Synthesis of siloxanes

XII *. Cleavage of siloxanes by hydrogen chloride

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(Received March 23rd, 1988)

Abstract

^{1}H NMR spectroscopy has been used in a kinetic study of the cleavage of siloxane bonds by hydrogen chloride in dioxane. The cleavages show an induction period which is associated with the autocatalytic effect of the water formed during the reaction. The kinetic behavior can be expressed in terms of a rate law that includes rate constants for cleavage by both dioxane · HCl (k_1) and H$_2$O · HCl (k_2). The k_1' ($k_1' = k_1 \cdot [\text{HCl}]^{-4}$) and k_2' ($k_2' = k_2 \cdot [\text{HCl}]^{-3}$) values correlate with $\sigma^\star$ values; thus $\rho^\star$ values of -1.4 and -0.7 were obtained for k_1' and k_2', respectively. The $\sigma^\star$ value of 0.35 that we previously derived for the Me$_3$SiO group applies in this reaction.

The reaction of 1,3-bis(*p*-methoxyphenyl)tetramethyldisiloxane with hydrogen chloride involves cleavage of silicon–aryl rather than Si–O bonds.

Introduction

The industrial production of polysiloxanes by hydrolysis of chlorosilanes is mainly carried out in acidic media, and so in addition to hydrolysis and condensation reactions cleavages of siloxane bonds may also occur. In the equilibration processes that often represent a subsequent process in the production of siloxanes, cleavages and reformations of siloxane bonds are the most important reactions.

The cleavage of siloxane bonds by hydrogen halides was first observed by Krieble and Elliot [2]. The cleavage of siloxanes was subsequently utilized for preparative

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* For Part XI see ref. 1.

purposes; e.g. Müller et al. obtained a 70% yield of dimethylchlorosilane by passing HCl into tetramethyldisiloxane [3]. The equilibration of $Me_3Si(OSiMe_2)_2OSiMe_3$ by hydrogen chloride in the presence of various quantities of water or methanol was investigated by Mayo, who found that oligomeric siloxanes $Me_3Si(OSiMe_2)_nOSiMe_3$ ($n = 0, 1, 2, ...$) and (Me_2SiO) are formed [4].

The first quantitative investigations on the siloxane-HCl system were carried out by Hyde et al. [5]. They observed that equilibria are established between siloxanes and chlorosilanes, and they determined the equilibrium constants for the reactions of several substituted disiloxanes with aqueous HCl. They found that the equilibria generally lie far over to the side of the disiloxanes and are shifted further in this direction by electron-withdrawing substituents on silicon. They also noted a linear correlation between the equilibrium constants and the Si–H stretching vibrations of the corresponding silanes.

To the best of our knowledge no results of kinetic investigations in the siloxane-HCl system have been published up to now. Our aim was to study the influence of substituents on the rate of the siloxane cleavage. In this connection we were especially interested in whether the σ^* values for siloxy groups that we determined spectroscopically [6] and found to apply in the cleavage of siloxanes by BF_3 [1], would also apply to the cleavage by HCl.

Experimental

Preparation of the HCl-dioxane solution

Hydrogen chloride, prepared from sodium chloride and concentrated sulphuric acid, was dried by passage through sulphuric acid and introduced into ice-cooled dioxane which had been dried over sodium. Appropriate amounts of the stock

Table 1

Chemical shifts of the methyl protons used in determining the relative concentrations of reactants and products

