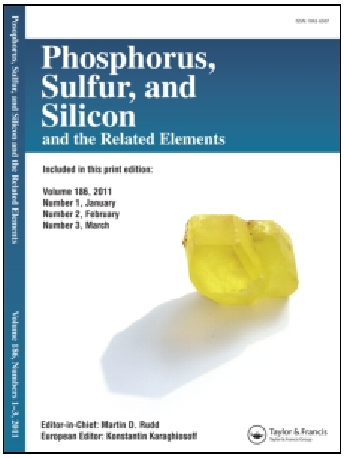


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTIONS IN THE CHLOROSILANE-SILANOL-SILOXANE SYSTEM

K. Rühlmann[a]
[a] Sektion Chemie, Technische Universität Dresden, Dresden, German Democratic Republic

To cite this Article Rühlmann, K.(1986) 'REACTIONS IN THE CHLOROSILANE-SILANOL-SILOXANE SYSTEM', Phosphorus, Sulfur, and Silicon and the Related Elements, 27: 1, 139 — 152
To link to this Article: DOI: 10.1080/03086648608072767
URL: http://dx.doi.org/10.1080/03086648608072767

Phosphorus and Sulfur, 1986, Vol. 27, pp. 139–152
0308-664X/86/2702-0139/$20.00/0

REACTIONS IN THE CHLOROSILANE-SILANOL-SILOXANE SYSTEM

K. RÜHLMANN

Technische Universität Dresden, Sektion Chemie, Mommsenstr. 13,
DDR-8027 Dresden, German Democratic Republic

We obtained the first σ^*-values and E_s-values for siloxy groups by spectroscopic and kinetic methods. Detailed mechanistic investigations are performed on the hydrolysis of chlorosiloxanes, the cleavage of Si—O—Si bonds by HCl, and the substituent exchange reaction between silanols and chlorosilanes.

INTRODUCTION

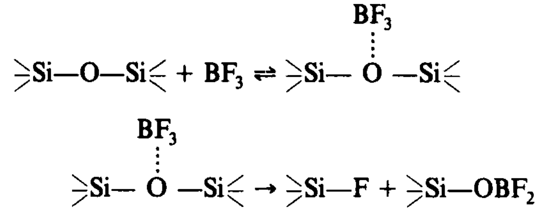
In spite of the growing importance of silicones details of the mechanisms of the reactions which are involved in their technical production by hydrolysis of chlorosilanes and condensation of the silanols formed are widely unknown. This is especially true for the influence of inductive and steric effects as well as of the medium on the direction and the rate of these reactions. In addition, there is a complete lack of inductive and steric substituent constants for siloxy groups in literature. Thus the first topic of our work in this field was the evaluation of those constants, which should give us a basic tool for further kinetical and mechanistical investigations.

DETERMINATION OF INDUCTIVE AND STERIC SUBSTITUENT CONSTANTS FOR SILOXY GROUPS

We could obtain the first inductive substituent constants for siloxy groups by a method developed by Engelhardt and coworkers.[1] These authors found a linear correlation between the ^{29}Si-NMR shifts of compounds of the type $(Me_3SiO)_3Si—X$ and the σ^*-values of X.[2] Correlation is especially good with the shift values of the monofunctional silicon atoms. Of interest is the σ^*-value of the phenyl group, which was found to be 0.5. That is significantly smaller than the value known in carbon chemistry. In this connection we recalculated the correlation between Si–H-coupling constants and σ^*-values found by Nagai[3] at a larger number of silanes with alkyl, aryl, and halogenated alkyl groups at silicon. In this investigation Nagai used the value of 0.6 for a phenyl group at carbon. But if correlation is taken without the phenyl group, it is much better. And now from the coupling constant found for a phenylsilane a value of 0.48 was calculated by us. This lower σ^*-value is well understandable, because there is a significant back donation of charge from the phenyl group to silicon by $(p \rightarrow d)_\pi$-interaction.

From the data found in the literature[1] the equation $\delta(M) = 1.75 \cdot \sigma^* + 7.5$ could be derived. Now from the known value for the monofunctional silicon atoms of tetrakis(trimethylsiloxy)silane,[4] we calculated the σ^*-value of the trimethylsiloxy group. And from shift values measured by us a series of σ^*-values for siloxy groups could be obtained using the equation given (Table I).

These inductive substituent constants had to be confirmed by a kinetical investigation. Thus it was necessary to find a kinetically easily evaluatable reaction, which was not, or only to a small extent, influenced by steric effects. We found it in the cleavage of siloxanes by boron trifluroide. This reaction follows the mechanism (1) and the rate law (2).



$$\geq Si{-}O{-}Si\leq + BF_3 \rightleftharpoons \geq Si{-}\overset{\overset{BF_3}{\vdots}}{O}{-}Si\leq$$

$$\geq Si{-}\overset{\overset{BF_3}{\vdots}}{O}{-}Si\leq \rightarrow \geq Si{-}F + \geq Si{-}OBF_2 \qquad (1)$$

$$-\frac{d[\geq SiOSi\leq]}{dt} = k \cdot [BF_3]^{4.6} \cdot [\geq SiOSi\leq]$$
$$= k' \cdot [\geq SiOSi\leq] \qquad (2)$$

