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SOLVOLYSIS OF ARYLDIMETHYLPHENOXYSILANES

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SUMMARY

The logarithms of the rate constants for the acid- and base-catalysed solvolysis of phenoxysilanes $(p\text{-}XC_6H_4)Me_2SiOPh$ (X = F, Cl, Br, H, Me, MeO) in absolute ethanol correlate with the σ^0 constants of the substituents, the ρ values being -0.57 for the acid- and $+0.19$ for the base-catalysed process. The results are discussed in terms of bimolecular mechanisms, in which pentacoordinate intermediates may possibly play a part in the acid-catalysed reaction, but are considered unimportant for the base-catalysed reaction.

INTRODUCTION

The hydrolysis of trialkylphenoxysilanes was studied by Akerman[1,2], who found that the reaction was catalysed by both acid and base. Schowen and Latham found that the methanolysis of phenoxytriphenylsilanes was subject to general base catalysis[3], and observed a curvature in the plot of the free energy of activation *versus* the free energy of ionisation of the corresponding phenol[4]. For an extended range of substituents in the phenoxy group of triethylphenoxysilanes, Humffray and Ryan[5] found that the rates for base-catalyzed hydrolysis correlated better with a four-parameter equation involving σ and σ^- than with the standard Hammett equation.

In the work described below, the effects of substituents in an aryl group attached to silicon, in the compounds $(p\text{-}XC_6H_4)Me_2SiOPh$, have been measured in order to assess the electronic situation at silicon in the activated complex.

RESULTS AND DISCUSSION

The reaction between aryldimethylphenoxysilanes and absolute ethanol containing a little acid or base is represented in eqn. (1). It is first-order with respect to the organosilane under both sets of conditions.

$$(p\text{-}XC_6H_4)Me_2SiOPh + EtOH \xrightarrow{\text{A or B}} (p\text{-}XC_6H_4)Me_2SiOEt + PhOH \qquad (1)$$

(X = F, Cl, Br, H, Me, MeO) A = acid, B = base

A. Acid-catalysed solvolysis

The reaction in absolute ethanol containing between 3×10^{-3} and 60×10^{-3}

N H_2SO_4 is of first-order with respect to hydrogen ion over the concentration range studied, as shown by the constancy of $k_{obs}/[H_2SO_4]$ (Table 1). The rate constants are consistent with the Hammett equation (2).

$$\log k = \log k_0 - 0.57\ \sigma^0 \tag{2}$$

The use of σ^0 constants instead of σ constants gives a somewhat higher correlation coefficient. The difference is not, in fact, statistically significant for a single reaction series, but work now in progress has shown that for several series of compounds having substituents in the aryl group attached to silicon, σ^0 constants give somewhat better correlations in each case for reactions having positive ρ values, and it seems σ^0 correlations are, indeed, significantly better than σ correlations. The applicability of σ^0 constants indicates that there is little change in the electronic interactions between the silicon atom and the aryl system on going from the initial to the excited state. The use of σ^0 constants was recently found to give better results in the case of the acid-catalysed solvolysis of 2-aryl-2-methyl-1,3,2-dioxasilacyclopentanes[6].

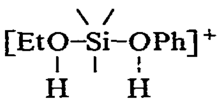
The rates are slightly increased by electron-donation from substituents in the *para*-position, as shown by the sign and magnitude of the reaction constant. This implies that there is slightly more positive charge on silicon in the transition state than in the initial state, a result which can be explained in terms of the mechanism proposed by Akerman[2] for the solvolysis of phenoxysilanes containing substituents in the phenoxy group. According to this mechanism, either the formation or breakdown of the intermediate protonated complex (I) is rate determining.

$$[(p\text{-}XC_6H_4)Me_2Si(OHPh)]^+ \tag{I}$$

If the proton transfer were rate-determining, as in eqn. (3), there would clearly be development of positive charge around the oxygen atom of the phenoxy part of the system and this would account for the negative ρ-value found by Akerman for variation of Y in $Me_3SiOC_6H_4Y$ compounds, although a higher absolute value of ρ might have been expected than was observed (*viz.* -0.53). However, it is difficult to see how this

$$EtOH_2^+ + (p\text{-}X_6H_4)Me_2SiOPh \xrightarrow{\text{slow}} EtOH + [(p\text{-}XC_6H_4)Me_2Si(OHPh)]^+ \tag{3}$$

mechanism would give rise to a similar degree of positive charge on the silicon atom in the case of $(XC_6H_4)Me_2SiOPh$ compounds (ρ -0.57, Table 1). The most plausible mechanism is thus one which involves a rate-determining attack by EtOH on the protonated complex (I). This still leaves a choice for this step between a simple S_N2-*Si* mechanism or one involving the prior formation of a pentacoordinate complex. If such coordination of ethanol to silicon occurs the complex will be of type (II).



