EQUILIBRIA BETWEEN Me_xSiCl_{4-x}, $x = 3, 2, 1, 0$ AND ALKYL CARBOXYLATE ESTERS *
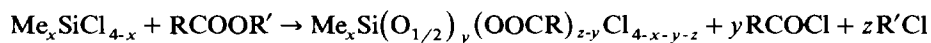
GODFREY C. MBAH and JOHN L. SPEIER

Dow Corning Corporation, Midland, Michigan 48640 (U.S.A.)

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Summary

At 150°C equilibria are established between chlorosilanes and alkyl esters according to the equation:

$$Me_xSiCl_{4-x} + RCOOR' \rightarrow Me_xSi(O_{1/2})_y(OOCR)_{z-y}Cl_{4-x-y-z} + yRCOCl + zR'Cl$$

When $x = 3$, $y = 0$, $z = 0.56$; when $x = 2$, $y = 0.26$, $z = 098$
When $x = 1$, $y = z = 0.56$; when $x = 0$, $y = z = 0.53$

Lewis acid salts such as $ZnCl_2$ or $FeCl_3$ are effective catalysts for the reactions leading to mixtures of these compounds.

Introduction

For about eight years the use of Me_3SiI and Me_3SiBr in organic syntheses has been increasing dramatically. These reagents dealkylate carboxylate esters quantitatively under extremely mild conditions. Excellent reviews of their uses have been published [1,2] recently. We had occasion to observe that chlorosilanes also react with alkyl esters. Because we could find no literature on such systems we briefly studied the systems $Me_xSiCl_{4-x} + RCOOR'$, where $x = 0$, 1, 2 and 3; R = Me, Et; R' = n-Bu, Me.

Results

Standard mixtures of chlorosilanes of the formula Me_xSiCl_{4-x}, $x = 0$, 1, 2, and 3 and alkyl carboxylates were heated in sealed Pyrex tubes alone or with various salts as catalysts for various times and the mixtures analysed by gas liquid chromatography (GLC).

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* This paper is dedicated to Professor M. Kumada on the occasion of his retirement.

Reactions of trimethylchlorosilane

Trimethylchlorosilane and n-butyl acetate, equimolar with 2% by wt. $FeCl_3$ at 150 °C, reacted very cleanly to consume 0.44 moles of each reagent to form 0.44 moles of Me_3SiOAc and n-butyl chloride within 3 h. No further change was detected during more than 16 h thereafter. The following reversible process was the only reaction detected. $Me_3SiCl + n\text{-}BuOAc \rightarrow Me_3SiOAc + n\text{-}BuCl$, $K \approx 0.62$.

The experiment was repeated with reagents in a mole ratio of 4/1. Equilibrium was achieved within 3 h with mole fractions of products: $K = [Me_3SiOAc][n\text{-}BuCl]/[Me_3SiCl][n\text{-}BuOAc] = [0.74]^2/[3.26][0.26] \approx 0.65$

The experiments were repeated with ethyl acetate and ethyl proprionate. With ethyl acetate, the equilibrium constant calculated in this way was 1.2. With ethyl proprionate it was 0.9.

Reactions of dimethyldichlorosilane

Equimolar amounts of dimethyldichlorosilane and n-butyl acetate led to a much more complex mixture of products. The percentage of the n-butyl acetate converted to n-butyl chloride under various conditions is shown in Table 1.

Thus, about 98% of the ester was converted to n-butyl chloride by one mole of Me_2SiCl_2. The principal other products identified were $Me_2Si(OAc)_2$, AcCl and $(ClMe_2Si)_2O$. Many more compounds thought to be chloroacetoxysiloxanes were indicated by GLC.

This experiment was repeated with methyl acetate and ethyl proprionate with $ZnCl_2$. Results seemed very closely the same.

The formation of acetyl chloride and siloxanes must have been from an equilibrium such as $ClMe_2SiOAc \rightarrow Me_2SiO_{2/2} + AcCl$. To see if this was likely, equivalents of acetyl chloride and octamethylcyclotetrasiloxane, $(Me_2SiO)_4$, were heated in sealed Pyrex tubes at 150 °C with and without catalysts for various times and analyzed by GLC. Table 2 shows the fraction of the acetyl chloride that was consumed under various conditions.

