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On the synthesis of siloxanes

XXI *. Verification of inductive and steric substituent constants for siloxy groups by reaction of triorganylchlorosilanes and chlorosiloxanes with lithium silanolates and lithium isopropylate **

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Abstract

In order to verify the substituent constants for siloxy groups determined previously, kinetic studies have been made of the reactions of triorganylchlorosilanes and monochlorosiloxanes with lithium silanolates and lithium isopropylate Relative rate constants were determined by turbidimetric measurements. Comparison of these values with those determined by means of ^{1}H-NMR spectroscopy shows that the easily performed turbidimetry is a suitable method. Initially the steric (δ) and inductive (ρ) reaction constants for the reactions were determined with triorganylchlorosilanes, then the chlorosiloxanes were investigated kinetically. The chlorosiloxanes reacted up to 10 times faster than expected from the substituent constants we previously determined, and so we conclude that the inductive effect of the siloxy groups can vary when the charge at the reaction centre is changed.

Introduction

We previously determined inductive and steric substituent constants for siloxy groups in order to provide a basis for investigations of important reactions involved in production of silicones [2,3]. To confirm these values easily studied model

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* For Part XX see ref. 1.

** Dedicated to Professor U. Wannagat on the occasion of his 70th birthday in recognition of his pioneering contributions to organosilicon chemistry.

reactions are needed, and the reactions (1) between organylchlorosilanes and lithium silanolates or lithium isopropylate seemed appropriate.

$$R^1Me_2SiCl + R^2OLi \longrightarrow R^1Me_2SiOR^2 + LiCl \qquad (1)$$

(R^1 = various substituted alkyl, aryl, siloxy, $R^2 = Me_3Si$, $PhMe_2Si$, Me_2HC)

These reactions give high yields, without formation of by-products, and the rates are substantially influenced by inductive and steric effects of the substituents at the reaction centre [4,5]; thus we obtained a steric susceptibility δ of 1.32 and an inductive reaction constant ρ of 0.45 for the reactions of organyldimethylchlorosilanes with lithium trimethylsilanolate [6]. To gain more insight into the influence of substituents on reactions of this type we have now studied the kinetics of the reactions of triorganylchlorosilanes and monochlorosiloxanes with lithium trimethylsilanolate, lithium dimethylphenylsilanolate and lithium isopropylate.

Experimental

^1H NMR spectroscopic measurements

The reactions of organyldimethylchlorosilanes with lithium trimethylsilanolate were monitored by measuring the intensities of the ^1H NMR signals from the Si–Me protons (Bruker WP 80 SY, 80.13 MHz; 4 scans). Reactions were performed up to 80% conversion. The decrease in the concentration was calculated either from the relative intensities of the signals of the starting compound and the product or by use of an internal standard (Me_4Si).

A solution of lithium trimethylsilanolate in diethylether (300 μl, 0.5 $mol \cdot l^{-1}$) was placed into the NMR-tube, with 100 μl $CDCl_3$ and a small amount of Me_4Si. The reaction was started by injecting the chlorosilane (0.15 mmol), the tube was shaken three times, and immediately introduced into the spectrometer. The first spectrum was taken about 20 s after the addition of the chlorosilane. Further spectra (8 to 20) were recorded at intervals of 30 to 120 s, depending on the reaction rate. The second order rate constants were calculated from the peak areas as usual (regression coefficients 0.98 to 0.99). The measurements were repeated four to eight times. The data are accurate to within $\pm 10\%$.

Gas chromatographic measurements

Relative rate constants for reactions between chlorosilanes and lithium trimethylsilanolate were determined by GLC. Equimolar amounts of two different chlorosilanes were dissolved in diethylether ($[R_3SiCl]_0$ 0.8–1.2 $mol \cdot l^{-1}$) and the reactions started by adding one tenth of that amount of an ethereal solution (1 $mol \cdot l^{-1}$) of lithium trimethylsilanolate which would be required for complete conversion of the chlorosilanes. When the reactions were finished the resulting lithium chloride was removed by centrifuging and the solution was examined by GLC (Chromatron GCHF 18.3 with FID; temperature 100–200°C; carrier gas: N_2 (flow 40 ml/min); column: 3 m, filled with 10% SE30 on Chromosorb W AW-DMCS). Under these conditions the ratio of the peak areas is equal to the ratio of the rate constants of the chlorosilanes used [7]. It was not necessary to correct the peak areas because the detection sensitivity was constant for all the disiloxanes formed, as shown in separate experiments involving use of an internal standard.

