

Nucleophilic Cleavage of the Silicon–Oxygen Bond: Acid-catalysed Hydrolysis of Tributylphenoxysilanes in Aqueous Organic Solvents

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The kinetics of acid-catalysed hydrolysis of tributylphenoxysilanes have been studied in aqueous dioxan, aqueous propan-2-ol, and aqueous acetonitrile. In aqueous dioxan, when allowance has been made for changes of acidity functions with solvent composition, the hydrolysis is shown to be at least second-order in water. Substituent effects are consistent with a mechanism involving fast protonation of the phenoxysilane followed by rate-limiting hydrolysis of the protonated species. The similarity of rates of hydrolysis in each solvent indicates that solvation differences between initial and transition states are either small or constant.

THERE have been a number of kinetic studies on the solvolysis of compounds of the type R_3MX ($R =$ alkyl or aryl; $M =$ Si or Ge; X includes halogeno, carboxylato, 2-pyridyl, hydrido, amino, phenylthio, and phenoxy), and the principal results have been reviewed recently.¹ The kinetics have generally been interpreted in terms of a bimolecular solvolysis reaction, similar to the S_N2 mechanism for nucleophilic substitution at carbon. There is no evidence that these reactions proceed *via* a cation (*e.g.* R_3Si^+) as in the S_N1 mechanism at carbon.

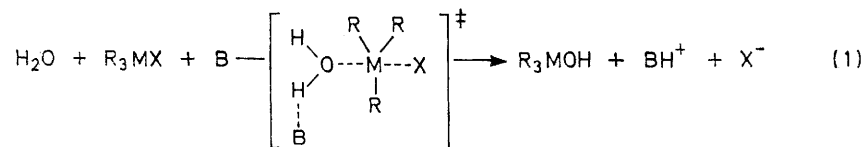
¹ R. H. Prince, M.T.P. International Reviews of Science: Inorganic Chemistry, Series One, ed. M. L. Tobe, Butterworths, London, 1972, vol. 9, p. 353.

The reaction scheme for hydrolysis can be written as in equation (1), where B is a base which can accept H^+ . When hydrolysis reactions are carried out in a protolytic solvent such as propan-2-ol the solvent itself can act as the base B . The reaction is then first-order with respect to R_3MX and almost first-order with respect to H_2O .^{2,3} Hydrolysis reactions in mixtures of water and organic solvents such as acetone, dioxan, and ether, which do not readily act as B , are first-order with respect to R_3MX and the order of reaction (n) with respect to H_2O varies

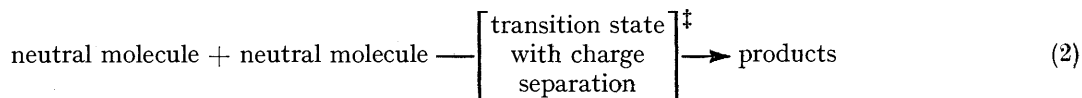
² R. H. Prince, *J. Chem. Soc.*, 1959, 1783.

³ R. H. Prince and R. E. Timms, *Inorg. Chim. Acta*, 1968, 2, 260.

between 1 and 6. These n values have been interpreted as evidence that water polymers are formed in these partly aqueous solvents, and that these polymers act both as nucleophile and as base B.³⁻⁶



The hydrolysis reactions which have been studied to find n values have all been of the charge type shown in equation (2). The rates of such reactions are very sensitive to the polarity of the solvent as there is a large



difference in solvation between the initial state and the transition state. n Values have not been measured for reactions of other charge types (e.g. positive ion + neutral molecule).^{*} There has been comparatively little work done on the mechanism of making and breaking Si-O bonds. The main work has been on the hydrolysis of organosilicon acetates, R_3SiOAc ,^{3,5,6,8} for which kinetics can be easily studied by titration of the acetic acid formed.

Åkerman^{9,10} has shown that hydrolysis of phenoxy-silanes, $\text{R}_3\text{SiOC}_6\text{H}_4\text{X}$ (R = alkyl, X = substituent) in aqueous ethanol is catalysed by H^+ and OH^- and obeys the rate equation (3), where k_a and k_b are the acid- and

$$\text{Rate} = (k_a[\text{H}^+] + k_{sp} + k_b[\text{OH}^-])[\text{R}_3\text{SiOPh}] \quad (3)$$

base-catalytic coefficients and k_{sp} is the rate coefficient for uncatalysed hydrolysis. For the acid-catalysed hydrolysis Åkerman proposed that R_3SiOPh was protonated to give $\text{R}_3\text{SiO(Ph)H}^+$; this was then hydrolysed to give $\text{R}_3\text{SiOH}_2^+$, which lost a proton to give R_3SiOH as product. The rate-limiting step was probably the hydrolysis of $\text{R}_3\text{SiO(Ph)H}^+$, although a slow initial protonation was not ruled out.

We have studied the kinetics of the acid-catalysed hydrolysis of tri-*n*-butylphenoxysilanes in organic solvents in order to compare the results with those for uncatalysed hydrolysis of Si-O bonds and for acid-catalysed hydrolysis of organic esters.

RESULTS AND DISCUSSION

Tributylphenoxysilane was chosen as a typical phenoxysilane which was easy to prepare and gave convenient hydrolysis rates. Under the conditions

^{*} In a recent study of the hydrolysis of trialkyl(phenylthio)silanes⁷ an n value of 1.51 was obtained in acidic (HCl) aqueous dioxan over the very limited range 1.32–2.7% H_2O .

