On the Hydrolysis of Trialkylphenoxysilanes. II

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The hydrolysis of twelve substituted triethylphenoxysilanes in aqueous ethanol has been studied spectrophotometrically. The reaction is catalysed by both acid and alkali. The catalytic constants for the *meta*- and *para*-substituted compounds agree well with the Hammett equation. Dimethyl-*t*-butylphenoxysilane has been prepared and its hydrolysis studied. The mechanisms of the reactions are discussed and the ultraviolet spectra are described.

In a previous paper¹ the preparation and hydrolysis of five trialkylphenoxysilanes was described, the alkyl groups being methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl. The specific rate of the reaction was found to be proportional to the hydrogen ion concentration in acid solution and the sum of hydroxide and ethoxide ion concentrations in alkaline solution and to diminish with increasing length of the alkyl groups. The investigation has now been extended to phenoxysilanes with substituents in the phenoxy group in order to acquire better knowledge of the mechanism of the reactions and, if possible, to obtain a quantitative relationship between rate constants and substituents according to Hammett's equation². Some reactions of substituted aryl- and benzylsilanes have been reported, where the rate constants satisfy the Hammett equation. Gilman and Dunn³ investigated the hydrolysis of six triarylsilanes in wet piperidine and found a reaction constant $\rho = 3.09$, but the rate constant for one of the substituents, the *para*-dimethylamino group, did not satisfy the equation when the σ -value from Hammett's table was used. Eaborn and Parker⁴ studied spectrophotometrically the alkali-catalysed cleavage of seventeen substituted benzyltrimethylsilanes in aqueous methanol. They found the substituent effects to agree well with Hammett's σ constants and they calculated a reaction constant $\rho = 4.88$.

The reaction now examined is described by the over-all reaction formula

From the five trialkylphenoxysilanes previously measured triethylphenoxysilane was chosen as the unsubstituted compound, as it has the most convenient rate of reaction. The corresponding trimethyl compound was not chosen, as its rate constants are much too great to be measured with accuracy. The

Fig. 1. Catalytic constants versus Hammett's σ -constants.

● Alkaline hydrolysis of triethylphenoxysilanes.
○ Acid

following twelve substituents have been introduced in the phenoxy group: *o*-CH₃, *m*-CH₃, *p*-CH₃, *p*-t-C₄H₉, *o*-CH₃O, *m*-CH₃O, *p*-CH₃O, *o*-Cl, *m*-Cl, *p*-Cl, 1,3(CH₃)₂ (α -naphthyl) and 2,4(CH₃)₂ (β -naphthyl). The rate constants k were determined for at least five different concentrations of hydrogen ions and five concentrations of hydroxyl ions. The catalytic constants $k_a = k/[\text{acid}]$ and $k_b = k/[\text{base}]$ were calculated and were found to be reasonably constant for each compound. Consequently none of the compounds have any spontaneous hydrolysis rapid enough to be noticed at the actual concentrations. These results are collected in Table 1.

According to Hammett² the quantitative relationship between the rate constants k' for the reaction of a *meta*- or *para*-substituted benzene derivative and the so called substituent constant σ is expressed by the formula

$$\log k' - \log k'_0 = \rho \sigma$$

where k'_0 is the rate constant of the unsubstituted compound, ρ is a constant, the reaction constant, and σ is defined from the equation

$$\sigma = \log K - \log K_0$$

K and K_0 being the dissociation constants of the benzoic acid with the same substituent and that of unsubstituted benzoic acid, respectively. A plot of the catalytic constants k_a and k_b of the *meta*- and *para*-substituted phenoxysilanes in Table 1 against σ is shown in Fig. 1. (The two small circles at $\sigma = -0.27$ refer to the *para*-methoxy group, *cf* below). The σ values are taken from Jaffé's review on the Hammett equation⁵. The plot shows that the expected

Table 1. Acid and alkaline hydrolysis of $\text{Et}_3\text{SiOC}_6\text{H}_4\text{R}$.

