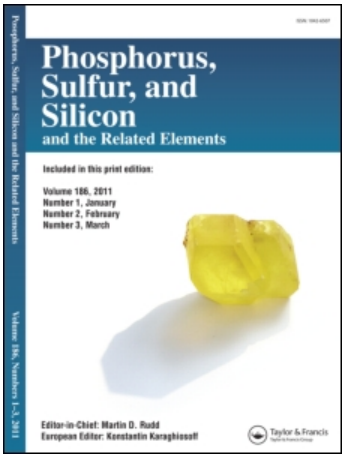

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ON THE SYNTHESIS OF SILOXANES XXIV. VERIFICATION OF INDUCTIVE AND STERIC SUBSTITUENT CONSTANTS FOR SILOXY GROUPS BY REACTION OF DI- AND TRICHLOROSILANES AND -SILOXANES WITH LITHIUM *T*-BUTOXIDE

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ON THE SYNTHESIS OF SILOXANES XXIV.* VERIFICATION OF INDUCTIVE AND STERIC SUBSTITUENT CONSTANTS FOR SILOXY GROUPS BY REACTION OF DI- AND TRICHLOROSILANES AND -SILOXANES WITH LITHIUM *T*-BUTOXIDE

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The reactions of dichloromethylorganylsilanes ($RSiMeCl_2$) and dichlorosiloxanes ($\equiv SiOSiMeCl_2$) as well as of trichloroorganylsilanes ($RSiCl_3$) and trichlorosiloxanes ($\equiv SiOSiCl_3$) with lithium *t*-butoxide in diethyl ether were investigated kinetically by turbidimetric measurements in order to verify the inductive substituent constants σ^* for siloxy groups determined earlier by the ^{29}Si NMR shifts of compounds $(Me_3SiO)_3Si—Y$ (Y = siloxy group) and the steric substituent constants E_s for siloxy groups which were obtained by the rate constants of the acetolysis reactions of compounds $ClMe_2Si—Y$ (Y = siloxy group). The reaction constants were determined using chloroorganylsilanes to be: ρ^* ($RSiMeCl_2$) = 0.85; δ ($RSiMeCl_2$) = 0.85; ρ^* ($RSiCl_3$) = 1.02; δ ($RSiCl_3$) = 1.28. The correlation of $\lg k_{rel} - \rho^* \cdot \sigma^*$ values of the corresponding chlorosiloxanes with E_s values using σ^*- and E_s-constants of siloxy groups determined earlier gave correlation straight lines with the slope of 0.81 ($\equiv SiOSiMeCl_2$) or 1.12 ($\equiv SiOSiCl_3$), respectively, that means the δ-values of the silanes and siloxanes are nearly identical. But the reactivity of the di- and trichlorosiloxanes is only about one tenth of the values expected by the reaction constants and the σ^*- and E_s-constants of siloxy groups previously determined. We suggest that this behavior is caused by an electron donating effect of the siloxy groups connected with silicon atoms bearing two or three chlorine atoms. As this influence is contrary to the electron attracting effect of siloxy groups at silicon atoms with only one chlorine atom, we assume that the inductive effect of siloxy groups is extremely sensitive to changes in electron density at the silicon atom with which they are connected. As the correlation straight lines are only parallel shifted, obviously the electron density at a silicon atom is mainly determined by the first generation of substituents.

Key words: Chlorosilane, chlorosiloxane, lithium alkoxide, reaction constant, substituent constant, kinetics.

INTRODUCTION

We previously studied the reactions of chlorodimethylorganylsilanes and chlorodimethylsiloxanes with lithium trimethylsilanolate, lithium dimethylphenylsilanolate and lithium *i*-propoxide[2] to prove the values of inductive and steric substituent constants for siloxy groups we determined.[3,4] It was found that the chlorodimethylsiloxanes react up to ten times faster than expected by the inductive substituent constants σ^* of the siloxy groups evaluated using the ^{29}Si NMR shifts of compounds $(Me_3SiO)_3Si—R$ (R = organyl or siloxy group)[3,5] and the steric sub-

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stituent constants E_s of the siloxy groups, derived from the acetolysis reactions of compounds $ClMe_2Si—R$ (R = organyl or siloxy group).[4] We suggest that the inductive effects of siloxy groups vary with the total electron density which is determined by the substituents at the reaction center, whereas the steric effects remain constant.