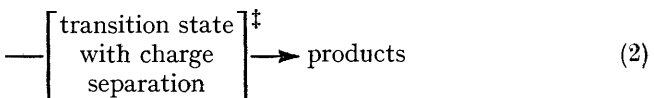
⁴ J. R. Chipperfield and R. H. Prince, *J. Chem. Soc.*, 1963, 3567.

⁵ R. H. Prince and R. E. Timms, *Inorg. Chim. Acta*, 1967, 1, 129.

⁶ R. H. Prince and R. E. Timms, *Inorg. Chim. Acta*, 1968, 2, 257.

used k_{sp} was very small in comparison with $k_a[\text{H}^+]$, and the rate equation could be written as equation (4). With HClO_4 or HCl as catalyst, hydrolysis rates were measured in aqueous dioxan, aqueous propan-2-ol, and

aqueous acetonitrile. Kinetics were studied under first-order conditions with acid concentrations at least ten times greater than $[\text{Bu}_3\text{SiOPh}]$. Values of k_a were calculated by dividing the observed first-order rate



$$\text{Rate} = k_a[\text{H}^+][\text{Bu}_3\text{SiOPh}] \quad (4)$$

$$\text{Rate} = k_1^{\text{obs}}[\text{Bu}_3\text{SiOPh}] \quad (5)$$

product, phenol, was characterised by its u.v. spectrum. The u.v. spectrum in the range 250–300 nm of a solution of Bu_3SiOPh after hydrolysis was compared with the

TABLE 1

Acid-catalysed hydrolysis of Bu_3SiOPh in aqueous dioxan: variation of k_a with temperature and with H_2O concentration ($[\text{acid}] = 0.01\text{M}$)

$t/^\circ\text{C}$	$[\text{H}_2\text{O}]/\%$ v/v	$k_a/1 \text{ mol}^{-1} \text{ min}^{-1} \text{ }^a$	$t/^\circ\text{C}$	$[\text{H}_2\text{O}]/\%$ v/v	$k_a/1 \text{ mol}^{-1} \text{ min}^{-1} \text{ }^a$
25.0	10	1.46	40.0	10	3.51
25.0	15	1.93	40.0	15	4.87
25.0	20	2.62	40.0	25	7.90
25.0	40	8.65	40.0	40	17.7
25.0	50	13.1	45.0	40	23.2
30.0	1	2.87	50.0	10	6.29
30.0	2	2.22	50.0	20	9.9
30.0	5	1.80	55.0	10	7.6
30.0	10	1.97	60.0	10	10.1
30.0	20	3.47	30.0	10	0.68 ^b
30.0	30	6.20	30.0	20	2.00 ^b
30.0	35	8.35	30.0	30	4.75 ^b
30.0	40	11.5	30.0	35	7.16 ^b
30.0	45	15.3	30.0	40	10.8 ^b
35.0	20	4.55	30.0	45	15.3 ^b
35.0	40	13.7			

^a HClO_4 used as catalyst except where otherwise indicated

^b HCl used as catalyst.

spectrum of an equimolar solution of phenol in the same solvent. The two spectra were identical in both shape and absorbance, which shows that phenol is one product and that the hydrolysis goes to completion. G.l.c. analysis showed that phenol and Bu_3SiOH were the only products.

There is considerable evidence that the Si-O bond

⁷ R. Danieli and A. Ricci, *J.C.S. Perkin II*, 1972, 1471.

⁸ G. Schott, H. Kelling, and R. Schild, *Chem. Ber.*, 1966, 99, 291; G. Schott and K. Deibel, *ibid.*, p. 301.

⁹ E. Åkerman, *Acta Chem. Scand.*, 1956, 10, 298.

¹⁰ E. Åkerman, *Acta Chem. Scand.*, 1957, 11, 373.

will be broken in the hydrolysis reaction and not the phenolic C-O bond. The acidic hydrolysis of dimethylbis-(*D*-1-methylpropoxy)silane gives butan-2-ol with the same optical configuration as the original 1-methylpropoxy-group.¹¹ The C-O bond in aryl ethers is stable to hydrolysis and the breakdown pattern of phenoxy-silanes in a mass spectrometer shows that under these

If protonation of Bu₃SiOPh takes place by reaction with an acid HA, rather than with H⁺ [equation (11)],



the rate of hydrolysis will be given by equation (12). Substitution of [H⁺]/K_a^{HA} for [HA]/A⁻ gives equation

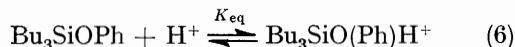
TABLE 2
Acid-catalysed hydrolysis of Bu₃SiOPh: variation of *k*_a with H₂O concentration in acetonitrile and propan-2-ol at 30.0° ([acid] = 0.01M)

[H ₂ O]/% v/v	1	2	5	10	20	30	40	50
<i>k</i> _a /l mol ⁻¹ min ⁻¹ in MeCN ^a	44.3		15.8	10.7	8.27	7.8	8.7	9.5
<i>k</i> _a /l mol ⁻¹ min ⁻¹ in Pr ⁱ OH ^b	2.65	3.60	4.10	3.70	3.30	3.23	3.30	

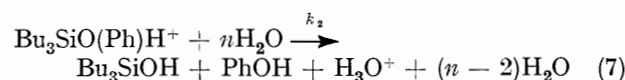
^a HCl catalyst. ^b HClO₄ catalyst.

conditions the Si-O bond is broken much more readily than the C-O bond.¹² Prince and Timms⁵ used ¹⁸O labelling to show that the Si-O bond and not the acyl C-O bond is broken in the hydrolysis of Ph₃SiOAc.

