725. *Nucleophilic Substitution Reactions of Organosilicon Compounds. Part II.*[1] *Reaction Mechanisms of Some Sterically Hindered Organosilicon Chlorides.*

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A kinetic study has been made of the reactions of several sterically hindered trisubstituted silyl chlorides with alcohols, water, and chloride ion in various solvents. Orders of reactivity, both of the silyl chlorides and the reagents, indicate that steric hindrance is important. Generally a high order with respect to hydroxylic reagents is observed, and the reactions are facilitated by increasing polarity of the medium. At low (hydroxylic) reagent concentrations we observed autocatalysis, strong catalysis by added halide ion, and very low temperature coefficients. Hydrolysis of triphenylsilyl chloride catalysed by chloride ion is of first order with respect to both the chloride-ion and water concentrations. The rapid exchange reactions with ^{36}Cl in dioxan and nitromethane solutions follow second-order kinetics. The exchange reaction of triphenylsilanol with $H_2{}^{18}O$ in neutral 10% aqueous dioxan is very slow; in acid solutions the rate of reaction is increased. Possible mechanisms for these reactions are discussed, and an S_N2 type mechanism is proposed in which the reagent is associated with a basic molecule.

In order to obtain a more detailed picture of the mechanism of nucleophilic substitution of chlorine from organosilicon chlorides, the work described in the previous paper [1] was extended to include both less reactive and more reactive compounds.

*Tri-*1*-naphthylsilyl Chloride.*—This compound was reported [2] to resist hydrolysis in 5% aqueous acetone over a period of five days. We find that it is sparingly soluble in acetone, and in nitromethane, but that the reaction in 5% aqueous dioxan is rapid at room temperature. An investigation was made of the reactions with water and various alcohols in dioxan and butan-2-one, including the effect of adding salts (cf. Table 1).

Table 1. *Reactions of tri-*1*-naphthylsilyl chloride with alcohols and water in inert solvents at* 25°.

Solvent	R_3SiCl (M)	Reagent ROH	Reagent Vol. %	Salt	(M)	10^4k_1 (sec.$^{-1}$)
Dioxan	0·01	MeOH	22·5	—	—	0·44
,, ...	,,	H_2O	1·8	—	—	0·07
,, ...	,,	,,	4·5	—	—	5·2
COMeEt	0·05	MeOH	10	—	—	3·8
,, ...	,,	,,	10	$NaClO_4$	0·1	4·8
,, ...	,,	,,	10	LiCl	0·1	5·5
,, ...	,,	,,	25	—	—	55
,, ...	,,	Pr^nOH	10	—	—	0·21
,, ...	,,	,,	25	—	—	2·6
,, ...	,,	Hexanol	10	—	—	0·025
,, ...	,,	,,	25	—	—	0·19

The rates observed with this compound are slower than those found for tri*iso*propylsilyl chloride, but the same general pattern of behaviour is evident. Reactions are faster in the more polar solvent, but salt effects in butan-2-one solution are insignificant. Particularly noteworthy is the sensitivity to the nature and concentration of the reagent, ROH. These may be placed in order of efficiency: $H_2O \gg MeOH > Pr^nOH >$ hexanol $> Pr^iOH$.

The high reactivity of water, and the very low reactivity of *iso*propyl alcohol, may be due to steric factors. Changes in the basic strength of these alcohols may also be important. The specific rôle of hydroxylic molecules in the medium is illustrated clearly by the high

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[1] Part I, Allen, Charlton, Eaborn, and Modena, preceding paper.

[2] Gilman and Brannen, *J. Amer. Chem. Soc.*, 1951, **73**, 4640.

order with respect to the weakly polar hexanol in butan-2-one. This is despite the general reduction in polarity of the medium as the hexanol content is increased.