As we used a large excess of BF_3, kinetical data could be evaluated with a pseudo first order kinetic law. From the rate constants of a series of substituted diaryldisiloxanes the ρ-value of this reaction was determined to be -1 (Figure 1) using the Hammett constants of Jaffe.[5] To determine σ^*-values from kinetical data, we had to change from Hammett to Taft constants[2] (Table II). The σ^*-values for substituted aryl groups could be calculated by the equation: $\sigma^*(X{-}Ph) = \sigma^*(X) + 0.48$ and 0.48 indeed is the σ^*-value of the phenyl group. From the octamethyltrisiloxane once more a value of nearly 0.35 was found for one trimethylsiloxy group at silicon and from the tris(trimethylsiloxy)methylsilane a value of 0.65 for two trimethylsiloxy groups at one silicon atom. That means firstly that the spectroscopically found σ^*-values could be used also in kinetics and secondly because of the good correlation that the cleavage of siloxanes by BF_3 is not or only to a very low extent

TABLE I

^{29}Si-NMR shift values δ of the monofunctional silicon atoms of compounds of the type $(Me_3SiO)_3Si{-}X$ and the σ^*-values of X

X	δ (ppm)	σ^*
H	8.34	0.48
$OSiMe_3$	8.08	0.35
$OSi(OSiMe_3)_3$	9.08	0.91
$OSiMe_2OSi(OSiMe_3)_3$	8.80	0.74
$OSiMe_2Cl$	9.63	1.22
$OSiMe_2OSiMe_2Cl$	9.09	0.91
$O(SiMe_2O)_2SiMe_2Cl$	8.90	0.80
$O(SiMe_2O)_3SiMe_2Cl$	8.86	0.78
$OSiMeCl_2$	10.50	1.71
$OSiCl_3$	11.40	2.23
$OSiMe(OH)_2$	9.70	1.26

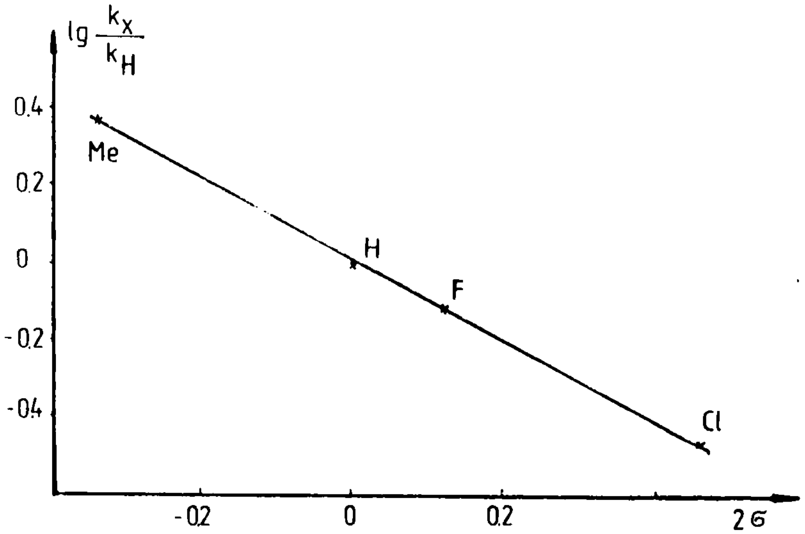


FIGURE 1 Determination of the ρ-value for the cleavage of the disiloxanes p-X—$C_6H_4Si(Me_2)$—O—$Si(Me)_2C_6H_4$-p-X by BF_3.

influenced by steric effects, though the second step of (1) is a nucleophilic substitution reaction, which should be sensitive to steric hindrance.

For the determination of steric substituent constants once more we had to find a suitable model reaction. As we intended investigations on the hydrolysis reactions of chlorosiloxanes, this model reaction should be mechanistically similar to the hydrolysis reaction and easy to evaluate. We have chosen the well-known acetolysis of chlorosilanes with acetic acid in acetic anhydride. Our first experiments showed that this reaction can be described by the Scheme (3).

$$\begin{gathered} \geqslant Si{-}Cl + AcOH \rightarrow \geqslant Si{-}OAc + HCl \\ Ac_2O + HCl \rightleftharpoons AcCl + AcOH \end{gathered} \tag{3}$$

TABLE II

Determination of σ*-values by cleavage of siloxanes $XSi(Me_2)OSiMe(Y)Z$ (0.1 mol · l^{-1}) by BF_3 (4.25 mol · l^{-1}) in dioxane $T = 30°C$

X	Y	Z	$10^3 \cdot k_i$ (min^{-1})	$\lg \frac{k_i}{k_{Me}}$	Σσ*
Me	Me	Me	180	0	0
p-Me—C_6H_4	p-Me—C_6H_4	Me	44	−0.61	0.62
Ph	Ph	Me	20	−0.96	0.96
p-F—C_6H_4	p-F—C_6H_4	Me	16	−1.05	1.08
p-Cl—C_6H_4	p-Cl—C_6H_4	Me	6.3	−1.46	1.42
Me	$OSiMe_3$	Me	82	−0.34	0.34
Me	$OSiMe_3$	$OSiMe_3$	62	−0.65	0.65
Me	Ph	Me	60	−0.48	0.48

Reacting monofunctional chlorosilanes with different concentrations of acetic acid we found that there is no reaction with acetic anhydride. And reactions of acetic anhydride with hydrochloric acid in acetic acid showed us that the equilibrium of the second reaction is established very fast and shifted far to the right side. As acetic anhydride is present in a large excess and the concentration of acetic acid remains constant because of the fast establishment of the equilibrium, the acetolysis reaction should obey a pseudo first order rate law (4).

$$\begin{aligned} -\frac{d[\geqslant\mathrm{SiCl}]}{dt} &= k\cdot[\mathrm{AcOH}]\cdot[\geqslant\mathrm{SiCl}] \\ &= k'\cdot[\geqslant\mathrm{SiCl}] \end{aligned} \tag{4}$$