Uncatalysed hydrolysis reactions of chloro- and acetoxy-silanes have been explained in terms of reaction with *n* water molecules, possibly present as a polymer (H₂O)_{*n*},¹ and a possible scheme for acid-catalysed hydrolysis of phenoxy-silanes is shown in equations (6)



and (7). The protonation reaction (6) will be fast in



comparison with the hydrolysis (7), as no substantial electron reorganisation or change in hybridisation is required, and Bu₃SiOPh contains no internal hydrogen bonds. Compounds of the type R₃SiOPh are weak bases¹³ and *K*_{eq} will be small. This scheme leads to the rate equations (8) and (9), and the observed catalytic coefficient, *k*_a, is given by equation (10).

$$\text{Rate of hydrolysis} = k_2[\text{H}_2\text{O}]^n[\text{Bu}_3\text{SiO(Ph)H}^+] \quad (8)$$

$$= k_2K_{\text{eq}}[\text{H}^+][\text{H}_2\text{O}]^n[\text{Bu}_3\text{SiOPh}] \quad (9)$$

$$k_a = k_2K_{\text{eq}}[\text{H}_2\text{O}]^n \quad (10)$$

As expected from Åkerman's studies we found that the hydrolysis reaction was first-order in Bu₃SiOPh and in acid (up to 0.01M). Table I shows that HCl and HClO₄ are equally effective as catalysts in 45% aqueous dioxan, but that HCl is less effective at lower water concentrations. HClO₄ is completely ionised in aqueous dioxan. Electrochemical measurements show that HCl is completely ionised in 45% aqueous dioxan but is increasingly present as un-ionised molecules as water concentration decreases.¹⁴

¹¹ R. H. Kriehle and C. A. Burkhard, *J. Amer. Chem. Soc.*, 1947, **69**, 2689.

¹² G. E. Gould, Ph.D. Thesis, University of Hull, 1971.

¹³ N. A. Matwiyoff and R. S. Drago, *J. Organometallic Chem.*, 1965, **3**, 393.

(13), and *K*_{eq}^{HA}/*K*_a^{HA} is equal to *K*_{eq}, so equation (13)

$$\text{Rate} = k_2K_{\text{eq}}^{\text{HA}}[\text{H}_2\text{O}]^n[\text{Bu}_3\text{SiOPh}][\text{HA}]/[\text{A}^-] \quad (12)$$

$$= k_2K_{\text{eq}}^{\text{HA}}[\text{H}_2\text{O}]^n[\text{Bu}_3\text{SiOPh}][\text{H}^+]/K_{\text{a}}^{\text{HA}} \quad (13)$$

becomes identical with equation (9) and our results cannot distinguish between protonation by H⁺ or HA.

By analogy with studies on uncatalysed hydrolysis we would expect a graph of log *k*_a against log [H₂O] to be a straight line of slope *n*. Figure 1 shows that this is not

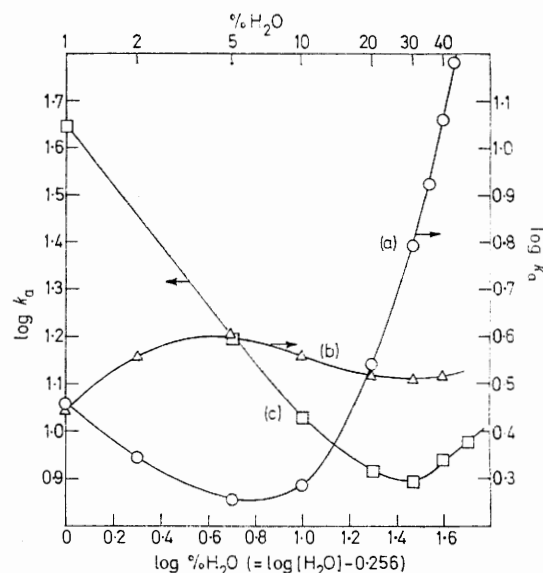


FIGURE 1 Acid-catalysed hydrolysis of Bu₃SiOPh in aqueous organic solvents at 30.0°; plots of log *k*_a against log [H₂O]; (a) dioxan, (b) propan-2-ol, (c) acetonitrile

so for any of the three solvents used. In aqueous dioxan over the range 30–40% water the slope is about 2, suggesting that 2 molecules of water are involved in the hydrolysis.

In equation (9) the equilibrium constant, *K*_{eq}, for the protonation of Bu₃SiOPh [equation (6)] has been expressed in terms of the concentrations of species present. In aqueous organic solvents activity co-

¹⁴ H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions,' 3rd edn., Reinhold, New York, 1958, ch. 11.

efficients are often far from unity and K_{eq} should be expressed as in equation (14), where S stands for

$$K_{eq} = c_{SH^+} f_{SH^+} / a_{H^+} \cdot c_S f_S \quad (14)$$

Bu_3SiOPh . Acidity functions h_0 have been measured in aqueous dioxan using substituted anilines as indicator.