$$[\underset{\displaystyle H}{\mathrm{EtO}}{-}\overset{\diagdown\,\diagup}{\underset{|}{\mathrm{Si}}}{-}\underset{\displaystyle H}{\mathrm{OPh}}]^+ \tag{II}$$

If the positive charge is assumed to be more stable in the ethoxy group than in the phenoxy group (or, equivalently, that phenol is more easily expelled than ethanol), it follows that the transition state for the formation of the complex (II) will have a higher energy than that for the breakdown of the complex. Thus if a pentacoordinate

TABLE 1

FIRST-ORDER CONSTANTS AT 25.0° FOR THE SOLVOLYSIS OF (p-XC_6H_4)Me_2SiOPh IN ABSOLUTE ETHANOL CONTAINING H_2SO_4[a]

X	[H_2SO_4] (10^3 *N*)	$k \cdot 10^3$ (sec^{-1})	$k/[H_2SO_4]$	$\bar{k}$
MeO	3.03	1.60	0.528	
	6.06	3.28	0.541	
	12.12	6.53	0.531	
	24.24	12.62	0.521	0.530
Me	6.06	3.11	0.514	
	12.12	6.10	0.505	0.510
H	6.06	2.57	0.424	
	12.12	4.90	0.406	
	24.24	10.3	0.421	
	60.60	24.9	0.412	0.421
F	6.06	2.04	0.337	
	12.12	3.66	0.302	
	24.24	7.49	0.309	0.316
Br	6.06	1.78	0.294	
	12.12	3.57	0.294	
	24.24	7.58	0.313	
	48.48	13.2	0.274	0.294
Cl	3.03	0.97	0.320	
	6.06	1.88	0.310	
	12.12	3.84	0.317	
	24.24	7.70	0.317	0.316

[a] $\rho = -0.57$; standard deviation 0.02; correlation coefficient −0.986.

TABLE 2

VALUES OF THE OBSERVED FIRST-ORDER RATE CONSTANTS, k, AND OF THE SPECIFIC RATE CONSTANT, k^B, IN THE SOLVOLYSIS AT 30.0° OF (p-XC_6H_4)Me_2SiOPh IN ABSOLUTE ETHANOL CONTAINING BUTYLAMINE BUFFERS[a,b]

X	10^4 *k* (sec^{-1}), *concn. of* $BuNH_2$[c] (*M*)				10^2k^B ($sec^{-1} \cdot mole^{-1}$)
	0.020	0.015	0.010	0.005	
MeO	6.10	3.86	2.77	0.569	3.53
Me	6.16	4.02	3.01	0.582	3.65
H	7.27	4.15	3.27	0.603	3.73
F	8.14	4.78	3.53	0.686	4.10
Br	8.38	5.02	3.49	0.726	4.24
Cl	8.28	4.84	3.62	0.775	4.34

[a] $\rho = +0.19$; standard deviation 0.01; correlation coefficient 0.982. [b] $\mu = 0.05$ by addition of $LiClO_4$. [c] In each case an equal concentration of $BuNH_3^+ Cl^-$ was also present.

complex is involved, its formation, not its breakdown, must be rate-determining. (Similar reasoning was used used by Schowen and Latham[3], in their discussion of the base-catalysed methanolysis of phenoxytriphenylsilane.) If the formation of the complex (II) were rate-determining, a new bond to silicon would be partly formed in the transition state; this would reduce the positive charge on silicon, but the latter might still be slightly positive in the transition state, and thus there would again be a small negative ρ value, as observed. It follows that the experimental data do not permit a firm choice between an S_N2–Si mechanism for the rate-determining step and one involving a pentacoordinate complex.

B. Base-catalysed solvolysis

In buffer solutions at variable base concentrations, [B], but at constant [B]/[BH] ratios, eqn. (4) was found to be valid in absolute ethanol.

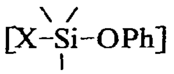
$$k_{obs} = k' + k^B \cdot [B] \qquad (4)$$

The rate constant k^B was found to follow the Hammett equation (5). As in the case

$$\log k^B = \log k_0^B + 0.19\,\sigma^0 \qquad (5)$$

of the acid-catalysed reaction, the applicability of the σ^0 constants indicates the absence of additional conjugation between the silicon atom and the aryl system in the transition state.