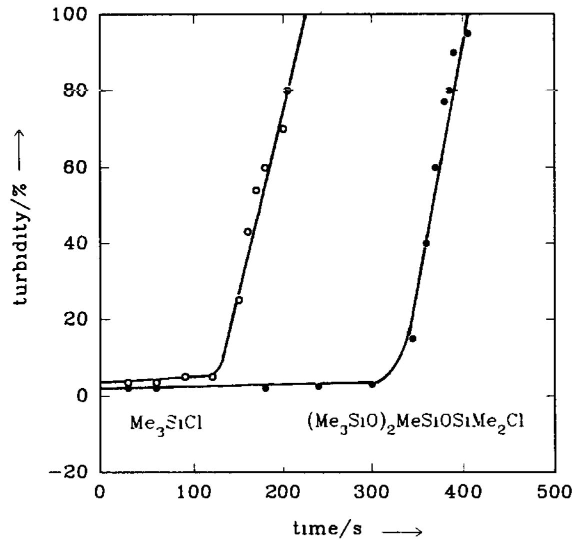

Fig. 1. Time-dependence of the turbidity of the reaction of Me_3SiCl (○) and $(Me_3SiO)_2MeSiOSiMe_2Cl$ (●) with lithium trimethylsilanolate.

Turbidimetric measurements

The turbidimetric measurements were carried out by use of 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. In order to determine the time in which a defined turbidity (80%) was reached, a solution of the corresponding lithium silanolate or lithium isopropylate in diethyl ether (0.3–0.6 mol l^{-1}) was thermostated at the reaction temperature and the reaction was started by adding an equimolar amount of a chlorosilane. The relative rate constants were calculated as quotients of the turbidity times for the standard substance (Me_3SiCl) and the other members of the series (Fig. 1).

Temperature

Experiments carried out at various temperatures (10°C to 30°C) showed that over this range the relative rate constants are independent of the reaction temperature within experimental error. Thus we were able to adjust the reaction temperature to a value that allowed the best reproducibility.

Preparations

Li-silanolates and Li-isopropylate. Lithium silanolate solutions were obtained by treating trimethylsilanol [6] or dimethylphenylsilanol [8] with lithium metal in diethylether. The lithium isopropylate solution was obtained analogously from isopropanol. The concentrations were in the range 0.5–1 mol l^{-1}.

Organyldimethylchlorosilanes. The chlorosilanes RMe_2SiCl **1–4**, **6**, **8–14**, **20**, **21** (the numbers as in Table 2) were prepared from Me_2SiCl_2 and the appropriate Grignard reagents (R = Et, ^{n}Pr, ^{n}Bu, $C_6H_5CH_2$, Me_3SiCH_2, X-C_6H_4) or lithium compounds (R = ^{i}Pr, ^{t}Bu, ^{s}Bu) derived from corresponding chlorides RCl.

^{t}BuMe$_2$SiCl (**4**); 36%; b.p. 133°C; d_4^{20} 0.865; $C_6H_{15}ClSi$; hydrolyzable Cl found: 23.20; calc.: 23.50; δ^{29}Si: 30.95 ppm; δ^1H: 0.338 ppm. ^{s}BuMe$_2$SiCl (**8**); 30%; b.p. 149°C; d_4^{20} 0.862; n_D^{20} 1.4250; $C_6H_{15}ClSi$; hydrolyzable Cl found: 23.00; calc.: 23.50; δ^{29}Si: 33.81 ppm; δ^1H: 0.298 ppm.

Cyclopentyldimethylchlorosilane (**5**) and cyclohexyldimethylchlorosilane (**7**) were prepared by hydrosilylation of cyclopentene or cyclohexene with dichloromethylsilane or trichlorosilane [*cf.* ref. 9] followed by reaction with methylmagnesium chloride. *cyclo*-PentMe$_2$SiCl (**5**); 33%; b.p. 134°C/13.3 kPa; d_4^{20} 0.950; n_D^{20} 1.4550; $C_7H_{15}ClSi$; hydrolyzable Cl found 21.40; calc.: 21.80; δ^{29}Si: 32.21 ppm.

Dimethylchlorosilane (**15**) was synthesized as previously described [10], as was bromomethyldimethylchlorosilane (**16**) [11]. Photochemical chlorination of trimethylchlorosilane yielded chloromethyldimethylchlorosilane (**17**) and dichloromethyldimethylchlorosilane (**18**). Reaction of hexamethyldisilane with concentrated sulphuric acid, followed by treatment with NH_4Cl gave chloropentamethyldisilane (**19**) [12]. The physical data for the known substances agreed with those previously given.

Chlorosiloxanes

1-Chloro-1,1,3,3,3-pentamethyldisiloxane (**22**) (MM^{Cl}) was obtained by equilibration of Me_2SiCl_2 with hexamethyldisiloxane in methylene chloride with HMPT as catalyst [13].

