724. *Nucleophilic Substitution Reactions of Organosilicon Compounds. Part I. Reactions of Tri*iso*propylsilyl Chloride.*

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The rates of the reactions of tri*iso*propylsilyl chloride with alcohols and water in various solvents have been studied. Solvolytic rates vary greatly, being in the order : methanol > ethanol ≫ *iso*propyl alcohol. Comparison of the reactions with methanol (10%) in nitromethane and in dioxan solution shows that the reaction is strongly facilitated by the more polar solvent. In these solvents the first-order rate increases more rapidly than the concentration of the reagent, but in *iso*propyl alcohol the reaction is of the first order with respect to methanol and water. In this solvent an S_N2 mechanism is proposed.

THERE are no published rate studies on the hydrolysis of organosilicon chlorides. Kinetic investigations have been made of the hydrolysis of organosilicon fluorides [1] and hydrides,[2] and also the analogous condensations of silanols to siloxanes.[3] Generally steric hindrance and electron supply to the silicon atom depress the rate of these reactions. It has been suggested [1] that hydrolysis of the fluorides requires pre-equilibrium formation of an intermediate involving quinquecovalent silicon, which breaks down to give products in a rate-determining step. The data on which this suggestion are based can, however, be interpreted equally on the basis of an S_N2 reaction.[4]

The compound chosen for our initial investigation, tri*iso*propylsilyl chloride, was reported [5] as " resistant to hydrolysis by ordinary means." This overstates the stability of the compound towards hydrolysis, for conditions can be chosen in which the reaction proceeds at a convenient rate. Preliminary experiments indicated that the rate of solvolytic reactions in various alcohols varies greatly with the alcohol used. Relative rates at 0° are approximately : Pr^{i}OH 1, EtOH 10^3, MeOH 10^4.

Addition of small amounts of pyridine to these solutions displaced the equilibrium towards complete reaction, but had little effect on the rate. Since large changes of medium are involved in this comparison, a more detailed study of some reactions in inert solvents was made, including salt effects. With water as the reagent these reactions go

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[1] Swain, Esteve, and Jones, *J. Amer. Chem. Soc.*, 1949, **71**, 965.
[2] Baines and Eaborn, *J.*, 1956, 1436.
[3] Grubb, *J. Amer. Chem. Soc.*, 1954, **76**, 3408.
[4] Hughes, *Quart. Rev.*, 1951, **5**, 245.
[5] Gilman and Dunn, *Chem. Rev.*, 1953, **52**, 99; Gilman and Clark, *J. Amer. Chem. Soc.*, 1947, **69**, 1499.

substantially to completion, but with methanol an equilibrium is reached. Where necessary, initial rates were calculated to overcome this difficulty. The reactions were followed by quenching samples in a large excess of dry ether, in which the reaction is negligibly slow, and titrating the acid liberated with triethylamine in benzene. The results are shown in Table 1.

TABLE 1. *Reactions of tri*iso*propylsilyl chloride with methanol and water in inert solvents at* 25·1°.

R_3SiCl (M)	MeOH (vol. %)	Et_4NX X	Et_4NX M	10^4k_2 (sec.$^{-1}$)	R_3SiCl (M)	ROH (vol. %)	Et_4NCl (M)	10^4k_1 (sec.$^{-1}$)
	In $MeNO_2$–MeOH					*In dioxan*		
0·03	5	—	—	1·65	0·01—0·02	MeOH (10)	—	0·04
,,	10	—	—	7·6	0·03	,, (10)	0·01	0·46
,,	10	Cl	0·01	10·5	,,	,, (22·5)	—	1·6
,,	10	ClO_4	0·01	9·0	0·01	H_2O (2)	—	2·9
,,	15	—	—	18·7	0·03	,, (3)	—	16·0
					,,	,, (4)	—	51
					0·01	,, (4·5)	—	90

Comparison of the results in nitromethane and dioxan shows that the reaction is strongly facilitated by the more polar solvent. The first-order rate coefficient increases more rapidly than the concentration of the reagent; this could be the result of a multiple order with respect to the reagent, or of a medium effect, or both. The greater reactivity of water than of methanol, as the reagent, is clearly shown by the results in dioxan. Salt effects are positive, and, as expected, are more pronounced in dioxan than in nitromethane. Variation of the initial concentration of the silicon halide does not affect the rate. In mixtures of the two solvents, with 10% of methanol as the reagent, a steady increase in the rate coefficient was observed as the nitromethane content was increased:

Solvent, nitromethane (%)	0	25	50	75	100
10^4k_1 (sec.$^{-1}$)	0·04	2·0	3·55	5·45	7·6

This solvent effect is similar to that observed for substitution at a carbon centre by the S_N2 mechanism when the reagent is neutral.

In order to clarify the problem of the high order with respect to the reagent, a study was made of the reactions in *iso*propyl alcohol. As we have seen, the solvolytic reaction in this alcohol is extremely slow, and it is possible to measure the reactions with small amounts of water and methanol against the background of the solvolysis. For the reaction with methanol the silicon halide was first allowed to react with the traces of water present in (dry) *iso*propyl alcohol before adding the reagent. The results are shown in Table 2.

