Organometallics **1993,** *12,* 1981-1982

Relative Consecutive Competitive Rates of Alkoxylation of Chlorosilanes

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Received November 23, 1992

Summary: Methanol or ethanol reacts irreversibly at great speed with warm liquid chlorosilanes as hydrogen chloride is expelled as a gas. The rates of ethoxylation relative to k for Me_3SiCl equal to 1 for the most important chlorosilanes in the silicone industry were determined.

Introduction

About 150 years ago Ebelman[1] discovered that ethanol reacted vigorously with tetrachlorosilane to form hydrogen chloride and tetraethoxysilane. Thus the first organic silicon compound was made, and it is made today in much the same way. Alcoholysis of chlorosilanes has long been a very important process in the manufacture of organosilicon intermediates for the silicone industry.

Fuoss[2] described the mathematics for calculating the relative amounts of each product that is formed when a given number of equivalents of a monofunctional reagent reacts irreversibly with a polyfunctional reagent. This is exactly the situation when an alcohol reacts with a di-, tri-, or tetrachlorosilane.

An attempt to measure the relative consecutive rates of ethanolysis of Me_2SiCl_2 and $MeSiCl_3$ was published in 1959.[3] In these experiments, ethanol and chlorosilanes were stirred at 0 °C for about 1 h; then the mixture was heated at reflux for 2 h "to drive away gaseous hydrogen chloride completely". The chloride-free mixtures were then analyzed by fractional distillation. The calculated k_2/k_1 for Me_2SiCl_2 was about 17/2 and $k_3/k_2/k_1$ for $MeSiCl_3$ was about 7/3/1. These values are far from those determined in this study (Table I) most likely because the quantities found by distillation after refluxing, etc. were not those produced kinetically but those obtained near equilibrium by redistribution reactions. Redistribution of chloride and ethoxy groups on silicon has been studied carefully and reviewed.[4]

Results

When methanol or ethanol was pumped through a capillary tube positioned below the surface of a stirred chlorosilane, at 60 °C or at reflux, the mixture bubbled furiously and hydrogen chloride was very quickly and quantitatively expelled through a reflux condenser at 0 °C. Reaction 1 is extremely fast and irreversible so long as the concentration of HCl remains near zero.

$$\equiv SiCl + ROH \rightarrow \equiv SiOR + HCl \text{ (bp 84 °C)} \quad (1)$$

After about 95% of the chloride is eliminated, HCl forms a high-boiling azeotrope with methanol (bp 84 °C) and a high-boiling solution with ethanol. These tend to separate as a second liquid phase. When this happens, alcoholysis stops, but redistribution proceeds.

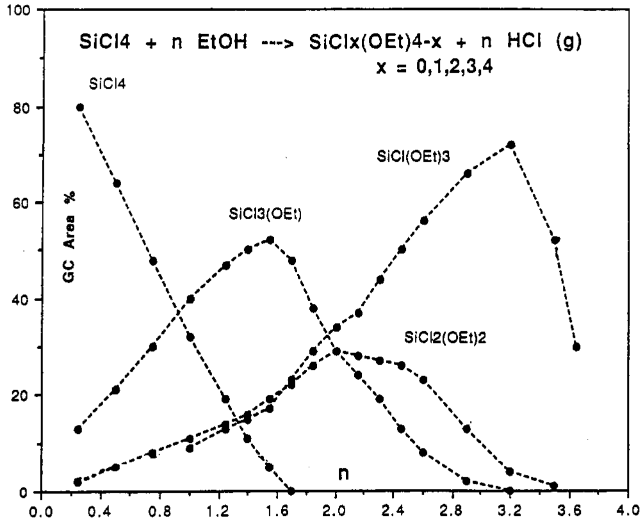

Figure 1.

When ROH reacts with R'_aSiCl_{4-a}, a = 0–2, the rate of formation of $R'_aSiCl_{3-a}OR'$ is

$$d[R'_aSiCl_{3-a}OR]/dt = k_{4-a}[R'_aSiCl_{4-a}][ROH] - k_{3-a}[R'_aSiCl_{3-a}OR][ROH]$$

Thus, the rate of appearance of the first product is the rate of disappearance of the original chlorosilane minus the rate of appearance of the second alkoxysilane. When $a = 2$; $d[R'_2SiClOR]dt = k_2[R'_2SiCl_2][ROH] - k_1[R'_2SiClOR][ROH]$. When $d[R'_2SiClOR]/dt = 0$, $k_2/k_1 = [R'_2SiClOR]/[R'_2SiCl_2]$. When $a = 1$, $k_3/k_2 = [R'SiCl_2OR]/[R'SiCl_3]$ and $k_2/k_1 = [R'SiCl(OR)_2]/[R'SiCl_2OR]$. When $a = 0$, $k_4/k_3 = [SiCl_2(OR)_2]/[SiCl_3OR]$, and $k_2/k_3 = [SiCl(OR)_3)]/[SiCl_2(OR)_2]$.

From a plot of the area percent on a gas liquid chromatograph of each chlorosilane and chloroalkoxysilane versus equivalents of alcohol added, the consecutive relative rates were approximated as the ratio of the area percent for the maximum concentration of each consecutive product to its antecedent reagent. For example see Figure 1. For relative consecutive rates for most industrially important chlorosilanes, see Table I.