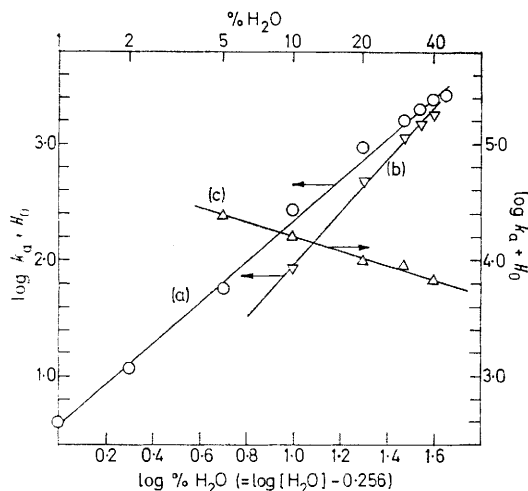


FIGURE 2 Plots of $\log k_a + H_0$ (at constant [acid]) against $\log [H_2O]$: (a) catalyst $HClO_4$, solvent aqueous dioxan; (b) catalyst HCl , solvent aqueous dioxan; (c) catalyst $HClO_4$, solvent aqueous propan-2-ol

If the ratio f_{SH^+}/f_S is the same as f_{inH^+}/f_{in} for the indicator, then K_{eq} can be expressed as in equation (15).

$$K_{eq} = c_{SH^+}/c_S \cdot h_0 \quad (15)$$

Substitution into equation (8) gives (16). By comparison with equation (4) we get (17), where c is the

$$\text{Rate of hydrolysis} = k_2 K_{eq} c_S h_0 [H_2O]^n \quad (16)$$

$$k_2 K_{eq} h_0 [H_2O]^n = k_a c \quad (17)$$

stoichiometric concentration of added acid. Taking logarithms in (17) gives (18). Hence for a constant

$$\log k_2 + \log K_{eq} - H_0 + n \log [H_2O] = \log k_a + \log c \quad (18)$$

concentration of catalyst, c , a plot of $\log k_a + H_0$ against $\log [H_2O]$ should be a straight line of slope n . Hammett acidity functions for $HClO_4$ in aqueous dioxan have been measured mainly for $c = 0.1M$, but the data show that h_0 is a linear function of c up to $0.1M$.^{15,16} Hence H_0 values for $c = 0.01M$ and $c = 0.1M$ differ only by a constant. Thus a plot of $\log k_a + H_0$ [where k_a was determined with $c = 0.01M$ ($HClO_4$) and H_0 refers to $0.1M$ - $HClO_4$] against $\log [H_2O]$ should have slope n .

A fairly linear plot is found from 1 to 45% dioxan with $n = 1.8$ (Figure 2). A similar plot using k_a with HCl

¹⁵ L. L. Leveson and C. W. Thomas, *J. Chem. Soc. (B)*, 1969, 1051; J. Koskikallio and A. Ervasti, *Acta Chem. Scand.*, 1962, **16**, 701.

¹⁶ C. W. Thomas and L. L. Leveson, *J.C.S. Perkin II*, 1973, 20.

¹⁷ E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1948, 1976.

¹⁸ H. Sadek and F. Y. Khalil, *Z. phys. Chem. (Frankfurt)*, 1968, **57**, 306.

as catalyst and acidity functions for HCl ^{17,18} is linear from 10 to 45% aqueous dioxan with $n = 2.2$. These n values of around 2 fit in well with results which show that acid-catalysed hydrolysis of carboxylic esters is second-order in water.¹⁹ One water molecule acts as nucleophile and the other helps to remove a proton from the transition state.

In hydrolysis reactions in aqueous organic solvents water can have a number of roles. It is a reactant, it contributes to the polarity of the medium, and it may be involved in specific solvent effects in the ground or transition states. Changes in hydrolysis rates of organo-silicon compounds with water concentration have been accounted for in terms of water as a reactant. As hydrolysis rate is proportional to $[H_2O]^n$, n molecules of water, possibly present as water polymers, are presumed to be reactant. This treatment does not consider polarity changes in the solvent. A reaction between neutral molecules is strongly accelerated by increase in solvent polarity, and equations similar to (19) (p and q

$$\log k = p(\epsilon - 1)/(2\epsilon + 1) + q \quad (19)$$

are constants; ϵ is the dielectric constant of the medium) can account for variations of rate with solvent changes.²⁰ Over the range 5–40% aqueous dioxan a graph of $\log [H_2O]$ against $(\epsilon - 1)/(2\epsilon + 1)$ is a straight line. This leads to the situation where the data of Prince and Timms on the hydrolysis of Pr_3SiOAc over the range 5–25% aqueous dioxan can be expressed either as (20) or (21). In equation (21) the role of water as a reactant

$$\log k = 4.4 \log [H_2O] - 8.3 \quad (20)$$

$$\log k = 24.6(\epsilon - 1)/(2\epsilon + 1) - 13.3 \quad (21)$$

is completely ignored. It would seem reasonable to account for the data with a composite equation containing terms for polarity and $[H_2O]$.

In acid-catalysed hydrolysis, where the charge type of the reaction is 'positive ion + neutral molecule,' the rate should decrease slightly with increase in solvent polarity. Ingold²¹ reports a ten-fold retardation in the reaction of Me_3S^+ with NMe_3 when changing from ethanol ($\epsilon = 24$) to water ($\epsilon = 80$). If we assume that change in solvent polarity will lower k_2 by a factor of about 10 as water content increases from 5 to 40% in aqueous dioxan, the observed $k_a^{40\%}/k_a^{5\%}$ value of 6.5 would increase to about 65 if the effect of solvent polarity is eliminated. A plot of $\log k_a + H_0$ (at constant acid concentration) against $\log [H_2O]$ has a slope of about 3 when k_a values are used in which the effect of solvent polarity has been removed. This indicates that 3 molecules of water are involved in reaction (7). Separation of the roles of water as reactant and as a contributor

¹⁹ A. J. Kirby, in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 10, p. 106.

