Nucleophilic Substitution at Silicon and Germanium: III. Hydrolysis of Tri-alkyl Silicon Acetates

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The rates of hydrolysis of the acetates, R_3SiOAc ($R =$ Me, Et, n–Pr, n–Bu) have been measured in dioxane and iso-propanol. Differences in activation energy account for the observed rate differences and steric factors are considered important. The dependence of the activation energy on the water concentration has been studied for $(n-Pr)_3SiOAc$ hydrolysis in dioxane. In iso-propanol this hydrolysis is close to first order in water, probably due to the ability of the alcohol to replace water molecules in the transition state. The hydrolysis of Me_3SiOAc in dioxane proceeds with a higher order in water than for the other acetates studied. It is suggested that the methyl group affords less «nonpolar protection» than other alkyl groups.

Introduction

Much evidence is available for the high reactivity of trimethyl silyl compounds relative to other trialkyl silicon compounds.[1] Presumably because of this, no quantitative kinetic rate comparisons have been made, although various independent rate studies of trimethyl silyl[2-4] and other trialkylsilyl compounds have been published.[4-10]

A suitable choice of water concentration enables us to compare the rate of hydrolysis of trimethylsilicon acetate with trimethyl, tri-propyl, and tributyl silicon acetates in dioxane as solvent. In iso-propanol the reaction is much faster and the trimethyl silicon acetate reacted too quickly for study by the technique described here.

Experimental Section

Kinetic measurements were made as described previously (Part I) except for Me_3SiOAc which was found to react during the extraction of the acetic acid.

(1) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 68, 2282 (1946).
(2) G. Schott and H. Werner, *Z. Anorg. Chem.*, 329, 299 (1964) and 331, 59 (1964).
(3) M. G. Voronkov and L. A. Zhagata, *Zhur. Obshchei Khim.*, 37, 1156 (1967).
(4) R. M. Pike and S. J. Weaver, *Rec. Trav. Chim.*, 86, 606 (1967).
(5) J. E. Baines and C. Eaborn, *J. Chem. Soc.*, 4023 (1955).
(6) O. W. Steward and O. R. Pierce, *J. Amer. Chem. Soc.*, 83, 1916 (1961).
(7) G. Schott and P. Ebel, *Z. Anorg. Chem.*, 325, 169 (1963).
(8) G. Schott and C. Harzdorf, *Z. Anorg. Chem.*, 306, 180 (1960).
(9) G. Schott, *Z. Chem.*, 6, 361 (1966).
(10) O. W. Steward and O. R. Pierce, *J. Amer. Chem. Soc.*, 83, 4932 (1961).

Instead, a spectrophotometric method was used. The reaction was started by mixing 5 ml of aqueous dioxane solution from a 5 ml syringe with 5 ml of Me_3SiOAc solution (.04 to .08 M) in a 25 ml flask. After shaking, the solution was poured into a 1 cm. quartz cell and the optical density measured at 232 mμ using a thermostatted Unicam SP 500 spectrophotometer. At this wavelength, both Me_3SiOAc and acetic acid absorb but with different extinction coefficients. The reference cell contained an aqueous dioxane solution of acetic acid whose concentration was adjusted to give an optical density change from about 0.8 to 0.3 during the reaction.

The silicon acetates were prepared by standard methods and purified by distillation on a spinning band column. Purity was checked by analysis for carbon, hydrogen and molecular weight and by the titre required for total saponification.

Acetone was purified by passing A.R. acetone through 5 ft.$\times$1″ column of molecular sieve, size 4A, at 510 mls/min. and then fractionally distilling from more molecular sieve. The specific conductivity was about 2×10^{-8} mho/cm.

Iso-propanol was purified similarly and distilled from calcium hydride. The specific conducticity was about 4×10^{-8} mho/cm.

Results and Discussion

Changing the Solvent. The rate of hydrolysis of $(n-Pr)_3SiOAc$ was measured in both acetone and iso-propanol. The results are given in Table I together with some data for dioxane reported previously, for comparison. In these solvents also, plots of log k_1 versus log (%H_2O) are linear and the orders, determined by a least squares method, are given in the table. Slow iso-propanolysis occurs in the absence of water. (If this «blank reaction» is due to traces of water remaining in the solvent, then it corresponds to about 0.01% H_2O). No correction for this was necessary, since even at 0.5% H_2O, the water concentration for the slowest hydrolysis studied, the hydrolysis reaction is fifty times more rapid than iso-propanolysis.