Ethanol was pumped into an equimolar mixture of two chlorosilanes in a small amount of toluene under the same conditions as described above. A plot was then made of the decrease in area of each chlorosilane relative to toluene as a standard as a function of the amount of alcohol that had been added. The plot was extrapolated to zero alcohol and the ratio of the two decreases was taken as the relative

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[1] Ebelman, J. J. *Compt. Rend.* **1844,** *19,* 398.

[2] Fuoss, R. M. *J. Am. Chem. Soc.* **1943,** *65,* 2406–2408.

[3] Chian, Yin-Yen; Lin, I.; Wang, Pao-Jen. *Hua Hsueh Hsueh Pao* **1959,** *25,* 197–204.

[4] Moedritzer, K. *J. Organomet. Chem. Rev.* **1966,** *179, 1.*

0276-7333/93/2312-1981$04.00/0

Table I. Rates of Competitive Consecutive Alcoholyses If Rate k_1[$\equiv$SiCl][ROH] Is Valued as 1

chlorosilane	ROH	k_4 × [$SiCl_4$] × [ROH]	k_3 × [$ROSiCl_3$] × [ROH]	k_2 × [$(RO)_2SiCl_2$] × [ROH]	k_1 × [$\equiv$SiCl] × [ROH]
$SiCl_4$	MeOH	120	15	15	1
	EtOH	198	18	18	1
$HSiCl_3$	EtOH		56	7	1
$MeSiCl_3$	MeOH		23	15	1
	EtOH		46	23	1
$PhSiCl_3$	EtOH		33	12	1
$MeHSiCl_2$	EtOH			8	1
Me_2SiCl_2	MeOH			15	1
	EtOH			16	1
$PhMeSiCl_2$	EtOH			12	1
Ph_2SiCl_2	MeOH			16	1
	EtOH			15	1

rate. In this way the following relative rates were measured.

k_4/k_3 for $SiCl_4/MeSiCl_3 = 12.5$

k_3/k_1 for $PhSiCl_3/Me_3SiCl = 90$

k_3/k_1 for $HSiCl_3/MeSiCl_3 = 56$

k_2/k_1 for $MeHSiCl_2/Me_2SiCl_2 = 4$

k_3/k_2 for $PhSiCl_3/Ph_2SiCl_2 = 43$

k_2/k_2 for $Me_2SiCl_2/PhMeSiCl_2 = 1.6$

k_3/k_1 for $MeSiCl_3/Me_3SiCl = 180$

k_3/k_3 for $MeSiCl_3/PhSiCl_3 = 2$

If the rate of ethoxylation of Me_3SiCl was taken as unity, the relative rate of the other chlorides were calculated as shown in Table II.

Discussion

The relative alcoholysis rates of a Si–Cl bond of type R_2ClSi–Cl is about 12–18 times faster than those of $R_2(R'O)Si$–Cl and $R(R'O)_2Si$–Cl when R = Me, Ph, or H, as though the extra Cl has an accelerating effect among these structures. This effect seems completely absent for the structure Si–Cl bonds of type RCl_2Si–Cl and $R(R'O)ClSi$–Cl. However, this accelerating effect returns forCl_3Si–Cl, which is more than 10 times more reactive than any other compound in the study.

Table II. Rates of Ethanolysis of Chlorosilanes Relative to the Rate for Me_3SiCl as Unity

	R_4	R_3	R_2	R_1
$SiCl_4$	2250	200	200	12
$HSiCl_3$		1080	135	19
$MeSiCl_3$		180	90	4
$PhSiCl_3$		90	33	3
$MeHSiCl_2$			44	5
$PhMeSiCl_2$			7	0.6
Me_2SiCl_2			11	0.7
Ph_2SiCl_2			3	0.2
Me_3SiCl				1

Experimental Section

All chlorosilanes were Dow Corning plant intermediates which had been analyzed by GC to be more than 98 area % pure. Methanol was Fisher Scientific, purified grade, and ethanol was Fisher Scientific absolute, 200 proof.

All analyses were effected with a Hewlett Packard 5890GC instrument equipped with a 20-ft × $^1/_8$-in. column packed with Chromosorb WHP, 80 mesh, with a thermal conductivity detector. GC area fractions were used as being equal to mole fractions for the mixtures of chloroalkoxysilanes. An error was introduced into the calculations in this way, but it should not be large.

Alkoxylations. Absolute ethanol was pumped with a Masterflex pump at the rate of 5 mL/min through a capillary tube which extended below the surface of stirred $SiCl_4$ (bp 58 °C, 116.6 g, 0.69 mol) in a three-necked round-bottom flask immersed in a water bath mainted at 60 °C. A reflux condenser cooled with ice water at 0 °C was attached to the flask as the vent to permit HCl to escape. Samples were taken by syringe through a diaphragm over one of the necks of the flask and injected into the gas chromatograph. The area percentages of each chlorosilane and each alkoxysilane were plotted against equivalents of alcohol that had been added. No alcohol was detected by the GC and also no HCl. The ratios of area percentages of alkoxysilane to antecedent chlorosilane at the point of maximum concentration of alkoxysilane were then taken as the relative competitive rates illustrated by Figure 1.

OM920738S