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Review

REACTIONS OF ORGANOPOLYSILANES WITH ORGANIC PEROXIDES *

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Contents

I. Introduction

There are few data on the reactions of halogeno(alkoxy)polysilanes with organic hydroperoxides and their salts. However, these reactions are of interest, because they enable one to study the comparative reactivity of halogenopolysilanes in oxidation and nucleophilic substitution reactions, as well as provide routes to peroxidic products containing polysilane chains in the molecule.

In this review, the main results of our investigations concerning reactions of chloropolysilanes, as well as some cyclic polysilanes, with t-butyl hydroperoxide and its lithium salt, lithium (t-butylperoxy)carbonate, lithium trimethylsilanolate and with peroxybenzoic acid, are presented.

Based on the reaction products, kinetic investigations, and studies of electronic effects in peralkylated and chloro-substituted polysilanes by IR and UV spectroscopic methods of their molecular complexes in the ground and transition state, the oxidation mechanisms of substituted polysilanes is discussed.

Kumada and Sakurai have studied the oxidation of linear and cyclic organodisilanes [1–5].

II. Interaction of organopolysilanes with t-butyl hydroperoxide and with its lithium salt

When we began our studies [6] there was only one published work [7], by Japanese authors, dealing with the interaction of two chlorodisilanes with t-butyl

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[*] Dedicated to Prof. M. Kumada.

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hydroperoxide. In that work it was attempted to obtain the peroxide with a silicon–silicon bond in the molecule, according to the reaction

$$Me_3SiSiMe_2Cl + Me_3COOH \xrightarrow[-C_5H_5N\cdot HCl]{C_5H_5N} Me_3SiSiMe_2OOCMe_3 \qquad (1)$$

Instead of the expected peroxide, t-butoxypentamethyldisiloxane was isolated. This product is thought to be formed as a result of the rearrangement of the unstable disilanyl peroxide intermediate

$$Me_3SiSiMe_2OOCMe_3 \xrightarrow{\Delta} Me_3SiOSiMe_2OCMe_3 \qquad (2)$$

The same reaction, carried out by us with equimolar quantities of reagents, gave t-butoxypentamethyldisiloxane and t-butylperoxypentamethyldisiloxane [6]. The yield of peroxide was 20%, and it increased up to 65% when a two-fold molar excess of t-butyl hydroperoxide was used.

The formation of the siloxane peroxide could not be accounted for by the mechanism assumed in the work [7].

The interaction of chloropentamethyldisilane with t-butylperoxylithium (TBPL) has been carried out in hexane or in ether at reactant mol ratios of 1/1 and 1/2. Kinetic curves of the consumption of substrate and accumulation of silicon-containing products have been measured by the GLC method. The results are shown in Fig. 1. In carrying out the reaction with equimolar amounts of reagents in ether, 40% of t-butylperoxypentamethyldisiloxane and 20% of t-butoxypentamethyldisiloxane were found. The peroxidic product yield increased up to 75% when the reaction was carried out with a two molar excess of TBPL. The interaction of chloropentamethyldisilane with t-butylperoxylithium in hexane leads to the same products, but proceeds somewhat more slowly. In this case, the use of GLC made it possible to follow the consumption and accumulation of the intermediately forming chloropentamethyldisiloxane as a function of time. Its maximum concentration in the reaction mixture is 10 mol%. The presence of this compound in the reaction products

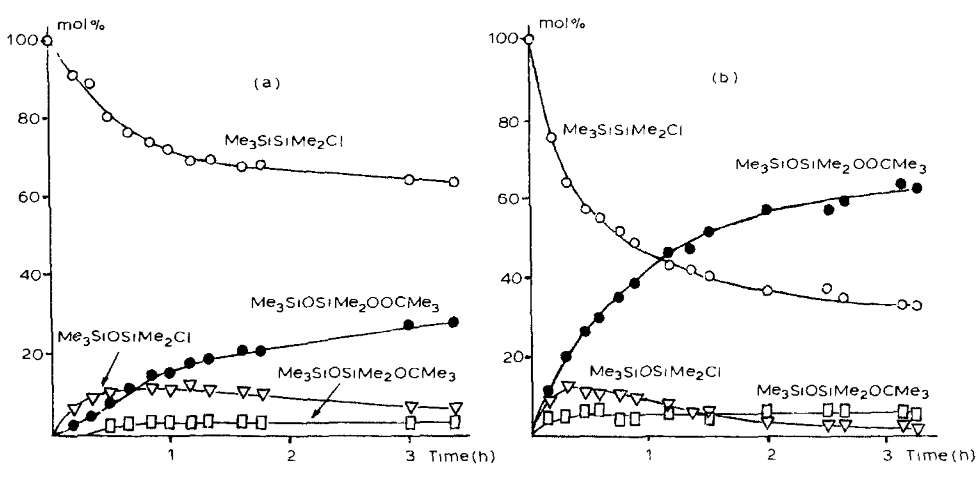


Fig. 1. Kinetic curves for the consumption of substrate and accumulation of the organosilicon products in the reaction of chloropentamethyldisilane with an equimolar quantity (a), or a double excess (b), of t-butylperoxylithium (hexane, 20 °C, $[Me_5Si_2Cl]_0$ 0.15 mol l^{-1}).

unambiguously indicates initial oxidation of the silicon–silicon bond in chloropentamethyldisilane.

$$Me_3SiSiMe_2Cl + Me_3COOLi \rightarrow Me_3SiOSiMe_2Cl + Me_3COLi \qquad (3)$$

It was found that the intermediate chlorosiloxane, as opposed to the initial chlorodisilane, readily enters into a nucleophilic substitution reaction with t-butylperoxylithium, and this results in a high content of the peroxidic siloxane in the reaction mixture

$$Me_3SiOSiMe_2Cl + Me_3COOLi \xrightarrow{k_1} Me_3SiOSiMe_2OOCMe_3 + LiCl \qquad (4)$$

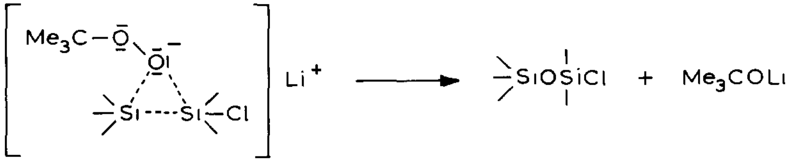
As the nucleophilic activity of TBPL is higher than that of lithium t-butylate (TBL), the yield of t-butylperoxypentamethyldisiloxane is considerably higher than that of t-butoxypentamethyldisiloxane.