Substrate	δ (ppm)	Cleavage products	δ (ppm)
$(PhMe_2Si)_2O$	0.320	$PhMe_2SiCl$	0.665
$(p\text{-}CH_3C_6H_4Me_2Si)_2O$	0.298	$p\text{-}CH_3C_6H_4Me_2SiCl$	0.645
$(p\text{-}ClC_6H_4Me_2Si)_2O$	0.320	$p\text{-}ClC_6H_4Me_2SiCl$	0.669
$(p\text{-}FC_6H_4Me_2Si)_2O$	0.318	$p\text{-}FC_6H_4Me_2SiCl$	0.687
$(ClCH_2Me_2Si)_2O$	0.183	$ClCH_2Me_2SiCl$	0.480
$(Me_3Si)_2O$	0.063	Me_3SiCl	0.378
$(Me_3SiO)_2SiMe_2$	0.095	$Me_3SiOSiMeCl$	0.137
	0.030		0.387
		Me_3SiCl	0.378
$(Me_3SiO)_3SiMe$	0.106	$(Me_3SiO)_2SiMeCl$	0.152
	0.009		0.349
		Me_3SiCl	0.378
$(p\text{-}MeOC_6H_4Me_2Si)_2O$	0.290	$p\text{-}MeOC_6H_4Me_2SiOSiMe_2Cl$	0.372
			0.378
		$(ClMe_2Si)_2O$	0.460
$MeSiCl_3$	1.017	–	
$MeSi(OH)Cl_2$	0.719	–	

solutions (6 to 8 mol · l⁻¹) thus made were diluted with anhydrous dioxane to give the solutions needed for the kinetic studies.

Preparation of siloxanes

The preparations of the siloxanes have been described previously [1].

Kinetic studies

The reactions were monitored by ^{1}H NMR spectroscopy by use of Bruker WH 90 DS or WP 80 SY spectrometers, operating at 90.02 or 80.13 MHz, respectively. The signals from the reagents and products used to monitor the reactions are shown in Table 1. Mixed solvent media were made up directly in a NMR tube: namely, a solution of Me$_4$Si in C$_6$H$_6$ (0.1 ml) was added to (i) a solution of HCl in dioxane (0.5 ml) or (ii) to a mixture of HCl in dioxane (0.45 ml), and H$_2$O in dioxane (0.05 ml). When methyltrichlorosilane was also used, it was added at this point. The NMR tubes were thermostatted in the spectrometer at 303 K. The reactions were initiated by the addition of 0.05 ml of the relevant siloxane for reactions with added water or 0.02 ml for those without added water.

Results and discussion

Initial examination on the cleavage of diphenyltetramethyldisiloxane with HCl in dioxane revealed a pronounced induction period. This is associated with the autocatalytic effect of the water formed during the reaction (see Fig. 1). This behaviour is due to the changes in the acidity of the media. In dioxane HCl has a relatively low acidity, but this rises significantly on addition of small quantities of water [7]. Since the acidity function of the dioxane-water-HCl system is known only
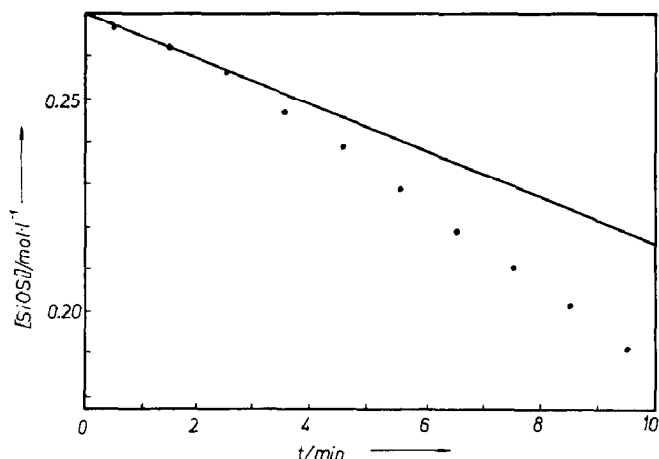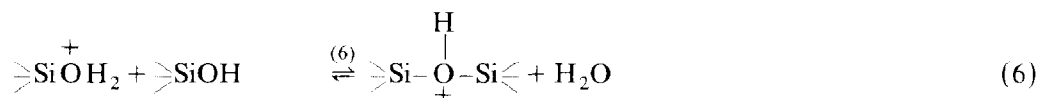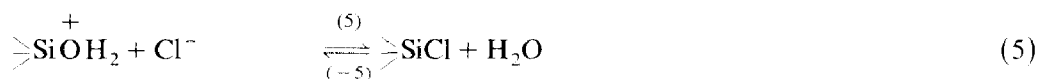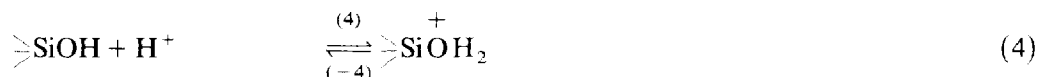