1,1,1,3,5,5,5-Heptamethyltrisiloxane M_2D^H and tris(trimethylsiloxy)silane M_3T^H were prepared by treating dichloromethylsilane or trichlorosilane with hexamethyldisiloxane and concentrated sulphuric acid [14].

3-Chloro-1,1,1,3,5,5,5-heptamethyltrisiloxane (**29**) (M_2D^{Cl}) and tris(trimethylsiloxy)chlorosilane (**35**) (M_3T^{Cl}) were made by chlorination of M_2D^H or M_3T^H as previously described [15].

Pentamethyldisiloxanol (MM^{OH}) and 1,1,1,3,5,5,5-heptamethyltrisiloxane-3-ol (M_2D^{OH}) were prepared by treating solutions of the corresponding chlorosiloxanes in diethyl ether with a suspension of $NaHCO_3$ in water [3].

Tris(trimethylsiloxy)silanol (M_3T^{OH}) was obtained by the hydrolysis of a solution of M_3T^{Cl} in diethylether with 0.5 *M* NaOH [3].

1,3-Dichloro-1,1,3,3-tetramethyldisiloxane ($^{Cl}MM^{Cl}$) and 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane ($^{Cl}MDM^{Cl}$) were synthesized by partial hydrolysis of Me_2SiCl_2 [16].

1,1-Dichloro-1,3,3,3-tetramethyldisiloxane ($MM^{Cl}{}_2$) was made by equilibration of $MeSiCl_3$ with hexamethyldisiloxane in the presence of $(PNCl_2)_x$ as catalyst [17].

The physical data for the siloxanes described above were as given in the literature.

3-Chloro-1,1,1,3,5,5,7,7,7-nonamethyltetrasiloxane (**30**) ($MD^{Cl}DM$) was prepared as follows. A solution of 32.9 g (0.2 mol) of pentamethyldisiloxanol (MM^{OH}) in 300 ml of diethylether was slowly added with vigorous stirring to a solution of 40.6 g (0.2 mol) of 1,1-dichloro-1,3,3,3-tetramethyldisiloxane ($MM^{Cl}{}_2$), in 300 ml of dry diethylether containing 15.8 g (0.2 mol) of pyridine. The mixture was heated under reflux for 2 h, the pyridine hydrochloride formed filtered off, and the filtrate distilled. 39.7 g (60%); b.p. 98°C/2.66 kPa; d_4^{20} 0.896; n_D^{20} 1.3989; $C_9H_{27}ClO_3Si_4$; hydrolyzable Cl found: 10.20; calc.: 10.71; δ^{29}Si/ppm: *M*D 8.4, D −45.4, D^{Cl} −19.3, $\mathit{M}D^{Cl}$ 11.9.

The following chlorosiloxanes were prepared similarly. 1-Chloro-1,1,3,3,5,5,5-heptamethyltrisiloxane (**23**) (MDM$^{\mathrm{Cl}}$) starting from trimethylsilanol and 1,3-dichloro-1,1,3,3-tetramethyldisiloxane ($^{\mathrm{Cl}}$MM$^{\mathrm{Cl}}$). 33%; b.p. 65–68°C/2.66 kPa; d_4^{20} 0.910; $C_7H_{21}ClO_2Si_3$; hydrolyzable Cl found: 13.40; calc.: 13.80; δ^{29}Si/ppm: M 8.2, D −18.5, M$^{\mathrm{Cl}}$ 3.4.

1-Chloro-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane (**24**) (MDDM$^{\mathrm{Cl}}$) starting from trimethylsilanol and 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane ($^{\mathrm{Cl}}$MDM$^{\mathrm{Cl}}$). 30%; b.p. 81–84°C/1.33 kPa; d_4^{20} 0.940; $C_9H_{27}ClO_3Si_4$; hydrolyzable Cl found: 10.37; calc.: 10.71; δ^{29}Si/ppm: M 7.5, D −19.3, D −20.9, M$^{\mathrm{Cl}}$ 3.5.

1-Chloro-1,1,3,3,5,7,7,7-octamethyl-5-trimethylsiloxytetrasiloxane (**25**) (M$_2$TDM$^{\mathrm{Cl}}$) starting from 1,1,1,3,5,5,5-heptamethyltrisiloxane-3-ol (M$_2$D$^{\mathrm{OH}}$) and 1,3-dichloro-1,1,3,3-tetramethyldisiloxane ($^{\mathrm{Cl}}$MM$^{\mathrm{Cl}}$). 50%; b.p. 115°C/2.0 kPa; d_4^{20} 0.920; n_D^{20} 1.3988; $C_{11}H_{33}ClO_4Si_5$; hydrolyzable Cl found: 8.35; calc.: 8.75; δ^{29}Si/ppm: M 8.0, T −65.0, D −19.3, M$^{\mathrm{Cl}}$ 3.6.

