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Nucleophilic substitution at silicon: the reaction of triphenylsilyl chloride with 2-propanol in CCl_4

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The reaction of triphenylsilyl chloride with 2-propanol in CCl_4 has been reinvestigated and a mechanism proposed. The HCl produced in the reaction is catalytic. The rate of the uncatalyzed reaction, as determined by extrapolations to zero time, increases more rapidly with 2-propanol concentration than would be required for an order of one in the alcohol. The rate of the HCl-catalyzed path is independent of the 2-propanol concentration in the range studied (5 to 15 volume %) but first order in the HCl concentration, suggesting that the reactive alcohol species in this case is of the form ROH...ClH.

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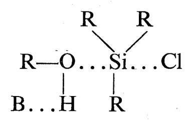
The reactions of triphenylsilyl chloride with H_2O in dioxan (1) and with 2-propanol in CCl_4 (2) are autocatalytic. The reactions may be represented generally by

$$(C_5H_6)_3SiCl + ROH \rightarrow (C_5H_6)_3SiOR + HCl$$

The HCl and chloride ions have been shown to be catalytic species (1, 2).

Petersen and Ross (2) concluded that there was little or no reaction of triphenylsilyl chloride and 2-propanol in the absence of HCl and that the order in the alcohol was one. They interpreted their results as support for a mechanism involving formation of a pentacovalent silicon intermediate followed by HCl-catalyzed decomposition to products.

Allen and Modena (1) assumed that no HCl was present initially in their reaction mixtures and obtained pseudo first-order rate constants for the uncatalyzed reaction of triphenylsilyl chloride and water in dioxan by extrapolation to zero time of plots of log $[R_3SiCl]$ against time. The initial slopes of these plots were constant at any one water concentration. The order in water was greater than one. Multiple orders in alcohol or water have been noted in a number of other systems (3–6) involving substitution at silicon in non-hydroxylic solvents. Allen and Modena proposed that in alcoholysis and hydrolysis, the reactive nucleophilic species is of the form ROH . . . B, where B is any entity that can act as a base and assist proton removal from the OH group.



$$\begin{array}{ccccc} & & R\ \ R & & \\ R{-}O & \cdots & Si & \cdots & Cl \\ | & & | & & \\ B\cdots H & & R & & \end{array}$$

Transition state

This type of mechanism has been used to explain the action of certain catalysts, the high order in the nucleophile, and temperature effects in a number of systems (1, 3–7).

Analyses of samples of triphenylsilyl chloride, combined with the observation that CCl_4 solutions of the silicon halide failed to show any detectable acid, led us to conclude that the samples used in this work did not contain HCl impurity. This suggested that, contrary to the arguments of Petersen and Ross, it should be possible to determine rate constants for the uncatalyzed reaction of triphenylsilyl chloride and 2-propanol in CCl_4 by extrapolations to zero time, and to determine the order in 2-propanol from the rate constants obtained. We have reinvestigated this reaction using a direct titrimetric method to determine the HCl produced in the reaction.

Results and Discussion

The reaction of 2-propanol and triphenylsilyl chloride in CCl_4 solvent is catalyzed by the HCl produced in the reaction, but HCl need not be present to initiate the reaction. The first-order plot shown in Fig. 1 is typical. Extrapolations to zero time on such plots for runs to which no HCl has been added give pseudo first-order rate constants, k_u, applicable to the uncatalyzed reaction. The results are summarized in Table I. All data were obtained at 25.2°.

From the data in Table I it can be seen that at any one alcohol concentration, k_u is reasonably constant. The rate increases with 2-propanol concentration more rapidly than would be required for an order of one in the alcohol. A plot of log k_u against log (volume % of ROH) is linear with slope equal to 2.4 in the range studied. The multiple order in 2-propanol is consistent with the mechanism proposed by Allen and Modena (1); B is another alcohol molecule. It is known that 2-propanol exists to a large extent as a polymer in CCl_4 (8, 9), and that the pseudo first-order rate constants for the 2-propanolysis of acetyl chloride in CCl_4 are proportional to the concentration of associated alcohol (9).

