<thead>
<tr>
<th>Run 6</th>
<th>(1.32 \times 10^{-4}) M</th>
<th>0.06 gms</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0  30  90  120  150</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>8.88 6.16 3.68 2.99 2.53</td>
<td></td>
</tr>
</tbody>
</table>

Initial \(k_1 = 1.40 \times 10^{-2}\), at \(T_\text{a} \), \(k_1 = 8.14 \times 10^{-2}\)

<table>
<thead>
<tr>
<th>Run 7</th>
<th>(1.32 \times 10^{-4}) M</th>
<th>0.04 gms</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0  34  60  90</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>8.44 5.68 4.46 3.50</td>
<td></td>
</tr>
</tbody>
</table>

Initial \(k_1 = 1.37 \times 10^{-2}\)

Triphenylsilanol (0.02 gms/200 mls) added
From the difference in initial first order rate constants between runs 4 and 7 due to the addition of triphenylsilanol it is possible to calculate a value for the equilibrium constant for the interaction between triphenylsilanol and hydroxide ion in 20% water:

80% acetone at 25°C

\[
\text{Ph}_3\text{SiOH} + \text{OH}^- \rightleftharpoons \text{Ph}_3\text{SiO}^- + \text{H}_2\text{O}
\]

Conc. of NaOH added = 1.32 x 10^{-4} M.
Conc. of Ph₃SiOH added = 3.62 x 10^{-4} M.
Conc. of water = 20% = 11.1 moles/litre.
Initial \( k_i \) in run 4 = 1.63 x 10^{-2} mins⁻¹ ± 50%.
Initial \( k_i \) in run 7 = 1.37 x 10^{-2} mins⁻¹ ± 50%.

(Errors of 50% have been arbitrarily assigned to the rate constants, see p. 39.)

Reduction in initial \( k_i \) = 0.26 ± 1.5 x 10^{-2} mins⁻¹
Since \( k_i = k_B [\text{OH}^-] \) and \( k_B = 360 ± 20\% \) litres.moles⁻¹ mins⁻¹ (see pp. 40, 41), this reduction in \( k_i \) represents an apparent reduction in hydroxide ion concentration of

\[
\frac{(0.26 ± 1.50) \times 10^{-2}}{360 ± 20\%} = (7.2 ± 54) \times 10^{-3} \text{ moles./litre.}
\]

So \( K = \frac{[\text{Ph}_3\text{SiO}^-] [\text{H}_2\text{O}]}{[\text{Ph}_3\text{SiOH}][\text{OH}^-]} \)

\[
= \frac{(7.2 ± 54) \times 10^{-3} (11.1)}{(3.62 - 0.07 ± 54) \times 10^{-4} \times (1.32 - 0.07 ± 54) \times 10^{-4}}
\]

\[= 1800 ± 30000.\]
To determine the nature of the reaction products, an aliquot was taken after the solution had reacted for over ten half-lives, extracted into toluene and washed in the usual way. It was dried, and the toluene boiled off to give a white solid, m. pt. 151.5° - 152.5°.

Melting point of triphenylsilanol: 155°.
(11) Acid Catalysed Hydrolysis of Triphenylsilyl Methoxides.

A solvent mixture of 10% water:90% acetone was used for the kinetics. Dilute hydrochloric acid for this mixture was prepared by diluting concentrated reagent grade acid with boiled out distilled water. It was standardised, using phenolphthalein indicator, with a dilute sodium hydroxide solution which in turn had been standardised with analytical reagent grade potassium hydrogen phthalate.

Aliquots were washed with 150, 100, 100, 50, 50 and 25 mls. volumes of water, and dried.

The plots of log D versus time were straight lines, the quoted value of $k_i$ (mins$^{-1}$) being derived from the slope. The concentration of triphenylsilyl methoxide was 0.04 gms./200 mls. in all the runs.

Run 12 Conc. of HCl, $1.080 \times 10^{-4}$ M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>6.61</td>
<td>4.60</td>
<td>3.21</td>
<td>2.31</td>
<td>1.59</td>
</tr>
</tbody>
</table>

$k_i = 1.19 \times 10^{-2}$

Run 13 $9.13 \times 10^{-4}$ M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>6.81</td>
<td>5.32</td>
<td>4.03</td>
<td>3.06</td>
<td>2.32</td>
</tr>
</tbody>
</table>

$k_i = 0.925 \times 10^{-2}$
<table>
<thead>
<tr>
<th>Run 14</th>
<th>(0.540 \times 10^{-4}) M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0 60 120 180 240</td>
</tr>
<tr>
<td>D</td>
<td>9.27 6.68 4.96 3.64 2.68</td>
</tr>
<tr>
<td>(k_1)</td>
<td>(= 5.11 \times 10^{-2})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 15</th>
<th>(2.23 \times 10^{-4}) M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0 20 40 60 80</td>
</tr>
<tr>
<td>D</td>
<td>8.63 5.55 3.39 2.18 1.37</td>
</tr>
<tr>
<td>(k_1)</td>
<td>(= 2.31 \times 10^{-2})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 16</th>
<th>(1.69 \times 10^{-4}) M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0 30 60 90 120</td>
</tr>
<tr>
<td>D</td>
<td>12.26 6.94 4.05 2.28 1.29</td>
</tr>
<tr>
<td>(k_1)</td>
<td>(= 1.86 \times 10^{-2})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 17</th>
<th>(1.16 \times 10^{-4}) M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0 30 60 90 120</td>
</tr>
<tr>
<td>D</td>
<td>11.99 8.20 5.69 3.95 2.61</td>
</tr>
<tr>
<td>(k_1)</td>
<td>(= 1.24 \times 10^{-2})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 18</th>
<th>(0.388 \times 10^{-4}) M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0 120 300 480 660</td>
</tr>
<tr>
<td>D</td>
<td>9.67 6.49 3.57 2.17 1.24</td>
</tr>
<tr>
<td>(k_1)</td>
<td>(= 3.10 \times 10^{-2})</td>
</tr>
<tr>
<td>Run</td>
<td>Concentration (M)</td>
</tr>
<tr>
<td>-------</td>
<td>-------------------</td>
</tr>
<tr>
<td>19</td>
<td>0.139 x 10⁻⁴</td>
</tr>
<tr>
<td>20</td>
<td>2.08 x 10⁻⁴</td>
</tr>
<tr>
<td>21</td>
<td>0.207 x 10⁻⁴</td>
</tr>
<tr>
<td>22</td>
<td>1.29 x 10⁻⁴</td>
</tr>
<tr>
<td>23</td>
<td>1.29 x 10⁻⁴</td>
</tr>
</tbody>
</table>
Run 24  

\[ \frac{1\cdot99 \times 10^{-4}}{} \text{ M.} \]

\begin{align*}
T & \quad 0 \quad 20 \quad 40 \quad 60 \quad 80 \\
D & \quad 7\cdot89 \quad 5\cdot11 \quad 3\cdot40 \quad 2\cdot25 \quad 1\cdot46
\end{align*}

\[ k_1 = 2\cdot11 \times 10^{-2} \]

Acid catalysed hydrolysis of the trisubstituted compounds.

The aliquots were washed with 150, 100 and 100 mls. of calcium chloride solution (5 gms./litre) and 50, 50 and 25 mls. of water.

The specific rate constants \( k_A = k_1/[H^+] \) (litres. moles. 'mins.' ) are quoted for each run.

Tri-\( \mu \)-chlorophenylsilyl methoxide (\( \cdot 2 \) gms./200 mls.).