*Tri*cyclo*hexylsilyl Chloride*.—With this compound[3] steric hindrance to the approach of the reagent should be intermediate between that in the tri*iso*propyl and the tri-1-naphthyl compounds. A brief study was made in order to determine their relative reactivities. For the reactions in dioxan solution at 25·1° the following rate coefficients were measured: Methanol (22·5%), 1·45; Water (1·8%), 0·40; (4·5%), 17·0 (all 10^4k_1 in sec.$^{-1}$).

Triphenylsilyl Chloride.—This compound is very much more reactive than those previously studied. On steric grounds alone there should be little difference between this and the tri*iso*propyl compound. Its reactivity indicates that the polarisability of the phenyl groups strongly facilitates the formation of the transition state. With this compound it was possible to study the reactions with very low concentrations of the reagents. Under these conditions salt effects are considerable and autocatalysis is observed in many cases. The latter, together with a significant back-reaction, necessitated measurement of initial rates by extrapolation to zero time. Because of this an overall maximum error of about 10% must be allowed for these rate coefficients.

TABLE 2. *Hydrolysis of triphenylsilyl chloride* (0·01M) *in nitromethane at* 25·1°.

[H_2O] (10^2M)	1·6	2·0	2·4	2·7	2·9	5·2	5·4	7·3	9·2	13·0
10^5k_1 (sec.$^{-1}$)	0·63	1·25	1·5	2·1	2·4	5·4	6·7	13·5	27	61
10^3k_2	0·40	0·61	0·63	0·78	0·83	1·05	1·25	1·85	2·9	4·7

Salt effects

[H_2O] (10^2M)	2·7	2·7	2·8	2·8	2·8	2·8	2·7	2·7	2·7	3·2
Et_4N^+ (10^4M) ClO_4^-	—	9	9 (Mg)	95	—	—	—	—	—	—
Et_4N^+ (10^4M) Br^- ...	—	—	—	—	1	4	—	—	—	—
Et_4N^+ (10^4M) Cl^- ...	—	—	—	—	—	—	0·45	3·4	9	9
10^5k_1 (sec.$^{-1}$)	2·1	2·2	2·6	3·7	12·5	37·5	10·5	59	95	120

In nitromethane (cf. Table 2), addition of tetraethylammonium perchlorate has a small effect on the rate, which may be interpreted as a simple salt effect. Substitution of magnesium for the cation does not alter this effect significantly. Halide ions, however, cause a very marked increase in rate; this catalysis may be related to the basic strength of the anion, since chloride is more effective than bromide. Unfortunately it was not possible to test this relation with more basic anions, since, in the low concentrations which must be used, the hydrogen chloride liberated would immediately convert them into their conjugate acids, and chloride-ion catalysis would be observed.

In dioxan the rate of hydrolysis is some 100 times shower than that in nitromethane

TABLE 3. *Hydrolysis of triphenylsilyl chloride* (0·01M) *in dioxan at* 25·1°.

[H_2O] (M) ...	0·25	0·38	0·50	0·75	1·0	[D_2O] (M)	0·45	0·68
10^5k_1 (sec.$^{-1}$)	0·33	1·95	7·25	85	1000	10^5k_1	2·2	26·5
10^5k_2	1·3	5·2	14·5	115	1000	k_1H/k_1D	2·0	1·9

Salt effects

Salt (10^4M)				10^5k_1	Salt (10^4M)				10^5k_1
[$Et_4N^+ClO_4^-$]	[$Et_4N^+Cl^-$]	[HCl]	[$HClO_4$]	(sec.$^{-1}$)	[$Et_4N^+ClO_4^-$]	[$Et_4N^+Cl^-$]	[HCl]	[$HClO_4$]	(sec.$^{-1}$)
	0·5M-H_2O					0·38M-H_2O			
—	—	—	—	7·3	—	—	—	—	2·0
0·9	—	—	—	21	1·35	—	—	—	6·8
—	0·9	—	—	124	2·7	—	—	—	18
—	—	10	—	15	—	1·1	—	—	127
—	—	21	—	24·5	—	—	—	0·85	12·4
	—	—	11	250	—	—	—	4·3	59
	0·25M-H_2O								
—	—	—	—	0·33					
0·9	—	—	—	5·5					
—	1·0	—	—	76·5					

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[3] Nebergall and Johnson, *J. Amer. Chem. Soc.*, 1949, **71**, 4022.

