On the Hydrolysis of Trialkylphenoxysilanes

EVERT AKERMAN

Department of Organic Chemistry, University of Lund, Lund, Sweden

The acid and base catalysed hydrolysis of $R_3SiOC_6H_5$ in aqueous ethanol has been studied for R = methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl. The specific rate of reaction follows the equation

$$k = k_a [H^+] + k_{sp} + k_b [\text{base}]$$

k_a being the catalytic constant for hydrogen ions, k_b that for a mixture of hydroxyl and ethoxide ions, k_{sp} the specific rate of the spontaneous hydrolysis, and $[\text{base}]$ the sum of hydroxyl and ethoxide ion concentrations. The first two members are negligible in alkaline solution and the last two members in acid solution. The rate of reaction diminishes with increasing length of the alkyl groups.

Kinetic investigations of the hydrolysis of silanes of the type R_3SiX where R is an alkyl or aryl group and X is a hydrolysable functional group are scarce. Swain, Esteve and Jones¹ found the rate of hydrolysis of triphenylsilyl fluoride in 50 % water, 50 % acetone to be proportional to the concentration of silane and that it is not influenced by hydrogen ions but accelerated by hydroxyl ions. From the influence of solvent, neutral salts and substituents they deduced that the hydrolysis possibly proceeded through a pentacovalent silicon intermediate. Krieble and Burkhard² found that the acid hydrolysis of dimethyldi-*n*-2-butoxysilane gave 2-butanol with the same optical activity as the original 2-butanol. This fact indicates that the silicon-oxygen bond is broken and not the carbon-oxygen bond.

As a part of the work in this laboratory five trialkylphenoxysilanes $R_3SiOC_6H_5$ with R = CH_3 , C_2H_5 , *n*- C_3H_7 , *n*- C_4H_9 , and *n*- C_5H_{11} have been investigated. The rate of hydrolysis of such compounds can be easily determined spectrophotometrically. In aqueous ethanol with water in great excess over the silane this is hydrolysed according to the formula

in some cases followed by formation of hexaalkyldisiloxanes and in alkaline solutions by the reaction

The phenol was identified from its ultraviolet spectrum. Trialkylsilanes and phenol — and the phenolate ion in alkaline solutions — absorb in the ultraviolet region, but the absorption maximum of the silanes is displaced by *ca.* 5 $m\mu$ from that of phenol, and the extinction coefficient at the maximum is only half that of phenol. Fig. 1 shows the absorption spectra of phenol, phenolate and trimethylphenoxy silane. The spectra of the other four alkylphenoxy silanes are very similar to that of trimethylphenoxy silane. Trialkylsilanol and hexaalkyldisiloxane do not absorb in this spectral region. The hydrolysis was carried out in water-ethanol mixture, (51.4 weight-% ethanol), since the silanes are insoluble in water, but with water in great excess, thus making the water concentration constant during the run. From the optical density D of the sample the expression $\log (D_{\infty} - D_t)$ was calculated, where D_t is the optical density at the time t and D_{∞} is the optical density at infinite time. This expression, when plotted against time, gives a straight line (Fig. 2 shows some typical plots). The reaction is consequently of the first order in silane, following the rate equation

$$k = \frac{1}{t} \log \frac{D_{\infty} - D_0}{D_{\infty} - D_t} \quad (1)$$

D_0 being the optical density at $t = 0$.

The hydrolysis was carried out in diluted HCl or NaOH or buffers of various composition. In the last-mentioned case the concentration of hydrogen and hydroxyl ions was measured electrometrically. In a water-ethanol solution of sodium hydroxide the anions are present partly as ethoxide ions and the

Fig. 1. Molar extinction coefficient ϵ vs wavelength

— = phenol
 - - - = phenolate ion
 - . - . - = trimethylphenoxy silane

Fig. 2. Acid hydrolysis of tri-n-butyl-phenoxy-silane. $\log (D_{\infty} - D_t)$ vs time.

