Kinetics and Mechanism of Hydrolysis of Trialkyl(phenylthio)silanes

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The hydrolysis in dioxan–water of some trialkyl(phenylthio)silanes has been studied quantitatively in the presence of small amounts of acid and base. The results are consistent with a mechanism which involves a fast protonation of the sulphur atom in acid followed by rate-determining attack of the solvent on the silicon atom and in slightly alkaline medium by a slow attack of the solvent on the sulphur atom concerted with a nucleophilic attack of the base.

THE mechanism of breaking of a carbon–silicon bond is well established [1] but little work has been done on the corresponding silicon–sulphur compounds, although their properties and chemical reactions are well known.[2] In order to elucidate the mechanism of cleavage of a sulphur–silicon bond, we have undertaken a kinetic study of the solvolysis of some thiosilanes and the results are herein reported.

RESULTS AND DISCUSSION

As expected from the high sensitivity of the S–Si bond of thiosilanes to hydrolysis,[2] the title compounds in aqueous dioxan rapidly give thiol and silanol [reaction (1)]. The reaction rate is strongly affected by the com-

$$H_2O + R_3Si\text{–}SPh \longrightarrow R_3Si\text{–}OH + HSPh \quad (1)$$

position of the medium (Table 1) and plots of log k against log $[H_2O]$ show good linearity over the range of

TABLE 1

First-order rate constants at 25 °C, $10^3 k/s^{-1}$, for hydrolysis of R_3Si–SPh

% H_2O [a]	Neutral medium R = Me	Neutral medium R = Et	Acid medium [b] R = Me	Alkaline medium [c] R = Me
1·33	0·40		6·92	5·01
1·86			10·72	33·11
2·67	7·28	0·32	19·05	
4·00	51·29	1·23		
5·33	158·50	4·27		

[a] Water (ml) per 100 ml solution. [b] 0·00133M-HCl. [c] 0·00133M-NaOH.

water concentrations used, according to the kinetic equation (2). The orders in water for the hydrolysis

$$\text{Rate} = k[\text{Substr.}][H_2O]^n \quad (2)$$

of trimethyl- and triethyl-(phenylthio)silane have been calculated from the data in Table 1 and the results are in Table 2. Multiple orders with respect to the nucleo-

TABLE 2

Kinetic orders in water for hydrolysis

R	Acid medium	Neutral medium	Alkaline medium
Me	1·51	4·35	5·00
Et		3·70	

phile, not unusual in the hydrolysis of organic [3] and organometallic substrates,[4] are consistent with a polymeric structure of the water molecules and the decrease in n, on changing from the basic to the acidic medium, can be ascribed to the different extent of hydrogen-bond formation when acids and bases are added to aqueous dioxan.

The effect of temperature on the reaction rate (Table 3)

TABLE 3

Effect of temperature on the hydrolysis of Me_3Si–SPh in aqueous dioxan (2·67% v/v water)

$t/°C$	18·3	25·0	38·2	45·0
$10^3 k/s^{-1}$	7·30	7·28	7·56	7·50

also supports the existence of large water-polymer aggregates. The simplest way to explain the lack of variation of reaction rate with temperature involves a water-polymer aggregate dissociation which will balance [4] the expected increase in the rate.

The change in the rate of hydrolysis with varying R is shown in Table 4.

TABLE 4

Relative rates for the hydrolysis of R_3Si–SPh in aqueous dioxan (2·67% v/v water)

R	Me	Et	Pr^n
$k_{rel.}$	87	1·4	1·0

[1] C. Eaborn, ' Organosilicon Compounds,' Butterworths, London, 1960, ch. 4.

[2] A. Haas, Angew. Chem. Internat. Edn., 1965, 14, 1014; E. W. Abel, J. Chem. Soc., 1960, 4406; H. J. Emeleus and L. E. Smythe, J. Chem. Soc., 1958, 609; M. Schmidt and M. Wieber, Inorg. Chem., 1962, 1, 909; H. Gilman and G. R. N. Smart, J. Org. Chem., 1951, 16, 424; D. Wittenberg, H. A. McNinth, and H. J. Gilman, J. Amer. Chem. Soc., 1958, 80, 5418.

[3] E. Tommila, E. Pakkala, V. K. Virtanen, A. Erva, and S. Varila, Ann. Acad. Sci. Fennicae, 1959, A2, 1; R. F. Hudson and B. Saville, J. Chem. Soc., 1955, 4114, 4121, 4130; R. F. Hudson and I. Steltzer, Trans. Faraday Soc., 1958, 54, 213.