$$Me_3SiOSiMe_2Cl + Me_3COLi \xrightarrow{k_2} Me_3SiOSiMe_2OCMe_3 + LiCl \qquad (5)$$
$$k_1 > k_2$$

It has been shown in special experiments, that an interchange reaction does not occur under our experimental conditions

$$Me_3SiOSiMe_2OCMe_3 + Me_3COOLi \nrightarrow Me_3SiOSiMe_2OOCMe_3 + Me_3COLi$$

Chlorodisilanes with butyl and phenyl substituents on the silicon atoms interact with TBPL in an analogous way [8,9]. In all cases the initial stage of the process is an oxidation of the chlorodisilane, with formation of the corresponding chlorosiloxane. The consumption of the latter in the reactions with TBPL and TBL proceeds comparatively rapidly. As a consequence of this, only small concentrations of chlorodisiloxanes are obtained in the reaction mixture.



Thus, peroxide forming reactions with the Si–Si bond in the molecule $RMe_2SiSiMe_2OOCMe_3$ and the further rearrangement do not occur, as chlorodisilanes show low reactivity towards nucleophilic reagents.

It may be assumed that the initial stage of the reaction of 1-chloroheptamethyltrisilane with TBPL is the oxidation of an Si–Si bond. It was of interest to establish which of two Si–Si bonds in 1-chloroheptamethyltrisilane would be oxidized in the first stage. With this aim, the interaction of the chlorotrisilane, as well as of two possible isomeric intermediate disilanes ($Me_3SiSiMe_2OSiMe_2Cl$ (**1**) and $Me_3SiOSiMe_2SiMe_2Cl$ (**2**)), with Me_3COOLi was carried out [10]; their reaction products were studied and the kinetics curves of their consumption and accumulation were plotted. The peroxidic compound **3** was found to be the main product of the reaction of the compound **1** with Me_3COOLi. The yield of **3** was 98%. Thus, the substitution of the chlorine atom by the t-butylperoxy group is the only process. The lithium salt, taken in excess, slowly oxidizes the Si–Si bond in the peroxide **3**:

$$\underset{(\mathbf{1})}{Me_3SiSiMeOSiMe_2Cl} + Me_3COOLi \rightarrow \underset{(\mathbf{3})}{Me_3SiSiMe_2OSiMe_2OOCMe_3} + LiCl \qquad (6)$$

$$\mathbf{3} + Me_3COOLi \rightarrow Me_3SiOSiMe_2OSiMe_2OOCMe_3 + LiOCMe_3 \qquad (7)$$

The initial stage of the reaction of the compound **2** with the peroxide salt, judging from the products formed, is oxidation of the Si–Si bond:

$$\underset{(\mathbf{2})}{Me_3SiOSiMe_2SiMe_2Cl} + Me_3COOLi \rightarrow \underset{(\mathbf{4})}{Me_3SiOSiMe_2OSiMe_2Cl} + Me_3COLi \qquad (8)$$

Then the reaction 9 proceeds easily.

$$\mathbf{4} + Me_3COOLi \rightarrow Me_3SiOSiMe_2OSiMe_2OOCMe_3 + LiCl \qquad (9)$$

In parallel with this, t-butoxyheptamethyltrisiloxane is being formed:

$$\mathbf{4} + Me_3COLi \rightarrow Me_3SiOSiMe_2OSiMe_2OCMe_3 + LiCl \qquad (10)$$

The yields of t-butylperoxy- and t-butoxy-heptamethyltrisiloxanes are 60 and 40%, respectively.

Kinetic curves of the consumption of substrate and the accumulation of the silicon-containing products of the interaction of 1-chloroheptamethyltrisilane with a triple excess of TBPL are presented in Fig. 2. An analysis of the kinetic curves, as well as the composition of the products, and a comparison of this data with the results on the oxidation of compounds **1** and **2**, suggests that the interaction of 1-chloroheptamethyltrisilane with TBPL is a multi-stage, consecutive-parallel process, starting with oxidation of the Si–Si bond located in the α-position to the

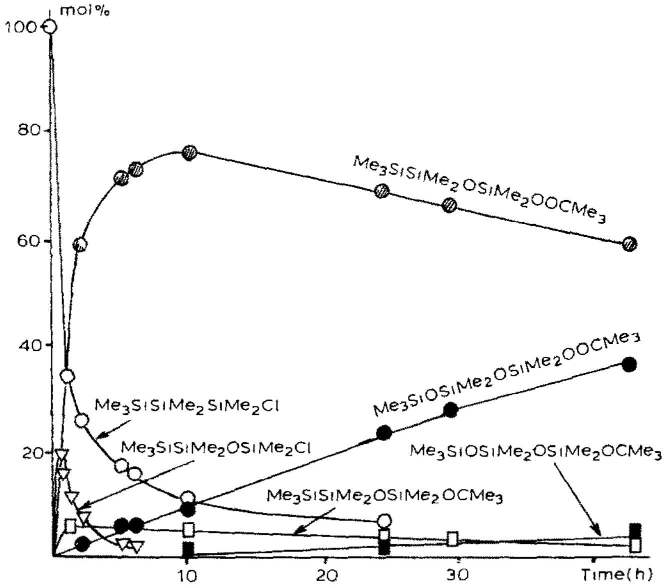


Fig. 2. Kinetic curves for the consumption of substrate and accumulation of the organosilicon products in the reaction of 1-chloroheptamethyltrisilane with a triple excess of t-butylperoxylithium (hexane, 20 °C, $[Me_3SiSiMe_2SiMe_2Cl]_0$ 0.15 mol l^{-1}).

chlorine atom, and proceeding according to the scheme represented by the equations 11–14 and 7.

$$\underset{}{Me_3SiSiMe_2SiMe_2Cl} + Me_3COOLi \rightarrow \underset{(\mathbf{1})}{Me_3SiSiMe_2OSiMe_2Cl} + Me_3COLi \qquad (11)$$

The chlorosiloxane **1**, so formed, enters into nucleophilic substitution reactions with TBPL and TBL:

$$\mathbf{1} \xrightarrow{Me_3COOLi} \underset{(\mathbf{3})}{Me_3SiSiMe_2OSiMe_2OOCMe_3} + LiCl \qquad (12)$$

$$\mathbf{1} \xrightarrow{Me_3COLi} \underset{(\mathbf{5})}{Me_3SiSiMe_2OSiMe_2OCMe_3} + LiCl \qquad (13)$$