Run 25  

\[ 6\cdot39 \times 10^{-5} \text{ M.} \]

\begin{align*}
T & \quad 0 \quad 30 \quad 60 \quad 90 \quad 120 \\
D & \quad 5\cdot34 \quad 3\cdot62 \quad 2\cdot48 \quad 1\cdot71 \quad 1\cdot18
\end{align*}

\[ k_1 = 1\cdot26 \times 10^{-2}, \quad k_A = 197. \]

Run 26  

\[ 6\cdot825 \times 10^{-5} \text{ M.} \]

\begin{align*}
T & \quad 0 \quad 30 \quad 60 \quad 90 \quad 120 \\
D & \quad 8\cdot01 \quad 5\cdot31 \quad 3\cdot53 \quad 2\cdot25 \quad 1\cdot51
\end{align*}

\[ k_1 = 1\cdot36 \times 10^{-2}, \quad k_A = 199. \]
Run 27  \( 6.74 \times 10^{-5} \) M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.36</td>
<td>5.59</td>
<td>3.77</td>
<td>2.49</td>
<td>1.68</td>
</tr>
</tbody>
</table>

\( k_i = 1.33 \times 10^{-2}, \quad k_A = 198. \)

Run 28  \( 6.85 \times 10^{-5} \) M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>31</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.22</td>
<td>5.37</td>
<td>3.74</td>
<td>2.41</td>
<td>1.58</td>
</tr>
</tbody>
</table>

\( k_i = 1.36 \times 10^{-2}, \quad k_A = 199. \)

Average \( k_A = 198 \)

Tri-\( \pi \)-tolylsilyl methoxide (\( \cdot 2 \) gms./200 mls.)

Run 29  \( 1.63 \times 10^{-4} \) M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>6.60</td>
<td>4.48</td>
<td>2.97</td>
<td>1.90</td>
<td>1.30</td>
</tr>
</tbody>
</table>

\( k_i = 1.36 \times 10^{-2}, \quad k_A = 83.2 \)

Run 30  \( 1.72 \times 10^{-4} \) M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>7.04</td>
<td>4.77</td>
<td>3.14</td>
<td>2.02</td>
<td>1.32</td>
</tr>
</tbody>
</table>

\( k_i = 1.425 \times 10^{-2}, \quad k_A = 83.0 \)

Average \( k_A = 83.1 \).

Tri-\( \pi \)-anisylsilyl methoxide (\( \cdot 05 \) gms./200 mls.)

Run 31  \( 1.81 \times 10^{-4} \) M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.50</td>
<td>5.80</td>
<td>3.91</td>
<td>2.53</td>
<td>1.58</td>
</tr>
</tbody>
</table>

\( k_i = 1.375 \times 10^{2}, \quad k_A = 76.0 \)
Run 32  

$$1.79 \times 10^{-4} \text{ M.}$$

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>7.28</td>
<td>4.61</td>
<td>3.17</td>
<td>2.16</td>
<td>1.43</td>
</tr>
</tbody>
</table>

$$k_1 = 1.355 \times 10^{-2}, \quad k_A = 75.6$$

Run 33  

$$1.95 \times 10^{-4} \text{ M.}$$

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>31.5</th>
<th>60</th>
<th>90</th>
<th>121.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.01</td>
<td>5.05</td>
<td>3.24</td>
<td>2.08</td>
<td>1.29</td>
</tr>
</tbody>
</table>

$$k_1 = 1.50 \times 10^{-2}, \quad k_A = 77.0$$

Run 34  

$$1.76 \times 10^{-4} \text{ M.}$$

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>7.62</td>
<td>5.06</td>
<td>3.40</td>
<td>2.26</td>
<td>1.49</td>
</tr>
</tbody>
</table>

$$k_1 = 1.35 \times 10^{-2}, \quad k_A = 76.6$$

**Average** $$k_A = 76.3$$

**Tri-m-chlorophenylethyl methoxide (0.05 gms./200 mls.)**

Run 35  

$$9.985 \times 10^{-5} \text{ M.}$$

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.80</td>
<td>5.86</td>
<td>3.83</td>
<td>2.49</td>
<td>1.65</td>
</tr>
</tbody>
</table>

$$k_1 = 1.39 \times 10^{-2}, \quad k_A = 139$$

Run 36  

$$9.145 \times 10^{-3} \text{ M.}$$

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.83</td>
<td>6.01</td>
<td>4.20</td>
<td>2.79</td>
<td>1.91</td>
</tr>
</tbody>
</table>

$$k_1 = 1.274 \times 10^{-2}, \quad k_A = 139.3$$

**Average** $$k_A = 139$$
(iii) Base Catalysed Hydrolysis of Triphenylsilyl Isopropoxides.

Acetone solvent was prepared by standing commercial acetone over potassium permanganate, sodium hydroxide pellets and anhydrous sodium sulphate for several days. It was then filtered into a 2 litre flask and anhydrous calcium sulphate was added to complete the desiccation. After 24 hours it was distilled through a 10" Dufton column.

Aliquots from the reaction mixture were added to scintillation solution (25 mls.) and washed with 150, 100 and 100 mls. of 0.01 N sulphuric acid, and three times with 100 mls. volumes of water.

From a reaction mixture which had reacted to completion, an aliquot was taken, extracted into toluene solution and washed in the usual way. After drying, the solvent was taken off to give a white solid, m. pt. 149°-151°. After one recrystallisation from light petroleum, the melting point was 153.5°-155° (melting point of triphenylsilanol: 155°).

Conc. of triphenylsilyl isopropoxide, (0.02 gms/200 mls.)

<table>
<thead>
<tr>
<th>Run 37</th>
<th>No catalyst.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (days)</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>10.33</td>
</tr>
</tbody>
</table>
The log D versus time plots for the sodium hydroxide catalysed reactions were curves. The quoted values of $k_i$ (mins$^{-1}$) are calculated from the slopes of the curves at $T = -2$ mins., the time of mixing of the components.

Run 38

$\text{NaOH conc. } 2.57 \times 10^{-3} \text{ M.}$

<table>
<thead>
<tr>
<th>T (mins.)</th>
<th>0</th>
<th>30.5</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>9.47</td>
<td>6.70</td>
<td>4.87</td>
<td>3.60</td>
<td>2.71</td>
</tr>
</tbody>
</table>

$k_i = 1.16 \times 10^{-2}$

The production of triphenylsilanol in the reaction mixture may be compared with the apparent reduction in hydroxide ion concentration.

At $T = 0$, $k_i = 1.160 \times 10^{-2}$

At $T = 60$, $k_i = 1.037 \times 10^{-2}$

Since $k_i = k_g [\text{OH}^-]$ and $k_g = 4.70 \text{ litres.moles}^{-1}\text{mins}^{-1}$ (see p. 48) this reduction in $k_i$ represents an apparent reduction of hydroxide ion concentration of:

$$[\text{OH}^-]_0 - [\text{OH}^-]_t = \frac{(1.160 - 1.037) \times 10^{-2}}{4.70} = 2.62 \times 10^{-4} \text{ M.}$$

At $T = 0$, $D = 9.47 \equiv 1 \text{ gms/litre Ph}_3\text{SiOPr}$

At $T = 60$, $D = 4.87$. This represents a reduction of the triphenylsilyl isopropoxide (M. W. = 318), and a corresponding increase in the triphenylsilanol concentration of $\frac{1}{318} \times (9.47 - 4.87) = 1.53 \times 10^{-4} \text{ M.}$
After 120 minutes.