R	$10^4 [\text{H}^+]$ M	$10^4 k$ sec^{-1}	k_a $\text{M}^{-1}\text{sec}^{-1}$	k_a mean $\text{M}^{-1}\text{sec}^{-1}$	$10^4 [\text{OH}^-]$ M	$10^4 k$ sec^{-1}	k_b $\text{M}^{-1}\text{sec}^{-1}$	k_b mean $\text{M}^{-1}\text{sec}^{-1}$
o-CH ₃	20.0	1.85	0.0925	0.0906	2.94	1.80	0.612	0.633
	30.0	2.65	.0883		6.22	3.98	.640	
	80.0	7.18	.0898		10.3	6.55	.636	
	120	11.0	.0916		15.9	10.3	.648	
	200	18.1	.0907		31.9	20.0	.627	
m-CH ₃	10.0	2.34	0.234	0.244	2.98	4.41	1.48	1.43
	20.0	4.90	.245		6.27	9.00	1.44	
	30.0	7.27	.242		9.96	13.5	1.36	
	50.0	12.9	.258		18.0	25.8	1.43	
	80.0	19.9	.249		24.6	35.7	1.45	
	120	28.5	.237					
p-CH ₃	10.2	3.17	0.311	0.317	2.87	3.50	1.22	1.20
	20.0	6.24	.312		6.19	7.15	1.16	
	50.0	16.0	.320		8.43	10.2	1.21	
	80.0	26.1	.326		29.9	35.5	1.19	
	120	37.8	.315		51.6	62.4	1.21	
p-t-C ₆ H ₄	9.77	2.78	0.284	0.290	2.86	3.35	1.17	1.19
	18.2	5.33	.293		6.37	7.43	1.17	
	50.3	14.8	.293		8.95	10.9	1.22	
	80.0	23.1	.289		16.4	19.4	1.18	
	120	34.7	.289		29.6	35.7	1.21	
o-CH ₃ O	9.57	1.84	0.192	0.207	2.79	2.06	0.737	0.729
	19.8	4.24	.214		6.31	4.49	.712	
	49.2	10.5	.214		10.0	7.38	.738	
	120	23.9	.199		15.1	11.0	.728	
	200	43.0	.215		30.1	22.0	.732	
m-CH ₃ O	9.57	1.97	0.206	0.196	1.30	3.61	2.79	2.67
	19.5	3.79	.194		2.66	7.38	2.78	
	29.4	5.80	.197		5.96	16.1	2.69	
	50.0	9.55	.191		9.93	25.1	2.53	
	80.0	15.8	.197		14.1	36.1	2.56	
	120	23.2	.193					
p-CH ₃ O	4.66	1.89	0.405	0.396	3.03	3.66	1.21	1.22
	19.1	7.87	.412		6.17	7.48	1.21	
	29.9	11.4	.382		9.12	11.1	1.22	
	50.1	19.3	.386		28.2	33.0	1.21	
	80.0	31.7	.396		50.0	64.7	1.25	
o-Cl	19.5	1.44	0.0738	0.0734	0.321	2.27	6.81	6.86
	50.0	3.65	.0730		0.767	5.33	6.95	
	80.0	5.92	.0739		1.50	10.2	6.80	
	120	8.78	.0732		3.06	20.6	6.73	
	200	14.6	.0730		6.25	43.7	6.99	
m-Cl	19.3	2.83	0.147	0.150	0.308	3.51	11.4	11.0
	28.9	4.30	.149		0.792	8.88	11.2	
	50.0	7.71	.154		1.23	13.9	11.3	
	120	17.7	.148		2.72	29.7	10.9	
	200	30.0	.150		6.21	64.8	10.4	

Table 1 continued.

<i>p</i> -Cl	10.0	1.73	0.173	0.170	0.296	2.12	7.15	7.17
	19.5	3.38	.173		0.762	5.57	7.30	
	50.0	8.40	.168		1.49	10.7	7.20	
	80.0	13.5	.169		2.82	20.0	7.09	
	120	20.2	.168		6.33	45.1	7.12	
1,3(CH) ₃ ^a	19.5	1.27	0.0649	0.0648	1.32	2.95	2.23	2.18
	30.0	1.95	.0648		2.78	6.13	2.22	
	80.0	5.23	.0654		6.28	13.1	2.09	
	120	7.77	.0647		10.3	21.8	2.12	
	200	12.8	.0640		16.3	36.2	2.22	
2,4(CH) ₃ ^b	10.0	2.13	0.213	0.209	1.24	4.14	3.34	3.39
	20.0	4.31	.215		2.68	9.35	3.49	
	49.8	10.4	.209		5.72	19.3	3.38	
	80.0	16.4	.206		9.68	32.5	3.36	
	120	24.9	.207		15.0	50.7	3.38	
H ^c	200	40.3	.202	0.219				2.05

a α -naphthyl, b β -naphthyl, c from Ref¹.