The products **3** and **5** are oxidized very slowly by the t-butylperoxylithium to give the corresponding siloxanes (eqs. 7 and 14).

$$\mathbf{5} + Me_3COOLi \rightarrow Me_3SiOSiMe_2OSiMe_2OCMe_3 + Me_3COLi \qquad (14)$$

In the reaction of 2-chloroheptamethyltrisilane with t-butylperoxylithium (Fig. 3), in contrast to the foregoing reaction, consecutive oxidation of both Si–Si bonds takes place (eqs. 15, 16) and the only product, 3-chloroheptamethyltrisiloxane, **7**, reacts with TBL and TBPL with the elimination of lithium chloride (eqs. 17, 18).

$$(Me_3Si)_2SiMeCl + Me_3COOLi \rightarrow \underset{(\mathbf{6})}{Me_3SiSiMe(Cl)OSiMe_3} + Me_3COLi \qquad (15)$$

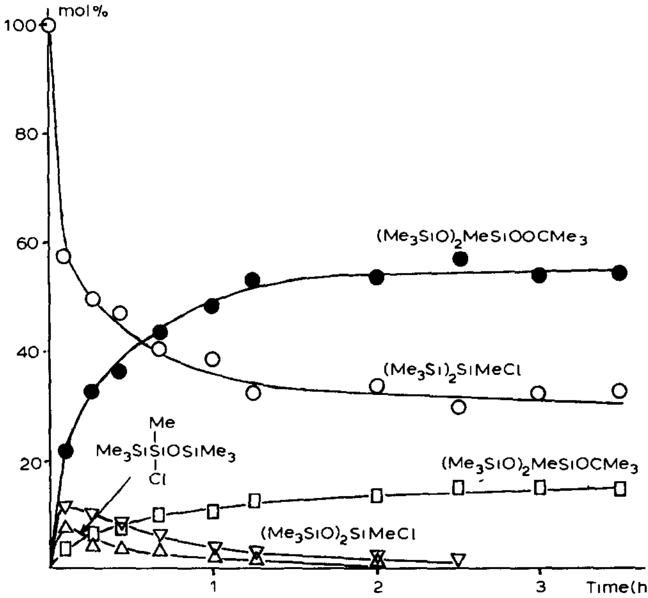


Fig. 3. Kinetic curves for the consumption of substrate and accumulation of the organosilicon products in the reaction of 2-chloroheptamethyltrisilane with a triple excess of t-butylperoxylithium (hexane, 20 °C, $[(Me_3Si)_2SiMeCl]_0$ 0.15 mol l^{-1}).

$$\mathbf{6} + \mathrm{Me_3COOLi} \rightarrow \underset{(\mathbf{7})}{(\mathrm{Me_3SiO})_2\mathrm{SiMeCl}} + \mathrm{Me_3COLi} \qquad (16)$$

$$\mathbf{7} \begin{cases} \xrightarrow{\mathrm{Me_3COOLi}} (\mathrm{Me_3SiO})_2\mathrm{MeSiOOCMe_3} & (17) \\ \xrightarrow{\mathrm{Me_3COLi}} (\mathrm{Me_3SiO})_2\mathrm{MeSiOCMe_3} & (18) \end{cases}$$

1,2-Dichlorotetramethyldisilane react with TBPL in a different manner [9]. At an equimolar reagent ratio (Fig. 4a), the main product is 1-chloro-3-t-butoxytetramethyldisiloxane, the formation of which may be explained by a mechanism involved rearrangement of the intermediate peroxidic compound with a Si–Si bond, which is consistent with ref. 7.

$$\mathrm{ClMe_2SiSiMe_2Cl} + \mathrm{Me_3COOLi} \rightarrow \underset{(\mathbf{8})}{\mathrm{ClMe_2SiSiMe_2(OOCMe_3)}} + \mathrm{LiCl} \qquad (19)$$

$$\mathbf{8} \looparrowright \underset{(\mathbf{9})}{\mathrm{ClMe_2SiOSiMe_2(OCMe_3)}} \qquad (20)$$

1-t-Butylperoxy-3-t-butoxytetramethyldisiloxane, **10**, becomes the main product with a two molar excess of $\mathrm{Me_3COOLi}$ (Fig. 4b):

$$\mathbf{9} + \mathrm{Me_3COOLi} \rightarrow \underset{(\mathbf{10})}{(\mathrm{Me_3COO})\mathrm{SiMe_2OSiMe_2(OCMe_3)}} + \mathrm{LiCl} \qquad (21)$$

The reactions described by the eqs. 22–24 proceed in parallel, but their share in

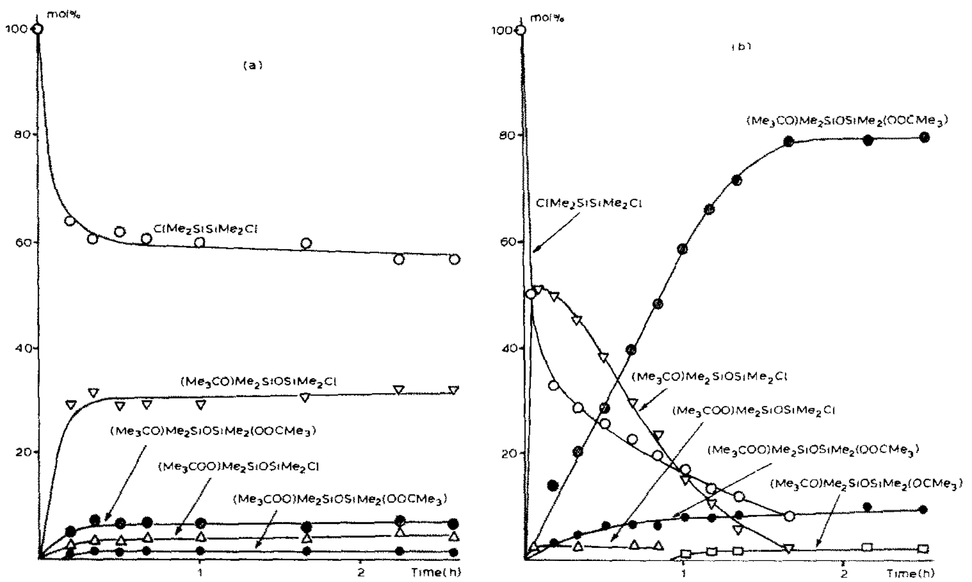


Fig. 4. Kinetic curves for the consumption of substrate and accumulation of the organosilicon products in the reaction of 1,2-dichlorotetramethyldisilane with an equimolar quantity (a), or a double excess (b), of t-butylperoxylithium (hexane, 20 °C, $[\mathrm{ClMe_2SiSiMe_2Cl}]_0$ 0.15 mol $\mathrm{l^{-1}}$).