Fig. 1. Plot of the concentration of the siloxane against time for the cleavage of (PhMe$_2$Si)$_2$O by HCl. [H$_2$O]$_0$ 0.036 mol·l⁻¹, [HCl]$_0$ 2.9 mol·l⁻¹, [(PhMe$_2$Si)$_2$O]$_0$ 0.272 mol·l⁻¹, T 303 K.

qualitatively [7], a model involving separate K values for the protonation of siloxane by $H^+ \cdot$ dioxane (eq. 1) and by H_3O^+ (eq. 2) was devised.

$$\text{>Si-O-Si<} + O\underbrace{\quad}O \cdot H^+ \underset{(-1)}{\overset{(1)}{\rightleftharpoons}} \text{>Si-}\overset{\overset{H}{|}}{\underset{+}{O}}\text{-Si<} + O\underbrace{\quad}O \tag{1}$$

$$\text{>Si-O-Si<} + H_3O^+ \underset{(-2)}{\overset{(2)}{\rightleftharpoons}} \text{>Si-}\overset{\overset{H}{|}}{\underset{+}{O}}\text{-Si<} + H_2O \tag{2}$$

$$\text{>Si-}\overset{\overset{H}{|}}{\underset{+}{O}}\text{-Si<} + Cl^- \overset{(3)}{\rightleftharpoons} \text{>SiCl} + \text{>SiOH} \tag{3}$$

$$\text{>SiOH} + H^+ \underset{(-4)}{\overset{(4)}{\rightleftharpoons}} \text{>Si}\overset{+}{O}H_2 \tag{4}$$

$$\text{>Si}\overset{+}{O}H_2 + Cl^- \underset{(-5)}{\overset{(5)}{\rightleftharpoons}} \text{>SiCl} + H_2O \tag{5}$$

$$\text{>Si}\overset{+}{O}H_2 + \text{>SiOH} \overset{(6)}{\rightleftharpoons} \text{>Si-}\overset{\overset{H}{|}}{\underset{+}{O}}\text{-Si<} + H_2O \tag{6}$$
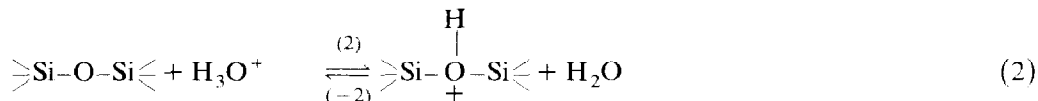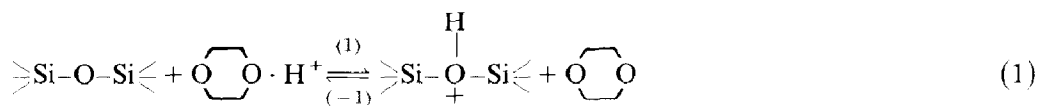
For simplicity the order with respect to both water and HCl in this scheme is shown as one. The correct values are given later in the text.

The reactions do not proceed to completion. As already noted by Hyde, equilibria are reached between the siloxanes and chlorosilanes [5]. For the cleavage of the Si–O bond, reaction 3 must be rate determining, and it is followed by fast reactions of the silanol (equations 4 and 5). Surprisingly, silanols could not be detected in the reaction mixtures by NMR spectroscopy, indicating the concentration of silanols present to be $< 1\%$.

Less clear are the reactions that lead to regeneration of siloxanes. The hydrolysis of the chlorosilane (reaction -5) must be important. The silanols formed by deprotonation (reaction -4) could further react with chlorosilanes (heterocondensation((reaction -3) or with protonated silanols (homocondensation) (reaction 6) to give disiloxanes. Reaction 6 is probably the main process. On the other hand, the reverse reaction (-6), i.e. the cleavage of the protonated siloxane by water, must be much less important than cleavage by Cl^- (eq. 3), since the water concentrations are very much lower than the Cl^- concentrations. Chlorosilane-silanol exchange reactions must also be taken into account [8].