²⁰ I. A. Koppel and V. A. Palm, 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, ch. 5.

²¹ C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 2nd edn., Bell, London, 1969, pp. 457–463.

to the polarity of the solvent is difficult as n can be made greater than 3 if increasing the solvent polarity is considered to retard reaction sufficiently. Reaction (7) involves at least two molecules of water, but additional water molecules may participate.

Values of k_a are almost constant between 1 and 40% aqueous propan-2-ol. Acidity functions for HClO_4 in aqueous propan-2-ol have not been measured, but as H_0 values for HCl and HClO_4 behave in a similar way with variation of water concentration in aqueous dioxan, H_0 values for 0.01M-HCl in aqueous propan-2-ol may be used as an approximation.²² A plot of $\log k_a + H_0$ (at constant acid concentration) against $\log [\text{H}_2\text{O}]$ is a straight line over the range 5–40% aqueous propan-2-ol with a slope of -0.6 . If one molecule of water is a reactant (the minimum requirement assuming that H^+ is removed from the transition state by solvent rather than by another water molecule) the plot of $\log k_a + H_0$ against $\log [\text{H}_2\text{O}]$ should have a slope of 1. For this to be so the value of $k_a^{40\%}/k_a^{5\%}$ should be 23, and not 0.8 as measured. A 29-fold retardation of rate as the solvent changes from 5% ($\epsilon = 19$) to 40% ($\epsilon = 37$) is reasonable.

Although H_0 values for 0.01M-HCl in aqueous acetonitrile are not available, it is likely that H_0 varies with solvent composition in a similar way to that seen in aqueous dioxan, and changes of k_a with water concentration can be accounted for in the same way.

Bunnett²³ derived the relationship (22) for acid-catalysed hydrolysis in strong acids where a_w is the

$$H_0 + \log k = \text{constant} + w \log a_w \quad (22)$$

activity of water in the solution, and w , the slope of a graph of $\log k + H_0$ against a_w , can be related to the mechanism of the hydrolysis reaction. The equation was derived for aqueous solutions but it has been applied to hydrolyses in aqueous dioxan.¹⁶ However, using our data, together with water activities in aqueous dioxan,²⁴ we find that a plot of $\log k_a + H_0$ against a_w is not linear and no conclusions can be drawn about mechanism.

Table 3 shows that there is a very small isotope effect

TABLE 3

Acid-catalysed hydrolysis of Bu_3SiOPh in D_2O -dioxan: variation of k_a with temperature, and with D_2O concentration ($[\text{HClO}_4] = 0.01\text{M}$)

$t/^\circ\text{C}$	$[\text{D}_2\text{O}]/\%$ v/v	$k_a^{\text{D}}/$ $\text{l mol}^{-1} \text{ min}^{-1}$	$k_a^{\text{H}}/k_a^{\text{D}}$
30.0	40	11.1	1.04
35.0	40	13.4	1.02
40.0	15	4.18	1.17
40.0	20	6.22	
40.0	25	7.8	1.02
40.0	40	17.2	1.03
45.0	40	20.5	1.13

if D_2O is used in place of H_2O . D^+ in D_2O is a stronger acid than H^+ in H_2O by a factor of 3 and hence K_{eq} should be increased to give $k_a^{\text{D}}/k_a^{\text{H}}$ a value of about 3. A value of $k_a^{\text{D}}/k_a^{\text{H}}$ of 1.5 has been measured for the acid-catalysed hydrolysis of some organic esters and this has

²² A. R. Tourky, A. A. Abdel-Hamid, and I. Z. Slim, *Z. phys. Chem. (Leipzig)*, 1972, **250**, 61.

been attributed to D_2O being a weaker nucleophile than H_2O , thus reducing $k_a^{\text{D}}/k_a^{\text{H}}$.²⁵ In addition, if the removal of a proton from the transition state by H_2O is involved in the rate-limiting step (as indicated from the order of reaction), the poorer proton-accepting ability of D_2O as compared with H_2O will also tend to decrease $k_a^{\text{D}}/k_a^{\text{H}}$.

For the three solvents studied the values of k_a at 30° in 40% aqueous solvent are: dioxan, 11.5 $\text{l mol}^{-1} \text{ min}^{-1}$; acetonitrile, 8.7 $\text{l mol}^{-1} \text{ min}^{-1}$; propan-2-ol, 3.3 $\text{l mol}^{-1} \text{ min}^{-1}$. This order changes slightly with $[\text{H}_2\text{O}]$ but the remarkable feature is the small range of k_a values found. These are consistent with the small solvent effects expected for a reaction between a positively charged ion and a neutral molecule, where there is little change in charge separation between the initial state and the transition state, and consequently only a small change in the number of molecules used in solvation.