linear relationship between $\log k$ and σ is rather well satisfied. One of the points, viz that for the *para*-methoxy group, has an obviously greater deviation than the others from the best straight line. This is, however, not uncommon (cf Ref. 5, p. 230), and so it seems reasonable to exclude this point when calculating the reaction constant. This constant ρ and the calculated catalytic constant for the unsubstituted compound k_0 were obtained according to the method of least squares. The results together with the standard deviation s and the correlation coefficient r (calculated in the same way as in Jaffé's review⁵) are given in Table 2. The figures in parenthesis are the values obtained when the rate constants for the *para*-methoxy group are included.

Attempts have been made to extend the Hammett equation to other reactions than those of *meta*- and *para*-substituted benzene derivatives. Thus Taft⁶⁻⁸ succeeded in modifying the equation by introducing a steric term E_s in such a way that the equation became valid also for *ortho* substituents:

$$\log k - \log k_0 = \rho\sigma^* + E_s \quad (1)$$

Table 2. Reaction constant ρ , $\log k_0$, standard deviation s and correlation coefficient r for the acid and base catalysed hydrolysis of triethylphenoxysilanes.

Catalysis	ρ	$\log k_0$	s	r
Acid	-0.533 (-0.600)	-0.632 (-0.621)	0.030 (0.038)	0.968 (0.964)
Base	1.742 (1.575)	0.337 (0.364)	0.094 (0.109)	0.970 (0.958)

The polar substituent in this equation was originally indicated by E_σ , but this was later ⁷ changed to σ^* . The substituent constants are evaluated by assuming that ρ has the same value as for *meta-para*-substituted derivatives and that E_s has the same value in alkaline as in acid hydrolysis. The agreement between Taft's values and those that can be calculated from the rate constants in Table 1 are, however, only qualitative. This is not unexpected as the validity of eqn. (1) is much more limited than that of the Hammett equation. Thus all the reactions investigated by Taft are of one single type, *viz.* esterification and ester hydrolysis.

It is still less probable that the hydrolysis of trialkylphenoxysilanes with different alkyl groups should fit eqn. (1). It is possible in the case of substituted acetates as shown by Taft ⁶⁻⁸, but here only *one* substituent is changed and in the compounds described in Part I ¹ of this work *three* substituents are changed. Even if polar effects might be additive as in the case of *meta-para*-substituted benzene derivatives, this is probably not true for steric effects.

In addition to the five compounds previously described, dimethyl-*t*-butylphenoxysilane has been prepared and its hydrolysis studied (Table 3). The rate constants of these six compounds cannot - as expected - be correlated with Taft's σ^* and E_s constants according to eqn. (1). It is interesting, however, to compare the specific rate constants of dimethyl-*t*-butylphenoxysilane with those of triethylphenoxysilane ($k_a = 0.219$, $k_b = 2.05$) and trimethylphenoxysilane ($k_a = 10.4$, $k_b \approx 330$). The substitution of a *t*-butyl group for a methyl group lowers the catalytic constants by a factor of 10^{-5} . But even in comparison with triethylphenoxysilane, dimethyl-*t*-butylphenoxysilane is hydrolysed very slowly, the ratio between the catalytic constants being less than 10^{-2} . If the polar effects in these two compounds are assumed to be of the same order of magnitude (the numbers of carbon atoms in α - and β -position to the silicon atom are the same, and according to Taft ⁷, σ^* for three ethyl groups is -0.72 , σ^* for two methyl groups plus one *t*-butyl group is -0.84), the low rate constants can at least to a large extent be ascribed to the steric influence of the *t*-butyl group.

From these facts several mechanisms of the reactions can be formulated. As the reaction constant for the alkaline hydrolysis has a rather high positive value, this reaction is obviously facilitated by a low electron density at the

Table 3. Acid and alkaline hydrolysis of $\text{Me}_2\text{-}t\text{-BuSiOC}_6\text{H}_5$.

