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THE MECHANISM OF THE ACID-CATALYZED PROPANOLYSIS OF 2-SILA-1,3-DIOXOLANES

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SUMMARY

Hexamethyl-2-sila-1,3-dioxolane reacts with an excess of isopropanol according to a first-order rate law. The reaction is acid-catalyzed, with a linear relation between the rate constant and the concentration of catalyst. The ring opening is fast, and is followed by a rate-determining step to give the products.

Rate constants for the propanolysis of 2,2-dialkyl-2-sila-1,3-dioxolanes decrease with the size of alkyl groups on silicon in the order Me > Et > Pr. The activation energy for reactions in propanol is about 6 kcal/mole, and for isopropanol about 11 kcal/mole, while the entropy of activation in both solvents has a high negative value of about −50 e.u. Rate constants for the acid-catalyzed reaction of $(p\text{-XC}_6H_4)CH_3Si[OC(CH_3)_2]_2$ with n-propanol (X=F, Cl, Br, H, CH_3, CH_3O) follow the Hammett equation ($\log(k/k_0) = -0.41\ \sigma^0$). (An analogous correlation was obtained for the phenyl–silicon IR vibration frequencies.) The reaction follows a bimolecular mechanism.

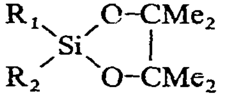
INTRODUCTION

The Si–OC bond in acyclic compounds readily undergoes solvolysis in the presence of acids or bases, but there have been few kinetic studies of this type of reaction. The acid-catalyzed reaction of trimethyl-tert-butoxysilane in absolute ethanol has been shown to be fast, the reaction being complete in less than half a minute[1]. The base-catalyzed solvolysis of triarylsilylacetates[2], and phenyldimethylsilyl acetates[3], has been studied by Schott and his co-workers. They found that electron-attracting substituents in either the acetate or the phenyl groups accelerated the reaction, showing that the ease of nucleophilic attack on silicon determines the order of reactivity. Prince and Timms[4] determined the activation parameters for the base-catalyzed hydrolysis of R_3SiOAc. They observed large negative values for the activation entropy, and attributed these to a high ordering of the water in the transition state. They discussed their results in terms of a bimolecular mechanism in which the bond-breaking process is important.

The methanolysis of menthoxysilanes was studied by Sommer *et al.*[5], who found that the reaction constant, ρ, had a much larger positive value in the acid than in the base-catalyzed solvolysis.

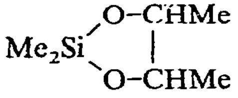
In the present work the rate of propanolysis of hexamethyl-2-sila-1,3-dioxolane, (Ia), has been compared with the rates for several acyclic $Me_2Si(OR)_2$ and Me_3SiOR

compounds in order to establish which is the rate-determining step in the solvolysis of (Ia). To throw light on the details of the mechanism of the reaction, (*a*) rates have been measured for the substituted 2-sila-1,3-dioxolanes (I) and (II), and activation parameters determined, and (*b*) the solvolysis of substituted phenylmethylsiladioxolanes $(p\text{-}XC_6H_4)CH_3Si[OC(CH_3)_2]_2$, (X=F, Cl, Br, H, CH_3, CH_3O) has been studied



(I)

(Ia), $R_1=R_2=Me$; (Ib), $R_1=R_2=Et$; (Ic), $R_1=R_2=Pr$; (Id), $R_1=Me$; $R_2=Ph$

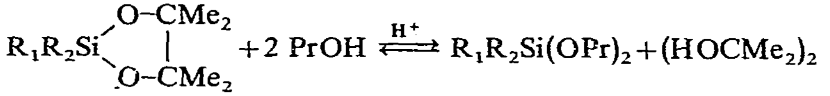


(II) (two isomers)

The latter study has given an indication of the relative importance of nucleophilic and electrophilic processes in a reaction in which one Si–O bond is being broken and another formed.