When HCl is added to the reaction mixtures, the pseudo first-order rate constants obtained by extrapolation, k_1, are higher than the k_u value at the same alcohol concentration. The increments, $k_1 - k_u$, are linear in HCl concentration, but appear to be independent of the alcohol concentration in the range studied (5 to 15 volume % 2-propanol), as can be seen from the k_c entries in column 6 of Table II. Catalysis by HCl is explained in terms of the increased basicity towards silicon of the oxygen of an alcohol molecule hydrogen-bonded through its proton to the chloride of the HCl. If this association of alcohol and HCl is virtually complete, so that the concentration of the reactive alcohol species is equal to the analytical concentration of HCl, then the independence of alcohol concentration shown by k_c is explained.

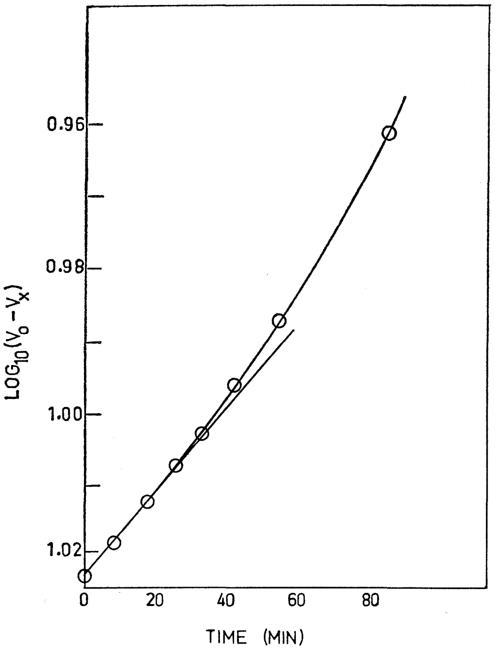


FIG. 1. First-order plot for 2-propanolysis $(C_6H_5)_3SiCl$ in CCl_4 at 25.2°; $[R_3SiCl]_0 = 1.374 \times 10^{-2}$ *M*, $[ROH]_0 = 10$ volume %, V_0 = volume of Et_3N solution corresponding to the initial silyl chloride concentration, V_x = volume of Et_3N solution corresponding to the HCl produced in the reaction.

TABLE I

Pseudo first-order rate constants for the uncatalyzed reaction of $(C_6H_5)_3SiCl$ and 2-propanol at 25.2°

$[R_3SiCl]_0 \times 10^3$ (*M*)	$[ROH]_0$ (volume %)	$k_u \times 10^5$ (s^{-1})
4.31	5.0	0.64
8.59	5.0	0.74
11.48	5.0	0.77
12.17	5.0	0.67
13.88	5.0	0.69
17.84	5.0	0.65
	Mean:	0.69
7.69	10.0	2.6
9.55	10.0	2.8
11.33	10.0	2.6
13.74	10.0	2.3
33.07	10.0	2.6
	Mean:	2.6
6.03	12.0	5.9
8.17	12.0	5.5
15.26	12.0	6.2
	Mean:	5.9
5.94	15.0	10.2
8.82	15.0	9.6
14.79	15.0	9.3
	Mean:	9.7

The rate equation appears to have the form

$$\begin{aligned} dx/dt &= k_u[R_3SiCl] + k_c[HCl]\,[R_3SiCl] \\ &= k_u(a_0 - x) \;\; + k_c(p_0 + x)\,(a_0 - x) \end{aligned}$$

where k_u varies with alcohol concentration but k_c does not. The first term refers to the uncatalyzed path, the second to the HCl-catalyzed path. For runs to which no HCl is added initially, p_0 equals zero. The integrated form of this rate law is

TABLE II

Rate constants for the HCl-catalyzed reaction of $(C_6H_5)_3SiCl$ and 2-propanol at 25.2°