1-Chloro-1,1,3,5,5,5-hexamethyl-3-trimethylsiloxytrisiloxane (**26**) (M$_2$TM$^{\mathrm{Cl}}$) starting from 1,1,1,3,5,5,5-heptamethyltrisiloxane-3-ol (M$_2$D$^{\mathrm{OH}}$) and dichlorodimethylsilane. 62%; b.p. 90°C/1.6 kPa; d_4^{20} 0.907; n_D^{20} 1.3958; $C_9H_{27}ClO_3Si_4$; hydrolyzable Cl found: 10.55; calc.: 10.71; δ^{29}Si/ppm; M 8.7, T −64.2, M$^{\mathrm{Cl}}$ 3.6.

1-Chloro-1,1,3,3,7,7,7-heptamethyl-5,5-bis(trimethylsiloxy)tetrasiloxane (**27**) (M$_3$QDM$^{\mathrm{Cl}}$) starting from tris(trimethylsiloxy)silanol (M$_3$T$^{\mathrm{OH}}$) and 1,3-dichloro-1,1,3,3-tetramethyldisiloxane ($^{\mathrm{Cl}}$MM$^{\mathrm{Cl}}$). 54%; b.p. 127°C/1.3 kPa; d_4^{20} 0.923; n_D^{20} 1.3988; $C_{13}H_{39}ClO_5Si_6$; hydrolyzable Cl found: 7.55; calc.: 7.39; δ^{29}Si/ppm: M 9.1, Q −105.6, D −18.6, M$^{\mathrm{Cl}}$ 3.8.

1-Chloro-1,1,5,5,5-pentamethyl-3,3-bis(trimethylsiloxy)trisiloxane (**28**) (M$_3$QM$^{\mathrm{Cl}}$) starting from tris(trimethylsiloxy)silanol (M$_3$T$^{\mathrm{OH}}$) and dichlorodimethylsilane. 60%; b.p. 102°C/1.6 kPa; d_4^{20} 0.898; n_D^{20} 1.3964; $C_{11}H_{33}ClO_4Si_5$; hydrolyzable Cl found: 8.55; calc.: 8.75; δ^{29}Si/ppm: M 9.5, Q −106.1; M$^{\mathrm{Cl}}$ 4.2.

5-Chloro-1,1,1,3,3,5,7,7,9,9,9-undecamethylpentasiloxane (**31**) ((MD)$_2$D$^{\mathrm{Cl}}$) starting from trichloromethylsilane and the double molar amount of pentamethyldisiloxanol (MM$^{\mathrm{OH}}$). 55%; b.p. 110°C/2.66 kPa; d_4^{20} 0.94; n_D^{20} 1.3988; $C_{11}H_{33}ClO_4Si_5$; hydrolyzable Cl found: 8.50; calc.: 8.75; δ^{29}Si/ppm: M 8.4, D$^{\mathrm{Cl}}$ −48.3, D −19.2.

3-Chloro-1,1,1,3,5,7,7,7-octamethyl-5-trimethylsiloxytetrasiloxane (**32**) (MD$^{\mathrm{Cl}}$TM$_2$) starting from 1,1,1,3,5,5,5-heptamethyltrisiloxane-3-ol (M$_2$D$^{\mathrm{OH}}$) and 1,1-dichloro-1,3,3,3-tetramethyldisiloxane (MM$^{\mathrm{Cl}}{}_2$). 68%; b.p. 100.5°C/1.07 kPa; d_4^{20} 0.924; n_D^{20} 1.3971; $C_{11}H_{33}ClO_4Si_5$; hydrolyzable Cl found: 8.50; calc.: 8.75; δ^{29}Si/ppm: *M*D$^{\mathrm{Cl}}$ 12.0, D$^{\mathrm{Cl}}$ −45.7, T −65.2, *M*T 8.7.

3-Chloro-1,1,1,3,7,7,7-heptamethyl-5,5-bis(trimethylsiloxy)tetrasiloxane (**33**) (MD$^{\mathrm{Cl}}$QM$_3$) starting from tris(trimethylsiloxy)silanol (M$_3$T$^{\mathrm{OH}}$) and 1,1-dichloro-1,3,3,3-tetramethyldisiloxane (MM$^{\mathrm{Cl}}{}_2$) 60%; b.p. 135°C/2.66 kPa; d_4^{20} 0.896; n_D^{20} 1.3963; $C_{13}H_{39}ClO_5Si_6$; hydrolyzable Cl found: 7.20; calc.: 7.39; δ^{29}Si/ppm: *M*D$^{\mathrm{Cl}}$ 12.2, D$^{\mathrm{Cl}}$ −45.3, Q −107.0, *M*Q 9.8.