the general process is less than 10%.

$$\mathrm{ClMe_2SiSiMe_2Cl + Me_3COOLi \rightarrow \underset{(\mathbf{11})}{ClMe_2SiOSiMe_2Cl} + Me_3COLi} \tag{22}$$

$$\mathbf{11}\mathrm{ + Me_3COOLi \rightarrow \underset{(\mathbf{12})}{ClMe_2SiOSiMe_2(OOCMe_3)} + LiCl} \tag{23}$$

$$\mathbf{12}\mathrm{ + Me_3COOLi \rightarrow (Me_3COO)Me_2SiOSiMe_2(OOCMe_3) + LiCl} \tag{24}$$

Thus, the results obtained point to the fact that monochloropolysilanes, in the reaction with Me_3COOLi, show a higher reactivity towards oxidation than in nucleophilic substitution. In contrast, dichloro-substituted disilane is more active in the nucleophilic substitution reaction. This is also confirmed by the kinetic results obtained for the reaction of various chlorosilanes with lithium trimethylsilanolate. This reaction is of the second-order, being first-order in each reactant. The results are given in Table 1. The general tendency observed, consisting of an increase in reaction rate with increasing total negative inductive effect of the substituents at the silicon atom, is in accordance with S_N2 reactions. From the k values it follows that monochloropolysilanes show very low reactivity in the reaction with lithium trimethylsilanolate compared with chlorosilanes and chlorosiloxanes. The highest reactivity in this reaction for all of the organosilicon compounds studied by us is exhibited by 1,2-dichlorotetramethyldisilane.

III. Reactions of organochloropolysilanes with lithium (t-butylperoxy)carbonate

The interaction of organochloropolysilanes with t-butylhydroperoxide, or with its lithium salt, does not lead to the formation of peroxidic compounds with a Si–SiOO group in the molecule [6], or such species are formed as unstable intermediate compounds [7,9,12]. It seemed probable that the compounds of this type could be obtained via peroxycarbonates according to reaction 25, as it is known [13], that

$$\mathrm{R_3SiSiR_2OC(O)OOCMe_3 \rightarrow R_3SiSiR_2OOCMe_3 + CO_2} \tag{25}$$

silicon-containing carbonates are unstable compounds at higher temperatures and

TABLE 1

THE RATE CONSTANTS FOR REACTIONS OF ORGANOCHLOROPOLYSILANES WITH Me_3SiOLi AT 20 °C IN BENZENE/ETHER [11]

Chlorosilanes	$\Sigma\sigma^*$ [a]	$k \times 10^3$ ($l\ mol^{-1}\ min^{-1}$)	Chlorosilanes	$\Sigma\sigma^*$	$k \times 10^3$ ($l\ mol^{-1}\ min^{-1}$)
$(Me_3Si)_2SiMeCl$	−1.44	$\ll 1$ [b]	$Me_3SiSiMeCl_2$	+2.18	5300
$Me_3SiSiMe_2SiMe_2Cl$		1	$ClMe_2SiSiMe_2Cl$	+0.32	8700
$Me_3SiSiMe_2Cl$	−0.72	10	$Me_3SiOSiMe_2SiMe_2Cl$		300
$n\text{-}BuMe_2SiSiMe_2Cl$		4	$Me_3SiSiMe_2OSiMe_2Cl$		1360
$PhMe_2SiSiMe_2Cl$		9	$Me_3SiOSiMe_2Cl$		5300
$Me_3SiSiMePhCl$	−0.12	20	$(Me_3SiO)_2SiMeCl$		270
Me_3SiCl	0.00	150	$n\text{-}BuMe_2SiOSiMe_2Cl$		1360
$PhMe_2SiCl$	+0.60	480	$PhMe_2SiOSiMe_2Cl$		2000
			$Me_3SiOSiMePhCl$		700

[a] The sum ($\Sigma\sigma^*$) of the Taft inductive constants of the three substituents bonded to the fragment $\geqslant$Si–Cl. [b] 2-Trimethylsiloxyheptamethyltrisilane is not detectable in the reaction mixture after 48 h.

TABLE 2

THE SILICON-CONTAINING PRODUCTS OF THE REACTIONS OF ORGANOCHLOROPOLYSILANES, $RMe_2SiSiMe_2Cl$, WITH LITHIUM (t-BUTYLPEROXY)CARBONATE AT 20–25 °C IN HEXANE

R	Mol ratio $\frac{RMe_2SiSiMe_2Cl}{Me_3COOC(O)OLi}$	Time (h)	Composition of reaction mixture (mol%)					
			$RSiOSiOOCMe_3$	$RSiOSiOCMe_3$	RSiSiCl	RSiOSiCl	$RSiSiOC(O)OCMe_3$	$RSiOSiOC(O)OCMe_3$
Me	1/1	200	15	53	31	1		
	1/2	200	23	74			0.5	2.5
n-Bu	1/1	71	13	23	36	28		
	1/2	46	19	41	25	15		
	1/4	27	19	71	3	7		
Me_3Si	1/2	240	35	65				
	1/3	240	29	71				

decompose according to the equation:

$$\mathrm{R_3SiOC(O)OR} \rightarrow \mathrm{R_3SiOR} + \mathrm{CO_2} \tag{26}$$

However, information on organosilicon peroxycarbonates is absent from the literature. With the aim of the synthesis of these compounds, the reactions of organochlorosilanes with lithium (t-butylperoxy)carbonate have been studied [14].

Lithium (t-butylperoxy)carbonate was obtained in 98% yield, according to the procedure proposed for the synthesis of lithium, sodium, and potassium (cumylperoxy)carbonates [15]:

$$\mathrm{Me_3COOLi} + \mathrm{CO_2} \rightarrow \mathrm{Me_3COOC(O)OLi} \tag{27}$$

Lithium (t-butylperoxy)carbonate is insoluble in ether, hexane or benzene; it is stable at room temperature and it decomposes slowly at 70 °C.