Kinetic experiments confirmed this assumption. The next step to the determination of steric substituent constants with this reaction had to be the evaluation of ρ, the inductive reaction constant of the acetolysis reaction. To exclude for the present steric effects, we determined at first the rate constants for a series of arylchlorodimethylsilanes. Table III shows, that within the limit of error, the rate constants of all arylchlorodimethylsilanes are equal. In other words, the acetolysis of chlorosilanes is insensitive to inductive effects and differences between the rate constants should be determined only by steric effects. Now δ, the constant of steric susceptibility, could be obtained by plotting the lg k-values of some alkylchlorodimethylsilanes against the known steric substituent constants of Taft.[2] These values led in our case to a better correlation than the E_s(Si)-values of Cartledge,[6] which were published in 1983 (Figure 2). The slope of the straight line of correlation, which means the constant of steric susceptibility, was found to be 1.3. Now we were able to calculate some new steric substituent constants for alkyl groups and further for a series of siloxy groups from kinetical data (Table IV). The reason for the unexpectedly high reactivity of 1.3-dichlorotetramethyl- and 1-acetoxy-3-chlorotetramethyldisiloxane has been unknown up to now. One explanation could be that the Si—O—Si-angle becomes stretched by electron attracting groups and thus the steric requirements diminish. Another reason may be that the acetolysis reaction changes the mechanism, if chlorosilanes with strong electron attracting groups are used. Thus we found that the ρ-value is no longer zero, if substances of the type $\mathrm{Me_3SiOSiMe(Ar)Cl}$ are used at higher concentrations of acetic acid. And in contrast to arylchlorodimethyl- and

TABLE III

Acetolysis of chlorosilanes $\mathrm{X{-}C_6H_4{-}SiMe_2Cl}$ (σ_0 0.38–0.42 mol · l^{-1}) with acetic acid (0.92 mol · l^{-1}) in acetic anhydride $T = 30°\mathrm{C}$

X	$10^4 \cdot k$ ($l \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1}$)	σ
p-Me	12.2	−0.17
H	12.0	0
p-F	11.1	0.06
p-Cl	11.7	0.23
m-Cl	12.8	0.37

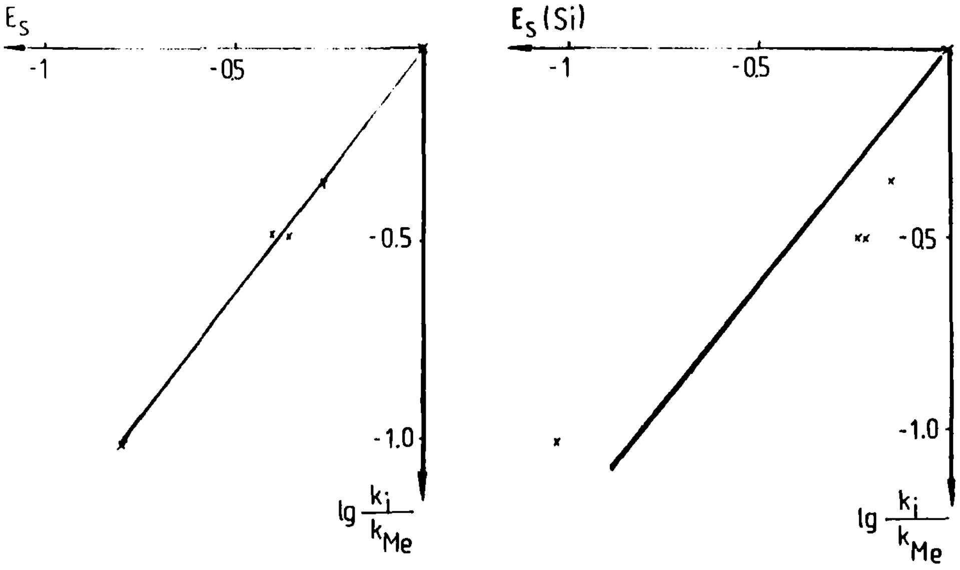


FIGURE 2 Determination of the constant of sterical susceptibility δ for the acetolysis of chlorosilanes.

TABLE IV

Determination of E_s-values from the acetolysis of chlorosilanes and -siloxanes of the type $RSiMe_2Cl$ (c_0 0.14–0.56 mol · l^{-1}) with acetic acid (0.92 mol · l^{-1}) in acetic anhydride $T = 30°C$

R	$k \cdot 10^4$ ($l \cdot mol^{-1} \cdot s^{-1}$)	E_s
Me	40	0.00
Et	18	−0.27
*i*Pr	9.8	−0.47
*i*Bu	11.7	−0.41
Ph	17.6	−0.27
Me_3SiO	11	−0.43
$Me_3SiOSiMe_2O$	10	−0.46
$Me_3SiO(SiMe_2O)_2$	7.7	−0.53
$(Me_3SiO)_2SiMeO$	4.0	−0.77
$(Me_3SiO)_2SiMeOSiMe_2O$	4.5	−0.73
$(Me_3SiO)_3SiO$	1.8	−1.04
$(Me_3SiO)_3SiOSiMe_2O$	2.6	−0.91
Cl	11	−0.43
$ClMe_2SiO$	26	−0.14
$Cl(Me_2SiO)_2$	22	−0.18
$Cl(Me_2SiO)_3$	14	−0.33
$Cl(Me_2SiO)_4$	10	−0.46
$ClMe_2SiO$ $SiMeO$ Me_3SiO	6.4	−0.59
AcO	22	−0.18
$AcOSiMe_2O$	19	−0.25

aryldichloromethylsilanes and aryltrichlorosilanes are reacting not only with acetic acid but also with acetic anhydride.