Continuing these studies we investigated the first step of the reactions of dichloromethylorganylsilanes and dichloromethylsiloxanes as well as of trichloroorganylsilanes and trichlorosiloxanes with lithium *t*-butoxide (1) in order to study the influence of strongly electron-attracting groups at the reaction center on the inductive effects of siloxy groups.

$$RMe_{3-n}SiCl_n + Me_3COLi \rightarrow RMe_{3-n}SiCl_{n-1}OCMe_3 + LiCl \qquad (1)$$

$$n = 2,\ 3 \qquad R = \text{alkyl, aryl, siloxy}$$

Lithium *t*-butoxide was used as nucleophile to avoid the reaction of more than one chlorine atom. Indeed, only reaction (1) took place as shown by gas chromatographic measurements.

RESULTS AND DISCUSSION

First of all inductive reaction constants ρ^* of the reactions (1) were determined from the k_{rel}-values of aryldichloromethylsilanes X-$C_6H_4SiMeCl_2$ (Table I, 5–9, $\rho^* = 0.85$) and of aryltrichlorosilanes X-$C_6H_4SiCl_3$, (Table II, 22–26, $\rho^* = 1.02$). Neglecting the inductive effects of the alkyl groups, which are about zero,[6] the correlation of the lg k_{rel}-values of alkyl substituted chlorosilanes with the E_s-values of the substituents gave the steric reaction constants δ of the reactions (1). We found δ-values of 0.85 for reactions of compounds $RSiMeCl_2$ with *t*-BuOLi (Table I, 1–4, $\delta = 0.85$) and of 1.28 for reactions of compounds $RSiCl_3$ with the same reagent (Table II, 14–21, $\delta = 1.28$). The rate constants of the siloxy substituted compounds show only small differences. This is due to the compensation of the influence of the inductive effects by the influence of the steric effects, because the reaction constants ρ and δ as well as the differences of the substituent constants σ and E_s are in the same order of magnitude (cf. Tables I and II).

In order to take into consideration the different inductive effects of the siloxy groups, the δ-values for the reactions with chlorosiloxanes were evaluated by correlating lg $k_{rel} - \rho^* \cdot \sigma^*$ with E_s. The results are shown in Figure 1 for compounds of the type $\equiv SiOSiMeCl_2$ and in Figure 2 for compounds of the type $\equiv SiOSiCl_3$. In both cases straight lines of correlation were obtained with siloxanes of the same slope as found with alkylchlorosilanes $RMeSiCl_2$ and $RSiCl_3$.

However, the lines are nearly parallel shifted to the correlation straight lines of the alkyl substituted compounds, as in the case of monochlorosilanes and monochlorosiloxanes.[2] But whereas the reactivities of monochlorosiloxanes were nearly ten times of those expected by the reaction constants and the substituent constants, the reactivities of the dichloro- and trichlorosiloxanes were only about one tenth of the expected ones.

We assume that the E_s-values of siloxy groups are constant in all series but their

TABLE I

Substituent constants for dichloromethylorganylsilanes or dichloromethylsiloxanes $RSiMeCl_2$ and relative rate constants for their reactions with lithium *t*-butoxide in diethyl ether at 30°C

No.	R	$\sigma^*(R)$	$E_s(R)$	k_{rel}
1	Me	0.00	0.0	1.00
2	Et	0.00	-0.28[4]	0.60
3	cPent	0.00	-0.70[2]	0.25
4	cHex	0.00	-0.79[7]	0.22
5	4-MeC_6H_4	0.31[a]	-0.40[4]	0.19
6	3-MeC_6H_4	0.41[a]	-0.40[4]	0.20
7	C_6H_5	0.48[3]	-0.40[4]	0.22
8	4-ClC_6H_4	0.71[a]	-0.40[4]	0.37
9	3-ClC_6H_4	0.85[a]	-0.40[4]	0.51
10	Me_3SiO	0.35[3]	-0.43[4]	0.15
11	$Me_3SiOSiMe_2O$	0.57[3]	-0.46[4]	0.15
12	$(Me_3SiO)_2SiMeO$	0.74[3]	-0.77[4]	0.14
13	$(Me_3SiO)_3SiO$	0.90[3]	-1.04[4]	0.12

steric susceptibility[b] δ:	0.85 (No. 1-4)
regression coefficient r:	0.99
significance level s:	0.0136
inductive reaction constant[c] ρ^*:	0.85 (No. 5-9)
regression coefficient r:	0.985
significance level s:	0.0373
steric susceptibility[d] δ:	0.81 (No.10-13)
regression coefficient r:	0.96
term C[d]:	-0.85
significance level s:	0.083