(cf. Table 3). Autocatalysis was observed, particularly with the lower concentrations of water used. Salt effects were even more marked, and the effect of added acid was studied. Substitution of deuterium oxide for water as the reagent reduced the rate by a factor or two.

In dioxan the increase in rate with increasing water concentration is very much more pronounced than that in nitromethane. This cannot be explained on the basis of a definite order with respect to the reagent. Obviously, changes due to the medium are very large in this weakly polar solvent. The dominating feature of the salt effects is again the strong catalysis by chloride ion. Since perchloric acid is more effective than tetraethylammonium perchlorate it seems that some electrophilic catalysis by the hydroxonium ion contributes to the reaction. The comparatively small effect of added hydrogen chloride shows (*a*) that the acid is virtually un-ionised in these media, and (*b*) that catalysis by associated hydrogen chloride is small. From this it follows that electrophilic catalysis by species other than the hydroxonium ion in the medium is not likely to be significant, and that the part played by any additional reagent molecules in the reaction is not electrophilic in character.

In an attempt to discover more precisely the nature of the chloride-ion catalysis, a more detailed study was made at various water concentrations, as reported in Table 4.

TABLE 4. *Hydrolysis of triphenylsilyl chloride catalysed by chloride ion in dioxan at* 25·1°

$[Et_4N^+Cl^-]$ (10^4M)	10^5k_1	10^5k_c	$k_2 = k_c/[Cl^-]$	$k_3 = k_2/[H_2O]$	$[Et_4N^+Cl^-]$ (10^4M)	10^5k_1	10^5k_c	$k_2 = k_c/[Cl^-]$	$k_3 = k_2/[H_2O]$
	0·5M-H_2O					0·25M-H_2O			
—	7	—	—	—	—	0·3	—	—	—
0·27	53	46	17	34	0·27	24	23·7	8·8	35
0·45	73	66	14	28	0·45	38	37·7	8·4	34
0·63	90	83	13	26	0·63	61	60·7	9·6	38
0·90	124	117	13	26	1·0	76·6	76·3	7·6	30
	0·38M-H_2O								
—	2	—	—	—					
0·36	49	47	13	35					
0·54	60	58	11	28					
1·10	127	125	11·5	30					

$k_c = k_1$ (catalysed) $- k_1$ (uncatalysed).

Two relations may be seen from these results : (*a*) for a given concentration of water, the increment of rate due to catalysis (k_c) is proportional to the chloride-ion concentration, and (*b*) the values of k_2 so obtained are proportional to the water concentration. The third-order coefficient, k_3, is reasonably constant over the range of concentrations studied. Thus, for the overall reaction, a rate equation may be written as :

$$\text{Rate} = k_{1(H_2O)}[R_3SiCl] + k_3[R_3SiCl][H_2O][Cl^-]$$

where $k_{1(H_2O)}$ is the first-order rate coefficient for the uncatalysed reaction at a given water concentration.

Temperature-dependence.—A qualitative study of the effect of temperature on some of these reactions is summarised in Table 5.

TABLE 5.

		Reagent			Temperature				
R in R_3SiCl	Solvent	ROH	Vol. %		0°	9·8°	25°	45°	60°
Pr^i	Pr^iOH	H_2O	[a]	10^2k_2 =	2·0	3·6	6·0	—	—
,,	$MeNO_2$	MeOH	10	10^4k_1 =	4·3	5·4	7·6	—	—
,,	Dioxan	H_2O	2	10^4k_1 =	—	—	2·6	2·9	—
,,	,,	MeOH	10	10^6k_1 =	—	—	3·7	4·8	—
1-$C_{10}H_7$	,,	H_2O	2	10^5k_1 =	—	—	0·9	—	1·2
Ph	,,	,,	0·9	10^5k_1 =	—	—	7·3	9·6	—
,,	,,	,, [b]	0·9	10^5k_1 =	—	—	73	88	—

[a] $[H_2O]$ between 0·01 and 0·05M. [b] $[Et_4N^+Cl^-]$ (0·4 × 10^{-4}M) added.