At $T = 0$, $k_1 = 1.160 \times 10^{-2}$

At $T = 120$, $k_1 = 9.37 \times 10^{-2}$

Then $[\text{OH}^-]_0 - [\text{OH}^-]_t = \frac{(1.160 - 9.37) \times 10^{-2}}{4.70} = 4.74 \times 10^{-4} \text{ M.}$

At $T = 0$, $D = 9.47$

At $T = 120$, $D = 2.71$

So $[\text{Ph}_3\text{SiOH}] = \frac{\frac{1}{318}}{9.47} (9.47 - 2.71) = 2.25 \times 10^{-4} \text{ M.}$

Run 39 \[3.46 \times 10^{-3} \text{ M.}\]

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>9.03</td>
<td>6.75</td>
<td>5.03</td>
<td>3.75</td>
<td>2.99</td>
</tr>
</tbody>
</table>

$k_1 = 1.625 \times 10^{-2}$

Run 40 \[0.930 \times 10^{-3} \text{ M.}\]

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>60</th>
<th>120</th>
<th>180</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.83</td>
<td>7.02</td>
<td>5.84</td>
<td>4.76</td>
<td>4.08</td>
</tr>
</tbody>
</table>

$k_1 = 3.99 \times 10^{-2}$

Run 41 \[0.439 \times 10^{-3} \text{ M.}\]

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>60</th>
<th>120</th>
<th>180</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>9.76</td>
<td>9.00</td>
<td>8.48</td>
<td>7.83</td>
<td>7.29</td>
</tr>
</tbody>
</table>

$k_1 = 1.27 \times 10^{-2}$
Comparison of the production of triphenylsilanol with
the apparent reduction of hydroxide ion concentration.

After 60 minutes.

At $T = 0$, $k_1 = 0.795 \times 10^{-2}$
At $T = 60$, $k_1 = 0.726 \times 10^{-2}$

Then $[OH^-]_0 - [OH^-]_t = (0.795 - 0.726) \times 10^{-2}$

$= 1.46 \times 10^{-4} \text{ M.}$

At $T = 0$, $D = 8.71 \equiv 0.1$ gms/litre $\text{Ph}_3\text{SiOH}$.
At $T = 60$, $D = 5.48$
So $[\text{Ph}_3\text{SiOH}] = 0.1 \times \frac{(8.71 - 5.48)}{318} = 1.17 \times 10^{-4} \text{ M}$

After 120 minutes

At $T = 0$, $k_1 = 0.795 \times 10^{-2}$
At $T = 120$, $k_1 = 0.691 \times 10^{-2}$

Then $[OH^-]_0 - [OH^-]_t = (0.795 - 0.691) \times 10^{-2}$

$= 2.21 \times 10^{-4} \text{ M.}$
At $T = 0$, $D = 6.71$
At $T = 120$, $D = 3.59$
So $[\text{Ph}_3\text{SiOH}] = \frac{1}{318} \times \frac{(6.71 - 3.59)}{8.71} = 1.85 \times 10^{-4}$ M.

<table>
<thead>
<tr>
<th>Run 44</th>
<th>$T$</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D$</td>
<td>9.64</td>
<td>7.68</td>
<td>6.27</td>
<td>5.16</td>
</tr>
<tr>
<td></td>
<td>$k_1$</td>
<td>$= \cdot784 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 45</th>
<th>$T$</th>
<th>0</th>
<th>29.5</th>
<th>59.5</th>
<th>89.5</th>
<th>119.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D$</td>
<td>7.06</td>
<td>5.59</td>
<td>4.39</td>
<td>3.44</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td>$k_1$</td>
<td>$= \cdot852 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 46</th>
<th>$T$</th>
<th>0</th>
<th>28</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D$</td>
<td>9.60</td>
<td>7.46</td>
<td>5.76</td>
<td>4.81</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td>$k_1$</td>
<td>$= \cdot864 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 47</th>
<th>$T$</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D$</td>
<td>8.56</td>
<td>6.64</td>
<td>5.28</td>
<td>4.21</td>
<td>3.29</td>
</tr>
<tr>
<td></td>
<td>$k_1$</td>
<td>$= \cdot864 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average $k_1$ (Runs 45–47) = $\cdot860 \times 10^{-2}$
Run 48  
\[1.91 \times 10^{-3} \text{ M.}\]

Added Triphenylsilanol (0.0429 gms/200 mls)

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.05</td>
<td>6.81</td>
<td>5.89</td>
<td>5.08</td>
<td>4.23</td>
</tr>
</tbody>
</table>

\[k_i = 0.565 \times 10^{-2}\]

Run 49  
\[1.91 \times 10^{-3} \text{ M.}\]

Added Triphenylsilanol (0.0559 gms/200 mls)

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>60</th>
<th>120</th>
<th>180</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>9.29</td>
<td>6.76</td>
<td>4.96</td>
<td>3.96</td>
<td>2.86</td>
</tr>
</tbody>
</table>

\[k_i = 0.553 \times 10^{-2}\]

From the differences in initial first order rate constant \(k_i\) between runs 45-47 and runs 48 and 49, due to the addition of triphenylsilanol, the equilibrium constant for the reaction

\[
\text{Ph}_3\text{SiOH} + \text{OH}^- \overset{K}{\rightleftharpoons} \text{Ph}_3\text{SiO}^- + \text{H}_2\text{O}
\]

may be calculated.

From Run 48.

Conc. of NaOH added = 1.91 \times 10^{-3} \text{ M.}

Conc. of Ph$_3$SiOH added = 7.77 \times 10^{-4} \text{ M.}

Conc. of water = 20\% = 11.1 \text{ moles/litre.}

Ave. initial \(k_i\) in runs 45-47 = 0.860 \times 10^{-2} \pm 1.5\%

Initial \(k_i\) in run 48 = 0.565 \times 10^{-2} \pm 1.5\%

Reduction in initial \(k_i\) = 0.295 \pm 0.021 \times 10^{-2}.

The error in the initial rate constants is based on
reproducibility, see p. 46.

Since \( k_{1} = k_{2}[\text{OH}^{-}] \) and \( k_{2} = 4.70 \pm 5\% \) (this theoretical error is arbitrary), this reduction in rate constant is equivalent to an apparent reduction of hydroxide ion concentration of

\[
\left( \frac{0.295 \pm 0.021}{4.70 \pm 0.22} \right) \times 10^{-2} = 6.27 \pm 0.71 \times 10^{-4} \text{ M}.
\]

So \( K = \frac{[\text{Ph}_{3}\text{SiO}^{-}][\text{H}_{2}\text{O}]}{[\text{Ph}_{3}\text{SiOH}][\text{OH}^{-}]} \)

\[
= \frac{(6.27 \pm 0.71) \times 10^{-4} \times (11.1)}{(7.77 - 6.27 \pm 0.71) \times 10^{-6} \times (19.1 - 6.27 \pm 0.71)}
\]

\[
= 36400 \pm 16000.
\]

From Run 49.

Conc. of NaOH added = 1.91 \times 10^{-3} \text{ M}.

Conc. of Ph_{3}SiOH added = 10.13 \times 10^{-4} \text{ M}.

Conc. of water = 11.1 \text{ M}.

Ave. initial \( k_{1} \) in runs 45-47 = \( 0.860 \times 10^{-2} \pm 1.5\% \)

Initial \( k_{1} \) in run 49 = \( 0.553 \times 10^{-2} \pm 1.5\% \)

Reduction in initial \( k_{1} \) = \( 0.307 \pm 0.021 \times 10^{-2} \).

This is equivalent to an apparent reduction of hydroxide ion concentration of

\[
\left( \frac{0.307 \pm 0.021}{4.70 \pm 0.22} \right) \times 10^{-2} = 6.53 \pm 0.80 \times 10^{-4} \text{ M}.
\]

So \( K = \frac{(6.53 \pm 0.80) \times 10^{-4} \times (11.1)}{(10.13 - 6.53 \pm 0.8) \times 10^{-6} \times (19.1 - 6.53 \pm 0.80)}
\]

\[
= 16000 \pm 9000.
\]
Base Catalysed Hydrolysis of the Substituted Compounds.