5-Chloro-1,1,1,3,5,7,9,9,9-nonamethyl-3,7-bis(trimethylsiloxy)pentasiloxane (**34**) ((M$_2$T)$_2$D$^{\mathrm{Cl}}$) starting from trichloromethylsilane and the double molar amount of 1,1,1,3,5,5,5-heptamethyltrisiloxane-3-ol (M$_2$D$^{\mathrm{OH}}$). 60%; b.p. 98°C/1.07 kPa; d_4^{20} 0.999; n_D^{20} 1.3996; $C_{15}H_{45}ClO_6Si_7$; hydrolyzable Cl found: 6.20; calc.: 6.40; δ^{29}Si/ppm: M 8.7, T −65.1, D$^{\mathrm{Cl}}$ −46.9.

Hexamethyldisiloxane, the chlorosilanes Me_nSiCl_{4-n} ($n = 1, 2, 3$) and chlorohy-

Table 1

Relative rate constants for the reactions of some chlorosilanes with lithium trimethylsilanolate determined by various methods (relative error ±10%)

Compound	relative rate constants k_{rel} determined by		
	^{1}H-NMR spectroscopy	gas chromatography	turbidimetry
$PhMe_2SiCl$	1.00	1.00	1.00
p-$TolMe_2SiCl$	0.75	0.77	0.80
p-$ClC_6H_4Me_2SiCl$	1.22	1.20	1.33
m-$ClC_6H_4Me_2SiCl$	1.82	1.40	1.74
Me_3SiCl	–	1.10	1.30
$(Me_3SiO)_2MeSiCl$	–	1.44	1.46

drogensilanes ($HSiCl_3$, $MeHSiCl_2$) were obtained commercially (Chemiewerk Nünchritz GmbH).

Results and discussion

Determination of relative rate constants k_{rel} by turbidimetric measurements

The reactions of chlorosilanes with lithium silanolates or lithium isopropylate in dilute ethereal solutions proceed with increasing turbidity of the solutions. At the beginning of the reactions the turbidity increases only slowly, and this is followed by a comparatively short phase in which the turbidity changes very rapidly. A plot of the intensity of the scattered light of the reactions of trimethylchlorosilane and $(Me_3SiO)_2SiMeOSiMe_2Cl$ (M_2TM^{Cl}) with lithium trimethylsilanolate against the reaction time is given in Fig. 1. To compare the reactivities of different compounds the time to reach the same turbidity was measured. Various measurements at comparable conditions show that the turbidity has a good reproducibility and depends on the reactivity of the compounds used, the temperature, and the concentration of the solutions. The time to yield a defined turbidity is inversely proportional to the rate constant of the reaction. The k_{rel} values obtained by this method are in good agreement with those determined by GLC or ^{1}H-NMR spectroscopy (Table 1).

Results

The reaction rates of the trialkylchlorosilanes RMe_2SiCl are almost exclusively influenced by the steric effects of the alkyl groups. Thus initially the steric susceptibilities, δ, for all the reaction series were determined by plotting the $\log(k_{rel})$ values of the reactions against the E_s constants of the alkyl groups (Table 2).

The $\lg(k_{rel})$ values of the compounds with R = Me, ^{n}Pr, ^{n}Bu and ^{c}Hex gave a satisfactory correlation with Taft's E_s values [18]. In the case of the ethyl group we used the E_s value that we previously found [3,6,19,20]. The δ-values determined in this way are listed in Table 2. The values are between 1.3 and 1.4. This means that the influence of steric effects on all these reactions is similar and fairly strong. Using the experimental k_{rel} values for R = ^{t}Bu, ^{c}Pent, ^{i}Pr and ^{s}Bu and the δ-values determined, we derived E_s values for these substituents that differed considerably from the Taft values [18]. For all series the same values were obtained

Table 2

Substituent constants for triorganylchlorosilanes RMe_2SiCl, relative rate constants $k(RMe_2SiCl)/k(Me_3SiCl)$ for their reactions with lithium silanolates and lithium isopropylate in diethyl ether at 20°C, and reaction constants for these reactions