The effect of a substituent X upon the rate of hydrolysis of $\text{Bu}_3\text{SiOC}_6\text{H}_4\text{X}$ is shown in Table 4, which contains

TABLE 4

Hydrolysis of substituted tributylphenoxysilanes, $\text{Bu}_3\text{SiOC}_6\text{H}_4\text{X}$, in 40% v/v aqueous dioxan at 30.0° ($[\text{HClO}_4] = 0.01\text{M}$)

X	λ/nm	$10^2 k_{\text{sp}}/$ min^{-1}	$k_a/$ $\text{l mol}^{-1} \text{ min}^{-1}$	k_a^{rel}
<i>p</i> -OMe	305	< 0.01	23.58	2.05
<i>p</i> -Me	280		15.62	1.36
<i>o</i> -Me	283		4.18	0.365
<i>p</i> - $[\text{CH}_2]_5\text{CH}$	286		10.97	0.954
H	280		11.50	1.00
<i>p</i> -F	293		11.70	1.02
<i>p</i> -CHO	293	1.00	4.73	0.411
<i>m</i> -CHO	325	0.02	7.60	0.660
<i>p</i> -Ph	295	< 0.01	9.14	0.795
<i>p</i> -CN	280	1.48	5.18	0.450
<i>p</i> -NO ₂	280	17.6	5.61	0.488
<i>o</i> -NO ₂	290	7.20	6.24	0.543
<i>p</i> -CO ₂ Et	285	0.09	5.20	0.452

values of k_a^{rel} (k_a values with respect to k_a for X = H) measured in 40% aqueous dioxan. Values of n are independent of X in this solvent within experimental error ($n = 2.4$ and 2.6 for X = H and *p*-NO₂, respectively) and k_a^{rel} values can be used to show the effect of X on k_2 and K_{eq} . Electron release by X should enhance K_{eq} and decrease k_2 . As k_a^{rel} decreases when X is electron-attracting, the effect of X upon K_{eq} outweighs its effect on k_2 . The small range of k_a^{rel} values implies either that the effects of X upon K_{eq} and k_2 almost cancel out for all substituents, or perhaps that the reactions are as insensitive to substituent changes as they are to solvent changes.

ortho- and *para*-Methyl substituents should have similar electronic effects upon the basicity of the phenolic oxygen atom and so change K_{eq} equally. The value of k_2 will probably be lowered by the *ortho*-methyl group as a result of steric hindrance in addition to its electronic properties, which should be similar to those in the *para*-methyl compound. There should be no steric effects

²³ J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, *et seq.*

²⁴ A. L. Vierk, *Z. anorg. Chem.*, 1950, **261**, 283.

²⁵ M. L. Bender, *Chem. Rev.*, 1960, **60**, 53.

upon K_{eq} in view of the small size of a proton. The value of k_a^{rel} for $X = o\text{-Me}$ (0.36) is lower than that for $X = p\text{-Me}$ (1.36), which confirms that reaction (7) is the rate-limiting step. The value of k_a^{rel} for 1-naphthoxy-silane is low (0.26) and probably arises from a lowering of k_2 by the large 1-naphthoxy-group. Plots of $\log k_a^{\text{rel}}$ against Hammett σ or σ^- constants are curved, as often found for reactions with more than one step.²⁶

Values of k_{sp} increase rapidly as X becomes more electron-withdrawing,²⁷ and for $p\text{-NO}_2\text{C}_6\text{H}_4\text{OSiBu}_3$ the rates of acid-catalysed ($[\text{H}^+] = 10^{-2}\text{M}$) and uncatalysed hydrolysis are similar. Table 5 shows the values of

TABLE 5

Values of k_{sp} and k_a for the hydrolysis of $p\text{-NO}_2\text{C}_6\text{H}_4\text{OSiBu}_3$ in aqueous dioxan and in aqueous propan-2-ol at 30.0° ($[\text{HClO}_4] = 0.01\text{M}$)

[H ₂ O]/% v/v	Aqueous dioxan			Aqueous propan-2-ol		
	30	35	40	20	30	40
10 ² k_{sp} /min ⁻¹	4.99	9.44	17.6	8.73	11.8	15.5
k_a /l mol ⁻¹ min ⁻¹	2.65	3.96	5.61	2.5	2.4	2.5

k_a and k_{sp} found. The slopes of graphs of $\log k_a$ and $\log k_{\text{sp}}$ against $\log [\text{H}_2\text{O}]$ over the range 30–40% aqueous dioxan give n values of 2.6 and 4.4, respectively. The value of 4.4 agrees well with values found for other uncatalysed hydrolysis reactions of silanes, and $n = 2.6$ confirms that protonated phenoxides need fewer water molecules for hydrolysis. In propan-2-ol the value of n

effects of R are similar in acid-catalysed and uncatalysed reactions of R_3SiX .

The activation parameters obtained (Table 6) are fairly similar to those obtained by Prince and Timms in their study of the hydrolysis of organosilicon acetates in aqueous dioxan.⁵ They attributed the high negative ΔS^\ddagger values to the high ordering of water molecules in the transition state. The mechanism of hydrolysis of organosilicon compounds in aqueous organic solvents is similar to that of some organic compounds. Thus n values for the hydrolysis of triphenylsilyl acetate are similar to those for the hydrolysis of benzyl chloride, but ΔS^\ddagger for benzyl chloride is of a magnitude normally found for bimolecular reactions. Table 6 shows some activation data for several hydrolysis reactions in aqueous organic solvents. There must be a specific factor associated with silicon which gives rise to the high negative ΔS^\ddagger values. Silicon can raise its co-ordination number above 4 (expanding its octet of electrons) and also forms bonds to fluorine and oxygen which have enhanced strength because of $p_\pi\text{-}d_\pi$ bonding. Silicon will expand its octet most readily when it is surrounded by electronegative atoms. Thus SiF_4 will form adducts with amines whereas Me_4Si will not. In the ground state the silicon atom in a phenoxysilane will be bonded to three carbon atoms and one oxygen atom. In the transition state of the hydrolysis of a phenoxysilane there will be two oxygen atoms near to the silicon,