In the reactions involving the siloxanes, $(Me_3SiO_2)SiMe_2$ and $((Me_3SiO)_3SiMe$ equilibria were not established between the initial products and the initial cleavage products. The chlorosiloxanes underwent further cleavage reactions, giving trimethylchlorosilane, and undefined higher molecular condensation products containing $SiMe_2O$ and $MeSiO_{1.5}$ units formed.

Because of the uncertainties about the back reactions involved in the equilibria, the rate data were used only up to 75% conversion. Since the proportions of siloxane in the equilibrium mixtures were always $< 10\%$, the reverse reactions can be neglected up to this extent of conversion, and so the rate law, given in equations 7–9
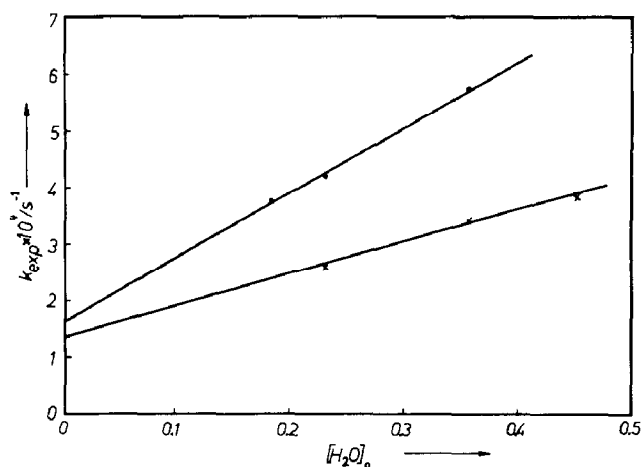
Fig. 2. Plot of the rate constant k_{exp} in the cleavage of $(PhMe_2Si)_2O$ by HCl against the initial concentration of water, $[H_2O]_0$; dots, ●, refer to an initial HCl concentration of 3.38 $mol \cdot l^{-1}$ and crosses, ×, to one of 2.90 $mol \cdot l^{-1}$.

(in which $K(1)$ and $k(3)$ etc. refer to the equilibria and reactions shown in equations 1–6) can be used.

$$-\frac{d[SiOSi]}{dt} = \left(k_1 + k_2 \cdot [H_2O]^a\right) \cdot [SiOSi] \tag{7}$$

with $k_1 = K(1) \cdot k(3) = k_1' \cdot [HCl]^b$ $\qquad(8)$

$k_2 = K(2) \cdot k(3) = k_2' \cdot [HCl]^c$ $\qquad(9)$

In some cases the cleavages were carried out in media involving known quantities of added water. The kinetics were then evaluated from the initial rates, r_0 (Fig. 1). The rate constant k_{exp} $(= r_0/[{>}SiOSi{<}]_0)$ were found to be directly proportional to the concentrations of the added water (Fig. 2), showing that there is an order of one with respect to H_2O in the range investigated. The slope of the plot of k_{exp} against $[H_2O]_0$ gives a rate constant k_2, and extrapolation to $[H_2O]_0 = 0$ gives k_1 (Fig. 2). The values of k_{exp} are given in Table 2, and the values of k_1 and k_2 in Table 3.

Other runs were carried out without added water. From the concentration of the siloxane at various times the two rate constants k_1 and k_2 were determined by a computer analysis based on the Runge–Kutta method (see Table 3).

From the rate constants determined at various HCl concentrations, the reaction orders, b and c, with respect to HCl were found (Fig. 3) to be approximately 4 and 3, respectively. The k' values (eq. 8 and 9) are shown in table 4.

Other reactions were performed in the presence of methyltrichlorosilane. This reacts immediately with the water formed, as in eq. 10. Equilibrium 10 lies almost

$$MeSiCl_3 + H_2O \rightleftharpoons MeSi(OH)Cl_2 + HCl \tag{10}$$

completely to the side of $MeSi(OH)Cl_2$ and HCl, thus very low water concentrations are present and so approximately constant acidities should be obtained. The possible condensation of $MeSi(OH)Cl_2$ (eq. 11) was not observed during the time

$$2\,MeSi(OH)Cl_2 \rightarrow (MeSiCl_2)_2O + H_2O \tag{11}$$

the reaction was followed. In the cleavages of $(Me_3SiO)_2SiMe_2$ and $(Me_3SiO)_3SiMe$,