Entry	R	σ^*(R)	E_S(R) [18]	Relative rate constants for reactions with		
				Me_3SiOLi	$PhMe_2SiOLi$ [a]	Me_2CHOLi [b]
0	Me	0.0	0.0	1.00 [c]	1.00	1.00
1	Et	0.0	−0.28 [3]	0.40 [c]	0.25	0.46
2	^{n}Pr	0.0	−0.36	0.30 [c]	0.25	0.38
3	^{n}Bu	0.0	−0.39	0.29 [c]	0.22	0.33
4	^{i}Bu	0.0	−0.55 [d]	0.08 [c]	0.17	0.25
5	^{c}Pent	0.0	−0.70 [d]	0.10	–	0.14
6	^{i}Pr	0.0	−0.76 [d]	0.10 [c]	0.07	0.11
7	^{c}Hex	0.0	−0.79	0.08 [c]	0.07	0.09
8	^{s}Bu	0.0	−0.87 [d]	0.09	0.06	0.07
9	$4\text{-}MeC_6H_4$	0.38 [e]	−0.40 [f]	0.69 [c]	0.85	0.51
10	C_6H_5	0.48 [i]	−0.40	0.91 [c]	0.95	0.58
11	$4\text{-}FC_6H_4$	0.54 [e]	−0.40	–	1.13	–
12	$3\text{-}MeOC_6H_4$	0.60 [e]	−0.40	–	0.94	–
13	$4\text{-}ClC_6H_4$	0.71 [e]	−0.40	1.11 [c]	1.35	1.1
14	$3\text{-}ClC_6H_4$	0.85 [e]	−0.40	1.66 [c]	1.75	1.52
15	H	0.94 [j]	1.00 [g]	240	410	375
16	$BrCH_2$	1.00 [35]	−0.27	4.80	4.00	6.00
17	$ClCH_2$	1.05 [35]	−0.24	6.70	5.50	5.00
18	Cl_2CH	1.94 [35]	−0.58	24	27	–
19	Me_3Si	−0.78 [33]	−0.63 [20]	0.08	0.07	0.13
20	Me_3SiCH_2	−0.26 [35]	−0.35 [h]	0.09	0.08	0.07
21	$C_6H_5CH_2$	0.215 [35]	−0.38	0.20	0.15	0.28
Steric susceptibility δ [k]:				1.32 ± 0.2	1.4 ± 0.35	1.32 ± 0.2
Regression coefficient:				0.99	0.97	0.99
Significance level				0.023	0.12	0.027
Inductive reaction constant ρ^* [k]:				1.04	1.1	0.94
Regression coefficient:				0.989	0.987	0.940
Significance level:				0.10	0.11	0.16

[a] Entries 0–8. 30°C. [b] Entries 0–14: 30°C. [c] ^1H-NMR spectroscopically at 30°C. [d] New calculated E_S values. [e] $\sigma^*(R\text{–}C_6H_4) = 0.48 + \sigma(R)$. [f] Determined from the rate constants for the acetolysis reaction: $k\{PhMe_2SiCl\} = 1.2 \times 10^{-3}$ l mol^{-1} s^{-1}. [g] Determined from the rate constants for the acetolysis reaction: $k\{Ph_2SiHCl\} = 7.6 \times 10^{-3}$ l mol^{-1} s^{-1}. [h] Determined from the rate constant for the acetolysis reaction: $k\{Me_3SiCH_2SiMe_2SiCl\} = 1.4 \times 10^{-3}$ l mol^{-1} s^{-1}. [i] Determined from $\delta^{29}Si((Me_3SiO)_3\text{-}Si\text{–}C_6H_5) = 8.48$ ppm [2,36] [j] Determined from $\delta^{29}Si((Me_3SiO)_3Si\text{–}H) = 9.14$ ppm [2,36] [k] See text

within experimental error. These new values are also listed in Table 2 (column 4, marked with ^{d}).

These E_S-values can also be applied to kinetic data for other reactions with a silicon atom as the reaction centre. In all the cases studied up to now the correlations are better than those with the original Taft values or other series of steric constants [21–23], including those which were used by Cartledge [24]. The reactions we reexamined include the solvolysis of alkylhydrogenosilanes catalysed by bases [25–28] or acids [29,30], the hydrolysis of alkylfluorosilanes [31], the acetolysis of alkyltrichlorosilanes [19] and the hydrolysis of trialkylacetoxysilanes [32].

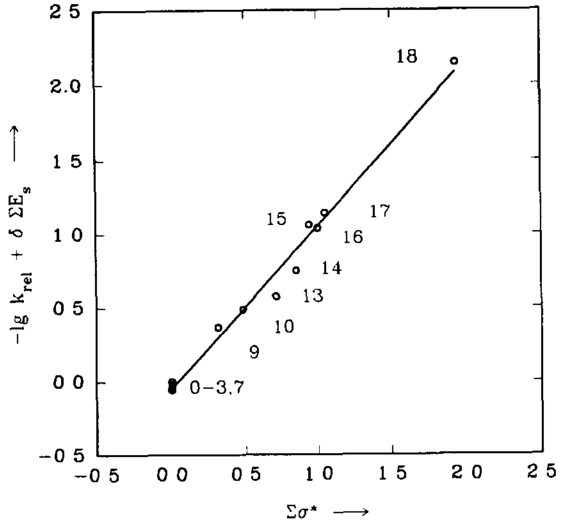

Fig. 2 Determination of the inductive reaction constant ρ^* for the reactions of organylchlorosilanes with lithium trimethylsilanolate (for numbering see Table 2).