It will be seen that the temperature-dependence varies with the medium used. In *iso*propyl alcohol a " normal " temperature coefficient is obtained. In nitromethane or dioxan with 10% of methanol, temperature is less important, and in these solvents with small water concentrations very small coefficients are observed. It is noteworthy that a similar dependence on temperature is shown by both the uncatalysed and the chloride-catalysed hydrolysis of the phenyl compound, despite the ten-fold rate factor. Such small temperature coefficients are generally associated with complex reactions, particularly those involving two or more stages. In our results there is a correlation between small temperature coefficients and high reaction order, both of which are consistent with a complex reaction. The only reactions showing simple second-order kinetics, *i.e.*, those in *iso*propyl alcohol solution, also have normal temperature coefficients.

TABLE 6. *Chloride-exchange reactions* at 25·1°.

Solvent		R in	$[R_3SiCl]$	$[Et_4NCl]$	k_2
Dioxan (%)	$MeNO_2$ (%)	R_3SiCl	(10^2M)	(10^2M)	(sec.$^{-1}$ mole^{-1} l.)
0	100	Pr^i	0·83	1·2	7
		,,	0·98	1·8	6·5
25	75	,,	0·65	0·58	10·4
		,,	0·75	0·98	12·5
		,,	0·61	1·9	11
		,,	0·80	0·64	11·2 [a]
50	50	,,	0·82	0·61	17
		,,	0·85	0·99	17
75	25	,,	0·80	0·61	16·5
		,,	0·79	1·0	15·6
50	50	$1-C_{10}H_7$	0·67	0·64	43
		,,	0·63	1·24	43
		,,	0·64	1·19	41
75	25	,,	0·71	0·77	18
		,,	0·47	0·69	22
50	50	*cyclo*Hexyl	0·40	0·22	5·4
		,,	0·41	0·88	4·6

[a] $[Et_4NClO_4]$ (0·01M) added.

Halogen-exchange Reactions.—Expecting that the chemical simplicity of halogen-exchange reactions might help to clarify the mechanism of these substitution reactions, we studied several exchange reactions, using ^{36}Cl-labelled tetraethylammonium chloride, with mixtures of dioxan and nitromethane as solvents (see Table 6).

Qualitative measurements with triphenyl- and trimethyl-silyl chloride in the 1 : 1 solvent mixture indicated complete reaction within 0·3 second.

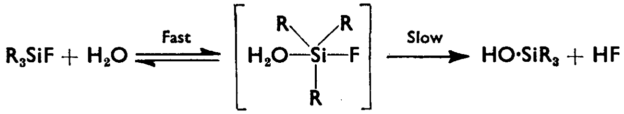
Good second-order kinetics were observed with all the compounds in all the solvents used. The order of reactivity towards chloride ion is different from that towards the hydroxylic reagents, being tri-1-naphthyl > tri*iso*propyl > tri*cyclo*hexyl. Steric factors may be less important with this small reagent, and dispersion of its negative charge will be facilitated by the polarisability of the naphthyl groups. Effects of the medium are small, the rate increasing with increasing dioxan content up to the 1 : 1 mixture. At higher dioxan contents the rate decreases again, possibly owing to association of the ionic species in such weakly polar media. The addition of tetraethylammonium perchlorate does not affect the rate.