RESULTS AND DISCUSSION

The overall reaction between 2-sila-1,3-dioxolanes and propanol containing a little sulphuric acid was found to be as represented in eqn. (1). Under these con-



$$R_1R_2Si\begin{matrix}O\text{-}CMe_2\\|\\O\text{-}CMe_2\end{matrix} + 2\ PrOH \overset{H^+}{\rightleftharpoons} R_1R_2Si(OPr)_2+(HOCMe_2)_2 \tag{1}$$

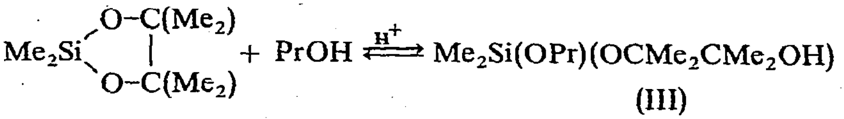
ditions the reaction with propanol went completely to the products, but with isopropanol about 35% of (Ia) remained after ten half-lives. With propanol in great excess and at a constant acid concentration the reaction was first order, according to eqn. (2).

$$d[I]/dt = -k[I] \tag{2}$$

Experiments with varying concentrations of acid catalyst showed that there was a linear relation between the rate constant and the concentration of catalyst (see Table 1).

$$k = k_0 + k_H[H^+] \tag{3}$$

From the stoichiometry of eqn. (1) it is apparent that the reaction involves rupture of two Si–O bonds and includes at least two proton-transfer reactions. Thus the simplest reaction scheme for hexamethyl-2-sila-1,3-dioxolane is the following:



$$Me_2Si\begin{matrix}O\text{-}C(Me_2)\\|\\O\text{-}C(Me_2)\end{matrix} + PrOH \overset{H^+}{\rightleftharpoons} Me_2Si(OPr)(OCMe_2CMe_2OH) \tag{4}$$

(III)

(Ia)

TABLE 1

THE ACID-CATALYZED SOLVOLYSIS OF HEXAMETHYL-2-SILA-1,3-DIOXOLANE IN PROPANOL/BENZENE (1/1 v/v) AT 35.0°[a]

$[H_2SO_4]$ (10^3N)	$k \cdot 10^5$ (sec^{-1})	$k/[H_2SO_4]$
0.25	5.28	21.1
0.50	12.1	24.2
1.0	22.1	22.1
2.0	40.5	20.3
4.0	90.4	22.6

[a] Calculated standard deviations are approx. 3%.

$$\underset{\text{(III)}}{Me_2Si(OPr)(OCMe_2CMe_2OH)} + PrOH \xrightleftharpoons{H^+} Me_2Si(OPr)_2 + (HOCMe_2)_2 \qquad (5)$$

If the postulated intermediate (III) were available, its reactivity relative to that of (Ia) would provide an answer to the question of whether step (4) or (5) is rate-determining, but several attempts at preparing it were unsuccessful. This was not surprising, since neat (III) can be expected to cyclise to form (Ia) or to polymerize. In order to answer this question, model compounds similar to (III), but lacking the nucleophilic hydroxyl group were examined. This permits a study of reactions of type (5) without any possibility of interference from the reversibility of a reaction of type (4). Various Me_3SiOR and $Me_2Si(OR)_2$ compounds were synthesized and their reactivities compared. Reactive compounds were treated with stoichiometric amounts of propanol in benzene without a catalyst, and the results are shown in Table 2. Less reactive compounds were

TABLE 2

REACTION OF Me_3SiOR (0.08 *M*) OR $Me_2Si(OR)_2$ (0.08 *M*) WITH PROPANOL (0.16 *M*) IN BENZENE AT 35.0°

$Me_nSi(OR)_{4-n}$	*Approx. percentages remaining after 2 min for R =*			
	CH_3CH_2	$HOCH_2CH_2$	$CH(CH_3)_2$	$CH(CH_3)_2C(CH_3)_2$
Me_3SiOR	25	25	25	60
$Me_2Si(OR)_2$	1		1	