[4] J. R. Chipperfield and R. H. Prince, J. Chem. Soc., 1963, 3567; R. H. Prince and R. E. Timms, Inorg. Chim. Acta, 1967, 129; 1968, 260.

The electronic effect of the Et_3Si group is not distinguishable [5] from that of the Me_3Si group and differences in rate listed in Table 4 cannot be interpreted by means of inductive factors but certainly account for an increasing steric hindrance with the branching of the aliphatic chain.

A significant influence is exerted by substituents in the benzene ring and Table 5 lists first-order rate

TABLE 5

First-order rate constants for the cleavage of XC_6H_4-S-SiMe$_3$ compounds by aqueous dioxan ($2\cdot67\%$ v/v water) presence of HCl, at $25 \pm 0\cdot1$ °C

X	$10^3[HCl]/M$	$10^3k/s^{-1}$	λ/nm
p-OMe	1·33	4·41	300
p-Me	1·33	5·02	285
H	0·26	1·99	280
H	1·33	6·92	280
H	2·66	13·70	280
H	5·32	27·80	280
m-OMe	1·33	8·28	293
p-Cl	1·33	15·67	285
m-Cl	1·33	24·32	285

constants for the acid-catalysed hydrolysis of XC_6H_4-S-SiMe$_3$ in aqueous dioxan. In acid medium (i) a plot of log k against σ_0 [6] gives a satisfactory straight line and, as expected for a nucleophilic substitution at a metal atom, the reaction rate is increased by electron-withdrawing substituents and lowered by electron-releasing groups in the benzene ring; (ii) a first-order dependence of the rate on the concentration of hydrochloric acid is observed (Table 5) over the range of acid concentrations examined; (iii) in dioxan containing 1·33% water, the reaction is 1·87 times faster when protium oxide is used instead of deuterium oxide (Table 6) and the value for k_H/k_D is unchanged in acid and neutral medium, accounted for by O–H bond breaking in the rate-determining step.

The simplest mechanism fitting the above observations

TABLE 6

Isotope effect on the hydrolysis of Me_3Si-SPh

		$10^3k/s^{-1}$	k_H/k_D
$H_2O = 1\cdot33\%$	$[HCl] = 0\cdot00133M$	6·92	1·87
$D_2O = 1\cdot33\%$	$[DCl] = 0\cdot00133M$	3·70	
$H_2O = 2\cdot67\%$	$[HCl] = 0$	7·28	1·88
$D_2O = 2\cdot67\%$	$[HCl] = 0$	3·87	

involves a fast acid–base equilibrium giving protonation of the sulphur atom, followed by slow nucleophilic attack of the water on the silicon atom (Scheme). This Scheme accounts for the acid catalysis, for the lower reactivity in heavy water, and for the substituent effect on the rate of hydrolysis; the low sensitivity to the substituent effect ($\rho = 1\cdot4$) can be rationalized in terms of the opposing effects of structural modifications of the aromatic portion on k_1/k_{-1} and k_2.

In the base-catalysed hydrolysis ($0\cdot00133M$-NaOH) of trialkyl(phenylthio)silanes, substituents in the benzene ring cause acceleration in all cases relative to the parent compound (Table 7). This anomalous variation induced by the substituents, similar to that observed by Eaborn

and his co-workers,[7] does not fit the usual pattern for nucleophilic substitutions and the remarkable increase in the rate caused by p-Me and p-OMe groups implies electrophilic participation in the rate-determining step.
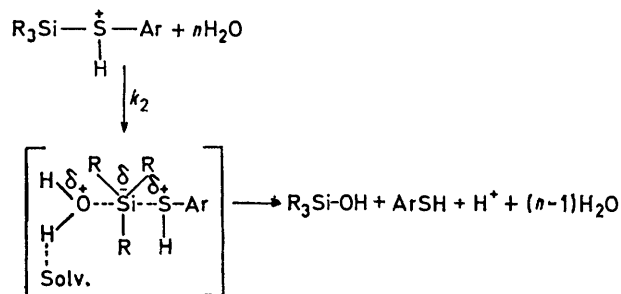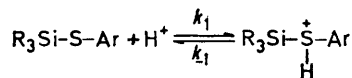
SCHEME

TABLE 7

First-order rate constants for the cleavage of XC_6H_4-S-SiMe$_3$ compounds in aqueous dioxan ($2\cdot67\%$ v/v water) in presence of $0\cdot00133M$-NaOH at $25 \pm 0\cdot1$ °C

X	$10^3k/s^{-1}$	λ/nm
p-OMe	12·16	320
p-Me	11·48	310
H	4·99	290
m-OMe	7·96	315
p-Cl	17·95	310
m-Cl	25·18	310