DISCUSSION

The more important features of our results may be summarised as follows : (*a*) The orders of reactivity, both of the silicon chlorides and of the reagents used, indicate that steric hindrance is important in these reactions. (*b*) Aryl groups (phenyl and naphthyl) facilitate the reactions, particulatly with chloride ion as the reagent. (*c*) Polarity of the medium increases the rate of reaction with neutral reagents, and depresses slightly the rate with negatively charged reagents. (*d*) In inert solvents the order with respect to hydroxylic reagents is always greater than one, but reactions in hydroxylic solvents are of first order with respect to these reagents. (*e*) In inert solvents, with low concentrations of hydroxylic reagents, strong catalysis by halide ions, together with low temperature coefficients, is observed. In *iso*propyl alcohol, temperature coefficients are normal and no catalysis by halide ion is observed. (*f*) Hydrolysis catalysed by chloride ion is of first order with respect to both halide ion and water. Chloride-ion exchange is of first order with respect to chloride ion.

Possible Reaction Mechanisms.—(1) *Unimolecular ionisation.* Since silicon is more electropositive than carbon, it might be expected that ionisation to give a siliconium ion would occur. So far, however, there is no evidence of such a process. Flowers, Gillespie, and Robinson[4] have carried out cryoscopic and conductivity measurements with several silanols in sulphuric acid, and shown that siliconium ion is not formed, at least to any measurable extent, in that solvent. Carbonium ions are stabilised by resonance between structures involving double-bond formation, and it was hoped that the structure of tri-1-naphthylsilyl chloride would be particularly suitable in this respect. Our failure to observe this mechanism with this compound seems to indicate that ionisation mechanisms, so frequently observed in organic compounds, do not occur in organosilicon compounds.

(2) *Formation of quinquecovalent silicon intermediates.* For the hydrolysis of triphenyl- and tri-*p*-tolyl-silyl fluoride in aqueous acetone, the rapid pre-equilibrium formation of a quinquecovalent intermediate, followed by its rate-determining unimolecular breakdown, has been proposed :[5]



$$R_3SiF + H_2O \overset{\text{Fast}}{\rightleftharpoons} \left[H_2O{-}SiR_3{-}F \right] \xrightarrow{\text{Slow}} HO{\cdot}SiR_3 + HF$$

The formation of stable or semi-stable compounds in which silicon has a covalency greater than four is well established with the fluoro- and chloro-silanes.[6] When one or more organic groups are attached to silicon, however, there is no evidence of further co-ordination. Eaborn[7] has shown that the ultraviolet absorption spectra of pyridine and *p*-toluidine in several organosilicon solvents do not differ significantly from the spectra in hexane. This indicates that, even under very favourable conditions, with little steric hindrance, no measurable co-ordination to silicon by these strong reagents occurs.

The simple kinetic form of the reaction cannot distinguish between a synchronous bimolecular process and a pre-equilibrium as proposed by Swain *et al.*[5] These authors considered both possibilities and decided in favour of the latter on the grounds that electron supply hinders the reaction, and that silyl fluorides are hydrolysed more slowly than the corresponding silyl chlorides. It has already been pointed out that depression of the rate by electron supply is consistent with certain S_N2 reaction mechanisms,[1] and it is well known that, under S_N2 conditions, organic fluorides are hydrolysed more slowly than the corresponding chlorides.[8] It is not possible to distinguish between the alternative mechanisms on this basis.

There are several objections to this type of mechanism for the reactions we have studied : (*a*) The unimolecular breakdown of the complex should be subject to general electrophilic catalysis. We have seen that, although there is slight catalysis by hydroxonium ion, other species, including hydrogen chloride, are ineffective. In particular, the high order with respect to hydroxylic reagents cannot be explained on the basis of electrophilic attack. (*b*) Steric hindrance is very great with these compounds :

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[4] Personal communication from Dr. R. J. Gillespie.

[5] Swain, Esteve, and Jones, *J. Amer. Chem. Soc.*, 1949, **71**, 965.