Organochlorosilanes, $\mathrm{RMe_2SiCl}$ (R = n-Bu, $\mathrm{Me_5Si_2O}$, n-$\mathrm{BuMe_2SiO}$) react with the peroxycarbonate in hexane (benzene) at 20 °C to give $\mathrm{CO_2}$ and the $\mathrm{RMe_2SiOOCMe_3}$ peroxide as the main products. These reactions proceed slowly. A quantitative yield of the products is obtained only after the reaction mixture has been stirred for several days. The reaction proceeds in accordance with eq. 28, via intermediate formation of the unstable (t-butylperoxy)carbonate **13**:

$$\mathrm{RMe_2SiCl} + \mathrm{Me_3COOC(O)OLi} \rightarrow \underset{(\mathbf{13})}{\mathrm{RMe_2SiOC(O)OOCMe_3}} + \mathrm{LiCl} \tag{28}$$

$$\mathbf{13} \rightarrow \mathrm{RMe_2SiOOCMe_3} + \mathrm{CO_2}$$

The reaction of chloro-di- and -tri-silanes with lithium (t-butylperoxy)carbonate is more complex. In these cases the final products of the reactions, under the condition of prolonged stirring of the reaction mixture and an excess of the peroxycarbonate, are $\mathrm{CO_2}$, the t-butoxysiloxane, **14**, and the t-butylperoxysiloxane, **15** (see Table 2 and Fig. 5).

It is possible that the compound **14** is formed in two independent ways, as represented by eqs. 29–30 and 31–33.

$$\mathrm{RMe_2SiSiMe_2Cl} + \mathrm{Me_3COOC(O)OLi} \rightarrow \mathrm{RMe_2SiSiMe_2OC(O)OOCMe_3} + \mathrm{LiCl} \tag{29}$$

$$\mathrm{RMe_2SiSiMe_2OC(O)OOCMe_3} \rightarrow \mathrm{CO_2} + \underset{\substack{\downarrow \\ \mathrm{RMe_2SiOSiMe_2OCMe_3} \\ (\mathbf{14})}}{\mathrm{RMe_2SiSiMe_2OOCMe_3}} \tag{30}$$

$$\mathrm{RMe_2SiSiMe_2Cl} + \mathrm{Me_3COOC(O)OLi} \rightarrow \mathrm{RMe_2SiOSiMe_2Cl} + \mathrm{Me_3COC(O)OLi} \tag{31}$$

$$\mathrm{RMe_2SiOSiMe_2Cl} + \mathrm{Me_3COC(O)OLi} \rightarrow \mathrm{RMe_2SiOSiMe_2OC(O)OCMe_3} + \mathrm{LiCl} \tag{32}$$

$$\downarrow \tag{33}$$

$$\underset{(\mathbf{14})}{\mathrm{CO_2} + \mathrm{RMe_2SiOSiMe_2OCMe_3}}$$

However, under the conditions of the experiment, from these reactions (eqs. 31–33) only one reaction (eq. 31) proceeds. This is confirmed by the presence of the chlorodisiloxane in, and the absence of the siloxanecarbonate from, the reaction mixture. The latter is a stable compound and does not decomposed at room temperature to the t-butoxydisiloxane **14** according to eq. 33. Therefore, the t-butoxydisiloxane **14** continues in the sequence of reactions 29–30. The chlorodisiloxane formed, enters into reaction with $Me_3COOC(O)OLi$, yielding the unstable siloxanylperoxycarbonate, which is transformed into the siloxane peroxide **15** (eq. 34).

$$\begin{array}{l} RMe_2SiOSiMe_2Cl + Me_3COOC(O)OLi \rightarrow \\ \quad RMe_2SiOSiMe_2OC(O)OOCMe_3 + LiCl \\ \qquad\qquad \downarrow \\ \quad RMe_2SiOSiMe_2OOCMe_3 + CO_2 \\ \qquad\qquad (\mathbf{15}) \end{array} \qquad (34)$$

Judging by the total content of the chlorodisiloxane and the siloxane peroxide **15** in the reaction mixture oxidation of the Si–Si bond (eq. 31) proceeds to 20–40%.

Similarly, 1-chloroheptamethyltrisilane reacts with lithium(t-butylperoxy)-carbonate, that is, the reaction described by eqs. 29–30, for approximately 70%, while oxidation of an Si–Si bond in the initial trisilane proceeds for 30% (eq. 35).

$$Me_3SiSiMe_2SiMe_2Cl + Me_3COOC(O)OLi \rightarrow Me_3SiSiMe_2OSiMe_2Cl + Me_3COC(O)OLi \qquad (35)$$

Moreover, the Si–Si bond located in the α-position to the chlorine atom is oxidized first. The Si–Si bond in alkoxydisilanes is not oxidized by lithium (t-butylperoxy)carbonate. So the mixture of 1,2-di(t-butoxy)tetramethyldisilane with an excess of $Me_3COOC(O)OLi$ in benzene at 20 °C for 25 days has not resulted in the formation of 1,3-di(t-butoxy)tetramethyldisiloxane.

Thus, if the initial stage of the reaction of organochloro-di- and -tri-silanes with lithium t-butyl peroxide is the oxidation of the Si–Si bond, and the nucleophilic substitution reaction of the Si–Cl bond is practically unobserved, lithium (t-butylperoxy)carbonate enters chiefly into nucleophilic substitution reaction with chloropolysilanes and oxidation of the Si–Si bond proceeds to approximately 30%. This leads to the presence in the reaction mixture of the t-butoxysiloxane **14**, which is formed as a result of rearrangement of the intermediate peroxide with the Si–Si–OO group in the molecule.