[a] calculated using the equation $\sigma^*(R\text{-}C_6H_4) = 0.48 + \sigma(R)$

[b] calculated using the equation $\log k_{rel} = \delta \cdot \Sigma E_s$

[c] calculated using the equation $\log k_{rel} = \rho^* \cdot \Sigma\sigma^*$

[d] calculated using the equation $\log k_{rel} - (\rho^* \cdot \Sigma\sigma^*) = \delta \cdot \Sigma E_s + C$

σ^*-values show systematic differences in different series. We suggest this behavior was caused by the electron density at the reaction center. While siloxy groups show a strong electron attracting effect in monochlorosiloxanes with comparatively high electron density at the silicon atom, they act as electron donors in di- and trichlorosiloxanes with comparatively low electron density at the silicon atom. To take these effects into consideration we introduced the term C into the Taft equation:

$$\lg k_{rel} = \rho^* \cdot \Sigma\sigma^* + \delta \cdot \Sigma E_s + C \qquad (2)$$

TABLE II

Substituent constants for trichloroorganylsilanes or trichlorosiloxanes $RSiCl_3$ and relative rate constants for their reactions with lithium *t*-butoxide in diethyl ether at 20°C

No.	R	$\sigma^*(R)$	$E_s(R)$	k_{rel}
14	Me	0.0	0.0	1.00
15	Et	0.0	-0.28[4]	0.41
16	^{n}Pr	0.0	-0.36[7]	0.36
17	^{n}Bu	0.0	-0.39[7]	0.32
18	^{i}Bu	0.0	-0.55[2]	0.19
19	^{i}Pr	0.0	-0.76[2]	0.11
20	^{c}Hex	0.0	-0.79[7]	0.10
21	^{s}Bu	0.0	-0.87[2]	0.07
22	4-MeC_6H_4	0.31[a]	-0.40[4]	0.08
23	C_6H_5	0.48[3]	-0.40[4]	0.12
24	4-FC_6H_4	0.54[a]	-0.40[4]	0.15
25	4-ClC_6H_4	0.71[a]	-0.40[4]	0.22
26	3-ClC_6H_4	0.85[a]	-0.40[4]	0.28
27	$ClCH_2$	1.05[8]	-0.24[7]	2.73
28	Cl_2CH	1.94[8]	-0.58[7]	6.50
29	$C_6H_5CH_2$	0.215[8]	-0.38[7]	0.56
30	Me_3SiO	0.35[3]	-0.43[4]	0.10
31	$Me_3SiOSiMe_2O$	0.57[3]	-0.46[4]	0.12
32	$(Me_3SiO)_2SiMeO$	0.74[3]	-0.77[4]	0.08
33	$(Me_3SiO)_3SiO$	0.90[3]	-1.04[4]	0.07

steric susceptibility[b] δ:	1.28	(No. 14-21)
regression coefficient r:	0.998	
significance level s:	0.023	
inductive reaction constant[c] ρ^*:	1.02	(No. 22-26)
regression coefficient r:	0.995	
significance level s:	0.023	
steric susceptibility[d] δ:	1.12	(No.30-33)
regression coefficient r:	0.98	
term C[d]:	-0.94	
significance level s:	0.07	

[a] calculated using the equation $\sigma^*(R\text{-}C_6H_4) = 0.48 + \sigma(R)$

[b] calculated using the equation $\log k_{rel} = \delta \cdot \Sigma E_s$

[c] calculated using the equation $\log k_{rel} = \rho^* \cdot \Sigma\sigma^*$

[d] calculated using the equation $\log k_{rel} - (\rho^* \cdot \Sigma\sigma^*) = \delta \cdot \Sigma E_s + C$