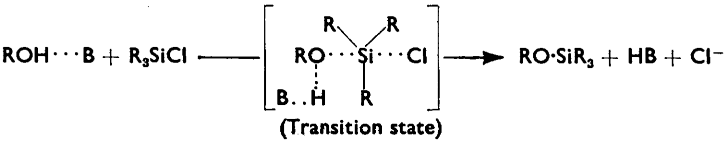
[6] Stone and Seyferth, *J. Inorg. Nuclear Chem.*, 1955, **1**, 112.

[7] Eaborn, *J.*, 1955, 2047.

[8] Chapman and Levy, *J.*, 1952, 1673.

e.g., tri*iso*propylsilyl chloride does not react with *iso*propyl-lithium to give tetra*iso*propylsilane.[9] Hence a kinetically rapid formation of the complex seems unlikely. (*c*) Such a pre-equilibrium would involve complete reaction for the symmetrical chloride exchange. Although the exchange is rapid, it is not kinetically " fast." Similarly we find that the exchange between $H_2{}^{18}O$ and triphenylsilanol is extremely slow in neutral 10% aqueous dioxan. This reaction is acid-catalysed, and work is in progress on the detailed kinetics. (*d*) It is difficult to accommodate chloride-ion catalysis in such a mechanism.

Proposed Reaction Mechanism.—The simplest scheme which can accommodate all the observed results is as follows :



The hydrogen-bonded association ROH • • B may be formed in a fast pre-equilibrium step, or it could occur during the approach of the reagent to silicon. B is any entity which can act as a base, *e.g.*, H_2O, ROH, halide ion. In this scheme the importance of the association in the reaction sequence is that the reagent is unable to displace chlorine unless a base is available to accept the proton. In hydroxylic solvents the latter process is unimportant, since all the reactants and transition state are highly solvated, and the proton transfer is kinetically fast. For this reason, although addition of traces of pyridine displaces the equilibrium in alcoholic solvents, no basic catalysis is observed. In such solvents the reaction is a simple bimolecular substitution, as we observe.

In inert solvents, with low concentrations of hydroxylic molecules, transfer of the proton to a base becomes kinetically important; hence the multiple order with respect to the reagent, and a possible correlation between their reactivity and basicity. At very low concentrations of hydroxylic species solvation of added halide ions will be low, and hence their basic properties will be enhanced. Consistently their catalytic effect falls off very rapidly as the concentration of solvating molecules increases, and a simple salt effect, similar to that of the perchlorate ion, is observed in more highly solvating media.

The small temperature coefficients observed at low concentrations of hydroxylic molecules would result from the decrease in concentration of the hydrogen-bonded complex as the temperature is increased. The first-order dependence on water concentration in the presence of chloride ion is strong evidence in favour of this mechanism. The reduction in rate by a factor of two when deuterium oxide is used in place of water as the reagent is consistent with a proton transfer involved in the transition state.

Somewhat similar schemes have been proposed for the acid- and base-catalysed hydration of acetaldehyde,[10] and for the alcoholysis of acid chlorides in inert solvents.[11]

EXPERIMENTAL

Materials.—Solvents, reagents, and salts were prepared and dried as described in Part I. The silyl chlorides have been previously reported. Physical properties of the products used were : tri-1-naphthylsilyl chloride, m. p. 210° (from light petroleum) ; tri*cyclo*hexylsilyl chloride, m. p. 102°, b. p. 156°/0·7 mm. ; triphenylsilyl chloride, " purified " grade, redistilled, b. p. 161°/0·6 mm. ; trimethylsilyl chloride, " purified " grade, used as supplied.