The rate-enhancing effect of electron-withdrawing substituents, on the other hand, is in line with the general accelerating effect produced by electron removal from the silicon atom which becomes more negative under attack by the nucleophile. The pattern for the substituents (Table 7) may be rationalized by the existence of two transition states, one, (I) involving mainly S $\cdots$ Si breaking, and the other, (II) involving S $\cdots$ H forming (or Si $\cdots$ $^+$SH breaking).
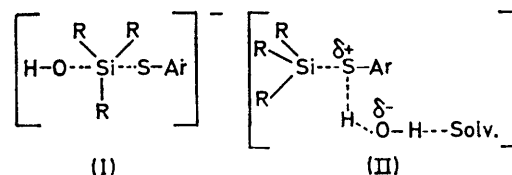
Electron-withdrawing substituents in the benzene ring will stabilize (I), whereas (II) will predominate with electron-releasing groups. Both transition states will involve a contribution from the other term and the V-shaped profile for the substituent effect in alkaline medium may be explained by proton transfer from the water to the sulphur atom, concerted with the cleavage

[5] J. Chatt and A. A. Williams, J. Chem. Soc., 1954, 4403.
[6] R. W. Taft, jun., J. Phys. Chem., 1960, 64, 1805.
[7] C. Eaborn, H. L. Hornfeld, and D. R. M. Walton, J. Chem. Soc. (B), 1967, 1036; E. Alexander, C. Eaborn, and T. G. Traylor, J. Organometallic Chem., 1970, 21, 65; A. R. Bassindale, C. Eaborn, R. Traylor, A. R. Thompson, D. R. M. Walton, J. Cretney, and G. J. Wright, J. Chem. Soc. (B), 1971, 1155.

of the S–Si bond by attack of the nucleophile on the silicon atom.

EXPERIMENTAL

Materials.—Reagent grade 1,4-dioxan was purified by standard procedures [8] and distilled before use. Conductivity water was used for all kinetic experiments. Triethyl(phenylthio)silane and substituted trimethyl(phenyl-thio)silanes were synthesized by adding to triethylamine (0·075 mol) and trialkylchlorosilane (0·050 mol) in dry ether the appropriate thiol (0·050 mol) and refluxing for 10 h under nitrogen. After cooling the solid was filtered off and washed with dry ether and the ether extracts were combined. After evaporation of the solvent, the residual oil was distilled under high vacuum. The physical properties and yields of the *products* are in Table 8. Trimethyl(phenylthio)silane [9] and tri-n-propyl(phenylthio)-silane [10] were synthesized by the literature methods.

Rate Measurements.—The kinetic runs were started in a thermostatted 1-cm quartz cell containing 2 ml of a dioxan solution of the thiosilane (3·0—6·5 × 10⁻⁴M) and 1 ml of aqueous dioxan. The reactions were followed by observing the change of the optical density of the solution at the suitable wavelength (Tables 5 and 7) with a Perkin-Elmer

[8] A. Weissberger, 'Technique of Organic Chemistry,' vol. 17, Interscience, New York, 1967.

TABLE 8

Analyses and physical properties of XC_6H_4–S–SiR_3 compounds

R	X	B.p./°C [a] at p/mmHg	Yield (%)	Found (%) C	Found (%) H	Required (%) C	Required (%) H
Et	H	102—103/0·3	41	64·3	9·3	64·2	8·60
Me	p-OMe	85—87/0·2	61	55·9	7·6	56·6	7·60
Me	p-Me	56—58/0·4	71	60·9	8·5	61·3	8·21
Me	m-OMe	78—79/0·3	49	57·1	7·6	56·6	7·60
Me	p-Cl	80—81/0·4	65	49·6	6·1	49·85	6·04
Me	m-Cl	66—68/0·4	58	50·2	6·0	49·85	6·04

[a] Uncorrected.

402 spectrophotometer. For fast reactions, the optical densities were recorded on a tape recorder with chart speeds between 60 and 500 mm min⁻¹, or when necessary, in a stopped flow apparatus. The first-order rate constants were evaluated by means of equation (3) where the symbols

$$kt = \ln (D_\infty - D_0)/(D_\infty - D_t) \qquad (3)$$

have their usual significance. Rate constants of duplicates agree within 3%.

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[9] K. A. Henry and A. Allred, *Inorg. Chem.*, 1965, **4**, 671.
[10] Larson and R. E. I. Marin, Swedish Pat. 138,357 (*Chem. Abs.*, 1954, **48**, 2761).