**Tri-m-tolylsilyl isopropoxide, (0.025 gms/200 mls)**

<table>
<thead>
<tr>
<th>Run 50</th>
<th>T</th>
<th>0</th>
<th>31</th>
<th>61</th>
<th>91</th>
<th>122</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td></td>
<td>4.53</td>
<td>4.02</td>
<td>3.63</td>
<td>3.23</td>
<td>2.89</td>
</tr>
</tbody>
</table>

\[ k_i = 3.99 \times 10^{-2} \]

<table>
<thead>
<tr>
<th>Run 51</th>
<th>T</th>
<th>0</th>
<th>60</th>
<th>120</th>
<th>180</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td></td>
<td>6.84</td>
<td>5.44</td>
<td>4.50</td>
<td>3.73</td>
<td>3.21</td>
</tr>
</tbody>
</table>

\[ k_i = 3.94 \times 10^{-2} \]

<table>
<thead>
<tr>
<th>Run 52</th>
<th>T</th>
<th>0</th>
<th>60</th>
<th>120</th>
<th>180</th>
<th>243</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td></td>
<td>8.92</td>
<td>7.15</td>
<td>5.72</td>
<td>4.85</td>
<td>4.05</td>
</tr>
</tbody>
</table>

\[ k_i = 3.92 \times 10^{-2} \]

**Average \( k_i = 3.95 \times 10^{-2} \), \( k_e = k_i/[\text{NaOH}] = 0.906 \).**

**Tris-p-trimethylsilylphenylsilyl isopropoxide, (0.025 gms/200 mls)**

<table>
<thead>
<tr>
<th>Run 53</th>
<th>T</th>
<th>0</th>
<th>32</th>
<th>60</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td></td>
<td>6.13</td>
<td>4.39</td>
<td>3.33</td>
<td>1.83</td>
</tr>
</tbody>
</table>

\[ k_i = 1.07 \times 10^{-2} \]

<table>
<thead>
<tr>
<th>Run 54</th>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td></td>
<td>6.00</td>
<td>4.38</td>
<td>3.25</td>
<td>2.41</td>
<td>1.75</td>
</tr>
</tbody>
</table>

\[ k_i = 1.06 \times 10^{-2} \]
<table>
<thead>
<tr>
<th>Run 55</th>
<th>T</th>
<th>0</th>
<th>31</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>5.99</td>
<td>4.35</td>
<td>3.21</td>
<td>2.37</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( = 1.065 \times 10^{-2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ave. ( k_1 )</td>
<td>( = 1.065 \times 10^{-2} ), ( k_8 = 2.45 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Tri-p-tolylsilyl isopropoxide, (0.03 gms/200 mls)**

**NaOH conc. = 1.750 \times 10^{-2} M.**

<table>
<thead>
<tr>
<th>Run 56</th>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>10.91</td>
<td>8.39</td>
<td>6.45</td>
<td>4.90</td>
<td>3.81</td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( = 0.878 \times 10^{-2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 57</th>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>9.03</td>
<td>6.98</td>
<td>5.31</td>
<td>4.11</td>
<td>3.11</td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( = 0.888 \times 10^{-2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 58</th>
<th>T</th>
<th>0</th>
<th>31.5</th>
<th>61</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>9.26</td>
<td>6.98</td>
<td>5.43</td>
<td>4.13</td>
<td>3.17</td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( = 0.896 \times 10^{-2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Ave. \( k_1 \) | \( = 0.887 \times 10^{-2} \), \( k_8 = 0.507 \) |

**Tri-p-anisylsilyl isopropoxide, (0.025 gms/200 mls)**

**NaOH conc. = 1.750 \times 10^{-2} M.**

<table>
<thead>
<tr>
<th>Run 59</th>
<th>T</th>
<th>0</th>
<th>31</th>
<th>90</th>
<th>120</th>
<th>151</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>7.73</td>
<td>6.46</td>
<td>4.59</td>
<td>3.84</td>
<td>3.27</td>
<td></td>
</tr>
<tr>
<td>( k_1 )</td>
<td>( = 0.575 \times 10^{-2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Run 60  
T  0  60  120  180  240  
D  8.10  5.63  4.03  2.84  2.00  
\[ k_1 = 5.84 \times 10^{-2} \]

Run 61  
T  0  30  60  92  120  
D  7.65  6.48  5.48  4.52  3.86  
\[ k_1 = 5.75 \times 10^{-2} \]
Ave. \[ k_1 = 5.75 \times 10^{-2} \], \[ k_B = 3.28 \].

Tri-p-trimethylsilylmethylphenylsilyl isopropoxide  
(0.03 gms/200 mls) \[ \text{NaOH conc. } = 1.750 \times 10^{-2} \text{ M.} \]

Run 62  
T  0  30  60  90  120  
D  6.34  5.91  5.49  5.07  4.71  
\[ k_1 = 2.38 \times 10^{-2} \]

Run 63  
T  0  66  120  180  240  
D  5.82  5.02  4.37  3.80  3.31  
\[ k_1 = 2.37 \times 10^{-2} \]
Ave \[ k_1 = 2.37 \times 10^{-2} \], \[ k_B = 1.35 \].

Tri-p-chlorophenylsilyl isopropoxide (0.03 gms/200 mls) \[ \text{NaOH conc. } = 1.090 \times 10^{-4} \text{ M.} \]

Run 64  
T  0  30  60  90  120  
D  8.86  7.33  6.46  6.10  5.79  
\[ k_1 = 8.25 \times 10^{-2} \]
<table>
<thead>
<tr>
<th>Run 65</th>
<th>T</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>4.92</td>
<td>4.29</td>
<td>3.93</td>
<td>3.75</td>
<td>3.61</td>
</tr>
<tr>
<td></td>
<td>$k_1 = \cdot 841 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ave. $k_1 = \cdot 833 \times 10^{-2}$, $k_b = 76.4$.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Tri-m-anisylsilyl isopropoxide (0.03 gms/200 mls)**

NaOH conc. $7.404 \times 10^{-4}$ M.

<table>
<thead>
<tr>
<th>Run 66</th>
<th>T</th>
<th>0</th>
<th>31</th>
<th>60</th>
<th>91</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>10.54</td>
<td>9.36</td>
<td>8.52</td>
<td>7.69</td>
<td>7.11</td>
</tr>
<tr>
<td>$k_1 = \cdot 418 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run 67

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>9.93</td>
<td>8.87</td>
<td>7.92</td>
<td>7.28</td>
<td>6.70</td>
</tr>
<tr>
<td>$k_1 = \cdot 417 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ave. $k_1 = \cdot 418 \times 10^{-2}$, $k_b = 5.65$

**Tri-p-t-butylphenylsilyl isopropoxide (0.05 gms/200 mls)**

NaOH conc. $1.778 \times 10^{-2}$ M.

<table>
<thead>
<tr>
<th>Run 68</th>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60.5</th>
<th>90.5</th>
<th>124.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>7.97</td>
<td>6.75</td>
<td>5.93</td>
<td>5.28</td>
<td>4.93</td>
</tr>
<tr>
<td>$k_1 = \cdot 614 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run 69

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>9.16</td>
<td>7.76</td>
<td>6.68</td>
<td>6.12</td>
<td>5.71</td>
</tr>
<tr>
<td>$k_1 = \cdot 616 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ave. $k_1 = \cdot 615 \times 10^{-2}$, $k_b = 0.346$. 