TABLE 3

FIRST-ORDER CONSTANTS FOR SOLVOLYSIS AT 35.0° OF $Me_2Si(OR)_2$ (0.08 *M*) IN ISOPROPANOL/BENZENE (1/1 v/v) CONTAINING 10^{-3} *N* H_2SO_4

R	k_1 (sec^{-1})
$CH_3CH_2CH_2$	10^{-3}
$(CH_3)_3C$	$<10^{-5}$
$(CH_3)_2CH(CH_3)_2C$	$<10^{-5}$
$(CH_3)_2C$, (Ia)	1.41×10^{-5}

treated with an excess of isopropanol containing 10^{-3} N sulfuric acid, and the results are shown in Table 3. From the results the following conclusions can be drawn.

(*a*). A hydroxyl group in R in a γ-position with respect to silicon has no effect on the reactivity of Me_3SiOR.

(*b*). The rates of reaction of $Me_2Si(OR)_2$ compounds are very dependent upon the nature of R. When R is a tertiary group, the reactivity is much lower than when R is primary or secondary.

(*c*). The $Me_2Si(OR)_2$ are more reactive than the Me_3SiOR compounds.

Compound (III) should be intermediate in reactivity between $Me_2Si(OPr)_2$ and $Me_2Si(OCMe_2CHMe_2)_2$, and thus the first-order rate constant for (III) should be of the order of 10^{-5} sec^{-1}. From Table 3, it will be seen that this is close to the rate constant found for (Ia), and this, together with the observations that the reaction between (Ia) and propanol goes to completion and that pinacol is formed in a first-order reaction shows that reaction (5) is rate-determining.

Calculations based upon the kinetic equations for the general case of reversible first-order reactions[6], considered together with the experimental facts, lead to the same conclusions.

The results obtained for the reaction of the dialkyl- and alkylarylsiladioxolanes (I) and (II) with propanol are given in Table 4. The reactivities of the siladioxolanes fall in the order (R =) Me > Et > Pr. This probably reflects increasing steric hindrance, since the results for the *p*-substituted dimethylphenylsiladioxolanes show that polar effects are small, and that increase in electron release to silicon raises the rate. The effect of R on the rate of alcoholysis of acetates R_3SiOAc was studied by Prince and Timms[4], who found that the compound with R = i-Pr was 100 times less reactive than that with R = Pr. The authors assumed that this was a result of the greater steric hindrance at silicon, although comparison of the effects of hexyl and cyclohexyl groups indicated the reverse.

TABLE 4

FIRST-ORDER CONSTANTS k_1 AND STANDARD DEVIATIONS s_k FOR THE SOLVOLYSIS AT 35.0° OF $R_1R_2Si(OCMe_2)_2$ IN PROPANOL/BENZENE (1/1 v/v) CONTAINING 10^{-3} N H_2SO_4

R_1	R_2	$10^5\ k_1\ (sec^{-1})$	$10^5\ s_k\ (sec^{-1})$
Me	Me	22.1	0.30
Et	Et	10.6	0.45
Pr	Pr	5.8	0.20
Me	Ph	8.2	0.34

The stability of (II) was relatively low. Molecular weight determinations showed that it polymerized on standing. Samples purified by GLC were found to be fairly stable, however, and it was possible to obtain semiquantitative data for its alcoholysis. The mixture of the two isomers of (II) obtained from GLC, was treated with isopropanol, and the results compared with those for hexamethyl-2-sila-1,3-dioxolane (Ia) (see Table 5). Because of limitations in the method of analysis, only approximate values could be obtained for the rate constants, but the following conclusions seem justified:

TABLE 5

FIRST-ORDER CONSTANTS AT 25.0° FOR THE SOLVOLYSIS OF $Me_3Si(OCRMe)_2$ (0.08 *M*) IN ISOPROPANOL/BENZENE CONTAINING 10^{-3} *N* H_2SO_4

R	$k_1 \cdot 10^6$ (*sec*$^{-1}$)
Me	8
H (isomer 1)	170
H (isomer 2)	300

(*i*). The reactivities of the two isomers of (II) are of the same order.