These data indicate that catalysts that were effective for the formation of alkyl chloride were also effective for formation of acetyl chloride. In this system equilibrium was achieved with about 74% of the acyl groups as chloride and 26% as acyloxysilanes or siloxanes. An equilibrium constant as the ratio of equivalents in

TABLE 1

CONVERSION (%) OF n-BuOAc TO n-BuCl AT 150 °C

Catalyst	Time (h)	n-BuCl (%)
None	2.5	None
n-Bu$_4$NBr	4	3
ZnCl$_2$	0.5	82
ZnCl$_2$	2	98
ZnCl$_2$	16	98
FeCl$_3$	2	82
FeCl$_3$	3	95
FeCl$_3$	4	98
FeCl$_3$	16	98

TABLE 2

$AcCl + \frac{1}{4}(Me_2SiO)_4 \rightarrow ClMe_2SiOAc$
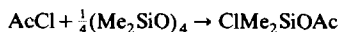
Catalyst	Time (h)	AcCl consumed (%)
None	2	16
n-Bu$_4$NBr	2	20
ZnBr$_2$	0.25	40
ZnBr$_2$	0.5	58
ZnBr$_2$	1.5	62
ZnCl$_2$	0.25	58
ZnCl$_2$	0.5	63
ZnCl$_2$	1.5	65
ZnCl$_2$	2.0	69
FeCl$_3$	0.25	65
FeCl$_3$	0.5	67
FeCl$_3$	1	74
FeCl$_3$	20	74

this case would be:

$$K = [\equiv\!Si\!-\!OAc]/[\equiv\!SiO_{2/2}] \times [\equiv\!Si\!-\!Cl]/[Ac\!-\!Cl] = [0.26]^2/[0.74]^2 \approx 0.13$$

GLC analyses showed less ClMe$_2$SiOAc than required by the equation of Table 2 and considerable Me$_2$Si(OAc)$_2$. To explain this equimolar amounts of Me$_2$SiCl$_2$ and Me$_2$Si(OAc)$_2$ were mixed in a vial and the mixture was analyzed periodically by both GLC and ^{1}H NMR. Results are shown in Table 3. No catalyst was added.

In each of these experiments in which siloxane bonds could form or react, a large number of siloxane polymers were formed. We suspected they were formed by equilibration, and to test this equivalent amounts of Me$_2$SiCl$_2$ and Me$_2$SiO$_{2/2}$ as (Me$_2$SiO)$_4$ were heated together at 150°C in sealed Pyrex tubes and the mixture was analyzed periodically by GLC. The fraction of the Me$_2$SiCl$_2$ consumed with time is shown in Table 4.

An equilibrium constant calculated from these data in the form $K = [ClMe_2SiO_{1/2}]^2/[Me_2SiCl_2][Me_2SiO_{2/2}] = [2 \times 0.61]^2/[0.39]^2 \approx 9.8$

The experiment was repeated with 4 equivalents of Me$_2$SiO$_{2/2}$, i.e., 1 mole Me$_2$SiCl$_2$ to 1 mole (Me$_2$SiO)$_4$ with FeCl$_3$. This mixture reached equilibrium in less

TABLE 3

$Me_2SiCl_2 + Me_2Si(OAc)_2 \rightarrow 2\ Me_2SiClOAc$

Reaction time at about 25°C	Me$_2$SiClOAc/Me$_2$SiCl$_2$		K (calcd.)	
	by GLC	by ^{1}H NMR	by GLC	by NMR
1 h	0.2			
1 d	1.0	1.2		
2 d	1.4	1.7		
6 d	1.4	1.6		
7 d	1.5	1.6	2.3	2.6

TABLE 4

$Me_2SiCl_2 + Me_2SiO_{2/2} \rightarrow 2ClMe_2SiO_{1/2}$
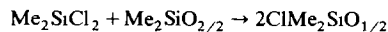
Catalyst	Time (h)	Me_2SiCl_2 consumed (%)
None	2.5	None
$ZnCl_2$	2	20
$Zn(OAc)_2$	0.25	25
$Zn(OAc)_2$	0.5	61
$FeCl_3$	0.25	61
$FeCl_3$	2	61

than 45 min, consuming 94% of the Me_2SiCl_2. For this example: $K = [2 \times 0.94]^2/[1 - 0.94][4 - 0.94] \approx 10$.

A scarcely detectable amount of $(Me_2SiO)_4$ remained at equilibrium, and GLC indicated a series of linear polysiloxanes, $Cl(Me_2SiO)_x Me_2SiCl$, $x = 0, 1, 2, 3$, etc.

Reactions of methyltrichlorosilane

Equimolar amounts of methyltrichlorosilane and n-butyl acetate were heated for 16 h with $FeCl_3$ and analyzed as having 52% of the n-butyl acetate consumed to form 52% n-butyl chloride and 52% acetyl chloride. No acyloxysilanes nor acyloxy-siloxanes were detected. This system apparently reacted cleanly but reversibly, according to the equation:

$MeSiCl_3 + n\text{-BuOAc} \rightarrow MeSiClO_{2/2} + n\text{-BuCl} + AcCl$

with an equilibrium constant:

$K = \left[MeSiClO_{2/2} \right][n\text{-BuCl}][AcCl]/[MeSiCl_3][n\text{-BuOAc}] =$

$$[0.52][0.52][0.52]/[0.48][0.48] \approx 0.6$$

The siloxanes appeared in GLC as a series of well separated peaks corresponding to $Cl[ClMeSiO]_x SiMeCl_2$ ($x = 0, 1, 2, 3$ etc.). Only the peaks corresponding to $x = 0$ and 1 were identified.