$[R_3SiCl]_0 \times 10^3$ (M)	$[ROH]_0$ (volume %)	$[HCl]_0 \times 10^3$ (M)	$k_1 \times 10^5$ (s^{-1})	$(k_1 - k_u) \times 10^5$ (s^{-1})	$\frac{(k_1 - k_u) \times 10^5}{[HCl]_0 \times 10^3} = k_c \times 10^2$ ($M^{-1}\,s^{-1}$)
11.50	5.0	0.742	1.65	0.96	1.3
10.19	5.0	0.742	1.62	0.93	1.3
16.87	5.0	1.29	2.25	1.56	1.2
10.83	5.0	3.31	5.07	4.38	1.3
16.73	5.0	5.02	6.30	5.61	1.1
10.72	5.0	5.33	6.84	6.15	1.2
10.04	10.0	3.21	6.6	4.0	1.3
18.14	10.0	3.63	8.3	5.7	1.6
8.13	10.0	3.89	7.2	4.6	1.2
10.30	10.0	4.23	7.3	4.7	1.1
10.43	10.0	6.33	11.7	9.1	1.4
10.58	12.0	1.60	7.7	1.8	1.1
17.35	12.0	2.19	9.7	3.8	1.7
9.37	12.0	5.78	12.4	6.5	1.1
8.29	15.0	2.68	14.6	4.9	1.8
11.89	15.0	7.20	22.1	12.4	1.7
16.74	15.0	11.80	29.6	19.9	1.7

$$\log_e\left[\frac{1-M}{1+M}\right] = (k_c a_0 + k_c p_0 + k_u)t + \log_e\left[\frac{1-B}{1+B}\right]$$

where

$$M = \frac{k_c a_0 - k_c p_0 - k_u - 2k_c x}{k_c a_0 + k_c p_0 + k_u}$$

and

$$B = \frac{k_c a_0 - k_c p_0 - k_u}{k_c a_0 + k_c p_0 + k_u}$$

If values for k_u and k_c are assumed, values of $\log_e [(1 - M)/(1 + M)]$ can be plotted against time for any run. Then the linearity of the plot can be checked and the slope of the least squares straight line through the points compared with the theoretical slope $(k_c a_0 + k_c p_0 + k_u)$. This was done for a wide range of k_c values at each of several k_u values for each run. In general, for each value of k_u there exists a value of k_c at which the theoretical and least squares slopes are essentially equal, and the deviation of points from the least squares straight line is very small. Other values of k_c with this k_u result in much greater deviations. However, for any one run several sets of k_u and k_c with different k_u values meet the requirements given above equally well. Despite this complication, the following points are evident (*a*) for k_u values within ±10% of the values obtained by extrapolation, the best k_c values are close to those calculated from the extrapolation data, (*b*) sets of k_u and k_c values for runs with and without added HCl at the same alcohol concentration show best agreement in the neighborhood of the values obtained by extrapolation, (*c*) the k_c values at any one alcohol concentration are reasonably constant, and (*d*) the k_c values appear to be independent of the alcohol concentration.

Data at various percentages of reaction are, therefore, consistent with the rate law deduced from extrapolations to zero time. Typical results are shown in Table III and a typical plot of $\log_e [(1 - M)/(1 + M)]$ is shown in Fig. 2.

When tetraethylammonium chloride is added to the reaction mixtures, the pseudo first-order rate constants obtained by extrapolation, k_1, are higher than those for the uncatalyzed reaction. The increments to the rate constant appear to be linear in salt concentration, as evidenced by the values of k_s at any one alcohol concentration in column 5 of Table IV. As in all other cases, runs containing Et_4NCl eventually showed autocatalysis by the HCl produced in the reaction.

Pseudo first-order rate constants obtained by extrapolation for runs with both HCl and Et_4NCl added show that the effect of one catalyst is not diminished in the presence of the other. This observation does not agree with the rate law for the