Tri-\textsubscript{m}-t-butyldiphenylisilyl isopropoxide (0.03 gms/200mls)

NaOH conc. \(1.778 \times 10^{-2}\) M.

Run 70
\begin{tabular}{lcccc}
T & 0 & 30 & 60 & 90.5 & 121 \\
D & 6.12 & 4.90 & 4.18 & 3.40 & 3.02 \\
\hline
\end{tabular}

\(k_1 = \cdot 798 \times 10^{-2}\)

Run 71
\begin{tabular}{lcccc}
T & 0 & 32 & 60 & 90 & 127 \\
D & 7.92 & 6.25 & 5.25 & 4.48 & 3.82 \\
\hline
\end{tabular}

\(k_1 = \cdot 801 \times 10^{-2}\)

Ave. \(k_1 = \cdot 800 \times 10^{-2}\), \(k_5 = \cdot 450\)

(iv) Acid Catalysed Hydrolysis of Triarylsilyl Isopropoxides.

The reaction medium was of the same composition for all the compounds; 20\% water: 80\% acetone containing \(1.24 \times 10^{-3}\) M. hydrochloric acid.

Aliquots were washed with 150, 100 and 100 mls. of dilute ammonium chloride solution (5 gms/litre) followed by three times 100 mls. of water.

The product of the hydrolysis of triphenylisilyl isopropoxide was determined by taking an aliquot from a reaction mixture which had reacted to completion, and adding to toluene. This solution was washed and dried in the same way as the other aliquots. The solvent was boiled off to leave a white solid, m. pt. 151\textdegree-152\textdegree. This was recrystallised once from light
petroleum, m. pt. 153·5°-155° (M. pt. triphenylsilanol (Ref 30) 155°).

All the graphs of log D versus time were straight lines, the quoted value of \( k_1 \) (mins\(^{-1}\)) being calculated from the slope.

**Triphenylsilyl isopropoxide** (0.02 gms/200 mls)

<table>
<thead>
<tr>
<th>Run 72</th>
<th>T</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>9.98</td>
<td>7.93</td>
<td>6.57</td>
<td>5.27</td>
<td>4.27</td>
</tr>
<tr>
<td></td>
<td>( k_1 = 1.05 \times 10^{-2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 73</th>
<th>T</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>8.95</td>
<td>7.52</td>
<td>6.17</td>
<td>4.98</td>
<td>4.05</td>
</tr>
<tr>
<td></td>
<td>( k_1 = 1.03 \times 10^{-2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 74</th>
<th>T</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>7.93</td>
<td>6.34</td>
<td>5.17</td>
<td>4.19</td>
<td>3.45</td>
</tr>
<tr>
<td></td>
<td>( k_1 = 1.04 \times 10^{-2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 75</th>
<th>T</th>
<th>0</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>9.31</td>
<td>6.13</td>
<td>4.94</td>
<td>3.98</td>
</tr>
<tr>
<td></td>
<td>( k_1 = 1.06 \times 10^{-2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ave. \( k_1 = 1.05 \times 10^{-2} \), \( k_A = \frac{k_1}{[HCl]} = 8.46 \text{ litres. moles.}^{-1} \text{ mins.}^{-1} \)

**Tri-\( \pi \)-chlorophenylsilyl isopropoxide** (0.025 gms/200 mls)
<table>
<thead>
<tr>
<th>Run 76</th>
<th>T</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>7.98</td>
<td>5.90</td>
<td>4.43</td>
<td>3.16</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td>$k_t$</td>
<td>$1.54 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 77</th>
<th>T</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>10.25</td>
<td>7.88</td>
<td>5.53</td>
<td>4.01</td>
<td>2.98</td>
<td></td>
</tr>
<tr>
<td>$k_t$</td>
<td>$1.55 \times 10^{-2}$, ave. $k_t = 1.545 \times 10^{-2}$.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tri-$\eta$-tolylsilyl isopropoxide (0.02 gms/200 mls)

<table>
<thead>
<tr>
<th>Run 78</th>
<th>T</th>
<th>0</th>
<th>30</th>
<th>62</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.14</td>
<td>6.41</td>
<td>5.03</td>
<td>4.06</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>$k_t$</td>
<td>$0.775 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 79</th>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90.5</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>11.25</td>
<td>8.90</td>
<td>7.08</td>
<td>5.54</td>
<td>4.40</td>
<td></td>
</tr>
<tr>
<td>$k_t$</td>
<td>$0.783 \times 10^{-2}$, ave. $k_t = 0.779 \times 10^{-2}$.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tri-$\eta$-anisylsilyl isopropoxide (0.025 gms/200 mls)

<table>
<thead>
<tr>
<th>Run 80</th>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>7.52</td>
<td>5.83</td>
<td>4.53</td>
<td>3.59</td>
<td>2.84</td>
<td></td>
</tr>
<tr>
<td>$k_t$</td>
<td>$0.811 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 81</th>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>9.03</td>
<td>7.22</td>
<td>5.70</td>
<td>4.39</td>
<td>3.46</td>
<td></td>
</tr>
<tr>
<td>$k_t$</td>
<td>$0.801 \times 10^{-2}$, ave $k_t = 0.806 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Tri-\text{-}m\text{-}anisylelsilyl isopropoxide

Run 82 (\text{\textbullet{0}}3\text{ gms/200 mls})

\begin{tabular}{c|ccccc}
T & 0 & 20 & 40 & 60 & 80 \\
D & 11.74 & 10.23 & 9.07 & 7.99 & 7.21 \\
\end{tabular}

\[ k_i = \cdot603 \times 10^{-2} \]

Run 83 (\text{\textbullet{0}}15\text{ gms/200 mls})

\begin{tabular}{c|ccccc}
T & 0 & 30 & 60 & 90 & 150 \\
D & 5.51 & 4.55 & 3.77 & 3.18 & 2.20 \\
\end{tabular}

\[ k_i = \cdot612 \times 10^{-2}, \text{ ave } k_i = \cdot608 \times 10^{-2} \]

Tri-\text{-}m\text{-}trimethylsilylel methylphenylsilyl isopropoxide

(\text{\textbullet{0}}35\text{ gms/200 mls})

Run 84 \ T \ 0 \ 30 \ 60 \ 91 \ 120 \\
D \ 7.61 \ 6.64 \ 5.83 \ 5.08 \ 4.43 \\

\[ k_i = \cdot446 \times 10^{-2} \]

Run 85 \ T \ 0 \ 30 \ 60 \ 120 \ 150 \\
D \ 7.28 \ 6.37 \ 5.51 \ 4.22 \ 3.62 \\

\[ k_i = \cdot455 \times 10^{-2}, \text{ ave } k_i = \cdot450 \times 10^{-2} \]

Tri-\text{-}m\text{-}chlorophenylelsilyl isopropoxide (\text{\textbullet{0}}25\text{ gms/200 mls})

Run 86 \ T \ 0 \ 20 \ 40 \ 60 \ 80 \\
D \ 9.42 \ 8.00 \ 6.77 \ 5.69 \ 4.88 \\

\[ k_i = \cdot824 \times 10^{-2} \]
Run 87 T 0 30 60 90 120
D 8.34 6.47 5.02 3.90 3.06
$k_1 = 0.844 \times 10^{-2}$, ave $k_1 = 0.834 \times 10^{-2}$

Tri-$\pi$-trimethylsilylphenylsilyl isopropoxide
(*035 gms/200 mls)

Run 88 T 0 30 60 180 300
D 9.68 8.97 8.31 6.28 4.68
$k_1 = 0.242 \times 10^{-2}$

Run 89 T 0 60 180 300 360
D 7.53 6.61 4.95 3.66 3.20
$k_1 = 0.243 \times 10^{-2}$, ave. $k_1 = 0.243 \times 10^{-2}$