It was of interest to study the reactivity of chloropolysilanes in the oxidation

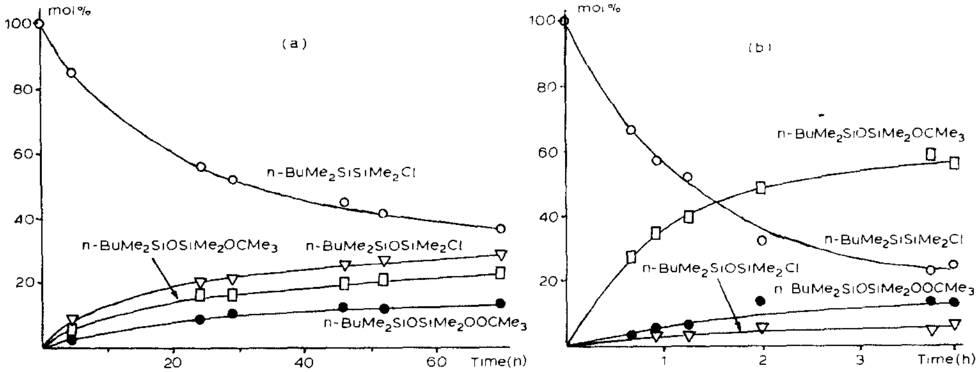


Fig. 5. Kinetic curves for the consumption of substrate and accumulation of the organosilicon products in the reaction of 1-n-butyl-2-chlorotetramethyldisilane with an equimolar quantity (a), or a four-fold excess (b), of lithium (t-butylperoxy)carbonate (hexane, 20 °C), $[n\text{-}BuMe_2SiSiMe_2Cl]_0$ 0.15 mol l^{-1}).

reaction in more detail. Therefore, the kinetics of the reactions of chloropolysilanes with peroxybenzoic acid have been studied.

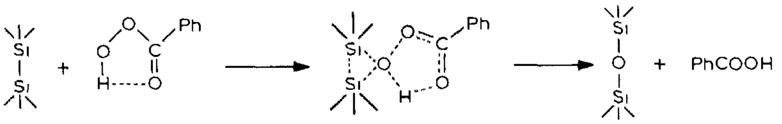
IV. The interaction of organochloropolysilanes with peroxybenzoic acid

The oxidation of some linear and cyclic organodisilanes by peroxy acids has been studied by Kumada and Sakurai [1–5,16].

Hexamethyldisilane and pentamethylphenyldisilane react slowly with peroxybenzoic acid (PBA) in dichloromethane [1]. The only products of this reaction are an acid and the corresponding siloxane. To determine the oxidation mechanism of organodisilanes Kumada and Sakurai studied the kinetics of reaction of *m*- and *p*-substituted phenyldisilanes, of the general formula $X{-}C_6H_4SiMe_2SiMe_3$ (X = Me, OMe, Cl), as well as of hexamethyldisilane with PBA, and found that the reaction is of the second-order, being first-order in each reactant. Electron-donating groups in the substituted pentamethylphenyldisilanes increased the reaction rate and a satisfactory correlation of log k vs. σ^+ was found. The reaction constant value, $\rho = -0.29$ characterizes the disilane and the peroxy acid as the nucleophilic and electrophilic reagents, respectively.

The authors proposed a mechanism, comprising electrophilic attack by an oxygen atom of the peroxybenzoic acid at the Si–Si bond (eq. 36), which is analogous to the mechanism previously suggested by Bartlett [17].

However, Kumada and Tamao [18] do not rule out the possibility of disilane



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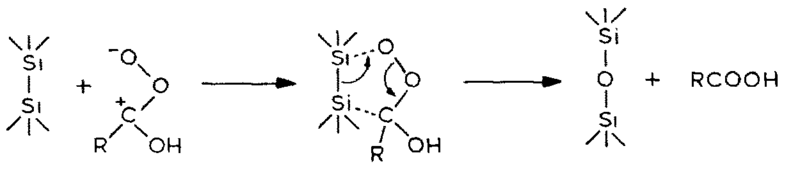
oxidation proceeding according to the mechanism of Kwart for the epoxidation of olefins [19]. According to this mechanism, peroxybenzoic acid reacts with the olefin as a 1,3-dipole:



(37)

It is probable that an electronegative substituent X in the organopolysilanes $R_3Si(SiR_2)_nX$ should decrease the oxidation rate of the Si–Si bond. However, we observed an opposite effect [11], for chloro-, bromo-, alkoxy- and benzoyloxy-disilanes are oxidized by peroxybenzoic acid more readily than are peralkylated disilanes. Octamethyltrisilane is also oxidized more slowly than its derivatives containing a halogen substituent (Table 3). In Figs. 6 and 7, kinetic curves of the consumption of substrate and the accumulation of oxidation products of the two isomeric compounds 1- and 2-chloroheptamethyltrisilanes are given. The character of these curves demonstrates that these reactions correspond to consecutive-parallel processes and begin with the oxidation of one Si–Si bond. The oxidation of the second Si–Si bond proceeds at a markedly slower rate. It was found that the Si–Si

TABLE 3

RATE CONSTANTS FOR REACTIONS OF ORGANOPOLYSILANES WITH PEROXYBENZOIC ACID AT 20 °C IN HEXANE (AT 35 °C IN BENZENE)[a]

Polysilane	$k \times 10^3$ ($l\ mol^{-1}\ min^{-1}$)	Polysilane	$k \times 10^3$ ($l\ mol^{-1}\ min^{-1}$)
$Me_3SiSiMe_3$	8	$ClMe_2SiSiMe_2Cl$	150
$n\text{-}BuMe_2SiSiMe_3$	6	$Me_3SiSiMeCl_2$	40
$n\text{-}BuMe_2SiSiMe_2(Bu\text{-}n)$	5	$Me_3SiSiMe_2OEt$	60
$Me_3SiSiMe_2Cl$	280	$Me_3SiSiMe_2OCMe_3$	(100)
$n\text{-}BuMe_2SiSiMe_2Cl$	150	$(Me_3CO)Me_2SiSiMe_2(OCMe_3)$	(130)
$s\text{-}BuMe_2SiSiMe_2Cl$	180	$Me_3SiSiMe_2OSiMe_2SiMe_3$	(340)
$PhMe_2SiSiMe_2Cl$	90	$Me_3SiOSiMe_2SiMe_3$	(190)
$Me_3SiSiMePhCl$	80	$Me_3SiOSiMe_2SiMe_2OSiMe_3$	(370)
$(Me_3Si)_2SiMeCl$	740	$Me_3SiSiMe_2OSiMe_2OSiMe_3$	(120)
$Me_3SiSiMe_2SiMe_2Cl$	420	$Me_3SiSiMe_2SiMe_2OSiMe_3$	(150)
$Me_3SiSiMe(Cl)OSiMe_3$	120	$Me_3SiSiMe_2SiMe_2SiMe_3$	(75)
$Me_3SiOSiMe_2SiMe_2Cl$	1240	$Me_3SiSiMe_2SiMe_3$	(54)
$Me_3SiSiMe_2OSiMe_2Cl$	60	$Me_3SiSiMe_2OC(O)Ph$	(510)