(*ii*). (II) is more reactive than (Ia).

Since reaction (5) is rate-determining, the enhanced reactivity of (II) compared with (Ia) would be expected, since the intermediate from (II) contains a secondary carbon β to silicon, while (Ia) contains a tertiary carbon. It was shown above that tertiary carbons β to silicon greatly reduce the rate of alcoholysis of $R_2Si(OR)_2$ compounds. Similar protective effects have been found in the hydrolysis of Me_3SiOR compounds[7].

The effects of temperature and medium on the reaction rate were investigated for the two compounds (Ia) and (Id) in n-propanol and isopropanol (Table 6). For both compounds the reactions are slower in isopropanol than in n-propanol. The entropy

TABLE 6

FIRST-ORDER CONSTANTS FOR THE SOLVOLYSIS OF $MeRSi(OCMe_2)_2$ IN PROPANOL/BENZENE AND ISOPROPANOL/BENZENE (1/1 v/v) CONTAINING 10^{-3} *N* H_2SO_4[a]

R	*Solvent*	$k_1 \cdot 10^5$ (*sec*$^{-1}$) *at various temperatures* (°*C*)				
		25	30	35	40	45
Me	PrOH/PhH	15.2	16.1	22.1	23.6	
	i-PrOH/PhH			1.41	2.06	2.60
Ph	PrOH/PhH	7.13	7.49	8.16	8.73	
	i-PrOH/PhH			3.50	4.38	5.89

[a] Calculated standard deviations are of the order of 1–7 %.

TABLE 7

ACTIVATION PARAMETERS AND (IN PARENTHESES) STANDARD DEVIATIONS FOR THE REACTION BETWEEN $MeRSi(OCMe_2)_2$ AND PROPANOL/BENZENE OR ISOPROPANOL/BENZENE (1/1 v/v)

R	*Solvent*	*E* (*kcal/mol*)	ΔS_{35} (*e.u.*)
Me	PrOH/PhH	6.1 (1.4)	−56.9 (13.1)
	i-PrOH/PhH	11.9 (1.5)	−43.2 (6.4)
Ph	PrOH/PhH	2.6 (0.2)	−70.7 (7.8)
	i-PrOH/PhH	10.2 (0.9)	−39.2 (6.2)

of activation has a high negative value in all cases, and the activation energy is considerably larger for isopropanolysis than for n-propanolysis (Table 7). The large negative value for the activation entropy indicates a high degree of order in the transition state, while the higher activation energy for reactions in isopropanol probably results from steric hindrance to nucleophilic attack at silicon; it cannot reasonably be ascribed to differences in general solvent properties, since these are rather similar for the two alcohols. For the phenylmethylsiladioxolanes the rate constants, shown in Table 8, fit the Hammett equation $\log(k/k_0) = \rho \cdot \sigma^0$ with $\rho = -0.41 \pm 0.02$ (correlation coefficient 0.99). The sign and magnitude of ρ show that the rate is slightly increased by electron-donating *para*-substituents. Previously σ^0 constants have been shown to correlate with the rate constants for the alkaline[8] and acid[9] solvolysis of substituted phenyldimethylsilanes, and the alkaline solvolysis of phenyldimethylsilyl acetates[3], while the bromination of phenyldimethylsilanes was correlated with the Hammett σ-constants[10]. In the cases in which σ^0 constants apply, the generally accepted interpretation is that the degree of interaction between the *d*-orbitals of silicon and the benzene system does not change between the ground and transition states.