Tri-$\pi$-t-butylphenylsilyl isopropoxide (*05 gms/200 mls)

Run 90 T 0 60 180 300 420
D 8.69 7.18 4.98 3.33 2.27
$k_1 = 0.323 \times 10^{-2}$

Run 91 T 0 120 240 360 480
D 8.16 5.67 3.89 2.62 1.79
$k_1 = 0.324 \times 10^{-2}$, ave. $k_1 = 0.324 \times 10^{-2}$

Tri-$\pi$-t-butylphenylsilyl isopropoxide (*05 gms/200 mls)

Run 92 T 0 110 230 350
D 7.99 4.89 3.12 1.94
$k_1 = 0.391 \times 10^{-2}$
Tri-\(\text{m}\)-tolylsilyl isopropoxide (0.03 gms/200 mls)

Run 94  
\begin{tabular}{cccccc}
T & 0 & 60 & 120 & 182 & 240 \\
D & 9.42 & 6.27 & 4.38 & 3.02 & 2.17 \\
\end{tabular}

\(k_1 = 0.595 \times 10^{-2}\)

(v) Base Catalysed Methoxyl Exchange of Triarylsilyl Methoxides.

A. Using Sodium Acetate Catalyst.

Methanol solvent was prepared by purifying the analytical reagent grade commercial material, first by shaking for four hours with anhydrous calcium sulphate and 3,5-dinitrobenzoic acid, and distilling. This was to effect a preliminary drying, and to remove basic impurities, amines and ammonia for example, from the methanol. Magnesium turnings (10 gms) were added to the distillate (2 litres). After reacting, the mixture was distilled through glass apparatus which had been washed with dilute acid and water and dried in an oven. During the distillation and during storage, in a Winchester fitted with a siphon, the system was protected from the atmosphere by drying tubes containing sodium hydroxide pellets, anhydrous magnesium per-
chlorate and activated alumina in series.

Anhydrous sodium acetate was prepared from the analytical reagent grade trihydrate. It was dried in an oven at 120° and then powdered and gently fused over the small flame of a microburner. As soon as it resolidified on cooling a small piece was chipped out and weighed in a stoppered weighing bottle.

The reaction vessels were dried in an oven and cooled in a vacuum. The methanol was added from a siphon and the sodium acetate was quickly transferred to the flask. The solution was left in the constant temperature bath to reach 25°.

Triphenylsilyl methoxide (0.04 gms.) was weighed out in a small sample tube, ca. 1 ml. capacity. To effect rapid dissolution of the silicon compound in the methanol, two drops of methanol were added to the compound and the mixture was heated until dissolved by placing the sample tube in a stoppered bottle in an oven. After cooling, the sample tube and its contents were added to the methanolic sodium acetate solution, and after mixing by inversion the initial aliquot was taken out.

The aliquots were pipetted onto scintillation solution (25 mls) as before, and washed with 150 mls.
of 0.005 N sulphuric acid containing 5 gms/litre of ammonium chloride (this was found to give a rapid separation of the toluene and water layers), and three times with 100 mls. of water; and dried.

The plots of log D versus time gave slight curves. The pseudo-first order rate constants (mins⁻¹) quoted were calculated from the slope of the curve at T = 0.

The concentrations of sodium acetate are given for each run.

<table>
<thead>
<tr>
<th>Run</th>
<th>Concentration</th>
<th>T</th>
<th>D</th>
<th>k₁</th>
</tr>
</thead>
</table>
| 95  | 0.983 x 10⁻³ M | 0     | 30   | 60   | 90   | 120
|     |               | 11.41 | 9.84 | 8.76 | 7.95 | 7.31
|     |               |       |      |      |      |     |
|     |               | ki = 0.53 x 10⁻² |
| 96  | 3.79 x 10⁻³ M  | 0     | 60   | 120  | 150  | 180 | 210 | 240
|     |               | 13.43 | 6.33 | 3.44 | 2.53 | 2.03 | 1.59 | 1.35
|     |               | ki = 1.32 x 10⁻² |
| 97  | 4.38 x 10⁻³ M  | 0     | 60   | 120  | 184  | 211 | 270
|     |               | 12.32 | 6.72 | 4.07 | 2.60 | 2.18 | 1.53
|     |               | ki = 1.07 x 10⁻² |
Run 98  \( 11.6 \times 10^{-3} \) M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.67</td>
<td>5.44</td>
<td>3.41</td>
<td>2.20</td>
<td>1.43</td>
</tr>
</tbody>
</table>

\[ k_1 = 1.66 \times 10^{-2} \]

Run 99  \( 17.5 \times 10^{-3} \) M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>7.81</td>
<td>4.12</td>
<td>2.35</td>
<td>1.49</td>
<td>.91</td>
</tr>
</tbody>
</table>

\[ k_1 = 3.39 \times 10^{-2} \]

Run 100  \( 23.6 \times 10^{-3} \) M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>13.25</td>
<td>7.72</td>
<td>4.42</td>
<td>2.81</td>
<td>1.83</td>
</tr>
</tbody>
</table>

\[ k_1 = 4.05 \times 10^{-2} \]

Run 101  \( 31.2 \times 10^{-3} \) M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>9.21</td>
<td>3.91</td>
<td>1.64</td>
<td>.85</td>
<td>.45</td>
</tr>
</tbody>
</table>

\[ k_1 = 5.96 \times 10^{-2} \]

Run 102  \( 37.1 \times 10^{-3} \) M.

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>10.59</td>
<td>4.60</td>
<td>2.11</td>
<td>1.06</td>
<td>.55</td>
</tr>
</tbody>
</table>

\[ k_1 = 5.85 \times 10^{-2} \]

B. Using Sodium Methoxide Catalyst.

The atmosphere was excluded from the reaction mix-
ture by using an atmosphere of nitrogen. Oxygen-free nitrogen was dried by passing through tubes containing sodium hydroxide pellets and magnesium perchlorate in series.

The reaction vessels were dried in an oven and blown out with nitrogen while cooling. This was repeated. After cooling finally, the flasks were filled with methanol from the siphon as nitrogen was blown into the flask through a drawn out glass tube.

Triphenylsilyl methoxide (20 gms.) was weighed out in a small sample tube which was added with its contents to the methanol. The reaction vessel was then placed in the water bath and left for the compound to dissolve and the solution to reach 25°C.

A solution of sodium methoxide in methanol was prepared by adding a piece of freshly cut sodium to purified methanol in a narrow necked flask stoppered with a rubber serum cap. This solution was standardised (0.02540 M) by titration with potassium hydrogen phthalate, using phenolphthalein indicator.

At the start of a run, sodium methoxide solution was taken from the flask with a Burroughs Wellcome and Co. Ltd. "Agla" Micrometer Hypodermic Syringe, needle type 214L, by piercing the cap, and a measured volume
was introduced into the reaction vessel. After shaking, the first aliquot was taken out.

Each time the reaction vessel was opened, to add catalyst or to take out an aliquot, nitrogen was blown in through a fine jet.

The plots of log \( D \) versus time were straight lines, \( k_i \) being calculated from the slope.

The concentration of sodium methoxide (moles/litre) and the first order rate constant \( k_i \) (\( \text{mins}^{-1} \)) are given for each run.