Table 2

Rate constants, k_{exp}, for the cleavage of siloxanes by HCl in the presence of various concentrations of H_2O

Siloxane	$[HCl]_0$ (mol·l⁻¹)	$[H_2O]_0$ (mol·l⁻¹)	$10^4 k_{exp}/s^{-1}$ [a]
$(PhMe_2Si)_2O$	3.38	0.036	5.75
		0.023	4.20
		0.018	3.75
	2.90	0.045	3.80
		0.036	3.45
		0.023	2.58
$(p\text{-}CH_3C_6H_4Me_2Si)_2O$	3.38	0.045	13.3
		0.036	11.2
		0.023	8.60
$(p\text{-}ClC_6H_4Me_2Si)_2O$	3.38	0.045	3.42
		0.036	2.62
		0.023	1.75
$(p\text{-}FC_6H_4Me_2Si)_2O$	3.38	0.045	4.27
		0.036	3.70
		0.023	2.83
$(ClCH_2Me_2Si)_2O$	3.38	0.045	0.333
		0.036	0.467
		0.023	0.0267

[a] $k_{exp} = r_0/[\text{>SiOSi<}]_0$.

the chlorosiloxanes formed are stable during the time of measurement. From these results, we conclude, that when water is not trapped, it is the siloxanols which are cleaved and not the chlorosiloxanes.

Table 3

Rate constants, k_1 and k_2, determined from the rate constant k_{exp} (Table 2) or (denoted by [a]) by the Runge–Kutta method

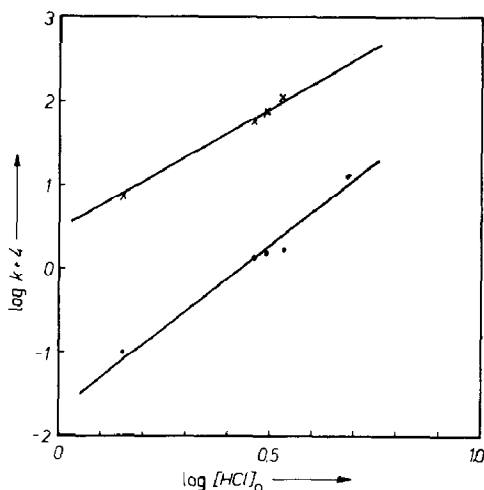| Siloxane	$[HCl]_0$ (mol·l⁻¹)	$k_1 \times 10^4$ (s⁻¹)	$k_2 \times 10^3$ (l·mol⁻¹ s⁻¹)
$(PhMe_2Si)_2O$	4.81	12.7	24.5
	3.38 [a]	1.67	11.3
	3.09	1.57	7.33
	2.90 [a]	1.33	5.63
	1.43	0.0983	0.733
$(p\text{-}CH_3C_6H_4Me_2Si)_2O$	4.81	28.3	35.0
	3.38 [a]	3.66	21.3
	3.09	3.50	8.50
	1.43	0.283	1.00
$(p\text{-}ClC_6H_4Me_2Si)_2O$	4.81	3.67	15.2
	3.38 [a]	0.670	6.18
	3.09	0.600	4.00
$(p\text{-}FC_6H_4Me_2Si)_2O$	3.99	2.17	8.50
	3.38 [a]	1.39	6.40
	2.64	0.700	4.20
$(ClCH_2Me_2Si)_2O$	3.38 [a]	0.0504	0.881
$(Me_3Si)_2O$	1.61	2.2	3.7
$(Me_3SiO)_2SiMe_2$	2.42	10.5	6.2
$(Me_3SiO)_3SiMe$	4.48	37	35
	4.03	18	22

Fig. 3. Determination of the reaction order with respect to HCl for the cleavage of $(PhMe_2Si)_2O$ by HCl. Plot of log k_1 (denoted by ●) and log k_2 (denoted by ×) against log $[HCl]_0$.

The k values in presence of added $MeSiCl_3$ are summarized in Table 5. They correspond to the k_1 values. The k' values also given in Table 5 were calculated in the same way as those for k_1' by assumption of a value of 4 for the order with respect to HCl.