Reaction of tetrachlorosilane

Equimolar amounts of tetrachlorosilane and n-butyl acetate were heated with $FeCl_3$ for various times and analyzed by GLC. Equilibrium was reached in less than 2 h and then remained unchanged during 16 h. About 53% of the n-butyl acetate was converted at equilibrum into n-butyl chloride and acetyl chloride, with formation of a large number of polychlorosiloxanes which were not well separated by GLC. An equilibrium constant calculated as above for this sytem would be:

$K = \left[Cl_2SiO_{2/2} \right][n\text{-BuCl}][AcCl]/[SiCl_4][n\text{-BuOAc}]$

$$= [0.53][0.53][0.53]/[0.47][0.47] \approx 0.7$$

This value is within experimental error, identical to that calculated for $MeSiCl_3$.

Discussion

Moedritzer [3] reviewed the equilibria $Me_2SiA_2 + Me_2SiB_2 \rightleftharpoons 2Me_2SiAB$ for many combinations of A and B groups on silicon. If the distribution of A and B on silicon

is random: $K = [Me_2SiAB]^2/[Me_2SiA_2][Me_2SiB_2] = 4$ and $[Me_2SiA_2]$: $[Me_2SiB_2] : [Me_2SiAB] = 1/1/2$. If A is chlorine, the value of K is 2.6 if B is Br; 2.9 with I; 4.6 with NC; 3.5 with NCO; 3.3 with NCS; 5.6 with SMe; 100 with OMe and 6667 with NMe_2. The first six of these groups equilibrate with Cl approximately randomly, but OMe and NMe_2 form $Me_2SiClOMe$ and $Me_2SiClNMe_2$ preferentially. Our results indicate that K lies between 2.3 and 2.6 if B is OAc and K is about 10 if B is $Me_2SiO_{2/2}$, placing these groups among those that distribute almost at random.

The exchange of groups between silicon and carbon $SiCl + RCOOR' \rightarrow SiOOCR + R'Cl$ (1) and $SiCl + SiOCCR \rightarrow SiOSi + RCOCl$ (2) was highly dependent upon the structure of the chlorosilane. Me_3SiCl gave only the products of eq. 1 with $K = 0.6$, so that slightly more than 1/2 of an equimolar mixture of reagents remained at equilibrium. Me_2SiCl_2 formed 98% $R'Cl$, but reaction 2 gave only 25% acyl chloride at equilibrium. These reactions gave rise to a system $Me_2SiCl_xB_{2-x}$ where $x = 0$, 1, or 2 and B was $OOCR'$ or $O_{1/2}$. The mixture of silicon compounds was nearly that of a statistically random distribution of values of x with B either $OOCR'$ or $O_{1/2}$.

$MeSiCl_3$ and $SiCl_4$ gave only about 50% RCl, almost the same as Me_3SiCl, but they also formed an equivalent of $R'COCl$ by reaction 2 which did not take place with Me_3SiCl and which went only to the extent of 25% with Me_2SiCl_2.

These systems formed siloxanes $Me_yCl_{x-y}Si(O_{1/2})_{4-x-y}$ with $y = 0$ or 1 and $x = 4$, 3, and 2.

These exchange reactions and redistribution reactions proceed very slowly if at all at 150°C in the absence of a catalyst, the best apparently being Lewis acid salts. With $FeCl_3$ for example, the reactions may proceed through highly polarized coordinated complexes such as:

Experimental

The chlorosilanes were very pure samples of our own manufacture. The esters were purchased from Eastman Kodak Co. and were pure as judged by our GLC analyses.

All GLC analyses were with a Hewlett–Packard 5710 A gas chromatograph equipped with a 20′ × 1/8″ stainless steel column, packed with 10% SE30 on chrom WHP 80/100 with a TC detector coupled to a Hewlett–Packard 3380 A integrator calibrated to automatically calculate the amount of each compound relative to an internal standard.

The ^{1}H NMR spectra were recorded neat with a Varian EM 390 spectrometer. The mole ratios of $Me_2SiCl_2/Me_2SiClOAc$ were taken as the integral ratios of the $SiCH_3$ groups for the two compounds. The ratio of $Me_2Si(OAc)_2/Me_2SiClOAc$ was determined at the same time, and the two ratios were very nearly the same.

General procedure

A standard solution of reagents was made up containing a known amount of a non-reactive standard selected to elute well away from reagents or products.

Portions of these solutions were sealed into 8 mm Pyrex tubes which sometimes contained salts in experiments made to see if the salts were catalytic. The tubes were kept for various lengths of time in an oven at 150°C, then cooled and opened, and the contents were analyzed.

References

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