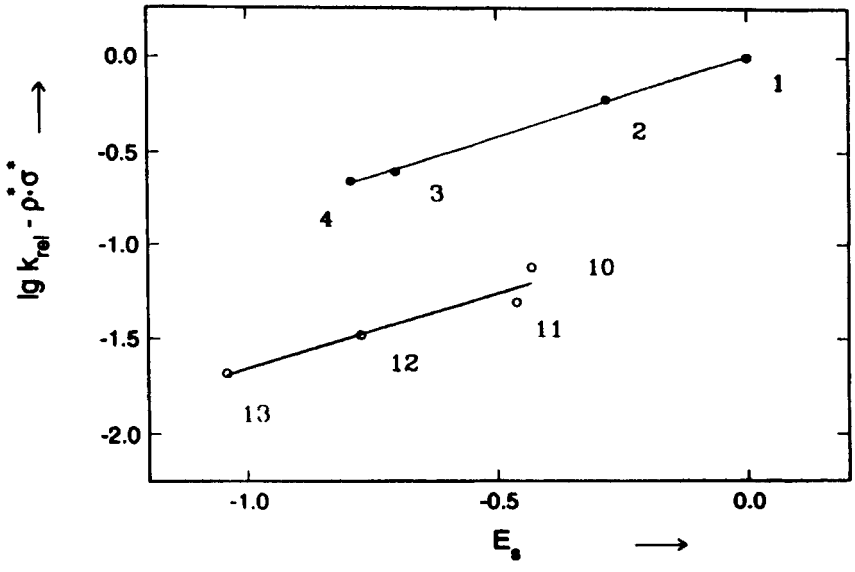

FIGURE 1 Correlation of the lg $k_{rel} - \rho^* \cdot \Sigma\sigma^*$ terms against the E_s-values of the substituents of dichloromethylorganylsilanes $RSiMeCl_2$ (●) and dichlorosiloxanes $\equiv SiOSiMeCl_2$ (○).

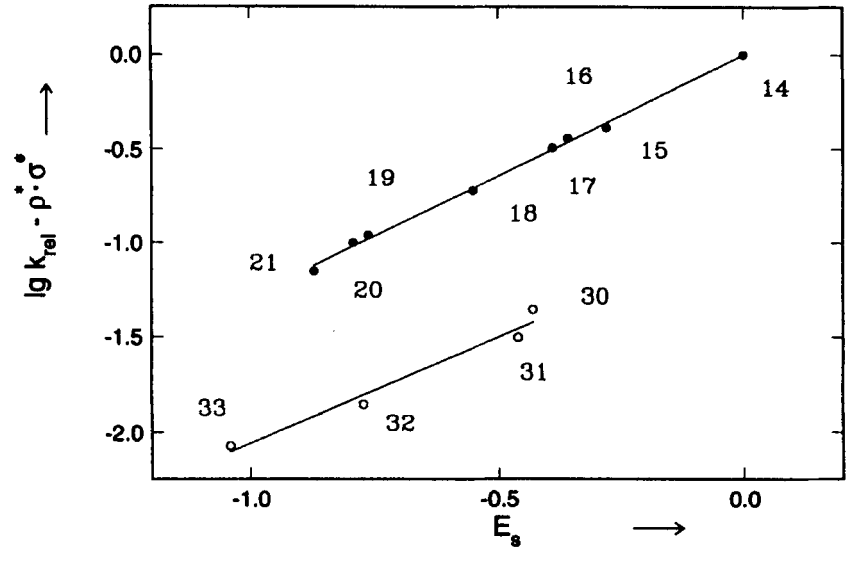

FIGURE 2 Correlation of the lg $k_{rel} - \rho^* \cdot \Sigma\sigma^*$ terms against the E_s-values of the substituents of trichloroorganylsilanes $RSiCl_3$ (●) and trichlorosiloxanes $\equiv SiOSiCl_3$ (○).

Because the correlation straight lines are nearly parallel shifted obviously this term C is determined mainly by the first generation of substituents around the reacting silicon atom. Although the σ^*-values of the siloxy groups are not constant in different series of compounds, they are useful to predict the relative reactivities within a series of siloxanes. On the other hand, the terms C calculated using

Equation (2) give insight into the total electron density at the reaction center. In order to calculate absolute rate constants besides the substituent constants σ^* and E_s the reaction constants ρ^* and δ as well as the constant C for the type of compounds studied are required.