[H ⁺] mM	10 ⁵ <i>k</i> sec ⁻¹	10 ⁴ <i>k_a</i> M ⁻¹ sec ⁻¹	10 ⁴ <i>k_a</i> mean M ⁻¹ sec ⁻¹	[OH ⁻] mM	10 ⁵ <i>k</i> sec ⁻¹	10 ³ <i>k_b</i> M ⁻¹ sec ⁻¹	10 ³ <i>k_b</i> mean M ⁻¹ sec ⁻¹
12.0	7.23	6.03	5.91	5.00	8.52	1.70	1.72
20.0	11.4	5.70		8.00	13.8	1.73	
25.0	14.7	5.88		12.0	20.4	1.70	
40.0	23.8	5.95		20.0	34.7	1.73	
50.0	30.0	6.00		30.0	52.2	1.74	

reaction centre. The simplest mechanism consistent with this is an S_N2 mechanism:

followed by the equilibrium

where R is H or Et.

The acid hydrolysis has a negative value of the reaction constant, so it must be facilitated by a high electron density at the reaction centre. A simple mechanism involves a fast proton transfer and a slow reaction between a charged complex and a solvent molecule:

However, the first step can also be rate determining and the second one rapid. R is also here H or Et.

In either case it is possible to formulate a mechanism involving a penta-covalent silicon atom. Eaborn and Parker⁴ did not exclude this possibility in the alkaline hydrolysis of benzyltrimethylsilanes, and Swain, Esteve and Jones⁹ made such an intermediate probable in the reaction between water and triphenylsilyl fluoride. According to this mechanism the alkaline hydrolysis could be represented by the formula

if the last step is assumed to be rate determining as in the hydrolysis of triphenylsilyl fluoride. A similar mechanism - with a positive intermediate - can be formulated for the acid hydrolysis.

In addition to these mechanisms there are also other possibilities where the carbon-oxygen bond is broken, but there is some indication that the cleavage of silicon-oxygen bond is favoured at least in the case of alkoxy-silanes¹⁰. The stability of aryl ethers against hydrolysis at room temperature also indicates a cleavage of the silicon-oxygen bond. It is true that *t*-butyl phenyl ether - the carbon analogue of trimethylphenoxysilane - is less stable than *n*-alkyl phenyl ethers, but the ease with which it is cleaved by mineral acids depends on the formation of *i*-butylene and phenol¹¹.

EXPERIMENTAL

The phenoxysilanes were prepared from triethylchlorosilane and the corresponding phenol according to the formula

Table 5. Extinction coefficient ϵ and wavelength λ for the absorption maxima of $\text{Et}_3\text{SiOC}_6\text{H}_4\text{R}$.

Substituent	Absolute maximum		Secondary maximum		Measuring Wavelength	
	ϵ	λ	ϵ	λ	acid	alkaline
H	267.5	1 050			280	280
<i>o</i> -CH ₃	270	1 200	275.5	1 080	280	285
<i>m</i> -CH ₃	270	1 000	275	910	280	285
<i>p</i> -CH ₃	274	1 240			285	290
<i>o</i> -CH ₃ O	274.5	2 380			285	285
<i>m</i> -CH ₃ O	273	1 960	280	1 660	284	285
<i>p</i> -CH ₃ O	286	2 350			300	302.5
<i>p</i> - <i>t</i> -C ₄ H ₉	272	1 200			285	285
<i>o</i> -Cl	272.5	1 440	278.5	1 320	285	290
<i>m</i> -Cl	274	1 250	278	1 120	285	290
<i>p</i> -Cl	278	1 230			290	292

Table 4. Physical constants and analyses of $\text{Et}_3\text{SiOC}_6\text{H}_4\text{R}$.