○ : $[H^+] = 1.52 \times 10^{-3} M$

● : " = 3.03 " "

+ : " = 10.0 " "

catalytic effect of hydroxyl and ethoxide ions is measured. The equilibrium constant for the reaction

has been determined by Caldin and Long³. Their values show that in 53 weight-% ethanol at 25° C about 17 % of added hydroxide is converted to ethoxide. If k_{OH} and k_{OEt} are the catalytic constants for hydroxide and ethoxide ions, the rate constant k of the reaction is supposed to be

$$k = k_{OH} [OH^-] + k_{OEt} [C_2H_5O^-]$$

For stoichiometric reasons the following equation is valid for solutions where the concentration of phenolate ion is negligible.

$$[Na^+] = [OH^-] + [C_2H_5O^-]$$

From equation (2) follows, as ionic strength, solvent and concentrations of water and ethanol are constant,

$$[C_2H_5O^-] = K [OH^-]$$

From these three equations follows

$$k = [Na^+] \frac{k_{OH} + Kk_{OEt}}{1 + K} = [Na^+] k'$$

Fig. 3. Acid hydrolysis of trimethylphenoxysilane. Rate constant vs hydrogen ion concentration.

○ : in glycine-HCl buffer.
 ● : in dil. HCl.

Thus the rate constant of the reaction is proportional to the amount of added sodium hydroxide, *i.e.*, [base].

The values k_a and k_b were calculated (Tables 1, 2) and are found to be constant for each compound. The hydrolysis of trimethylphenoxysilane is very rapid. Fig. 3 shows its acid hydrolysis and the slope of the line is $k_a = 10.4 \text{ M}^{-1} \text{ sec}^{-1}$. The alkaline hydrolysis of trimethylphenoxysilane is still more rapid and more complicated. The results obtained from reactions in glycine-NaOH buffers show that the ratio $\frac{k}{[\text{OH}^-]}$ is highly dependent on the buffer concentration, but still the reaction seems to be of the first order in hydroxyl ions with $k_b \approx 330 \text{ M}^{-1} \text{ sec}^{-1}$. Three runs at the neutral point in a Na_2HPO_4 - NaH_2PO_4 buffer seem to indicate a very slow spontaneous hydrolysis of trimethylphenoxysilane with a rate constant $k_{sp} \approx 10^{-5} \text{ sec}^{-1}$, but the rate of reaction here is also dependent on the buffer concentration. Thus the rate of hydrolysis of trimethylphenoxysilane follows the equation

$$k = k_a [\text{H}^+] + k_{sp} + k_b [\text{base}]$$

which probably is valid also for the other four compounds, but the spontaneous hydrolysis is too slow to be noticed. The values of k_a and k_b are collected in Table 3.

The investigation will be continued with examination of compounds with other alkyl or aryl groups and with substituents in the phenoxy group.

Table 1. Acid hydrolysis of $R_3SiOC_6H_5$ in 51.4 weight-% ethanol. $\mu = 0.05$ M.

R	[H ⁺] mM	$k \times 10^4$ sec ⁻¹	k_a M ⁻¹ sec ⁻¹	k_a mean M ⁻¹ sec ⁻¹
C ₆ H ₅	1.00	2.02	0.202	0.219
	3.03	6.90	.228	
	8.00	18.0	.225	
	10.0	22.3	.223	
<i>n</i> -C ₃ H ₇	1.00	1.21	0.121	0.115
	3.00	3.65	.121	
	10.0	11.0	.110	
	20.0	21.7	.108	
<i>n</i> -C ₄ H ₉	1.52	1.22	0.080	0.081
	3.03	2.40	.079	
	10.0	8.08	.081	
	20.0	16.5	.082	
<i>n</i> -C ₈ H ₁₇	2.00	1.21	0.061	0.060
	5.00	3.19	.064	
	10.0	6.44	.064	
	14.0	8.25	.059	
	20.0	12.0	.060	
	30.0	17.5	.057	

EXPERIMENTAL

The phenoxysilanes were prepared from phenol and trialkylethoxysilane (in the case of the *n*-propyl compound) or trialkylchlorosilane in the same way as similar compounds were prepared by Larsson ⁴ and Jörg and Stetter ⁵. One example is given.

*Tri-*n*-butylphenoxysilane.* 29.3 g (0.125 mole) of tri-*n*-butyl-chlorosilane and 11.8 g (0.125 mole) of phenol were refluxed in a dry atmosphere until no more hydrochloric acid was evolved (60 hours). The product was distilled at reduced pressure in a 33 cm glass helix packed column and gave 23 g (88% yield) of pure tri-*n*-butylphenoxysilane.