EXPERIMENTAL

Turbidimetric Measurements

The turbidimetric measurements[2] were carried out using a Spekol spectrocolorimeter (Carl Zeiss, Jena) (absorbing layer 0.5 cm, wave length 700 nm, receiver gain 50). The scattered light intensity was measured at an angle of 45° to the primary light beam.

A solution of lithium *t*-butoxide in diethyl ether (0.3 . . . 0.6 mol/l) was thermostated at the reaction temperature and the reaction was started by adding an equimolar amount of chlorosilane or chlorosiloxane. Time to attain turbidity of 80% was measured and defined as "turbidity time." The relative rate constants were calculated as quotients of the turbidity time values of the samples to those of the standard substances Me_2SiCl_2 or $MeSiCl_3$.

The measurements were repeated three to eight times. The k_{rel}-values show a relative error of ±10%.

Gas Chromatographic Measurements

The reactions of dichlorodimethylsilane or trichloromethylsilane, respectively, with lithium *t*-butoxide were studied by means of gas chromatography (Chromatron GCHF 18.3 with FID; temperature: 90°C; carrier gas: 40 ml/min, N_2); column: 3 m × 5 mm filled with 10% of SE30 on Chromosorb W AW-DMCS, 80–100 mesh ASTM). The chlorosilane was dissolved in diethyl ether (0.5 mol/l) and the reaction was started by adding an equimolar amount of lithium *t*-butoxide in ether. The lithium chloride formed was separated by centrifuging, subsequently, the solution was injected into the column. Only *t*-butoxychlorodimethylsilane or *t*-butoxydichloromethylsilane were observed as reaction products.

Preparations

Me_2SiCl_2, $MeSiCl_3$, $SiCl_4$, $MeHSiCl_2$, $HSiCl_3$ and hexamethyldisiloxane were gifts of the Chemiewerk Nünchritz GmbH.

Lithium-t-butoxide: Solutions of lithium-*t*-butoxide were obtained by treating *t*-butanol with lithium metal in diethyl ether. Concentrations in the range of 0.3 . . . 0.6 mol/l were used.

Dichloromethylorganylsilanes and trichloroorganylsilanes: The chlorosilanes $RMeSiCl_2$ (R = Et **2**, 4-MeC_6H_4 **5**, 3-MeC_6H_4 **6**, C_6H_5 **7**, 4-ClC_6H_4 **8**, 3-ClC_6H_4 **9**, were prepared from $MeSiCl_3$ and the appropriate Grignard reagents obtained by the corresponding chlorides RCl.

The chlorosilanes $RSiCl_3$ (R = Et **15**, *n*-Pr **16**, *n*-Bu **17**, 4-MeC_6H_4 **22**, C_6H_5 **23**, 4-FC_6H_4 **24**, 4-ClC_6H_4 **25**, 3-ClC_6H_4 **26** and $C_6H_4CH_2$ **29** were prepared in the same way from $SiCl_4$ and the appropriate Grignard reagents.

s-$BuSiCl_3$ **21** was obtained by the reaction of *s*-BuLi with $SiCl_4$. Dichlorocyclopentylmethylsilane **3**, dichlorocyclohexylmethylsilane **4** and trichlorocyclohexylsilane **20**, were prepared by hydrosilylation of cyclopentene or cyclohexene with dichloromethylsilane or trichlorosilane.[9]

In the following, the characteristic data of dichlorocyclopentylmethylsilane **3** were given:

Yield (31%), b.p. 62°C/2.66 kPa, d_4^{20} 1.05, n_D^{20} 1.4737, $C_6H_{12}Cl_2Si$, hydrolyzable Cl found: 38.50%, calc.: 38.71%, ^{29}Si NMR: δ 33.10 ppm

The data of the other compounds **4** and **20** were as published.

Trichloro(chloromethyl)silane **27** and trichloro(dichloromethyl)silane **28** were obtained by photochemical chlorination of trichloromethylsilane.[10] The physical data were as published.

Chlorosiloxanes: 1,1-Dichloro-1,3,3,3-tetramethyldisiloxane **10** as well as 1,1,1-trichloro-3,3,3-trimethyldisiloxane **30** were obtained by equilibrating $MeSiCl_3$ or $SiCl_4$ with hexamethyldisiloxane in the presence of $(PNCl_2)_x$ as catalyst.[11] The physical data were as published.