TABLE 8

FIRST-ORDER CONSTANTS FOR THE PROPANOLYSIS OF $(p\text{-}XC_6H_4)CH_3Si(OCMe_2)_2$ AT 35.0° AND 10^{-3} *N* H_2SO_4[a]

X	$k \cdot 10^5$ (*sec*$^{-1}$)	*log* k/k_0	σ^0
F	10.5	−0.073	0.17
Cl	9.2	−0.130	0.27
Br	9.8	−0.102	0.26
H	12.4	0.000	0.00
CH_3	14.1	0.056	−0.15
CH_3O	14.1	0.056	−0.16

[a] $\rho = -0.41$, standard deviation 0.02, correlation coefficient 0.99.

TABLE 9

IR ABSORPTION FREQUENCIES (cm^{-1}) FOR $(p\text{-}XC_6H_4)CH_2Si[OC(CH_3)_2]_2$

X	*Si–Ar*	*Si–CH₃*	*X*	*Si–Ar*	*Si–CH₃*
F	1585	1264	H	1592	1264
Cl	1573	1262	CH_3	1596	1264
Br	1570	1266	CH_3O	1590	1285

The IR frequencies of the phenyl vibrations of the siladioxolanes are given in Table 9. Absorption due to the silicon–aryl bond occurs in normal positions[11]. There is an analogy between the change in electron distribution in the molecule resulting from vibrational distortion and that which results from the influence of an attacking reagent. Electron-donating groups in the *para*-position shift the vibrational bands to higher wave numbers and there is a fair correlation between $\log[(\tilde{v}\text{-}v_0)/v_0]$ and σ^0. Shifts to higher wave numbers correspond to increased rates, and the effects of *para*-

substituents on IR vibrational bands may be compared to their effects on rates. The opening of the siladioxolane ring by alcoholysis, reaction (4) above, may be regarded as a convenient way of making alkoxysilanes with reactivities suitable for kinetic measurements, since it has been shown that the following step, reaction (5), is rate-determining. Reaction (5) involves the cleavage of one Si–O bond with simultaneous formation of another Si–O bond. If the bond-breaking were rate-determining, the reaction would be analogous to an S_N1 reaction and would involve the formation of a siliconium ion. There is no example of the operation of an S_N1-Si mechanism in the literature, and such a mechanism is most unlikely for the solvolysis studied[5]. In agreement with this, while positive or slightly negative entropies of activation would be expected for an S_N1 mechanism[12], values which are large and negative were in fact found for the siladioxolanes. Thus the S_N1-Si mechanism can be ruled out.

A bimolecular mechanism involving rapid protonation of an oxygen atom followed by rate-determining attack by ROH is consistent with the facts:

$$Me_2Si(OR)(OR') + H^+ \rightleftarrows [Me_2Si(OR)(OHR')]^+ \quad \text{(fast)}$$

$$[Me_2Si(OR)(OHR')]^+ + ROH \rightarrow \underset{\text{(IV)}}{[R\underset{H}{O}\text{---}Si\text{---}\underset{H}{O}R']^+} \rightarrow Me_2Si(OR)_2 + R'OH_2^+ \quad \text{(slow)}$$

In view of the symmetry of the transition state (IV), bond-breaking and making processes would be expected to be fairly synchronous, so that little charge would be located on the Si atom in the transition state. The small negative value of ρ is consistent with this.

EXPERIMENTAL

Materials

Acyclic compounds. Trimethylalkoxysilanes were made from trimethylchlorosilane and alcohols with tributylamine as hydrogen chloride acceptor. Diorganodialkoxysilanes were similarly made from diorganodichlorosilanes. Products were purified by rectification. Elemental analyses are given for new compounds. Trimethylethoxysilane b.p. 72–78° (lit.[13] b.p. 75.0°/745 mmHg). 2-(Trimethylsiloxy)ethanol b.p. 152° (lit.[14], b.p. 151–152°). Trimethylisopropoxysilane b.p. 86–88° (lit.[15] b.p. 87°). 1-(Trimethylsiloxy)-1,1,2-trimethylpropane b.p. 50–54°/40 mmHg. (Found: C, 64.61; H, 12.78. $C_9H_{22}OSi$ calcd.: C, 62.00; H, 12.72%.) Dimethyldipropoxysilane b.p. 152–154° (lit.[16] b.p. 152°). Dimethyldiisopropoxysilane b.p. 132° (lit.[17] b.p. 132.5°). Dimethyldi-tert-butoxysilane b.p. 157° (lit.[18] b.p. 50.5°/15 mmHg). Dimethylbis(1,1,2-trimethylpropoxy)silane. (Found: C, 64.13; H, 12.07. $C_{14}H_{32}OSi$ calcd.: C, 64.55; H, 12.38%.) Methylphenyldipropoxysilane b.p. 137°/25 mmHg, n_D^{20} 1.4701. (Found: C, 65.15; H, 9.15. $C_{13}H_{22}O_2Si$ calcd.: C, 65.49; H, 9.30%.)