<table>
<thead>
<tr>
<th>Run 103</th>
<th>( \text{Concentration} = 3.81 \times 10^{-8} \text{ M.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0 16 32 120 260 380</td>
</tr>
<tr>
<td>D</td>
<td>6.97 6.89 6.13 4.98 3.56 2.21</td>
</tr>
<tr>
<td>( k_i )</td>
<td>( \approx 0.242 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 104</th>
<th>( \text{Concentration} = 7.61 \times 10^{-8} \text{ M.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0 60 120 180 240 300</td>
</tr>
<tr>
<td>D</td>
<td>10.36 7.72 5.55 4.22 3.05 2.21</td>
</tr>
<tr>
<td>( k_i )</td>
<td>( \approx 0.511 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 105</th>
<th>( \text{Concentration} = 10.16 \times 10^{-8} \text{ M.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0 45 90 135 180 226</td>
</tr>
<tr>
<td>D</td>
<td>9.90 6.71 4.73 2.99 2.00 1.33</td>
</tr>
<tr>
<td>( k_i )</td>
<td>( \approx 0.895 \times 10^{-2} )</td>
</tr>
</tbody>
</table>
Run 106  
12.19 x 10^{-8} M.

T  0  15  30  63  105  145  165
D  9.83 8.39 7.02 4.58 2.85 1.67 1.29

k_1 = 1.23 x 10^{-2}

Run 107  
21.59 x 10^{-8} M.

T  0  20  40  60  80
D  9.68 5.99 3.90 2.72 1.46

k_1 = 2.35 x 10^{-2}

Run 108  
25.40 x 10^{-8} M.

T  0  20  40  63  81
D  8.70 5.00 2.72 1.39 0.99

k_1 = 2.91 x 10^{-2}

The rates of exchange of the unsubstituted and
three substituted compounds were measured in methanol
containing 4.06 x 10^{-8} M. sodium methoxide.

A solution of this concentration was made up in
the reservoir, and dried reaction vessels were filled
and placed in the constant temperature bath. To start
the run, solutions of 0.15 gms of compound were prep­
ared as described above under sodium acetate catalysis
and added to the methanol. Tri-\textsubscript{m}-chlorophenylsilyl
isopropoxide was insufficiently soluble to be added in
this manner. It was finely powdered in its weighing
tube, and dissolved in the reaction mixture by occasional shaking.

The plots of log D versus time were straight lines; 

$k_i$ (mins$^{-1}$) was calculated from the slope and is given for each run.

**Triphenylsilyl methoxide.**

Run 109  T  0  120  240  360  480  600  
D  12.03  10.90  9.52  8.37  7.34  6.23  

$k_i = 1.095 \times 10^{-2}$

Run 110  T  0  120  240  360  540  660  
D  12.69  11.19  9.84  9.04  7.36  6.31  

$k_i = 1.08 \times 10^{-2}$

Ave. $k_i = 1.08 \times 10^{-2}$

**Tri-$m$-chlorophenylsilyl methoxide**

Run 111  T  0  15  30  55  70  
D  13.17  9.03  6.42  3.70  2.63  

$k_i = 2.24 \times 10^{-2}$

Run 112  T  0  20  40  60  80.5  
D  9.50  6.01  3.74  2.33  1.58  

$k_i = 2.22 \times 10^{-2}$, ave. $k_i = 2.23 \times 10^{-2}$.

**Tri-$m$-anisylsilyl methoxide.**
Run 113  T  0  120  240  360  480  
D  12.32  11.15  10.45  9.70  8.92  
\[ k_1 = 0.0676 \times 10^{-2} \]

Run 114  T  0  120  240  360  484  604  690  
D  10.36  9.53  8.81  8.04  7.41  6.75  6.35  
\[ k_1 = 0.0710 \times 10^{-2} \]
Ave. \( k_1 = 0.0693 \times 10^{-2} \)

**Tri-p-chlorophenylsilyl methoxide**

Run 115  T  0  14  25  36  48  60  
D  8.71  6.24  4.52  3.57  2.80  1.98  
\[ k_1 = 2.46 \times 10^{-2} \]

Run 116  T  0  15  32  45  60  75  
D  8.51  6.14  4.11  2.89  2.03  1.40  
\[ k_1 = 2.46 \times 10^{-2}, \text{ ave } k_1 = 2.46 \times 10^{-2} \]

The rates of exchange of the unsubstituted and three substituted compounds were measured in methanol containing \( 22.0 \times 10^{-3} \) M. sodium methoxide.

**Triphenylsilyl methoxide.**

Run 117  T  0  15  32  45  60  
D  11.53  8.12  5.32  3.93  2.70  
\[ k_1 = 2.45 \times 10^{-2} \]
Run 118 T 0 20 35 65 80
   D 10.69 6.56 4.58 2.37 1.52
   k₁ = 2.44 x 10⁻², ave. k₁ = 2.45 x 10⁻²

Run 119 Water (•1 mls/200mls) added.
   T 0 15 30 45 60
   D 11.73 8.15 5.65 3.92 2.79
   k₁ = 2.44 x 10⁻²

Tri-œ-anisylsilyl methoxide
Run 120 T 0 120 240 365 484
   D 16.33 10.40 6.70 4.20 2.65
   k₁ = 3.73 x 10⁻²

Run 121 T 0 120 240 365 484
   D 16.34 10.55 6.62 4.20 2.69
   k₁ = 3.73 x 10⁻², ave. k₁ = 3.73 x 10⁻²

Tri-œ-tolylsilyl methoxide
Run 122 T 0 45 90 137 180 225
   D 9.52 6.78 4.67 3.10 2.21 1.52
   k₁ = 8.33 x 10⁻²

Run 123 T 0 50 91 136 180
   D 10.47 7.04 5.09 3.56 2.56
   k₁ = 7.91 x 10⁻², ave. k₁ = 8.12 x 10⁻²
Tri-\textit{p}-tolylsilyl methoxide

Run 124 T 0 61 135 195 255
D 8.44 5.80 3.62 2.45 1.69
\[ k_4 = 6.34 \times 10^{-2} \]

Run 125 T 0 60 135 195 256
D 7.40 5.10 3.32 2.20 1.57
\[ k_4 = 6.26 \times 10^{-2}, \text{ ave. } k_4 = 6.30 \]

(vi) Acid Catalysed Methoxyl Exchange of Triarylsilyl Methoxides.

A. Using Benzoic Acid Catalyst.

Methanol solvent was prepared as described above.

Analytical grade benzoic acid was gently fused over a small flame to dry it, and poured into a stoppered weighing bottle. It was weighed and dissolved in methanol (0.0942 M).

Reaction vessels were dried by heating and evacuating, and filled with solvent by adding a measured volume of benzoic acid/methanol from a self-filling burette and diluting to 200 mls.

After the solution had reached 25°, the run was started by adding triphenylsilyl methoxide (0.04 gms) dissolved in 2 drops of methanol, as described above under sodium acetate catalysis.

Aliquots were pipetted onto scintillation solution
and washed with 150 mls. ammonium chloride solution (5 gms/litre) and three times with water (100 mls); and dried.

The plots of log D versus time were straight lines; \( k_i \) (mins\(^{-1}\)), calculated from the slope is given. The concentration of benzoic acid (moles/litre) in the reaction mixture is also quoted.