[a] The values of the oxidation constant for the first Si–Si bond are given for compounds containing two or more Si–Si bonds.

bond situated in the α-position relative to the chlorine atom [20] in 1-chloroheptamethyltrisilane is oxidized first.

$$Me_3SiSiMe_2SiMe_2Cl \xrightarrow{PhCO_3H,\ k_1} Me_3SiSiMe_2OSiMe_2Cl \xrightarrow{PhCO_3H,\ k_2} Me_3SiOSiMe_2OSiMe_2Cl \qquad k_1 > k_2 \qquad (38)$$

The particular characteristic of the compounds studied is the presence of the

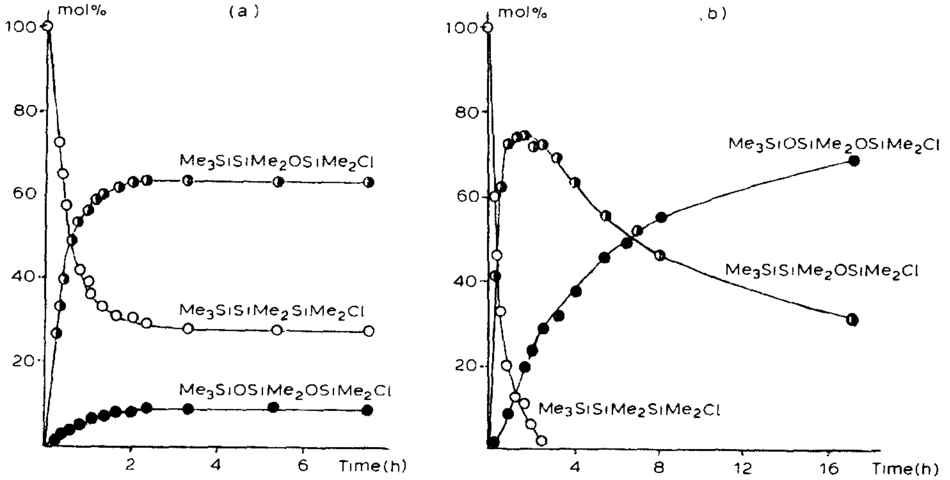
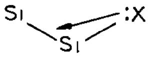


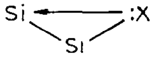
Fig. 6. Kinetic curves for the consumption of substrate and accumulation of the organosilicon products in the reaction of 1-chloroheptamethyltrisilane with an equimolar quantity ($[Me_3SiSiMe_2SiMe_2Cl]_0$ 0.08 mol l^{-1}) (a) or a double excess ($[Me_3SiSiMe_2SiMe_2Cl]_0$ 0.04 mol l^{-1}) (b) of peroxybenzoic acid (hexane, 20 °C).

Si–Si fragment conjugated with *n*-donor substituents. It is known that the silicon–silicon bond is more easily polarized than the σ(C–C) coupling in alkanes, in consequence of this the Si–Si bond is more reactive [21,22]. In some properties the Si–Si bond may be more successfully compared with the multiple C–C than with a σ(C–C) bond. This is indicated by the chemical behaviour of organopolysilanes, as well as by their UV spectra [23,24]. A number of interesting properties of polysilanes was found in studies of the UV, NMR and photoelectron spectra of these compounds. Among them, might be pointed out the chromophoric properties of the polysilane chain, the transfer of electronic effects with low fading via a chain of two–six silicon atoms [27], the ability of Si–Si bonds to enter into conjugation with π-electronic systems, as well as with free electron pairs of some substituents [28–37].

Taking into account the foregoing, it can be said that one of the reasons for the enhanced reactivity of chloro(alkoxy)polysilanes in the reaction with peroxybenzoic acid might be various intramolecular interactions, leading to enhancement of the nucleophilic properties of the Si–Si bond; for example, such as *n*,σ-conjugation (**A**) and intramolecular coordination (**B**):



(A)



(B)

Mechanism **B** presupposes the shift of a free electron pair of the X atom to a vacant *d*-orbital of the silicon atom. Intramolecular electronic effects in the derivatives of silane and germane have been studied and discussed in refs. 38–46.

To prove the presence or absence of intramolecular coordination in alkylchlorodisilanes, 1-chloro-2-hydrotetramethyldisilane has been studied [10] by the method developed by Egorochkin et al. [47,48].

This compound is chosen as a model because the modes of the Si–H vibration are highly characteristic. Therefore, the frequency and integrated intensity of the ν(Si–H) band is determined almost exclusively by the electronic effects of the substituents

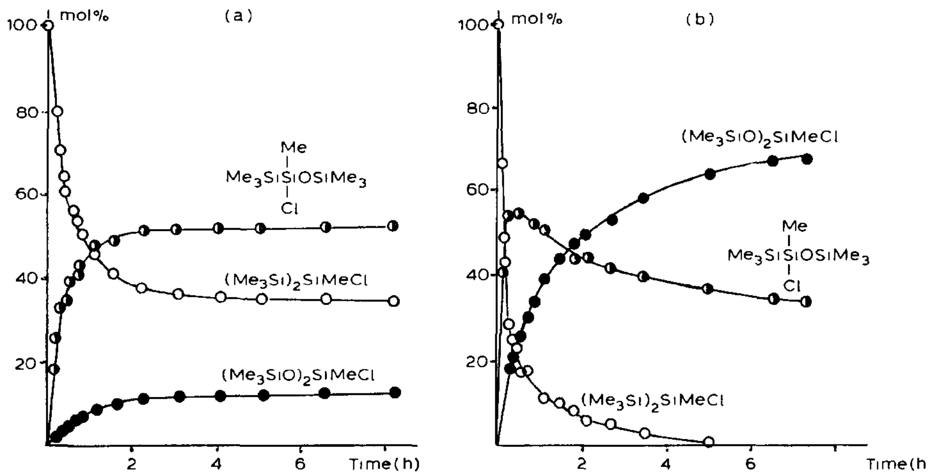


Fig. 7. Kinetic curves for the consumption of substrate and accumulation of the organosilicon products in the reaction of 2-chloroheptamethyltrisilane with an equimolar quantity ($[(Me_3Si)_2SiMeCl]_0$ 0.07 mol l^{-1}) (a) or a double excess ($[(Me_3Si)_2SiMeCl]_0$ 0.06 mol l^{-1}) (b) of peroxybenzoic acid (hexane, 20 °C).

bound to the Si atom; indeed the frequency and intensity of the ν(Si–H) band appear to be the sole sources of data on the electronic effects of the substituents in organosilicon compounds. The data thus obtained indicate that the Me_2SiCl fragment, besides inductive $-I$-effect, shows electron-donor properties and that about 50% of chlorotetramethyldisilane molecules contribute to intramolecular coordination.