Rate Measurements.—These were carried out as described in Part I, except as follows. The solid silyl chlorides and the reagents were dissolved separately in two portions of the solvent, brought to thermostat temperature, and mixed at zero time. For runs at 45° and 60° sealed Pyrex glass tubes were used, which were crushed under dry ether at room temperature; titration

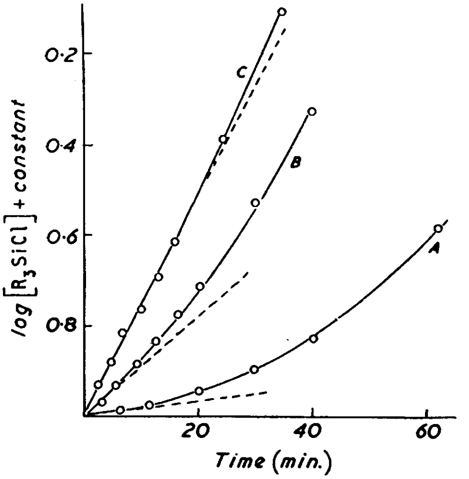
[9] Gilman and Clark, *J. Amer. Chem. Soc.*, 1947, **69**, 1499.

[10] Bell, Rand, and Wynne-Jones, *Trans. Faraday Soc.*, 1956, **52**, 1093; Bell and Darwent, *ibid.*, 1950, **46**, 34.

[11] Hudson and Saville, *J.*, 1955, 4121.

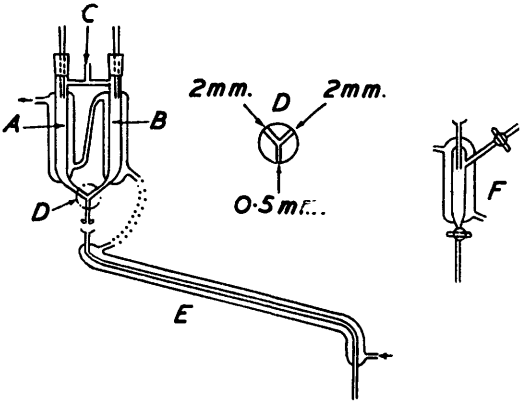
was as before. It was observed that, if these samples were " killed " by freezing at −80°, very high acid values were obtained, in some cases amounting to an additional 50% of the total reaction. It appeared that considerable reaction was occurring during the melting and freezing. Generally, first-order rate constants were calculated from the initial slope of the first-order log plot, and second-order constants by dividing the first-order constant by the initial concentration of the reagent, which was nearly always in large excess. For those runs which were free from autocatalysis and went to completion, good first-order kinetics were observed throughout.

FIG. 1. *Hydrolysis of triphenylsilyl chloride* (0·01M) *in* 1% *aqueous dioxan at* 25°.



A, Run without added salt, showing autocatalysis. *B*, Effect of addition of tetraethylammonium chloride (0·27 × 10^{-4}M). *C*, Effect of addition of tetraethylammonium chloride (0·63 × 10^{-4}M), showing almost complete elimination of autocatalysis.

FIG. 2. *Apparatus used for the measurement of very fast chloride-exchange.*



E.g., tri-1-naphthylsilyl chloride (0·005M) in 10% methanolic butan-2-one, at 25·1°; triethylamine = 0·053M :

Time (min.)	2	6	10	15	20	33	45	60	90	∞
Titre (ml.)	0·41	1·25	1·90	2·75	3·45	4·9	6·05	7·05	8·2	9·43
10^4k_1 (sec.$^{-1}$)	3·8	3·55	3·76	3·7	3·8	3·7	3·8	3·83	3·8	—

A series of runs in which autocatalysis and salt effects were observed are shown in Fig. 1. These show clearly the catalysis by halide ion, accompanied by depression of the autocatalysis as the halide-ion concentration is increased.

Chloride-exchange Reactions.—For these reactions, which involved measurements within 1 second in some cases, the flow apparatus shown in Fig. 2 was used.