In addition to the acetolysis experiments some attempts were made to use the values determined for the calculation of further steric substituent constants. At first an equation (5) was derived by linear regression for the calculation of E_s(R—CH$_2$)-values from E_s(R)-values, which means E_s-values for substances with stepwise introduction of methylene groups.

$$E_s(\mathrm{R{-}CH_2}) = 0.239 \cdot E_s(\mathrm{R}) - 0.293 \qquad (5)$$

By means of this equation new steric substituent constants can be calculated (Table V). The limiting value for infinitely long methylene chains should be −0.39. Quite the same is possible with the stepwise introduction of dimethylsiloxy groups. In this case the limiting value was estimated to be about −0.6. Materials to now were too limited to give a correct mathematical expression. Thus these attempts have to be confirmed with more extensive experimental material. This is also true for the following results. We began to investigate the acetolysis of cyclic chlorosiloxanes. The first example was the chlorotrimethylbis(trimethylsiloxy)-cyclotrisiloxane, which is obtained in three stereoisomers, one of which has a doubled statistical factor (Figure 3). In this case we could use ^{29}Si-NMR, because of the low reactivity of these compounds. Indeed we found three signals of various intensity (Table VI). The signal of I may be too large, because it is very close to the following strong signal of II. These signals disappeared with different velocity during acetolysis reaction and the signals arising appear in the order of the disappearing ones. This should speak for a retention mechanism of the acetolysis reaction. If this is accepted, two facts are in coincidence: At first substance I should be hindered in formation because of the steric hindrance in this compound. This would explain the nonstatistical relation between the three isomers. And secondly substance I should have a lower reactivity in reactions with retention stereochemistry, because of the steric hindrance towards the approaching substituent. But also in this case material was too small to draw general conclusions. But it should be very interesting to investigate stereochemistry of a whole set of reactions at cyclic siloxanes without the need of preparation of optically active compounds.

In the following part some reactions shall be discussed, which are important steps in the production of silicones.

TABLE V

Calculation of E_s-values for compounds of the type RCH$_2$SiMe$_2$Cl from the E_s-values of the compounds RSiMe$_2$Cl

R	E_s(R)	R—CH$_2$	E_s (R—CH$_2$) calc.	E_s (R—CH$_2$) found	Lit. data [2]
H	1.24	Me		0	0
Me	0	Et		−0.27	−0.07
Et	−0.27	*n*Pr		−0.36	−0.36
*n*Pr	−0.36	*n*Bu		−0.39	
*i*Pr	−0.47	*i*Bu	−0.41	−0.41	−0.97
C_6H_5	−0.28	$C_6H_5CH_2$	−0.36		−0.38

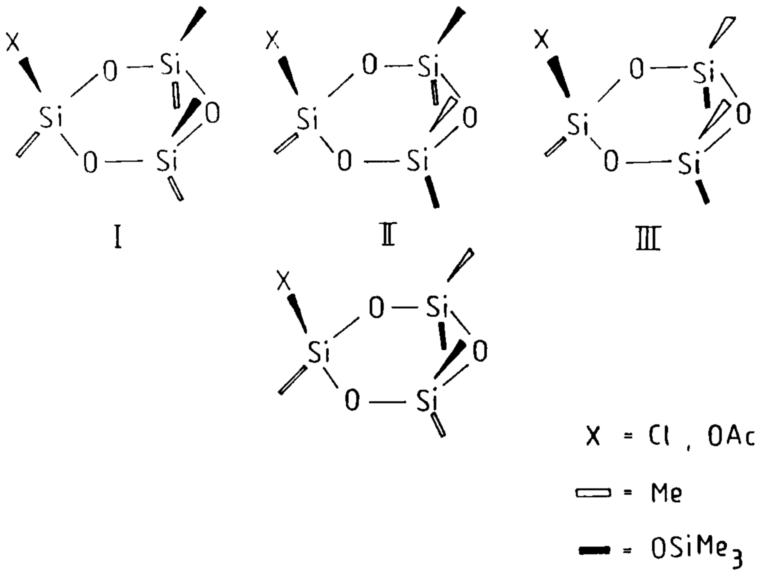


FIGURE 3 Stereoisomers of the chlorotrimethylbis(trimethylsiloxy)cyclotrisiloxane.

TABLE VI

^{29}Si-NMR shift values and rate constants for the acetolysis reaction of the chlorotrimethylbis(trimethylsiloxy)cyclotrisiloxane stereoisomers

X = Cl				X = OAc		
δ (ppm)	intensity (%)	stereoisomer	$k \cdot 10^6$ (s^{-1})	δ (ppm)	intensity (%)	stereoisomer
− 31.68	22	I	6.2	−49.75	14	I
−31.76	51	II	20	−49.53	53	II
−31.18	26	III	62	−48.59	33	III

HYDROLYSIS OF CHLOROSILOXANES IN ACIDIC MEDIUM

We studied the hydrolysis reaction of chlorosilanes in aqueous dioxane by ^{1}H-NMR spectroscopy. At first we tried to determine the ρ-value of the reaction, to get some insight into the mechanism, and intended to carry out these reactions under pseudo first order conditions, because of an easy evaluation, that means with about tenfold excess of water and hydrochloric acid. But our first model compounds, substituted diarylchlorodisiloxanes, reacted too fast. Thus they could be hydrolyzed only with equimolar amounts of water and without hydrochloric acid at the starting point. Surprisingly these reactions could be evaluated with a second order rate law in spite of the formation of hydrochloric acid during the reaction and an acid catalysis later observed. Thus the rate constants and the ρ-value calculated to be 0.35 can be used only in a tentative way (Table VII).