2-Alkyl-2-sila-1,3-dioxolanes

Method A. 2-Sila-1,3-dioxolanes were prepared by treatment of pinacol with the appropriate dichlorosilane in diethylether, with pyridine as acid acceptor. Diethyl- and dipropyldichlorosilane were prepared in 20–30% yields by Grignard reactions from silicon tetrachloride. Elemental analyses are given for new compounds. (Ib)

(Found: C, 57.24; H, 10.66. $C_{10}H_{16}O_2Si$ calcd.: C, 59.35; H, 10.96%.). (Ic) (Found: C, 60.25; H, 11.22. $C_{12}H_{20}O_2Si$ calcd.: C, 62.55; H, 11.37%.). (Id) (Found: C, 65.45; H, 8.63. $C_{13}H_{14}O_2Si$ calcd.: C, 66.05; H, 8.53%.).

Method B. In this method 2-sila-1,3-dioxolanes were prepared from glycols and dimethyldiethoxysilane by continuously distilling off the ethanol/diethoxysilane azeotrope. NMR spectra showed that (II) was a mixture of *cis* and *trans* isomers. This was expected, since the mixture of *d, l-* and *meso*-2,3-butanediol gives *cis-* and *trans*-4,4-dimethyl-2-phenyl-1,3-dioxolane when brought into reaction with benzaldehyde[19].

2-Aryl-2-sila-1,3-dioxolanes

The compounds $(p\text{-}XC_6H_4)CH_3Si(OC(CH_3)_2)_2$, (X = F, Cl, Br, CH_3, CH_3O) were made by treatment of pinacol with the appropriate arylmethyldichlorosilane in diethyl ether with pyridine as acid acceptor. Only the unsubstituted compound (X = H) has been previously reported. The arylmethyldichlorosilanes were made by Grignard reactions from methyltrichlorosilane and *para*-substituted bromobenzenes, by the method used for the preparation of dimethylchlorosilanes[3].

Dichlorosilanes. $(p\text{-}FC_6H_4)CH_3SiCl_2$ b.p. 94°/18 mmHg (lit.[21] b.p. 196–198°), n_D^{20} 1.4987 (lit.[21] n_D^{20} 1.5050). $(p\text{-}ClC_6H_4)CH_3SiCl_2$ b.p. 125–127°/25 mmHg (lit.[22] b.p. 161–164°/100 mmHg), n_D^{20} 1.5371 (lit.[23] n_D^{20} 1.5345). $(p\text{-}BrC_6H_4)CH_3SiCl_2$ b.p. 128°/25 mmHg (lit.[24] n_D^{20} 1.5628). $(p\text{-}CH_3C_6H_4)CH_3SiCl_2$ b.p. 103°/15 mmHg, n_D^{20} 1.5190. $(p\text{-}CH_3OC_6H_4)CH_3SiCl_2$ b.p. 154°/18 mmHg, n_D^{20} 1.5302.