<table>
<thead>
<tr>
<th>Run</th>
<th>Concentration (M)</th>
<th>T</th>
<th>D</th>
<th>k (_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>126</td>
<td>2.17 x 10(^{-3})</td>
<td>0</td>
<td>60</td>
<td>1.35 1.65 1.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.23</td>
<td>3.39</td>
<td>1.59 1.14 0.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( k_i = 1.01 \times 10^{-2} )</td>
</tr>
<tr>
<td>127</td>
<td>4.55 x 10(^{-3})</td>
<td>0</td>
<td>31</td>
<td>60  90 111</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.94</td>
<td>4.86</td>
<td>2.84 1.70 1.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( k_i = 1.96 \times 10^{-2} )</td>
</tr>
<tr>
<td>128</td>
<td>7.11 x 10(^{-3})</td>
<td>0</td>
<td>15</td>
<td>31  46 60.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.18</td>
<td>6.20</td>
<td>3.83 2.62 1.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( k_i = 2.73 \times 10^{-2} )</td>
</tr>
<tr>
<td>129</td>
<td>11.83 x 10(^{-3})</td>
<td>0</td>
<td>15</td>
<td>30  45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.63</td>
<td>2.82</td>
<td>1.44 0.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( k_i = 3.90 \times 10^{-2} )</td>
</tr>
</tbody>
</table>
Run 130

<table>
<thead>
<tr>
<th>T</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>6.64</td>
<td>3.93</td>
<td>2.28</td>
<td>1.26</td>
<td>1.28</td>
</tr>
</tbody>
</table>

\[ k_1 = 3.55 \times 10^{-2} \]

B. Using Hydrochloric Acid Catalyst.

Methanol solvent was prepared as before.

Hydrogen chloride was generated from sodium chloride and concentrated sulphuric acid. The gas was bubbled from a drawn out glass tube through methanol in a narrow necked flask, and stoppered with a rubber serum cap. It was standardised (0.02035 M.) by titration with standard sodium hydroxide solution using phenolphthalein indicator.

A nitrogen atmosphere was used throughout. Hot reaction vessels were blown out with dry nitrogen and filled with methanol as described for sodium methoxide catalysis, and triphenylsilyl methoxide (20 gms.) was added. After the solution had reached 25°, the run was started by adding a measured volume of methanolic hydrogen chloride with a micrometer syringe.

The plots of log D versus time were slightly curved, \( k_1 \) decreasing with time. The \( k_1 \) (mins.\(^{-1}\)) quoted is calculated from the initial slope. In runs 131 - 133 \( k_1 \) increases with time. Here the value quoted is
based on the reaction which occurred between the first and second reading.

The concentration of acid is quoted.

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Reactant</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>131</td>
<td>No</td>
<td>Ph₃SiOMe</td>
<td>(°206 gms/200 mls)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T (hours)</td>
<td>0</td>
<td>33.5</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>12.24</td>
<td>8.98</td>
</tr>
<tr>
<td>k₁ = 1.55 x 10⁻⁴ mins⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Reactant</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>132</td>
<td>No</td>
<td>Ph₃SiOMe</td>
<td>(°090 gms/100 mls)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T (hours)</td>
<td>0</td>
<td>70</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>10.70</td>
<td>5.66</td>
</tr>
<tr>
<td>k₁ = 1.51 x 10⁻⁴ mins⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>133</td>
<td>3.05 x 10⁻⁶ M.</td>
</tr>
<tr>
<td></td>
<td>T (mins)</td>
</tr>
<tr>
<td>D</td>
<td>12.24</td>
</tr>
<tr>
<td>k₁ = 0.053 x 10⁻²</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>134</td>
<td>4.06 x 10⁻⁶ M.</td>
</tr>
<tr>
<td></td>
<td>T</td>
</tr>
<tr>
<td>D</td>
<td>12.15</td>
</tr>
<tr>
<td>k₁ = 0.703 x 10⁻²</td>
<td></td>
</tr>
</tbody>
</table>

Footnote: This value was not measured, but calculated from the initial concentration by comparison with that of the previous run. 10.70 = 12.24 x °090 x 200 / °206 / 100
The unsubstituted and four substituted compounds were solvolysed in methanol containing $4.97 \times 10^{-6}$ M. hydrochloric acid. All operations were conducted under nitrogen.

A reservoir of solvent was made up of this concentration, and dried reaction vessels were blown out with nitrogen and filled with the solution. The compound (15 gms.) was weighed out in a small tube and dissolved in two drops of methanol, as described above for sodium acetate catalysis. This was added to the solvent to start the run.

### Run 135

<table>
<thead>
<tr>
<th>T (min)</th>
<th>0</th>
<th>15</th>
<th>60</th>
<th>151</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (sec)</td>
<td>8.70</td>
<td>7.00</td>
<td>3.87</td>
<td>1.32</td>
<td>0.93</td>
</tr>
<tr>
<td>$k_1 = 1.44 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Run 136

<table>
<thead>
<tr>
<th>T (min)</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (sec)</td>
<td>9.85</td>
<td>6.33</td>
<td>4.21</td>
<td>2.92</td>
<td>2.22</td>
</tr>
<tr>
<td>$k_1 = 3.14 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Run 137

<table>
<thead>
<tr>
<th>T (min)</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>61</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (sec)</td>
<td>10.13</td>
<td>5.63</td>
<td>3.13</td>
<td>1.74</td>
<td>1.28</td>
</tr>
<tr>
<td>$k_1 = 3.92 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The plots of log $D$ versus time were slight curves, $k_i$ (mins$^{-1}$) quoted below being calculated from the initial slope.

### Triphenylsilyl methoxide.

<table>
<thead>
<tr>
<th>Run 138</th>
<th>T</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>14.31</td>
<td>10.78</td>
<td>8.41</td>
<td>6.57</td>
<td>5.13</td>
<td></td>
</tr>
<tr>
<td>$k_i$</td>
<td>$1.47 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 139</th>
<th>T</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>64</th>
<th>84</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>13.33</td>
<td>8.60</td>
<td>5.59</td>
<td>3.48</td>
<td>2.44</td>
<td></td>
</tr>
<tr>
<td>$k_i$</td>
<td>$2.21 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 140</th>
<th>T</th>
<th>0</th>
<th>25</th>
<th>45</th>
<th>65</th>
<th>85</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>13.14</td>
<td>10.09</td>
<td>8.18</td>
<td>6.87</td>
<td>5.82</td>
<td></td>
</tr>
<tr>
<td>$k_i$</td>
<td>$1.07 \times 10^{-2}$</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

### Tri-m-tolylsilyl methoxide.

<table>
<thead>
<tr>
<th>Run 141</th>
<th>T</th>
<th>0</th>
<th>60</th>
<th>120</th>
<th>180</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>9.50</td>
<td>5.13</td>
<td>3.32</td>
<td>2.47</td>
<td>2.02</td>
<td></td>
</tr>
<tr>
<td>$k_i$</td>
<td>$1.24 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run 142</th>
<th>T</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>11.28</td>
<td>9.63</td>
<td>8.24</td>
<td>7.25</td>
<td>6.26</td>
<td></td>
</tr>
<tr>
<td>$k_i$</td>
<td>$5.30 \times 10^{-2}$</td>
<td></td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>
Tri-$m$-tolylsilyl methoxide

Run 143  T  0  30  60  90  120  
D  7.90  6.22  5.00  4.10  3.46

$$k_1 = 7.95 \times 10^{-2}$$

Run 144  T  0  30  62  90  120  
D  8.04  5.79  4.18  3.17  2.39

$$k_1 = 1.14 \times 10^{-2}$$

Tri-$m$-anisylsilyl methoxide

Run 145  T  0  31  60  90  120  
D  9.48  6.66  4.89  3.68  2.89

$$k_1 = 1.15 \times 10^{-2}$$

Run 146  T  0  30  60  90  120  
D  8.88  6.38  4.61  3.51  2.68

$$k_1 = 1.12 \times 10^{-2}$$

Tri-$m$-anisylsilyl methoxide

Run 147  T  0  30  62  90  120  
D  16.37  13.92  11.47  10.10  9.08

$$k_1 = 6.10 \times 10^{-2}$$

Run 148  T  0  30  60  90  120  
D  18.10  17.42  16.72  15.84  15.31

$$k_1 = 1.46 \times 10^{-2}$$
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