TABLE VII

Hydrolysis of chlorodisiloxanes $C_6H_5Si(CH_3)_2OSiCl(CH_3)p\text{-}X{-}C_6H_4$ (σ_0 0.127 mol · l^{-1}) with aqueous (σ_0 0.127 mol · l^{-1}) dioxane $T = 30°C$

X	$k \cdot 10^2$ ($l \cdot mol^{-1} \cdot s^{-1}$)
Cl	2.5
H	2.2
Me	1.8

To realize our program we had to turn to another model system and found it in diarylpentasiloxanes. Now the reaction rate was low enough to allow the investigation of the influence of hydrochloric acid and water. At first, at a tenfold excess of water, we varied the concentration of the hydrochloric acid from 6 to 12 fold excess. Using the following rate law for the acid catalysed reaction (6).

$$-\frac{d[CS]}{dt} = k \cdot [H_2O]^a \cdot [HCl]^b \cdot [CS]$$

$$= k' \cdot [HCl]^b \cdot CS \qquad (6)$$

$$|[CS] = [\text{chlorosiloxane}]$$

k'-values could be obtained from the first order rate constants k(exp) by plotting lg k(exp)-values towards lg[HCl] (Table VIII). Two things are important: firstly all these reactions are acid catalyzed, secondly the power of the concentration of the hydrochloric acid is about 0.5. To learn more about the character of the catalysis we carried out some reactions in the presence of perchloric acid and found that perchloric acid is a nearly 20 times stronger catalyst than hydrochloric acid (Table IX). Thus we assume that the essential contribution to acid catalysis is given by proton catalysis, and further that this catalysis should be expressable by an initial protonation equilibrium as in most other cases (7).

$$\text{chlorosiloxane} + H^+ \rightleftharpoons \text{chlorosiloxane} \cdot H^+ \qquad |K_1$$

$$\text{chlorosiloxane} \cdot H^+ + a\,H_2O \rightarrow \text{siloxanol} \cdot H^+ + HCl + a - 1\,H_2O$$

$$HCl \rightleftharpoons H^+ + Cl^- \qquad |K_2 \qquad (7)$$

TABLE VIII

Hydrolysis of chloropentasiloxanes $(Me_3SiO)_2Si(Me)OSiAr(Cl)OSiME_2Ar'$ (σ_0 = 0.07 mol · l^{-1}) with aqueous (σ_0 0.7 mol · l^{-1}) dioxane in the presence of different concentrations of HCl (σ_0 0.4 to 1.0 mol · l^{-1}) $T = 30°C$

Ar	Ar'	b	$k' \cdot 10^2$ (($l \cdot mol^{-1})^b \cdot s^{-1}$)
p-Cl—C_6H_4	Ph	0.70	2.2
Ph	Ph	0.53	1.5
p-Me—C_6H_4	Ph	0.70	1.2
Ph	p-Cl—C_6H_4	0.73	1.9
Ph	p-Me—C_6H_4	0.52	1.3

TABLE IX

Hydrolysis of (Me$_3$SiO)$_2$Si(Me)OSiPH(Cl)OSiMe$_2$Ph (σ_0 0.073 mol · l^{-1}) with aqueous (σ_0 0.73 mol · l^{-1}) dioxane in the presence of HCl or HClO$_4$ T = 30°C

$[HClO_4]_0$ (mol/l)	$k_{exp} \cdot 10^3$ (s^{-1})	$[HCl]_0$ (mol/l)	$k_{exp} \cdot 10^3$ (s^{-1})
0.01	6.7		
0.02	9.4		
0.04	14.4	0.4	7.8
0.06	21.0	0.6	10.8
0.08	27.5	0.8	13.7

This mechanism leads to the following rate law.[8]

$$-\frac{d[CS]}{dt} = K_{\uparrow} \cdot [H_2O]^a \cdot [CS \cdot H^+]$$

$$\left| \begin{array}{l} [CS \cdot H^+] = K_1 \cdot [CS]\ \ [H^+] \\ \quad [H^+] = \sqrt{K_2 \cdot [HCl]} \end{array} \right.$$

$$-\frac{d[CS]}{dt} = k_1 \cdot K_1 \cdot \sqrt{K_2} \cdot [H_2O]^a \cdot [HCl]^{0.5} \cdot [CS]$$

$$= k' \cdot [HCl]^{0.5} \cdot [CS] \qquad (8)$$

$$\|[CS] = [\text{chlorosiloxane}];\ [CS \cdot H^+] = [\text{chlorosiloxane} \cdot H^+]$$

The expression [H$^+$] equals square root of K$_2$ times concentration of HCl is possible, because in the medium used HCl dissociates only to a small extent and thus concentration of HCl is large in relation to concentration of proton and chloride anion, that means: nearly constant. Thus an expression is obtained from a mechanistical standpoint that is quite the same as that found from kinetical experiments.

As we found that hydrolysis reactions start also without addition of hydrochloric acid, a noncatalyzed reaction had to exist besides the acid catalyzed one. To get an impression of their extent, we performed a hydrolysis reaction of the diphenylchoropentasiloxane with a tenfold excess of water but without added hydrochloric acid. From a Runge-Kutta-treatment of the kinetic data according to the equation (9)

$$-\frac{d[CS]}{dt} = k_1 \cdot [H_2O]^a \cdot [HCl]^{0.5} \cdot [CS] + k_2 \cdot [H_2O]^c \cdot [CS]$$

$$= k_1' \cdot [HCl]^{0.5} \cdot [CS] + k_2' \cdot [CS]$$

$$\|[HCl] = [CS]_0 - [CS]$$

$$= k_1'([CS]_0 - [CS])^{0.5} \cdot [CS] + k_2' \cdot [CS] \qquad (9)$$

we found $k_1' = 1.5 \cdot 10^{-2}$ $(l \cdot mol^{-1})^{0.5} \cdot s^{-1}$ and $k_2 = 0.8 \cdot 10^{-5}$ s^{-1}. These values show that the noncatalyzed reaction gives noticeable contributions only at very low concentrations of hydrochloric acid. At higher concentrations the contributions of