The inductive reaction constants ρ^* were determined using compounds RMe_2SiCl with strong electron attracting groups R (Table 2, entries 9–18) and several alkyl-substituted compounds (Table 2, entries 0–3, 7). The σ^* values of the alkyl groups were set to 0 because their effects are small and approximately equal [37]. Since it was impossible to exclude the steric influence of the substituents we plotted $\log(k_{rel}) - \delta^* E_s$ against $\sigma^*(R)$ to give the reaction constants as the slope of the straight lines obtained. Fig. 2 shows an example. The k_{rel} values for the compounds RMe_2SiCl with $R = C_6H_5CH_2$, Me_3SiCH_2 and Me_3Si deviate systematically from the straight lines. We think that once more the known steric substituent constants cannot be used for these groups when they are on silicon atoms. Thus we calculated new E_s values for the substituents Me_3SiCH_2 ($E_s = -0.58$) and $C_6H_5CH_2$ ($E_s = -0.68$). The relative rate constants for the reactions with chloropentamethyldisilane enabled us to calculate E_s for the Me_3Si group ($E_s = -0.23$), but this is uncertain because it is based on a σ^* value (-0.78) for this substituent that is not generally accepted [20].

Using the reaction constants determined we studied some reactions with monochlorosiloxanes. The relative rate constants calculated from turbidimetric measurements are listed in Table 3. The correlation of $\log k_{rel} - \rho^*\sigma^*$ with ΣE_s for the reactions with lithium trimethylsilanolate, lithium dimethylphenylsilanolate, and lithium isopropylate are shown in Figs. 3–5. The data for the siloxy substituted compounds fit on one straight line, which means that the E_s values are correct, but, surprisingly, this line is nearly parallel shifted to that for the organo-substituted compounds. Depending on the reagent, the siloxy-substituted compounds react about 6–10 times faster than expected from the substituent constants (see Table 3 term C). We assume that this is due to the variable inductive effect of the siloxy groups. The σ^* values change depending on the total charge at the reaction centre, which is influenced by all the substituents. Compared with those derived from the system that we originally used to determine σ^* values for siloxy groups

Table 3

Substituent constants for monochlorosiloxanes, rate constants relative to Me_3SiCl for reactions with lithium silanolates and lithium isopropylate in diethylether at 20°C, and reaction constants

Entry	Chlorosiloxane [a]	$\Sigma\sigma^*$(siloxy) [2]	ΣE_s(siloxy) [3]	Relative rate constants for reactions with		
				Me_3SiOLi	$PhMe_2SiOLi$	Me_2CHOLi [b]
22	MM^{Cl}	0.35	−0.43	6.3	4.2	2.1
23	MDM^{Cl}	0.57	−0.46	4.6	3.6	2.5
24	$MDDM^{Cl}$	0.62	−0.52	3.6	3.3	2.2
25	M_2TDM^{Cl}	0.71	−0.73	2.0	1.7	1.1
26	M_2TM^{Cl}	0.74	−0.77	2.2	1.0	1.2
27	M_3QDM^{Cl}	0.74	−0.91	1.5	1.2	0.92
28	M_3QM^{Cl}	0.90	−1.04	1.4	0.79	0.57
29	M_2D^{Cl}	0.70	−0.86	1.1	0.72	0.63
30	$MD^{Cl}DM$	0.92	−0 89	1.4	0.80	0.50
31	$(MD)_2D^{Cl}$	1.14	−0.92	1.1	0.95	0.43
32	$MD^{Cl}TM_2$	1.09	−1.20	0.91	0.80	0.54
33	$MD^{Cl}QM_3$	1.25	−1.47	0.46	0.28	0.31
34	$(M_2T)_2D^{Cl}$	1.48	−1.52	0.58	0 54	0.38
35	M_3T^{Cl}	1.05	−1.29	0 02	0.02	0.02
Steric susceptibility δ [c]:				1.65±0.3	1 59±0.4	1.57±0 3
Term C [c]				0.81	0.49	0.58
Regression coefficient.				0.98	0.96	0.97

[a] $M = Me_3SiO_{1/2}$, $D = Me_2Si(O_{1/2})_2$, $T = MeSi(O_{1/2})_3$, $Q = Si(O_{1/2})_4$, $M^{Cl} = Me_2ClSiO_{1/2}$, $D^{Cl} = MeClSi(O_{1/2})_2$. [b] At 30°C. [c] Determined from $\log k_{rel} - (\rho^*\Sigma\sigma^*) = \delta\Sigma E_s + c$, entries 23–30, 32–34, ρ^* see Table 2.