Boiling points, refractive indices (determined with an Abbe refractometer), densities (determined with an Ostwald-Sprengler pycnometer of 1.5 ml), molecular refractivities (calculated from the Lorenz-Lorentz formula) and analyses are given in Table 4. For the calculated molecular refractivities the group refractivities given by Smith ⁶ have been used. Smith does not give the group refractivity $r\text{-SiOC}_6\text{H}_5$, but from his value of the group refractivity $r\text{-SiC}_6\text{H}_5$ and the bond refractivities Si-C aromatic, Si-O, and C-O ether given by Vogel ⁷ and Warrick ⁸, the group refractivity $r\text{-SiOC}_6\text{H}_5$ was calculated to 28.31 ml. The equivalent weight was determined by hydrolysing the silane in a mixture of glacial acetic acid and 1 N hydrochloric acid for some hours and determining the phenol according to Sprung ⁹. Silicon analyses were performed according to Smith ⁶. The reactions were carried out in 51.4 weight-% ethanol obtained from 20.00 ml of water made up with redistilled 96 % ethanol to 50.00 ml. Sodium chloride was added to give an ionic strength $\mu = 0.05$ M, calculated from the formula

$$\mu = \frac{1}{2} \sum_i c_i z_i^2$$

Table 2. Alkaline hydrolysis of $R_3SiOC_6H_5$ in 51.4 weight-% ethanol. $\mu = 0.05$ M.

R	Composition of solution	[OH ⁺] mM	$k \times 10^4$ sec ⁻¹	k_b M ⁻¹ sec ⁻¹	k_b mean M ⁻¹ sec ⁻¹
C ₂ H ₅	0.014 M glycinate	0.0463	0.954	2.06	2.05
	0.0011 M glycine				
	0.014 M glycinate	0.0750	1.60	2.13	
	0.0018 M glycine				
	0.01 M Na ₂ CO ₃	0.578	11.2	1.94	
n-C ₃ H ₇	0.01 M NaHCO ₃				0.66
	0.009 M NaHCO ₃				
	0.01 M Na ₂ CO ₃	1.27	8.37	0.66	
	0.005 M NaHCO ₃				
	0.01 M Na ₂ CO ₃	2.00	13.1	0.65	
n-C ₄ H ₉	0.003 M NaHCO ₃				0.41
	dil. NaOH	4.00	26.3	0.66	
	0.01 M Na ₂ CO ₃	0.578	2.30	0.40	
	0.01 M NaHCO ₃				
	dil. NaOH	1.99	7.96	0.40	
n-C ₅ H ₁₁	»	5.00	20.8	0.42	0.30
	»	8.00	33.7	0.42	
	0.01 M Na ₂ CO ₃	0.585	1.77	0.30	
	0.01 M NaHCO ₃				
	dil. NaOH	3.06	8.96	0.29	
n-C ₆ H ₁₃	»	8.00	24.7	0.31	0.30
	»	12.0	36.3	0.30	
	»				

where c = ion concentrations and z = valency. The concentration of silane was about 10^{-4} M, in some cases of alkaline solutions of low buffer capacity $0.5 \cdot 10^{-4}$ M. (It is not necessary to know the exact concentration, cf. eqn. (1)). The optical density was measured in a 1 cm quartz cell with a tight cover in a Beckman DU spectrophotometer provided with a 4 300 photomultiplier attachment. By means of an arrangement designed by the author the walls of the cell compartment were tempered with circulating water from a thermostat. The temperature of the solution was $25.0 \pm 0.2^\circ$ C. The slit width was 0.6 mm and the wave length generally 280 $m\mu$, in some cases of alkaline solutions 290 $m\mu$ (see Fig. 1). The first reading D_0 could be made one minute after mixing and the last

Table 3. The acid and base catalysed hydrolysis of $R_3SiOC_6H_5$.

R	k_a M ⁻¹ sec ⁻¹	k_b M ⁻¹ sec ⁻¹
CH ₃	10.4	~ 330
C ₂ H ₅	0.22	2.1
n-C ₃ H ₇	.12	0.66
n-C ₄ H ₉	.081	.41
n-C ₅ H ₁₁	.060	.30

one was made after a time equal to ten times the half life. For the reactions with a half life longer than one hour, King's¹¹ method was used. As a «blank» was used a solution of exactly the same composition as the sample, but where the reaction had started two to three half-lives earlier. The rate equation (1) is in this case transformed to

$$k = \frac{1}{t} \log \frac{D_0'}{D_t'}$$

D' being the optical density read on the photometer. Plotting $D't$ versus time gives a straight line, the slope of which is $-k$. The reactions were followed to at least 70 % hydrolysis. All constants were calculated from graphs.