TABLE X

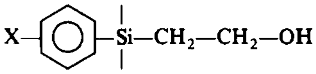
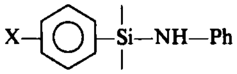
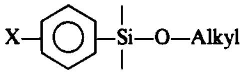
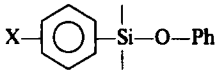
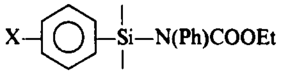
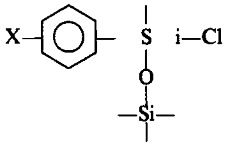
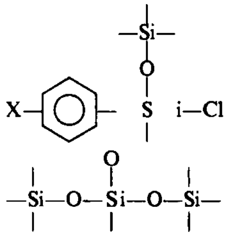
Hydrolysis of $PhMe_2Si—X—SiPH(cyc.hexyl)Cl$ (σ_0 0.11 mol · l^{-1}) with aqueous (σ_0 1.0 mol · l^{-1}) dioxane T = 30°C

X = 0			X = CH_2		
$[HCl]_0$ (mol/l)	$k_{exp} \cdot 10^3$ (s^{-1})	$[HCl]_0$ (mol/l)	$k_{exp} \cdot 10^3$ (s^{-1})	$[HClO_4]_0$ (mol/l)	$k_{exp} \cdot 10^3$ (s^{-1})
0	6.7	0	3.2	0.01	2.25
0.3		0.3	2.9	0.02	2.95
0.5	11.7	0.5	2.5	0.04	3.7
0.7		0.7	2.85	0.06	5.0
				0.08	9.15

the noncatalyzed reaction can be neglected. Thus the k'-values obtained (Table VIII) could be used for the calculation of ρ for the acid catalyzed reaction. Thus we obtained with the σ-values of Jaffé[5] for the variation of the phenyl groups at the reaction center a ρ-value of 0.7 and at the neighboring Si-atom a ρ-value of 0.3 and in consequence a coefficient of transmission for a dimethylsiloxy group of 0.43.

TABLE XI

ρ-Values of acid catalysed solvolysis reactions

Substrate	Reagent	Catalyst	ρ-value	Literature
	$MeOH/H_2O$	H_2SO_4	−1.44	[8]
	EtOH	H_2SO_4	−0.97	[8]
	*n*PrOH	H_2SO_4	−0.41	[8]
	EtOH	H_2SO_4	−0.57	[8]
	H_2O	HCl	−0.2	[9]
	H_2O	HCl	+0.35	
	H_2O	HCl	+0.7	

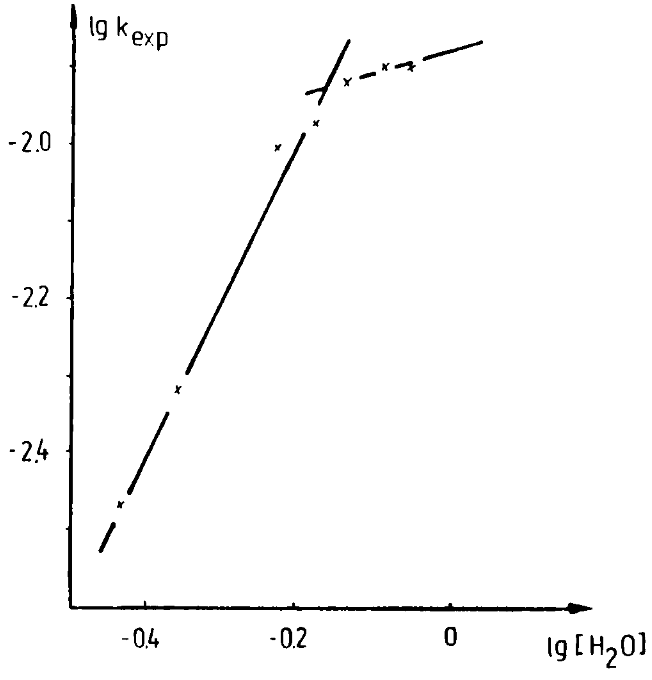


FIGURE 4 Hydrolysis of $(Me_3SiO)_2Si(Me)OSiPh(Cl)OSiMe_2Ph$ with aqueous dioxane in the presence of a tenfold excess of HCl. $T = 30°C$.

To answer the question where protonation takes place, at the leaving chlorine atom or at the siloxane oxygen atom, we simply did preliminary experiments with disiloxanes and analogous disilamethylenes and found that, in contrast to the hydrolysis of the chlorosiloxanes, hydrolysis of disilamethylenes shows nearly no catalysis by hydrochloric acid and only weak catalytic contributions by perchloric acid (Table X). This suggests a protonation at the oxygen atom as it was shown by Olah.[7]

Unusual is the positive ρ-value for a reaction with preceding protonation equilibrium. But from the literature can be seen that ρ-values of such reactions increase with decreasing basicity of the leaving group (Table XI). Further it should be taken into account that the attack of the proton takes place not at the leaving group but at an oxygen atom presumably at a larger distance to the reaction center because of the increasing basicity of oxygen atoms with increasing distance from the chlorine-bearing silicon. Figure 4 refers to the power of water concentration in the rate law. From experiments with an excess of hydrochloric acid we found, up to an eightfold excess of water, a nearly straight line with a slope of two. At higher concentrations the power is decreasing. Thus in the area investigated the correct rate law for the acid catalyzed reaction is:

$$-\frac{d[\mathrm{CS}]}{dt} = k_{\mathrm{H}} + \cdot [\mathrm{H_2O}]^2 \cdot [\mathrm{HCl}]^{0.5} \cdot [\mathrm{CS}]$$