Siladioxolanes. (X=) F (Found: C, 60.78; H, 7.59. $C_{13}H_{19}FO_2Si$ calcd.: C, 61.39; H, 7.56%.). Cl (Found: C, 57.16; H, 7.12. $C_{13}H_{19}ClO_2Si$ calcd.: C, 57.65; H, 7.07%.). Br (Found: C, 49.58; H, 6.18. $C_{13}H_{19}BrO_2Si$ calcd.: C, 49.52; H, 6.08%.). CH_3 (Found: C, 64.96; H, 8.93. $C_{14}H_{22}O_2Si$ calcd.: C, 67.15; H, 8.86%.). CH_3O (Found: C, 62.82; H, 8.47. $C_{14}H_{22}O_3Si$ calcd.: C, 63.12; H, 8.32%.).

Kinetic measurements

Organosilicon compounds were purified by GLC for all kinetic experiments. Reactions with reactive acyclic organosilicon compounds were run without a catalyst and with stoichiometric amounts of propanol in benzene. 0.08 mol/l acyclic compound was dissolved in benzene (Merck p.a. distilled from sodium), and 0.16 mol/l propanol (purified according to Schott *et al.*[3]) was added. After stirring, samples were withdrawn and analyzed. Rough values of the rate constants were obtained for the acyclic compounds by measuring peak heights of the organosilicon reactants as functions of time. Thus the rate constants given refer to the cleavage of the first Si–OC bond. Under these conditions, the 2-sila-1,3-dioxolanes and the $Me_2Si(OR)_2$ compounds in which R is tertiary were unreactive, and the solvolyses in these cases were carried out with propanol in large excess and containing a little sulphuric acid. 0.08 mol/l (I) or $Me_2Si(OR)_2$ was dissolved in benzene/propanol, 1/1 by volume, containing sulfuric acid at a concn. of 10^{-3} *N*. Substituted aryl compounds were run at three different concentrations, viz. 0.08, 0.06, and 0.04 mol/l, in propanol containing a little sulphuric acid.

Samples were withdrawn from the reaction mixture and analyzed by GLC on a 2 m × ¼″ column packed with 20% Apiezon L on 60–80 mesh Chromosorb W HMDS. Higher boiling compounds (b.p. > 200°) were analyzed on a 2 m × ¼″ column packed with 10% Apiezon L on 45–60 mesh Chromosorb W HMDS. Helium (40 ml/min) was used as the carrier gas in conjunction with a thermal conductivity detector (Varian Aerograph model P-90 gas chromatograph), and nitrogen (60 ml/min) in conjunction with a flame ionization detector (Varian Aerograph model 1740 gas chromatograph). Preliminary experiments showed that it was not necessary to stop the reaction by neutralizing the catalyst before the injection into the gas chromatograph, identical rate constants being obtained for neutralized and acidic solutions.

The decrease in concentration of the 2-sila-1,3-dioxolanes was followed by disc-integrating the peak area. Reactions in n-propanol were followed to about 80% completion, and in isopropanol to about 50% completion.

For some reactions it was possible to check the validity of the analytical method by measuring also the concentration of pinacol formed in the reactions. The first-order constants thus obtained were identical with those based on the concentrations of the 2-sila-1,3-dioxolanes.

Reaction products

The products from the reaction between hexamethyl-2-sila-1,3-dioxolane and the propanols were isolated by GLC and their identity established by comparing their IR spectra with those of authentic samples. The products from the reaction between $MePhSi[OC(CH_3)_2]_2$ and propanol were isolated by GLC and identified as pinacol and $MePhSi(OPr)_2$ by comparing IR spectra and retention times with those of authentic samples. The retention time for $MePhSi(OPr)_2$ (product) relative to $MePhSi[OC(CH_3)]_2$ (reactant) was t_R (prod.)/(react.) = 0.70. The reaction between $(p\text{-}XC_6H_4)CH_3Si[OC(CH_3)_2]_2$ and propanol was found to give only one product in each case; the retention times, t_R were of 0.69–0.70.

Treatment of data

First-order constants given in the tables are mean values based on three or four individual runs. Each run usually involved ten observations (range 8–33 obs.). The constants and standard deviations were obtained by means of a computer using a linear least-squares method.

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