TABLE 6

Activation data for hydrolysis reactions

Compound	Catalyst	Solvent	ΔH^\ddagger / kcal mol ⁻¹	ΔS^\ddagger / cal mol ⁻¹ K ⁻¹
Bu_3SiOPh	HClO_4	10% } v/v H ₂ O-dioxan	10.3	-31.3
Bu_3SiOPh	HClO_4	20% } v/v H ₂ O-dioxan	9.6	-32.6
Bu_3SiOPh	HClO_4	40% } v/v H ₂ O-dioxan	8.4	-34.3
Bu_3SiOPh	HClO_4	40% } v/v D ₂ O-dioxan	7.4	-37.3
$\text{Bu}_3\text{SiO(1-naphthyl)}$	HClO_4	40% } v/v H ₂ O-dioxan	7.6	-39.5
Pr_3SiOAc	None	30% } v/v H ₂ O-dioxan	9.9 ^a	-44.5 ^a
EtOAc	HCl	40% v/v H ₂ O-acetone	15.7 ^b	-25.5 ^b
PhCH_2Cl	None	40% v/v H ₂ O-dioxan	20.3 ^c	-23.5 ^c
PhCH_2Cl	None	40% v/v H ₂ O-dioxan	20.1 ^c	-23.3 ^c

^a From ref. 5. ^b E. Tommila and A. Hella, *Ann. Acad. Sci. Fennicae, AII*, 1954, 53. ^c E. Tommila, E. Paakkala, U. K. Virtanen, A. Erva, and S. Varila, *Ann. Acad. Sci. Fennicae, AII*, 1959, 91.

(0.8) for uncatalysed hydrolysis is in good agreement with that (1.2) found for hydrolysis of Pr_3SiCl in propan-2-ol.² Only 1 molecule of water is required for hydrolysis as propan-2-ol itself can accept the proton [equation (1)]. For acid-catalysed hydrolysis in propan-2-ol, $n = 0$, as found for the unsubstituted phenoxysilane, and this value arises in a similar way.

The value of k_a for the HClO_4 -catalysed hydrolysis of Ph_3SiOPh in 40% aqueous dioxan at 30° is 3.13 l mol⁻¹ min⁻¹. The relative rate in comparison with the tributyl compound [$k_a(\text{Ph}_3\text{SiOPh})/k_a(\text{Bu}_3\text{SiOPh})$] is 0.27. This is fairly similar to the value of 0.17 obtained for the uncatalysed hydrolysis of acetates⁵ [$k(\text{Ph}_3\text{SiOAc})/k(\text{Bu}_3\text{SiOAc})$] and shows that steric and electronic

²⁶ H. H. Jaffé, *Chem. Rev.*, 1953, 53, 191.

²⁷ A. A. Humffray and J. J. Ryan, *J. Chem. Soc. (B)*, 1969, 1138.

those of the departing phenol and of the incoming water. In this situation octet expansion will be favoured (with respect to the ground state) and also more $p_\pi\text{-}d_\pi$ bonding is possible. There is kinetic evidence that nucleophilic substitution reactions at silicon proceed through a transition state in which bond making is slightly more advanced than bond breaking.²⁸ The transition state for silicon is thus more complicated (more than four σ -bonds; $p_\pi\text{-}d_\pi$ bonding) and it is possibly this which gives rise to the large negative ΔS^\ddagger values for reactions of silicon compounds.

Low ΔH^\ddagger values for uncatalysed hydrolysis of organosilicon chlorides and acetates have been explained by proposing that ΔH^\ddagger is composed of two terms, one for the enthalpy of formation of a water polymer, and a second

²⁸ C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960, p. 111.

for the enthalpy of activation for hydrolysis of the silicon compound by the water polymer. The two terms tend to cancel each other and lead to the low observed values. Table 7 shows that low ΔH^\ddagger values are found for both catalysed and uncatalysed hydrolysis of organosilicon compounds, where reactions probably involve different numbers of water molecules. The low ΔH^\ddagger values seem specific to reactions of silicon compounds and may arise from the energy of the transition state being lowered relative to the ground state by formation of more than four σ -bonds in the former, where bond formation is more advanced than bond breaking.

Debye-Hückel theory predicts that there should be no salt effect when one of the reactants is uncharged. However when salts are added to such reactions taking place in solvents less polar than water there is a linear dependence of the rate coefficient k according to equation (23),²⁹ where k_0 is the rate coefficient in the absence of

$$k = k_0(1 + b[\text{salt}]) \quad (23)$$

added salt and b is a constant. For Bu_3SiOPh in 40% aqueous dioxan at 30° there is a linear relationship between k_a and $[\text{NaClO}_4]$ up to 0.2M- NaClO_4 , with $b = 2.6 \text{ l mol}^{-1}$. This salt effect probably arises from the increased activity of HClO_4 which has been demonstrated on addition of salts to aqueous dioxan.³⁰

Overall the mechanism of acid-catalysed hydrolysis of phenoxysilanes is similar to that of acid-catalysed hydrolysis of organic esters, with additional features caused by silicon's ability to use $3d$ orbitals.