TABLE III

k_u (s^{-1})	k_c (M^{-1} s^{-1})	Required slope (s^{-1})	Slope of least squares line (s^{-1})	$\log_e \frac{1-B}{1+B}$	Intercept of least squares line	% reaction followed
0.64×10^{-5}	0.82×10^{-2}	4.17×10^{-4}	4.16×10^{-4}	-1.71	-1.68	24
0.65×10^{-5}	0.90×10^{-2}	1.67×10^{-4}	1.67×10^{-4}	-3.21	-3.18	6.5
0.77×10^{-5}	1.18×10^{-2}	1.72×10^{-4}	1.72×10^{-4}	-3.06	-3.06	13
0.69×10^{-5}	1.38×10^{-2}	1.76×10^{-4}	1.76×10^{-4}	-2.23	-2.21	20
0.69×10^{-5}	1.18×10^{-2}	1.74×10^{-4}	1.74×10^{-4}	-1.03	-1.01	45
0.69×10^{-5}	0.93×10^{-2}	2.09×10^{-4}	2.08×10^{-4}	-1.07	-1.06	26
2.44×10^{-5}	1.03×10^{-2}	1.41×10^{-4}	1.41×10^{-4}	-1.57	-1.57	17
2.60×10^{-5}	0.83×10^{-2}	2.99×10^{-4}	2.99×10^{-4}	-2.35	-2.35	13
2.60×10^{-5}	1.27×10^{-2}	2.11×10^{-4}	2.11×10^{-4}	-0.495	-0.498	37
2.60×10^{-5}	1.24×10^{-2}	2.97×10^{-4}	2.97×10^{-4}	-1.15	-1.12	47
2.60×10^{-5}	1.42×10^{-2}	2.14×10^{-4}	2.14×10^{-4}	-0.689	-0.693	35
2.60×10^{-5}	1.40×10^{-2}	1.95×10^{-4}	1.95×10^{-4}	-0.346	-0.360	31
6.20×10^{-5}	1.18×10^{-2}	2.43×10^{-4}	2.43×10^{-4}	-1.07	-1.08	24
6.02×10^{-5}	1.51×10^{-2}	1.84×10^{-4}	1.84×10^{-4}	-0.717	-0.720	13
5.90×10^{-5}	1.30×10^{-2}	2.56×10^{-4}	2.56×10^{-4}	$+0.096$	$+0.089$	39
5.90×10^{-5}	1.36×10^{-2}	3.25×10^{-4}	3.24×10^{-4}	-0.978	-0.945	36
5.90×10^{-5}	1.38×10^{-2}	2.27×10^{-4}	2.27×10^{-4}	-0.589	-0.593	32
10.2×10^{-5}	1.38×10^{-2}	1.84×10^{-4}	1.84×10^{-4}	-0.216	-0.209	50
9.6×10^{-5}	1.17×10^{-2}	1.99×10^{-4}	1.99×10^{-4}	-0.072	-0.073	44
9.7×10^{-5}	1.32×10^{-2}	2.42×10^{-4}	2.42×10^{-4}	$+0.191$	$+0.197$	49
9.7×10^{-5}	1.29×10^{-2}	4.66×10^{-4}	4.66×10^{-4}	$+0.143$	$+0.167$	34
9.7×10^{-5}	1.29×10^{-2}	3.44×10^{-4}	3.44×10^{-4}	$+0.212$	$+0.230$	44

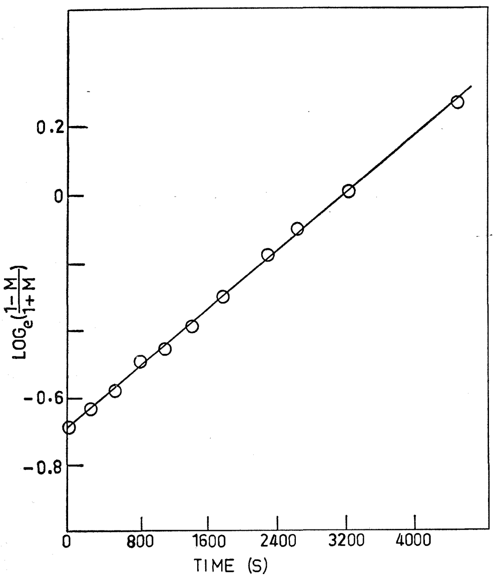


FIG. 2. Plot of $\log_e [(1 - M)/(1 + M)]$ against time with least squares line shown; $[R_3SiCl]_0 = 1.040 \times 10^{-2}$ $M = a_0$, $[ROH]_0 = 10$ volume %, $[HCl]_0 = 3.21 \times 10^{-3}$ $M = p_0$.

salt-catalyzed reaction proposed by Petersen and Ross (2). The results for samples containing both catalysts are shown in Table V.

Since $k_s > k_c$, Et_4NCl is more effective as a catalyst than HCl. It seems reasonable to conclude that the Cl in both catalysts acts by association with the proton of the alcohol OH group. Such association is known to occur between quaternary ammonium halides and alcohols in CCl_4 (10). The HCl may not be appreciably dissociated (2), while the tetraethylammonium chloride may be present as ion pairs (11).