Samples of exactly equal volume (from two automatic pipettes) were placed in the jacketed arms *A* and *B*. One of these contained the silyl chloride and the other the ^{36}Cl-labelled tetraethylammonium chloride. A (measured) pressure of nitrogen was exerted equally on the samples *via* the inlet *C*. A reservoir (5 l.) and adjustable fine leak were used to maintain constant pressure during each measurement. Water at 25° was circulated continuously through all the jackets. After 20 min., when temperature equilibrium had been established, the tap *D* was fully opened (at zero time) and the reactants were forced through the reaction tube *E* into 100 ml. of sodium-dried ether contained in a No. 4 sintered-glass filter funnel. The time *t′* for total outflow of the liquid was recorded. The salt was precipitated immediately on contact with the ether. As soon as outflow ceased, suction was applied to a Buchner flask below the filter, and the salt was separated from the solvent within 5 seconds of precipitation. After the salt had been washed with several small amounts of dry ether, it was dissolved in approximately 15 ml. of distilled water and set aside for counting and potentiometric titration of chloride with silver nitrate solution. Reaction times were varied both by changing the pressure and by the use of several reaction tubes (E) of different volumes. The reaction time (t) is given by: $t = t' \times v/V$, where t' = measured time of total outflow, v = volume of the reaction tube, and V = total volume of the reaction solutions. Hence if the ratio v/V is small (in our apparatus 0·1—0·03) very short reaction times can be measured accurately. For the longer reaction times, and for infinity values, a reservoir F was used in place of the reaction tube. Good agreement was found between the two systems when it was possible to duplicate reaction times by both methods. A ball-and-socket joint facilitated changes of the reaction vessel, and proved to be leakproof under pressure. The efficiency of the "killing" of the reaction by precipitation of the salt was checked by dispensing with the reaction vessels and running the mixed samples directly on to the ether from the ball joint. Such tests gave 1—2% reaction, which is approximately correct for the time of contact of the solutions.

E.g., tri-1-naphthylsilyl chloride (0·0063M) + $Et_4N^{+\,36}Cl^-$ (0·0124M) *in* 50 : 50 *dioxan* : *nitromethane at* 25°.

t (sec.)	0	0·39	0·70	0·75	0·90	0·99	1·13	2·01	2·55	3·61
$(C - X)$ *	9002	8409	8106	7971	7668	7582	7296	6767	6540	6255
k_2 (sec.$^{-1}$ mole^{-1} l.)...	—	46	37	39	43	42	47	43	43	49

* C = Initial specific count for $Et_4N^+Cl^-$; $(C - X)$ = specific count for $Et_4N^+Cl^-$ at time t (measured); X = specific count for R_3SiCl at time t (calculated).

$H_2{}^{18}O$ *Exchange.*—Triphenylsilanol (2 g.) was dissolved in dry dioxan (90 ml.) with $H_2{}^{18}O$ (10 ml.) (1·07 atom % enriched in ^{18}O). After 24 hr. at 25° the solvent was removed by evaporation in a vacuum at room temperature. The solid was dried at 50°/0·1 mm. over magnesium perchlorate. Portions of the solid, with a little ammonium chloride as catalyst, were sealed in a (measured) carbon dioxide atmosphere in Pyrex ampoules, and heated at 250° for 7 days. The ^{18}O content of the carbon dioxide was measured (by Dr. C. A. Bunton) by mass-spectrometer, and was found to be normal, indicating that no exchange had occurred. The method was checked by starting with prepared triphenylsilanol containing 1·07 atom % excess of ^{18}O, which was allowed to react with normal water exactly as above. On analysis the carbon dioxide was found to contain 1·06 atom % excess of ^{18}O, due allowance being made for dilution, confirming the absence of exchange.

The same reactions were carried out, with normal triphenylsilanol and 1·07 atom % enriched water, in the presence of (*a*) 0·1M-hydrochloric acid and (*b*) 0·1M-perchloric acid. After 3 hr. at 25° the silanol was precipitated by adding normal water, washed with small amounts of water to remove traces of acid, and dried as before. On analysis the carbon dioxide contained (*a*) 0·54 and (*b*) 0·47 atom % excess of ^{18}O, indicating that considerable exchange had taken place in both cases.

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