CLEAVAGE OF SILOXANES BY HCL

The second reaction we investigated is the cleavage of the siloxane bond by HCl, which is important for the preparation of silicones in acidic medium, especially for the equilibration reactions. Kinetic data obtained couldn't be evaluated with a simple rate law. A significant induction period suggested autocatalytic effects caused by the water formed during the reaction. Further establishment of an equilibrium could be observed. Thus we assumed the following mechanism (10).

$$\geqslant\text{Si—O—Si}\leqslant + \text{HCl}\cdot\text{L} \xrightarrow{k_1} \text{products } (\geqslant\text{SiCl})$$

$$\geqslant\text{Si—O—Si}\leqslant + \text{HCl}\cdot\text{H}_2\text{O} \xrightarrow{k_2} \text{products } (\geqslant\text{SiCl})$$

back reaction

$$\geqslant\text{SiCl} + \text{H}_2\text{O} \xrightarrow{k_3} \tfrac{1}{2}\geqslant\text{Si—O—Si}\leqslant + \text{HCl} + \tfrac{1}{2}\,\text{H}_2\text{O} \qquad (10)$$

$$\left|\begin{array}{l} \text{L} = \text{dioxane} \\ [\text{HCl}\cdot\text{L}] = \text{const., because large in relation} \\ \qquad\text{to the other concentrations} \end{array}\right.$$

The idea of mechanism (10), is that there are two species reacting with the siloxanes, adducts of hydrochloric acid with dioxane and adducts of hydrochloric acid with H_2O. Surprisingly no trace of silanol signals could be found in the proton resonance spectra. For they have to be formed, their concentration must be too low under these conditions of high concentration of hydrochloric acid to appear in the spectra. From mechanism and stoichiometry the rate law (11) could be derived

$$\|[\geqslant\text{Si—O—Si}\leqslant] = c; \qquad \text{L} = \text{dioxane}$$

$$-\frac{dc}{dt} = (k_1 + k_2\cdot[\text{HCl}\cdot\text{H}_2\text{O}])\cdot c - \tfrac{1}{2}k_3\cdot[\leqslant\text{SiCl}]\cdot[\text{H}_2\text{O}_{\text{free}}]. \qquad (11)$$

$$\left|\begin{array}{l} [\geqslant\text{SiCl}] = 2(c_0 - c) \\ [\text{H}_2\text{O}_{\text{stöch}}] = [\text{H}_2\text{O}_{\text{free}}] + [\text{HCl}\cdot\text{H}_2\text{O}] = c_0 - c \\ \text{HCl}\cdot\text{L} + \text{H}_2\text{O}_{\text{free}} \rightleftharpoons \text{L} + \text{HCl}\cdot\text{H}_2\text{O}|\text{K}' \\ |\text{K}' = \text{L}\cdot\text{K} \end{array}\right.$$

$$-\frac{dc}{dt} = [k_1' + k_2'\cdot(c_0 - c)]\cdot c - k_3'\cdot(c_0 - c)^2$$

$$\left|\begin{array}{l} k_1' = k_1;\ k_2' = k_2\cdot\dfrac{\text{K}\cdot[\text{HCl}\cdot\text{L}]}{1 + \text{K}\cdot[\text{HCl}\cdot\text{L}]};\ k_3' = k_3\cdot\dfrac{1}{1 + \text{K}\cdot[\text{HCl}\cdot\text{L}]} \\ k_1' = k_1^*\cdot[\text{HCl}\cdot\text{L}]^4;\ k_2' = k_2^*\cdot[\text{HCl}\cdot\text{L}]^3;\ k_3' = k_3^* \end{array}\right.$$

This equation allows determination of the rate constants for the three reactions by nonlinear regression. Table XII shows these rate constants for substituted aryldisiloxanes and the ρ-values obtained from them. To include pure methylsiloxanes we

TABLE XII

Cleavage of substituted diaryldisiloxanes (p-X—C_6H_4)$SiMe_2$—O—$SiMe_2$(p-X—C_6H_4) (σ_0 0.1 mol · l^{-1}) with HCl (σ_0 1.5 to 5 mol · l^{-1}) in dioxane T = 30°C

X	$k_1^* \cdot 10^5$ ($l^4 \cdot mol^{-4} \cdot min^{-1}$)	$k_2^* \cdot 10^5$ ($l^4 \cdot mol^{-4} \cdot min^{-1}$)	$k_3^* \cdot 10^5$ ($l \cdot mol^{-1} \cdot min^{-1}$)	$\sum\sigma$
Me	32	1900	5000	−0.34
H	13	1400	6400	0
F	9.2	1300	6800	+0.12
Cl	4.0	820	8000	+0.46

$\rho_1 = -1.13$ $\rho_2 = -0.45$ $\rho_3 = 0.52$.