The rate constants k_1' and k_2' correlate satisfactorily with the Taft σ^*-constants (Fig. 4, 5). A σ^* value of 0.48 was used for the phenyl group [1]. The value for

Table 4

Rate constants k_1' and k_2' for the cleavage of siloxanes by HCl

Siloxane	$k_1' \times 10^6$ $(l^4 \cdot mol^{-4} \cdot s^{-1})$	$k_2' \times 10^4$ $(l^4 \cdot mol^{-4} \cdot s^{-1})$	σ^*
$(PhMe_2Si)_2O$	1.9	2.5	0.96
$(p\text{-}CH_3C_6H_4Me_2Si)_2O$	4.7	3.7	0.62
$(p\text{-}ClC_6H_4Me_2Si)_2O$	0.62	1.4	1.42
$(p\text{-}FC_6H_4Me_2Si)_2O$	1.1	1.8	1.08
$(ClCH_2Me_2Si)_2O$	0.039	0.23	2.10
$(Me_3Si)_2O$	32　(49 [a])	8.9	0.00
$(Me_3SiO)_2SiMe_2$	30　(14 [a])	4.4	0.35
$(Me_3SiO)_3SiMe$	8.0 (8.3 [a])	3.6	0.70

[a] Values in the presence of $MeSiCl_3$.

Table 5

Cleavage of the siloxanes in the presence of $MeSiCl_3$

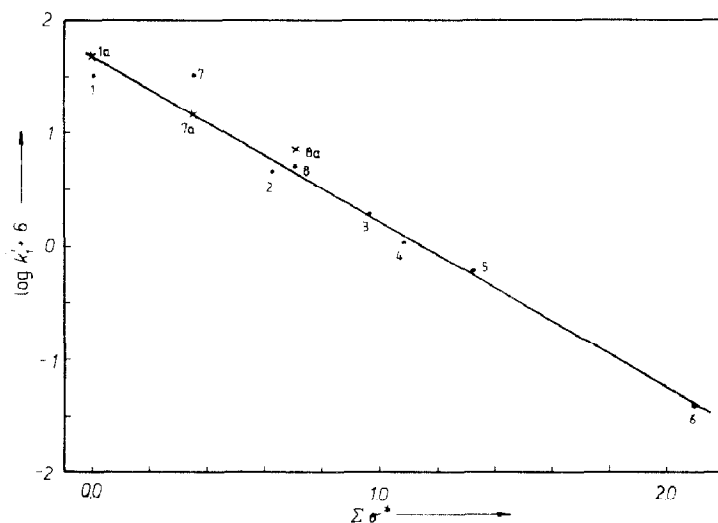| Siloxane	$[HCl]_0$ $(mol \cdot l^{-1})$	$k \times 10^4$ (s^{-1})	$k' \times 10^5$ $(l^4 \cdot mol^{-4} \cdot s^{-1})$
$(Me_3SiO)_2SiMe_2$	2.03	2.64	1.55
	1.26	0.294	1.17
$(Me_3SiO)_3SiMe$	2.11	1.65	0.832
$(Me_3Si)_2O$	1.87	5.40	4.92

Fig. 4. Plot of log k'_1 against the σ^* or $\Sigma\sigma^*$ values of the substituents; dots, ●, refer to reactions in the absence of MeSiCl$_3$ and crosses, ×, to those in its presence 1, (Me$_3$Si)$_2$O; 2. (p-CH$_3$C$_6$H$_4$Me$_2$Si)$_2$O; 3, (PhMe$_2$Si)$_2$O; 4. (p-FC$_6$H$_4$Me$_2$Si)$_2$O; 5. (p-ClC$_6$H$_4$Me$_2$Si)$_2$O; 6. (ClCH$_2$Me$_2$Si)$_2$O; 7. (Me$_3$SiO)$_2$SiMe$_2$; 8, (Me$_3$SiO)$_3$SiMe.