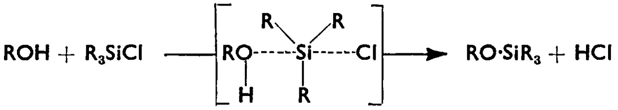
TABLE 2. *Reactions of tri*iso*propylsilyl chloride* (0·03M) *with methanol and water in* iso*propyl alcohol at* 25·1°.

[MeOH] (M)	0	0·96	1·32	2·25	2·25	3·25	2·25 [a]	2·25 [b]
10^4k_1 (sec.$^{-1}$)	0·03	1·43	1·92	3·72	3·95	5·30	4·33	4·13
10^4k_2	—	1·49	1·45	1·65	1·75	1·63	1·92 [a]	1·83 [b]

[a] 0·11M-LiCl added. [b] 0·08M-$LiClO_4$ added.

$[H_2O]$ (M)	0	1·53	1·73	1·87	2·84	3·87	5·83
10^4k_1 (sec.$^{-1}$)	0·03	8·9	10·0	11·5	17·8	25·1	36·4
10^4k_2	—	5·8	5·8	6·15	6·25	6·5	6·25

The second-order rate coefficients, k_2, obtained by dividing the first-order coefficients by the initial concentration of the reagent, do not vary significantly over the range studied. Salt effects are small, positive, and independent of the nature of the anion. No autocatalysis by the hydrogen chloride liberated during the reaction was observed. From these results it is reasonable to assume that the high order with respect to the hydroxylic reagent in inert solvents is related to some property of the reagent which may be taken over by an (unreactive) hydroxylic solvent. Ignoring, for the time being, the rôle of the solvent, we may postulate an S_N2 mechanism in which chloride is displaced directly in a one-stage process by the reagent:



In order to accommodate the depression of the rate of nucleophilic substitution reactions of silicon halides by electron supply to the silicon atom, it is only necessary to remember that, in an S_N2 reaction, the electron requirements depend on whether the bond-making or the bond-breaking process is the more important.[4, 6] For these reactions it appears that the emphasis is on the bond-making process, which is hindered by electron supply.

EXPERIMENTAL

Materials.—Alcohols were dried by reaction with magnesium or lithium, and fractionated through a 40 in. helix-packed column. Purity was checked by constancy of b. p. on change to total reflux. Nitromethane was shaken with anhydrous calcium sulphate and charcoal granules for several hours, run slowly through a 24 in. column of chromatographic alumina (dried at 350° for 6—8 hr.), and fractionated as above. To minimise decomposition this solvent was taken off under reduced pressure. If slight acidity was found in the distillate it was removed by re-passage through a short column of dried alumina. Purity was checked by conductivity not greater than 4×10^{-7} ohm^{-1} at 25°. Dioxan of " purified " grade was fractionated directly from sodium until the metal remained bright: it had m. p. $\nless$ 11·6°. Ether and benzene were distilled from sodium. The water content of all " dry " solvents, and the concentration of water in aqueous reagent solutions, was checked by Karl Fischer titration.

Salts were of " AnalaR " grade, or prepared from " AnalaR " reagents, and were dried in vacuum over phosphoric oxide or magnesium perchlorate at suitable temperatures.

Tri*iso*propylsilyl chloride was prepared as previously described,[5] and had b. p. 80°/10 mm., n_D^{25} 1·4515. Its purity was checked by chloride titration.

Rate Measurements.—Reagent and solvent were mixed in a stoppered flask and brought to thermostat temperature. At zero time the tri*iso*propylsilyl chloride was added from a micro-pipette to the well-stirred solution. For the slower runs samples (5 or 10 ml.) were withdrawn by pipette at suitable time intervals and run into about 100 ml. of dry ether. The acid liberated was titrated with standard (0·01—0·05M) triethylamine in dry benzene, with neutral-red as indicator. For the faster runs an automatic pipette was used which enabled samples to be withdrawn at 30 sec. intervals. The reaction is virtually stopped in dry ether, no acidity being developed in the neutralised solution within 30 min. Infinity values were measured on several samples by adding aqueous alcohol to the ether solution (after initial titration as above) and titrating the total acid liberated.

E.g., tri*iso*propylsilyl chloride (0·03M) in 4% aqueous dioxan; 25°; titrated with 0·0371M-triethylamine in benzene:

Time (min.)	1·05	2·0	2·35	3·15	4·0	5·40	8·20	11·20	∞
Titre (ml.)	2·60	4·0	4·95	5·65	6·25	7·30	8·10	8·65	8·80

k_1 (graphically) = 51×10^{-4} sec.$^{-1}$.

For the reactions with methanol in *iso*propyl alcohol, the silyl chloride was added first to the *iso*propyl alcohol, and the solution was kept at thermostat temperature for about 3 hr. to complete any initial reaction with traces of water in the solvent. The acidity was then measured, and the methanol added at zero time.

E.g., tri*iso*propylsilyl chloride (0·03M) + methanol (2·25M) in *iso*propyl alcohol; 25·1°:

Time (min.)	0	1·00	3·00	4·40	9·20	14·10	20	31	60	∞
Titre (ml.)	3·25	3·35	3·55	3·75	3·97	4·48	4·80	5·30	6·16	8·20

k_1 (graphically) = $3·95 \times 10^{-4}$ sec.$^{-1}$.

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[*Received, March 5th,* 1957.]

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[6] Ašperger and Ingold, *J.*, 1956, 2862.