Hydrogen and hydroxyl ion concentrations greater than 0.001 M were obtained by diluting standardized hydrochloric acid and carbonate-free sodium hydroxide solutions. In buffer solutions the concentrations were determined electrometrically using a glass electrode with a saturated calomel electrode as reference electrode and with exclusion of the carbon dioxide of the air. Nernst's equation gives the relation between electromotive force E and activity, but as the ionic strength was constant this relation is supposed to be valid also for concentrations

$$E_{\text{OH}} = E - \frac{RT}{F} \ln [\text{H}^+] \quad (3)$$

The equation

$$k_w = [\text{H}^+] \cdot [\text{OH}^-] \quad (4)$$

is supposed to be valid in this ethanol-water mixture. Eqns. (3) and (4) give the equation

$$E_{\text{OH}} = E + \frac{RT}{F} \ln [\text{OH}^-] \quad (5)$$

These assumptions are verified in Tables 5 and 6. The electromotive forces were measured in diluted hydrochloric acid and sodium hydroxide and sodium chloride was added to give an ionic strength of 0.05 M. Each value of the electromotive force E is a mean of at least two readings. In the most alkaline solutions the E.M.F. measured with the glass electrode does not exactly follow eqn. (5), but these high concentrations were never used for the kinetics. Besides the constancy of E_{OH} is not very good, although sufficient, especially in poorly buffered solutions.

The author is indebted to Professor Erik Larsson for suggesting the subject of this investigation and his kind interest during its course.

Table 4. Physical constants and analyses of $R_3\text{SiOC}_6\text{H}_5$.

R	B.p. °C	Pressure mm Hg	n_D^{20}	d_4^{20}	MR _D		% Si		Equiv. wt.	
					found	calc.	found	calc.	found	calc.
CH ₃ ¹	68—9	13	1.4787	0.9265	50.89	51.06	16.5	16.9	27.9	27.6
C ₂ H ₅	145	20	1.4883	0.9288	64.69	64.60	13.6	13.5	34.4	34.7
<i>n</i> -C ₃ H ₇	121—2	1.5	1.4837	0.9120	78.54	78.84	11.2	11.2	42.0	41.8
<i>n</i> -C ₄ H ₉	145	3	1.4820	0.8993	92.72	92.74	9.5	9.6	49.0	48.8
<i>n</i> -C ₅ H ₁₁	153	1.5	1.4800	0.8904	106.76	106.65	8.4	8.4	55.7	55.8

1. this compound is previously described by Speier¹⁰.

Table 5. Electromotive forces in dilute hydrochloric acid.

[HCl] M	temp ° C	— <i>E</i> mV	<i>E</i> _{oH} mV
0.0300	22.2	5.9	83.4
.0200	22.0	16.4	83.4
.0120	22.0	29.2	83.5
.0080	22.0	39.3	83.2
.0050	21.9	51.6	83.2
.0030	22.1	64.6	83.3
.0020	22.0	74.4	83.7

Table 6. Electromotive forces in dilute sodium hydroxide.

[NaOH] M	temp ° C	— <i>E</i> mV	<i>E</i> _{oOH} mV
0.0300	22.8	679.4	768.4
.0200	22.0	670.8	770.3
.0120	21.7	661.3	773.7
.0080	22.4	650.3	773.2
.0050	22.0	639.6	774.4
.0030	22.0	625.4	773.2
.0020	22.3	614.2	772.2

REFERENCES

1. Swain, G., Esteve, R. M. and Jones, R. H. *J. Am. Chem. Soc.* **71** (1949) 965.
2. Kriebble, R. H. and Burkhard, C. A. *J. Am. Chem. Soc.* **69** (1947) 2689.
3. Caldin, E. F. and Long, G. *J. Chem. Soc.* **1954** 3737.
4. Larsson, E. *Chem. Ber.* **86** (1953) 1382.
5. Jörg, H. and Stetter, J. *J. prakt. Chem.* **117** (1927) 305.
6. Smith, B. *Kiselorganiska studier* (Diss.) Chalmers University of Technology, Gothenburg 1951.
7. Vogel, A. I. *A Textbook of Practical Organic Chemistry*, 2nd Ed., Longmans, Green and Co., London 1951.
8. Warrick, E. L. *J. Am. Chem. Soc.* **68** (1946) 2455.
9. Sprung, M. M. *Ind. Eng. Chem. Anal. Ed.* **13** (1941) 35.
10. Speier, J. L. *J. Am. Chem. Soc.* **74** (1952) 1003.
11. King, E. L. *J. Am. Chem. Soc.* **74** (1952) 563.

Received November 10, 1955.