The base-catalysed hydrolysis of phenoxysilanes [equations (24) and (25)] has already been studied.^{9,10,27,31,32}



In alkaline solution $k_b[\text{OH}^-] \gg k_{sp}$ and rate equation (3) can be simplified to equation (26). No previous workers

$$\text{Rate} = k_b[\text{R}_3\text{SiOPh}][\text{OH}^-] \quad (26)$$

have studied the effect of variation of water concentration upon k_b , so we have made a few preliminary measurements which are given in Table 7. A graph of

TABLE 7

Base-catalysed hydrolysis of Bu_3SiOPh in aqueous dioxan at 30.0°: variation of k_b with H_2O concentration

$[\text{H}_2\text{O}]/\%$ v/v	15	20	25
$k_b/\text{l mol}^{-1} \text{ min}^{-1}$	3.76	4.75	5.25

log k_b against log $[\text{H}_2\text{O}]$ over the range 15–25% aqueous dioxan has a slope of about 0.65. There are formally no water molecules required for hydrolysis, as under experimental conditions $[\text{OH}^-] > [\text{R}_3\text{SiOPh}]$ and equilibrium (25) lies well over to the left. Values of n other than

²⁹ C. L. Perrin and J. Pressing, *J. Amer. Chem. Soc.*, 1971, **93**, 5705.

³⁰ J. P. H. Boyer, R. J. P. Corriu, and R. J. M. Perz, *Tetrahedron*, 1971, **27**, 5255.

³¹ R. L. Schowen and K. S. Latham, *J. Amer. Chem. Soc.*, 1966, **88**, 3795.

0 may arise either from a variation of activity coefficients of OH^- with water concentration, or from participation of water in the reaction, perhaps in assisting the removal of OPh^- from the activated complex. Values of n between 0 and 1 have also been found for the base-catalysed hydrolysis of ethyl acetate in aqueous dioxan.³³ We have measured the rates of base-catalysed hydrolysis of $\text{Bu}_3\text{SiOC}_6\text{H}_4\text{X}$ ($\text{X} = \text{H}$ or $p\text{-OMe}$) in aqueous dioxan. Table 8 shows the relative rates of

TABLE 8

Base-catalysed solvolysis of $\text{R}_3\text{SiOC}_6\text{H}_4\text{X}$: relative rates of solvolysis for $\text{X} = \text{H}$ and $\text{X} = p\text{-OMe}$ with change of solvent and R

R	Solvent	$t/^\circ\text{C}$	$k_b^{p\text{-OMe}}/k_b^{\text{H}}$	Ref.
Ph	MeOH	27.4	0.49	32
Bu	40% v/v H_2O -dioxan	30.0	0.53	
Et	40% v/v H_2O -EtOH	25.0	0.59	10

base-catalysed solvolysis for three systems. The almost constant value of $k_b^{p\text{-OMe}}/k_b^{\text{H}}$ is good evidence that there is no dramatic change of mechanism among these three systems, and consequently that there are no specific effects associated with the butyl groups.

EXPERIMENTAL

Tributylphenoxysilanes were prepared by the method of Larsson,³⁴ in which ethanol is distilled from a mixture of tributylethoxysilane and the phenol. For phenols containing electron-donating substituents a small piece of sodium (0.2 g) was added to the ethoxysilane-phenol mixture. This promoted the ionisation of the phenol, and accelerated the reaction. The products were purified by fractional distillation under reduced pressure followed by preparative g.l.c. The identity and purity of the products were confirmed by i.r., n.m.r., and mass spectroscopy and g.l.c. Purity was found to be about 97% before preparative g.l.c. and over 99% after. The main impurity was phenol, and no significant differences in rate coefficients were found between reactions of samples which had received g.l.c. purification, and those of samples which had not.

Triphenylphenoxysilane was prepared by stirring together at 120° for 4 h sodium (0.70 g, 0.03 g atom), phenol (30 g, 0.32 mol), and chlorotriphenylsilane (9.3 g, 0.03 mol). The cooled mixture was shaken with water, and the residue filtered off and extracted with light petroleum (b.p. 60–80°). Filtration (hot) and cooling yielded crystalline triphenylphenoxysilane. Hydrolysis gave Ph_3SiOH and PhOH , confirmed by t.l.c.

Dioxan was purified by boiling under reflux with sodium for 48 h. It was distilled from the sodium and then distilled from sodium a second time. Acetonitrile and AnalaR propan-2-ol were used without further purification, as g.l.c. analysis showed them both to be well over 99% pure.

Solutions of $x\%$ v/v aqueous solvent were made up by making x ml of water (containing HClO_4 or HCl at an appropriate concentration) up to 100 ml with solvent. The solvent (25 ml) was preheated to the temperature

³² R. L. Schowen and K. S. Latham, *J. Amer. Chem. Soc.*, 1967, **89**, 4677.

³³ Calculated from data in E. Tommila, A. Koivisto, J. P. Lyyra, K. Antell, and S. Heimo, *Ann. Acad. Sci. Fennicae, AII*, 1952, **47**.

³⁴ E. Larsson, *Chem. Ber.*, 1953, **86**, 1382.

required for the kinetic run. The liquid phenoxysilane (1 or 2 μ l) was then added from a Drummond Microcaps pipette, the mixture was shaken, and a 10 mm u.v. spectrophotometer cell was quickly filled. Optical density measurements were taken at suitable times with a Unicam SP 500 spectrophotometer fitted with a thermostatted cell holder. The wavelengths at which measurements were made are shown in Table 4. Apparent first-order rate coefficients, k_1^{obs} , were calculated in the usual way, and were reproducible to $\pm 3\%$. For phenoxysilanes contain-

ing strongly electron-attracting substituents k_{sp} [equation (1)] contributes substantially to the observed rate of hydrolysis; k_{sp} values were measured separately by hydrolysis in the appropriate acid-free solvent and suitable allowance was made in the calculation of k_a values (Table 4).

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