TABLE XIII

Cleavage of siloxanes $XMe_2SiOSiMe(Y)Z$ (σ_0 0.1 mol · l^{-1}) with HCl (σ_0 1.5 to 5 mol · l^{-1}) in dioxane T = 30°C

X	Y	Z	lg $k^*_{1(i)}/k^*_{1(Me)}$	lg $k^*_{2(i)}/k^*_{2(Me)}$	$\sum\sigma^*$
Me	Me	Me	0	0	0
Me	$OSiMe_3$	Me	−0.36	−0.15	0.35
Me	$OSiMe_3$	$OSiMe_3$	−0.68	−0.28	0.65
Me—C_6H_4	Me—C_6H_4	Me	−0.54	−0.27	0.62
Ph	Ph	Me	−0.92	−0.40	0.96
F—C_6H_4	F—C_6H_4	Me	−1.08	−0.47	1.08
Cl—C_6H_4	Cl—C_6H_4	Me	−1.44	−0.63	1.42
			$\rho_1 = -1$	$\rho_2 = -0.43$	

had again to change from Hammett to Taft constants (Table XIII). From the rate constants we found a good correlation using once more the value of 0.48 for the phenyl and $\sigma_X^* + 0.48$ for the substituted phenyl groups and further the value of 0.35 for one and 0.65 for two trimethylsiloxy groups at silicon.

SUBSTITUENT EXCHANGE REACTIONS BETWEEN SILANOLS AND CHLOROSILANES

In alkaline medium the formation of siloxane bonds from silanols and chlorosilanes is one of the most frequently used reactions for the synthesis of oligosiloxanes. But nothing could be found in the literature about this reaction in acidic medium. First experiments showed, surprisingly to us, that there is without any doubt no condensation at all. But a very quick exchange of chlorine atoms and hydroxyl groups. In addition slower condensation reactions of the silanols take place, at first only of the starting silanol, later on also of the starting silanol with the silanol formed in the exchange reaction and finally, with a clear induction period, also of the silanol formed. Finally, silanol concentration goes to zero, as we could observe also in the cleavage reaction of siloxanes by hydrochloric acid, and equilibria established between chlorosilanes and siloxanes, as described by Hyde.[10] Substituent exchange reactions are well known and mostly interpreted with a four center mechanism. The

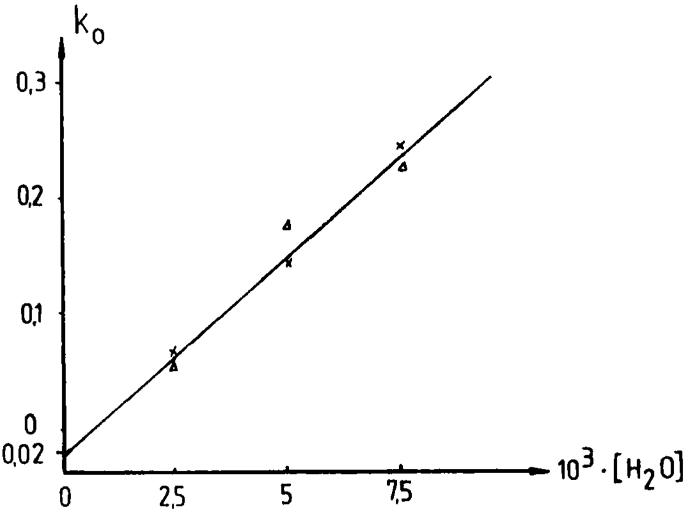


FIGURE 5 Dependance of the initial rate constant k_0 for the substituent exchange reaction between $PhMe_2SiCl$ and $BzMe_2SiOH$ from the concentration of water. Δ, $PhMe_2SiCl$; x, $BzMe_2SiOH$.

special case, Cl—OH-exchange was published in 1982 by Vasil'eva as a direct exchange of the functional groups.[11] From the reaction of $PhMe_2SiCl$ with $BzMe_2SiOH$ in a 3 : 1 mixture of C_6D_6 and dioxane we found that in the starting phase of the substituent exchange reaction condensation reactions can be neglected. Now reactions with different amounts of water gave a very interesting result (Figure 5). The initial rate constant for the decrease of both chlorosilane and silanol concentration goes to zero without added water. Thus mechanism of this exchange reaction should be hydrolysis of chlorosilane and reaction of silanol with hydrochloric acid (12).

$$\begin{array}{c} \geq SiCl + H_2O \rightleftharpoons \geq SiOH + HCl \\ \geq Si'OH + HCl \rightleftharpoons \geq Si'Cl + H_2O \\ \hline \geq SiCl + \geq Si'OH \rightleftharpoons \geq SiOH + \geq Si'Cl \end{array} \tag{12}$$

We assume the same mechanism also for other substituent exchange reactions.

REFERENCES

1. G. Engelhardt, H. Jancke, R. Radeglia, H. Kriegsmann, M. F. Larin, V. A. Pestunovich, E. I. Dubinskaya and M. G. Voronkov, *Z. Chem.*, **17**, 376 (1977).
2. R. W. Taft, in *Steric Effects in Organic Chemistry*, M. S. Newman, Ed. (J. Wiley and Sons, New York, 1956), Chap. 13.
3. Y. Nagai, H. Matsumoto, T. Nakano and H. Watanabe, *Bull. Chem. Soc. Japan*, **45**, 2560 (1972).
4. G. Engelhardt and H. Jancke, *J. Organomet. Chem.*, **28**, 293 (1971).
5. H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
6. F. K. Cartledge, *Organometallics*, **2**, 425 (1983).
7. G. A. Olah, D. H. O'Brien and C. Y. Lui, *J. Amer. Chem. Soc.*, **91**, 701 (1969).
8. B. Bøe, *J. Organomet. Chem.*, **107**, 139 (1976).
9. K. Hänig, H. Große-Ruyken, K. Rühlmann and J. Schlapa, *J. Organomet. Chem.*, **263**, 145 (1984).
10. J. F. Hyde, P. L. Brown and A. L. Smith, *J. Amer. Chem. Soc.*, **82**, 5854 (1960).
11. T. V. Vasil'eva, V. Ya, Stolyarenko, G. N. Yakovleva and V. V. Yastrebov, *Zh. Obshch. Khim.*, **52**, 2570 (1982).