The magnitude of the negative charge developed on silicon in the transition state, as indicated by the ρ value, is much smaller than that of the charge developed on the phenoxy group, as indicated by the rates for the compounds $Me_3SiOC_6H_4Y$ having substituents in the phenoxy group, for which Akerman[2] observed a ρ value of $+1.74$ in the solvolysis by 51.4 weight % ethanol/water. Again, Schowen and Latham[4] observed a ρ value of 1.2 for the methanolysis of triarylphenoxysilanes, and it seems reasonable to assume that a ρ value in the region $+1.2$ to $+1.7$ would apply to the reaction of $(XC_6H_4)Me_2SiOPh$ compounds in absolute ethanol. The ratio $\rho(Si)/\rho(OPh)$ is thus in the region of $0.11-0.19$, which shows that the charge development is much less pronounced in the silicon part than in the phenoxy part of the activated complex, in contrast to the results for the acid-catalysed reaction. For the reactions in absolute ethanol the transition state may be formulated as (III).



$$[X\text{–}\overset{\diagdown\ \diagup}{\underset{|}{Si}}\text{–}OPh] \qquad (III)$$

X=EtO–HB or X=B

Solvolysis of the separating phenoxide anion will reduce the amount of charge concentrated on the oxygen atom, and in less protic media one would expect less charge dispersion by hydrogen bonding, and consequently a higher ρ value for substituents in the phenoxy group. For reactions of $Et_3SiOC_6H_4Y$ compounds in 60% dioxane/water, Humffray and Ryan[5] obtained a ρ value of 3.2, which shows that in this medium more of the negative charge is centred on the oxygen atom of the phenoxy group.

The existence of a pentacoordinate complex will now be considered. Since OPh is a better leaving group than EtO, it follows that if such a complex were involved, its formation would probably be rate-determining; the negative charge transferred from the ethoxide ion would thus reside substantially on the silicon atom, and this would give rise to a high positive ρ value, contrary to what is observed. If, on the other hand, the decomposition of the complex to give the products were rate-determining, so that the complex usually reverted to the starting materials, racemisation without reaction would be expected in appropriate systems, and this is not observed[7]. The involvement of a pentacoordinate complex is thus unlikely, and we are left with a bimolecular S_N2-*Si* mechanism. Synchronous bond-making and bond-breaking would clearly place little charge on silicon in the transition state, and would account nicely for the smallness of the observed positive value of ρ.

Akerman observed that in both the acid- and base-catalysed reactions of R_3Si-OPh where R = alkyl, the methyl compound (R = Me) reacted very much faster than the other compounds. The low ρ values obtained in this study show that the polar effects of substituents attached to silicon are small, and the rate differences observed by Akerman cannot thus be attributed to such effects, and must, therefore, be ascribed to the differing steric influences of the alkyl groups.

EXPERIMENTAL

Materials

The phenoxysilanes (p-XC_6H_4)Me_2SiOPh were made by treatment of phenol with the appropriate chlorosilane in diethyl ether with pyridine as acid acceptor; the chlorosilanes were prepared by Grignard reactions from dimethyldichlorosilane[8]. The phenoxysilanes, all of which are new compounds, were purified by fractional distillation, and for the kinetics studies small samples were further purified by GLC. They had the following properties: (X=) F, b.p. 170–173°/15 mm (Found: C, 68.62; H, 6.52. $SiC_{14}H_{15}FO$ calcd.; C, 68.21; H, 6.14%.); Cl, b.p. 160–170°/20 mm (Found: C, 64.25; H, 5.93. $SiC_{14}H_{15}ClO$ calcd.: C, 63.98; H, 5.75%.); Br, b.p. 176–186°/15 mm (Found: C, 52.80; H, 4.18. $SiC_{14}H_{15}BrO$ calcd.: C, 53.16; H, 4.18%.); H, b.p. 184–188°/50 mm (Found: C, 73.42; H, 7.26. $SiC_{14}H_{16}O$ calcd.: C, 73.63; H, 7.00%.); Me, b.p. 160–170°/25 mm (Found: C, 74.92; H, 7.32. $SiC_{15}H_{18}O$ calcd.: C, 74.33; H, 7.49%.); MeO, b.p. 142–154°/15 mm (Found: C, 69.20; H, 7.39. $SiC_{15}H_{18}O_2$ calcd.: C, 69.72; H, 7.02%.).

Rate measurements

All reactions were carried out in absolute ethanol. Acid solutions were made up by adding 5–100 μl of 5% H_2SO_4 in ethanol to known volumes of ethanol in the absorption cell, which was placed in a thermostated cell holder of a Unicam SP500 spectrophotometer. After the mixture had reached the appropriate temperature, about 0.2 μl phenoxysilane was introduced, and the increase in absorption at 280 nm, which is due to the formation of phenol, was followed. Ethanol containing acid was used in the reference cell. Temperature control was within ±0.1°. For the p-F compound, it was confirmed that varying the wavelength used between 278 and 282 nm did not affect the observed rate constant.

For the base-catalysed reactions a buffer system consisting of butylamine and its hydrochloride was used. The ionic strength was adjusted to μ 0.05 by the appropriate addition of $LiClO_4$. Absorbance readings were taken during the first half-life of the reactions and infinity readings were determined after ten half-lives.

Reaction Products

The spectra of the final mixtures were identical with the spectrum of phenol above 240 nm under the same conditions.

Treatment of data

First order constants given in the tables are mean values for at least two runs. Rate constants were obtained graphically.

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