The hydrolysis is faster in these two more polar solvents, than in dioxane, as expected for a reaction in which considerable ionic character is developed in the transition state. In acetone the rate is only

Table I. Rate constants for hydrolysis of (n—Pr)₃SiOAc at 25°C

%H₂O	Acetone	$10^4 k_1$ (sec⁻¹) Iso-propanol	Dioxane
0	—	.026 ± .001	—
0.5	—	1.48 ± .05	—
1	—	3.19 ± .05	—
2.5	—	10.2 ± .1	—
5	0.79 ± .02	25.8 ± .3	.046 ± .001
7.5	1.56 ± .03	—	—
10	4.43 ± .07	51 ± 1	1.11 ± .01
15	18.1 ± .3	—	5.80 ± .04
20	47.5 ± .7	139 ± 3	19.3 ± .2
Order	3.48 ± .04	1.23 ± .02	4.39 ± .06

slightly faster than in dioxane, this difference decreasing with increasing water concentration since the order in water is lower at 3.48. This lower order suggests that perhaps acetone molecules are more effective than dioxane molecules in solvating the transition state and thus fewer water molecules are necessary.

In iso-propanol the rate is strikingly greater than in the other two solvents and the dependence on water is close to first order. Since acetone and iso-propanol have similar dielectric constants, the dielectric constant must be only a minor factor in determining the rate. Similarly the hydrolysis of chloro-silanes and -germanes in acetone-ether solvents is little dependent on the dielectric constant of the medium.

Prince[11] found a similar low order for the hydrolysis of (i—Pr)₃SiCl in iso-propanol. He suggested that iso-propanol was hydrogen bonding with the water and could replace water molecules in the transition state solvation shell, except for the one water molecule necessary for the attack at the silicon atom. Two further results confirm this model: (i) at 5% H₂O we may compare the activation parameters in the two solvents (Table II). We see that the large rate difference is explained by the activation entropy difference of 13.5 e.u. suggesting that the ground state is more ordered in iso-propanol because of the extra hydrogen bonding; (ii) at 5% H₂O in the presence of potassium acetate, concentration $5.3 \times 10^{-4} M$, $k_1 = 2.67 \pm .02 \times 10^{-3}$ sec⁻¹—virtually the same as the rate in the absence of the acetate. In dioxane, such low sensitivity to catalysis by acetate was found only

at high water concentrations, showing that the alcohol molecules can act effectively as the base B (see Part I) independently of the concentration of water molecules present. Allen and Modena[12] observed a similar lack of catalysis when studying chlorosilane hydrolysis in iso-propanol.

Changing R. Table II gives the rates and activation parameters for the silicon acetates studied at 5% H₂O in dioxane and iso-propanol.

Considering the data for dioxane first, the relative rates are (including a value for (n—hex)₃SiOAc obtained by extrapolation):

R	Me	Et	n—Pr	n—Bu	n—Hex
k_{rel}	171	4.5	1	0.53	0.14

Trimethyl silicon acetate is extremely sensitive to hydrolysis compared with the other acetates. The activation energies show steadily decreasing increments from R = Me to Bu, while ΔS^*_{obs} is virtually constant. Both steric and inductive factors are involved here, although we consider that steric factors are probably the more important. Our data does not correlate well with Taft σ^* [9] values showing that inductive effects alone are not able to account for the relative rates.

After R = n—Pr, the decrease in rate is roughly proportional to the number of CH₂ groups added. At this chain length, steric and polar effects should be negligible and the small decrease in rate reflects the increasing mass.

For the alkaline hydrolysis of tri-alkyl silanes Baines and Eaborn[5] found the relative rates

Et	Pr	Bu
2.5	1	.67

suggesting less steric hindrance in this reaction than in our acetate solvolysis involving a highly ordered and crowded transition state.

The slightly lower, but probably significant, ΔS^*_{obs} for the hydrolysis of Me₃SiOAc indicates the effect of decreased steric hindrance on the entropy of activation as discussed by Price[13] for the hydrolysis of trialkylsilanes. Another interesting aspect of this hydrolysis is that the order in water, deduced from the data in Table III, is signficantly higher at $4.97 \pm .04$ than for

Table II. Apparent activation parameters for hydrolysis of R₃SiOAc at 25°C and 5% H₂O in dioxane and isopropanol

R	Dioxane $10^5 k_1$	ΔH^*_{obs}	ΔS^*_{obs}	Iso-propanol $10^3 k_1$	ΔH^*_{obs}	ΔS^*_{obs}
Me	78.6 ± .8	1.1 ± .1	−65.1 ± .1	—	—	—
Et	2.08 ± .02	2.7 ± .2	−66.8 ± .2	5.8 ± .1	3.9 ± .4	−52 ± 1
Pr	.46 ± .01	3.6 ± .1	−66.8 ± .3	2.58 ± .03	3.9 ± .1	−53.3 ± .3
Bu	.244 ± .002	4.2 ± .7	−66 ± 2	1.76 ± .08	3.9 ± .4	−54 ± 1

Table III. The rate of hydrolysis of Me₃SiOAc in Dioxane at 25°C

%H₂O	3	3.5	4	5	6	7	8.5
$10^4 k_1$ (sec⁻¹)	.56 ± .01	1.29 ± .01	2.44 ± .02	7.86 ± .08	18.2 ± .1	39.1 ± .2	101 ± 1

(11) R. H. Prince, *J. Chem. Soc.*, 1783 (1959).