(Me$_3$SiO)$_3$SiMe was statistically corrected [1]. It was found that the σ^*-constant for Me$_3$SiO of 0.35 determined spectroscopically [6] is also applicable in the cleavage of siloxanes by HCl, as it was in the cleavage of the siloxanes by BF$_3$ [1]. Values of ρ^* -1.4 and -0.7 were calculated for k'_1 and k'_2, respectively. These negative values reflect the fact that the protonation step of the siloxane preceding the rate-determining step has a large negative ρ^* value which is not fully counteracted by that of the subsequent nucleophilic substitution.
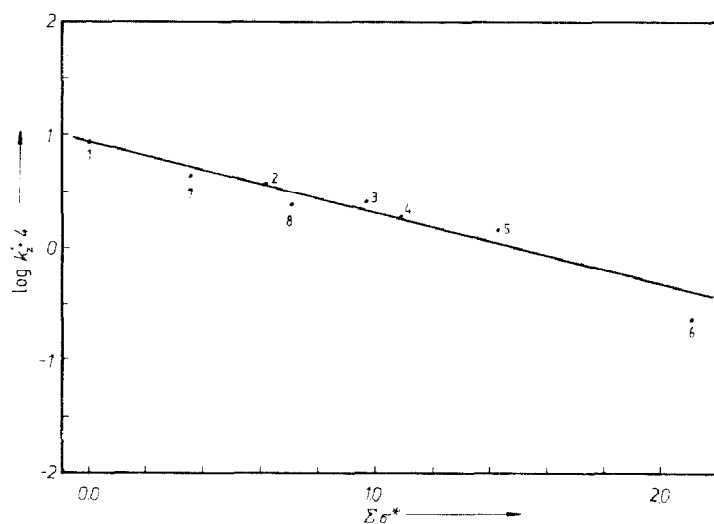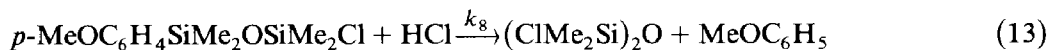

Fig. 5. Plot of log k'_2 against the σ^* or $\Sigma\sigma^*$ values of the substituents. 1, (Me$_3$Si)$_2$O; 2. (p-CH$_3$C$_6$H$_4$Me$_2$Si)$_2$O; 3, (PhMe$_2$Si)$_2$O; 4, (p-FC$_6$H$_4$Me$_2$Si)$_2$O; 5, (p-ClC$_6$H$_4$Me$_2$Si)$_2$O; 6. (ClCH$_2$Me$_2$Si)$_2$O; 7, (Me$_3$SiO)$_2$SiMe$_2$; 8, (Me$_3$SiO)$_3$SiMe.

In the reaction with HCl the behaviour of 1,3-bis(*p*-methoxyphenyl)tetramethyl-disiloxane was exceptional in that instead of Si–O bonds the Si–aryl bonds are cleaved:

$$(p\text{-MeOC}_6\text{H}_4\text{SiMe}_2)_2\text{O} + \text{HCl} \xrightarrow{k_7} p\text{-MeOC}_6\text{H}_4\text{SiMe}_2\text{OSiMe}_2\text{Cl} + \text{MeOC}_6\text{H}_5 \quad (12)$$

$$p\text{-MeOC}_6\text{H}_4\text{SiMe}_2\text{OSiMe}_2\text{Cl} + \text{HCl} \xrightarrow{k_8} (\text{ClMe}_2\text{Si})_2\text{O} + \text{MeOC}_6\text{H}_5 \quad (13)$$

At an HCl concentration of 1.75 mol · l^{-1} values of k_7 and k_8 were found to be 4.54×10^{-3} and 4.0×10^{-4} s^{-1}.

The much greater rate of cleavage of *p*-MeOC$_6$H$_4$–Si than of Ph–Si bonds by electrophiles is well documented [10]. Protonation at oxygen (eq. 1,2), while very fast, has to be followed by a much slower rate determining step (eq. 3), whereas protonation a carbon, while much slower than at oxygen is always followed by cleavage and so is rate determining.

A comparison of the two *k* values, after a statistical correction of k_7 shows that the first step is about six times faster than the second. This is due to electron withdrawal by the chlorine atom in the chloro(methoxyphenyl)siloxane which reduces the ease of protonation of the carbon atom of the aryl–Si bond [10].

Acknowledgement

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