It is impossible to tell from our kinetic data whether the reaction of the silyl chloride and ROH . . . B proceeds by an S_N2 mechanism or by formation of a pentacovalent silicon intermediate. We favor the former after considering collectively the information dealing with substitution of chloride at silicon by more basic groups as presented in refs. 1, 3, 7, 12–14.

Experimental Details

A. Solvents

Carbon Tetrachloride. Reagent grade CCl_4 was used without further purification or drying. Numerous blanks containing only triphenylsilyl chloride and CCl_4 were run, and in all cases no more than 1% reaction occurred over a 24 h period; there was no detectable acidity produced in the length of time for which normal kinetic runs were followed.

2-Propanol. Molecular sieves were used for drying. The water content was reduced to 0.008% or less (Karl Fisher titration) in 3 to 4 days.

Dioxan. Reagent grade dioxan was refluxed with sodium until formation of resin ceased and the sodium remained shiny. It was then distilled.

TABLE IV

Rate constants for the Et_4NCl-catalyzed reaction of $(C_6H_5)_3SiCl$ with 2-propanol at 25.2°

$[R_3SiCl]_0 \times 10^3$ (M)	$[ROH]_0$ (volume %)	$[Salt] \times 10^4$ (M)	$k_1 \times 10^5$ (s^{-1})	$\frac{(k_1 - k_u) \times 10^5}{[Salt] \times 10^4} = k_s \times 10$ (M^{-1} s^{-1})
11.74	5.0	0.422	2.69	4.7
12.51	10.0	0.712	5.4	3.9
12.37	10.0	0.929	6.6	4.3
10.07	10.0	1.85	9.1	3.5
8.02	10.0	4.04	16.6	3.5
11.97	15.0	1.04	13.7	3.8
9.19	15.0	3.87	22.1	3.2
12.56	15.0	5.44	25.0	2.8

TABLE V

Rate constants for the Et_4NCl-catalyzed reaction of $(C_6H_5)_3SiCl$ with 2-propanol as determined from runs containing added HCl

$[R_3SiCl]_0 \times 10^3$ [M]	$[ROH]_0$ (volume %)	$[HCl]_0 \times 10^3$ (M)	$[Salt] \times 10^4$ (M)	$k_1 \times 10^5$ (s^{-1})	$\frac{(k_1 - k_u - k_c p_0) \times 10^5}{[Salt] \times 10^4} = k_s \times 10$ (M^{-1} s^{-1})
8.82	10.0	2.08	1.77	12.6	4.1
10.76	12.0	1.64	3.03	14.4	3.2
8.32	15.0	0.684	2.06	20.2	4.7

Benzene. Reagent grade benzene was dried by distillation from sodium.

Diethyl Ether. Anhydrous diethyl ether was distilled from sodium or used as obtained from Mallinckrodt (A.R., A.C.S., 0.01% H_2O).

B. Preparation of Triphenylsilyl Chloride

$(C_6H_5)_3SiCl$ was prepared by chlorination of $(C_6H_5)_3SiH$ in CCl_4.

The reaction vessel was immersed in an ice-water bath. The CCl_4, Cl_2, and dissolved HCl were pumped off following completion of the reaction. The crude product was recrystallized from benzene and petroleum ether and then distilled at reduced pressure (boiling point 147 °C at 0.01 mm Hg).

Anal. Calcd. for $(C_6H_5)_3SiCl$: C, 73.33; H, 5.12; Cl, 12.03. Found: C, 73.41; H, 5.21; Cl, 11.92.

C. Procedure Followed in Kinetic Runs

Separate solutions of $(C_6H_5)_3SiCl$ and 2-propanol in CCl_4 were made up quantitatively at 25.2° and then mixed. Aliquots were removed from the reaction mixture at intervals, quenched in dry benzene or ether, and titrated immediately for HCl with a dioxan solution of Et_3N. Neutral red dissolved in 2-propanol was used as the indicator. Total acid values were obtained by titration of an aliquot run into 95% ethanol; production of HCl was complete and rapid in the ethanol.

Solutions of HCl in CCl_4 were prepared with HCl which had been passed through a H_2SO_4 drying train.

Tetraethylammonium chloride was dried over P_2O_5 under vacuum at the temperature of boiling methanol for several hours.

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