R	B.p. °C	Pressure mm Hg	n_D^{20}	d_4^{20}	MR _D		% Si		% C		% H	
					found	calc.	found	calc.	found	calc.	found	calc.
<i>o</i> -CH ₃	126	13	1.4913	0.9292	69.37	69.25	12.7	12.6	69.9	70.2	9.9	10.0
<i>m</i> -CH ₃	125	13	1.4893	0.9240	69.50	69.25	12.8	12.6	70.1	70.2	10.0	10.0
<i>p</i> -CH ₃	128—9	13	1.4891	0.9240	69.50	69.25	12.8	12.6	70.0	70.2	9.8	10.0
<i>o</i> -CH ₃ O	133	12	1.4949	0.9736	71.38	71.02	11.7	11.8	65.5	65.5	9.2	9.3
<i>m</i> -CH ₃ O	138—9	10	1.4962	0.9762	71.36	71.02	11.8	11.8	65.6	65.5	9.4	9.3
<i>p</i> -CH ₃ O	150—1	13	1.4955	0.9772	71.20	71.02	11.6	11.8	65.2	65.5	9.3	9.3
<i>p</i> - <i>t</i> -C ₄ H ₉	150	11	1.4885	0.9127	83.58	83.42	10.7	10.6	72.4	72.7	10.6	10.7
<i>o</i> -Cl ^a	134—5	12	1.5035	1.0334	69.51	69.42	11.6	11.6	59.5	59.4	8.0	7.9
<i>m</i> -Cl ^a	137—8	14	1.5017	1.0268	69.75	69.42	11.6	11.6	59.4	59.4	8.0	7.9
<i>p</i> -Cl ^b	140	13	1.5021	1.0288	69.66	69.42	11.6	11.6	59.3	59.4	7.9	7.9
1,3(CH) ₄	168—9	10	1.5550	1.0017	82.82	—	10.9	10.9	74.1	74.4	8.6	8.6
2,4(CH) ₄	172	10	1.5537	0.9962	83.08	—	10.9	10.9	74.3	74.4	8.7	8.6

^a % Cl found 14.6; calc. 14.6.^b " " " 14.7; " 14.6.

Fig. 2. Ultraviolet spectra of triethylnaphthoxysilane in 51.4 weight-% ethanol.
 — the α -compound, - - - the β -compound.

as previously described¹. If the evolution of hydrochloric acid was very slow, as in the case of dimethyl-*t*-butylphenoxysilane, the reaction was carried out in pyridine.

Dimethyl-*t*-butylphenoxysilane. To 6.6 g (0.07 mole) of phenol in 5 g of pyridine were added 10.6 g (0.07 mole) of dimethyl-*t*-butylchlorosilane prepared according to Sommer and Tyler¹² dissolved in 15 g of pyridine, and the mixture was refluxed for half an hour. The precipitated pyridine hydrochloride (6.0 g, calc. 8.1 g) was filtered off and washed with dry ether. The ether and pyridine was distilled off and the residue distilled *in vacuo*. 3.0 g = 45 % of phenol were recovered and the yield of the silane was 6.8 g = 48 %. B. p. 100–101°/15 mm, $n_D^{20} = 1.4812$, $d_4^{20} = 0.9127$, $MR_D = 64.97$. (Found: C 69.3; H 9.7; Si 13.6; Calc. for $C_{14}H_{18}OSi$: C 69.2; H 9.7; Si 13.5). Analyses and physical constants for the other compounds are found in Table 4. The agreement between the found and calculated molecular refractivity is not very good, the found value being on the average 0.2 ml too high, but it is known that the phenoxy group attached to silicon has no constant group refractivity as shown by Smith¹³ in the case of mixed alkoxy-phenoxysilanes.

The rate constants were determined as in Ref.¹ and thus the temperature was 25.0°C, the ionic strength 0.05 M and the solvent 51.4 wt.-% ethanol. As examples of buffers used in the alkaline hydrolysis at low hydroxyl ion concentrations can be mentioned: in 0.013 M glycinate + 0.003 M glycine $[OH^-]$ is equal to 3×10^{-5} M, in 0.012 M $NaHCO_3$ + 0.006 M Na_2CO_3 , $[OH^-]$ is equal to 3×10^{-4} and in 0.005 M $NaHCO_3$ + 0.010 M Na_2CO_3 , $[OH^-]$ is equal to 10^{-3} M.

The ultraviolet spectra were determined and are generally similar to those of unsubstituted phenoxysilane in having only one maximum in the region 250–320 mμ, but five of the compounds have a secondary maximum. The wavelengths and extinction coefficients of these maxima are given in Table 5 together with the wavelengths used for the kinetics. The spectra of the naphthoxysilanes are more complicated (Fig. 2). The rate of hydrolysis for the α -naphthoxy compound was determined at 325 mμ and that for the β -naphthoxy compound at 335 mμ in acid and 340 mμ in alkaline solution.

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