(12) A. D. Allen and G. Modena, *J. Chem. Soc.*, 3671 (1957).

(n—Pr)₃SiOAc (4.39±.04). We believe this to be
due to the smaller shielding effect or «non-polar
protection» of methyl relative to other alkyl groups,
allowing greater solvation of the acetate by the more
polar water molecules. Alkyl groups, by their nature,
will be water repelling and seek preferential solvation
by dioxane molecules.

In iso-propanol, the relative rate differences are
smaller and neither the activation energies nor entro-
pies are sufficiently accurate to show any significant
trend.

Et	Pr	Bu
2.2	1	.68

Assuming the order in water bears some relation to
the number of water molecules in the transition state,
as discussed in Part I, than the transition state in iso-
propanol will be less crowded than in dioxane and
hence steric hindrance less important. These relative
rates are in good agreement with those of Baines and
Eaborn[5] which were measured in aqueous ethanol,
suggesting similar steric effects in the two reactions.

Changing the Water Concentration. In Part I we
considered the effect of changing the water concen-
tration on the temperature dependence of the hydro-
lysis. We have now made further studies of the
temperature dependence of the (n—Pr)₃SiOAc hydro-
lysis. The complete results are given in Table IV and
are shown plotted in the Figure 1 against log(%H₂O).*

Table IV. Activation Parameters for (n—Pr)₃SiOAc

%H₂O	ΔG^*_{obs}	ΔH^*_{obs}	ΔS^*_{obs}
25	20.48 (kcals)	—	—
20	21.14	6.18±.18	—46.1± .6
17.5	21.46	—	—
15	21.85	6.29±.3	—48.2±1
12.5	22.8	6.12±.14	—50.1± .5
10	22.83	5.42±.27	—54.4± .9
5	24.73	3.6 ±.1	—66.8± .3

(*) If the data is plotted against the water concentration directly,
the pattern is little changed except that the ΔG^*_{obs} plot is distinctly
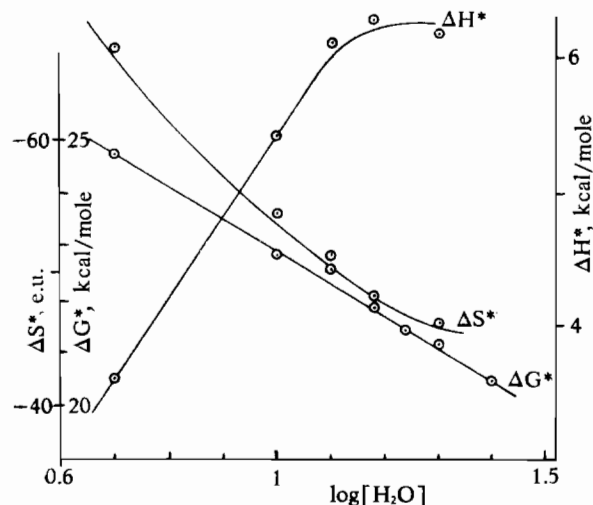curved.

Figure 1. Observed activation parameters for the hydrolysis
of n-Pr₃SiOAc in dioxan at 25°C.

The observed free energy of activation, ΔG^*_{obs}, is
calculated from the equation

$$k_1 = \frac{kT}{h} \exp \frac{-\Delta G^*_{obs}}{RT}$$

We see that although ΔH^*_{obs} reaches a limiting
value at the higher water concentrations, ΔS^*_{obs} does
not but shows a roughly linear dependence on log
(%H₂O) over the range studied. The shape of the
ΔH^*_{obs} curve is just that expected from the simple
theory of Chipperfield and Prince,[14] fully confirming
the suggestions put forward in Part I. The linearity
of the ΔG^*_{obs} plot is seen to be derived from the
two opposing effects of ΔH^*_{obs} and ΔS^*_{obs}. This
linearity may not be a fundamental property of the
hydrolysis but does seem to be an important feature
of solvolysis reactions at a silicon or germanium atom.