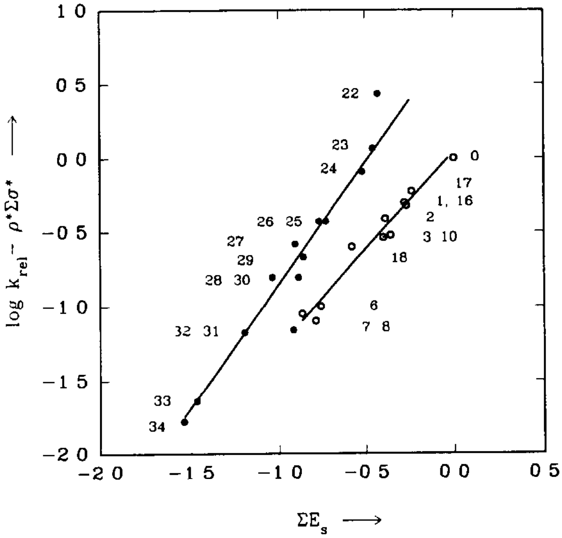

Fig. 3. Correlation of the lg $k_{rel} - \rho^*\Sigma\sigma^*$ terms against steric substituent constants E_s of the substituents for reactions of chlorosilanes (○) and chlorosiloxanes (●) with lithium trimethylsilanolate (for numbering see Tables 2 and 3).

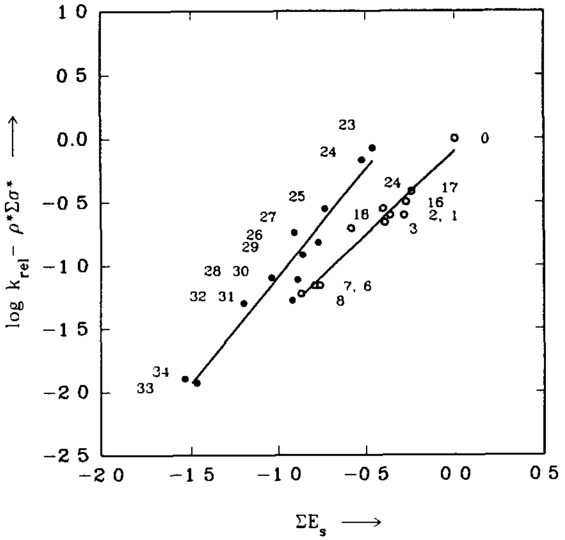

Fig. 4. Plot of lg $k_{rel} - \rho^*\Sigma\sigma^*$ against the steric substituent constant E_s of the substituents for reactions of chlorosilanes (○) and chlorosiloxanes (●) with lithium dimethylphenylsilanolate (for numbering see Tables 2 and 3).

($(Me_3SiO)_3SiR$ with R = various organic or siloxy groups [2]), all the values are about 0.65 higher; that is, all siloxy groups have a stronger electron attracting effect in the system now described.

Although the σ^* values for the siloxy groups are not constant they can be used to predict relative reactivities within a series of siloxanes having a similar sub-

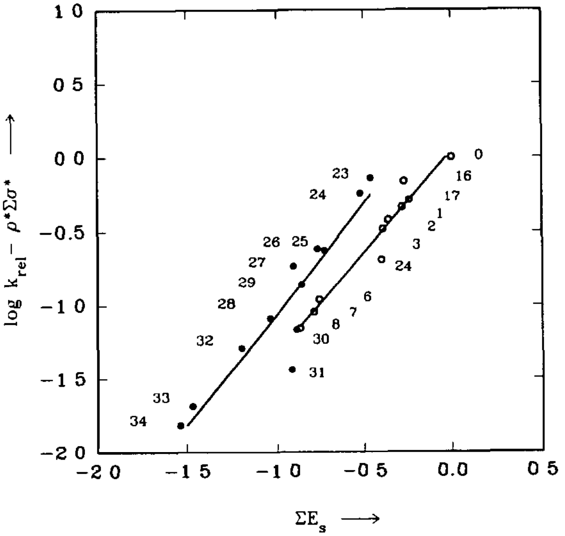

Fig. 5. Correlation of the lg $k_{rel} - \rho^*\Sigma\sigma^*$ terms against the steric substituent constants E_s of the substituents at chlorosilanes (○) and chlorosiloxanes (●) for the reaction with lithium isopropylate (for numbering see Tables 2 and 3).

stituent pattern at the reaction centre. More data are needed before further discussion is justified.

We are continuing our work by investigating the reactions of di- and trichlorosiloxanes in order to study the effect of strongly electron-attracting groups on the reaction centre. We also intend to carry out some theoretical calculations to throw light on these effects.

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