1,1-Dichloro-1,3,3,5,5,5-hexamethyltrisiloxane (MDM^{Cl_2}) **11**: A solution of 32.9 g (0.2 mol) pentamethyldisiloxanol in 300 ml of dry diethyl ether was slowly added to a vigorously stirred solution of 30 g (0.2 mol) of trichloromethylsilane in 300 ml of dry diethyl ether containing 15.8 g (0.2 mol) of pyridine. The mixture was boiled for 2 h, the pyridine hydrochloride formed, was filtered off, and the filtrate was distilled.

Yield (27%), b.p. 53°C/1.07 kPa, d_4^{20} 0.988, n_D^{20} 1.4020, $C_6H_{18}Cl_2O_2Si_3$, hydrolyzable Cl found: 25.10%, calc.: 25.56%, ^{29}Si NMR: δ 9.25 ppm (M), −16.84 ppm (D), −19.89 ppm (M^{Cl_2})

The following chlorosiloxanes were prepared similarly:

1,1-Dichloro-1,3,5,5,5-pentamethyl-3-trimethylsiloxytrisiloxane ($M_2TM^{Cl_2}$) **12**: starting from 1,1,1,3,5,5,5-heptamethyltrisiloxane-3-ol and trichloromethylsilane.

Yield (60%), b.p. 94°C/1.6 kPa, d_4^{20} 0.976, n_D^{20} 1.4005, $C_8H_{24}Cl_2O_3Si_4$, hydrolyzable Cl found: 19.80%, calc.: 20.17%, ^{29}Si NMR: δ 9.75 ppm (M), −19.72 ppm (M^{Cl_2}), −64.43 ppm (T)

1,1-Dichloro-1,5,5,5-tetramethyl-3,3-bis(trimethylsiloxy)trisiloxane ($M_3QM^{Cl_2}$) **13**: starting from tris(trimethylsiloxy)silanol and trichloromethylsilane.

Yield (65%), b.p. 113°C/2.0 kPa, d_4^{20} 0.970, n_D^{20} 1.3991, $C_{10}H_{30}Cl_2O_4Si_5$, hydrolyzable Cl found: 16.42%, calc.: 16.66%, ^{29}Si NMR: δ 10.65 ppm (M), −19.11 ppm (M^{Cl_2}), −107.31 ppm (Q)

1,1,1-Trichloro-3,3,5,5,5-pentamethyltrisiloxane (MDM^{Cl_3}) **31**: starting from pentamethyldisiloxanol and tetrachlorosilane.

Yield (22%), b.p. 55°C/1.07 kPa, d_4^{20} 1.025, n_D^{20} 1.4005, $C_5H_{15}Cl_3O_2Si_3$, hydrolyzable Cl found: 33.60%, calc.: 35.72%, ^{29}Si NMR: δ 10.25 ppm (M), −15.29 ppm (D), −48.89 ppm (M^{Cl_3})

1,1,1-Trichloro-3,5,5,5-tetramethyl-3-trimethylsiloxytrisiloxane ($M_2TM^{Cl_3}$) **32**: starting from 1,1,1,3,5,5,5-heptamethyltrisiloxane-3-ol and tetrachlorosilane.

Yield (40%), b.p. 92°C/0.93 kPa, d_4^{20} 1.030, n_D^{20} 1.4007, $C_7H_{21}Cl_3O_3Si_4$, hydrolyzable Cl found: 26.80%, calc.: 28.60%, ^{29}Si NMR: δ 10.58 ppm (M), −49.74 ppm (M^{Cl_3}), −64.66 ppm (T)

1,1,1-Trichloro-5,5,5-trimethyl-3,3-bis(trimethylsiloxy)trisiloxane ($M_3QM^{Cl_3}$) **33**: starting from tris(trimethylsiloxy)silanol and tetrachlorosiloxane.

Yield (56%), b.p. 115°C/1.73 kPa, d_4^{20} 1.028, n_D^{20} 1.4001, $C_9H_{27}Cl_3O_4Si_5$, hydrolyzable Cl found: 22.15%, calc.: 23.84%, ^{29}Si NMR: δ 11.55 ppm (M), −49.22 ppm (M^{Cl_3}), −108.36 ppm (Q)

All substances used for kinetic measurements had a higher purity than 98% as determined by gas chromatography.

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