Thus, the observed acceleration of the oxidation rate may be due to the availability of n,σ-conjugation or to intramolecular coordination in substituted polysilanes. Such effects may lead to increasing energy of the highest occupied molecular orbital (HOMO) of the polysilane and so enhancing its donor-ability towards electrophilic reagents. It is known, for example, that the first ionization potential (I_1^D) is decreased on substitution of methyl group by RO in hexamethyldisilane [49].

Me_6Si_2	8.69 eV
$(MeO)SiMe_2SiMe_3$	8.60 eV
$(PhO)SiMe_2SiMe_3$	8.36 eV
$MeOC_6H_4OSiMe_2SiMe_3$	7.76 eV

To obtain some information about the energy change of the HOMO of polysilanes, which, as it known [28,50], is localized at the Si–Si bond, the charge-transfer complexes of tetracyanoethylene (TCE) with some peralkylated and chloro-substituted polysilanes (Table 4) were studied [51]. Charge-transfer complexes of organopolysilanes with TCE were studied earlier [36,49,52–54], and a linear correla-

TABLE 4

CHARGE TRANSFER FREQUENCIES (ν_{CT}), FIRST IONIZATION POTENTIALS (I_1^D), STABILITY CONSTANTS OF THE COMPLEXES (K_{ST}), AND ENTHALPY OF FORMATION (ΔH) OF THE COMPLEXES OF ORGANOPOLYSILANES WITH TETRACYANOETHYLENE, AND THE RATE CONSTANTS (k) FOR THE REACTION OF ORGANOPOLYSILANES WITH PEROXYBENZOIC ACID

Polysilane	$\nu_{CT}\times10^{-3}$ (cm^{-1})	I_1^D (eV)		K_{ST} [c] (l mol^{-1})	ΔH (kcal mol^{-1})	$k\times10^3$ [d] (l mol^{-1} min^{-1})
		Calcd. [a]	Lit. [b]			
$Me_3SiSiMe_3$	23.8	8.68	8.69			8 (25)
n-$BuMe_2SiSiMe_3$	23.3	8.57		0.15 ± 0.05	2	6
n-$BuMe_2SiSiMe_2$(Bu-n)	22.6	8.45		0.20 ± 0.15	3	5
$Et_3SiSiEt_3$	21.7	8.31		0.03 ± 0.03	2	
$Me_3SiSiMe_2SiMe_3$	21.1	8.19	8.19			(54)
$Me_3Si(SiMe_2)_2SiMe_3$	19.2	7.90	7.98			(75)
$Me_3SiSiMe_2Cl$	26.5	9.08				280 (330)
n-$BuMe_2SiSiMe_2Cl$	26.3	9.05		0.10 ± 0.10	2	150
s-$BuMe_2SiSiMe_2Cl$	26.3	9.05				180
$Me_3SiSiMe_2SiMe_2Cl$	23.8	8.65				420
$(Me_3Si)_2SiMeCl$	22.1	8.37	8.42			740
$ClMe_2SiSiMe_2Cl$	29.0	9.48				150
$Me_3SiSiMeCl_2$	28.8	9.48				40

[a] The first ionization potential values were calculated from the linear correlation between I_1^D and ν_{CT}, accordingly to ref. 53. [b] Ref. 28. [c] For the other compounds the values of K_{ST} are nearly zero and these cannot be calculated exactly because of the negative values of $1/\epsilon$ in the Benesi-Hildebrant equation [75]. [d] The rate constants of the reaction of organopolysilanes with peroxybenzoic acid at 20 °C in hexane (at 35 °C in benzene).

tion of the ionization potentials with charge-transfer frequencies (ν_{CT}) was found. Some additional characteristics of formation of these complexes were established [51]. For example, peralkylated polysilanes and organochloropolysilanes form weak complexes with TCE of the contact type, with stability constants (K_{ST}) equal to 0.2 l mol^{-1} or less; the ΔH values of such complexes do not exceed 3 kcal mol^{-1}. When passing from peralkylated polysilanes to chloro-substituted polysilanes, a considerable decrease of polysilane HOMO energy occurs, resulting in an increase of the charge-transfer frequency and hence to increasing the first ionization potential values of chloropolysilanes, and indicating a substantial decrease of the Si–Si bond-donor property. A further decrease of HOMO energy occurs upon introduction of the second chlorine atom into the molecule.

From a comparison of the charge-transfer frequencies, or I_1^D-values, with the oxidation rate constants (k) (Table 4), it follows that, in spite of the considerable increase of I_1^D-values when passing from permethylated-polysilanes to chloropolysilanes, the rate constant of the latter is the larger. However, it might be pointed out that in the series of permethylated-polysilanes, as well as in the chloropolysilane series, there is a tendency towards a slowing down of reaction with increasing I_1^D-values (Fig. 8). An approximately linear correlation of ln k with charge-transfer frequencies is observed for each of these series:

$$\ln k = -(0.24 \pm 0.03) \times 10^{-3}\, \nu_{CT} + (2.11 \pm 0.66) \quad (n = 3, r = 0.992)$$

$$\ln k = -(0.32 \pm 0.08) \times 10^{-3}\, \nu_{CT} + (6.85 \pm 2.02) \quad (n = 7, r = 0.883)$$

All this indicates that in the process of the oxidation of Si–Si bonds by a peroxy acid, the formation of charge-transfer complexes, analogous to the σ,π-type of complex studied with TCE, may take place. But this is not the only factor determining the oxidation rate.

Thus, considering the oxidation reactions of Si–Si bonds in terms of the mechanism proposed in refs. 1, 16 does not provide an explanation for the increase of the reaction rate on the introduction of a chlorine atom or RO group into a polysilane

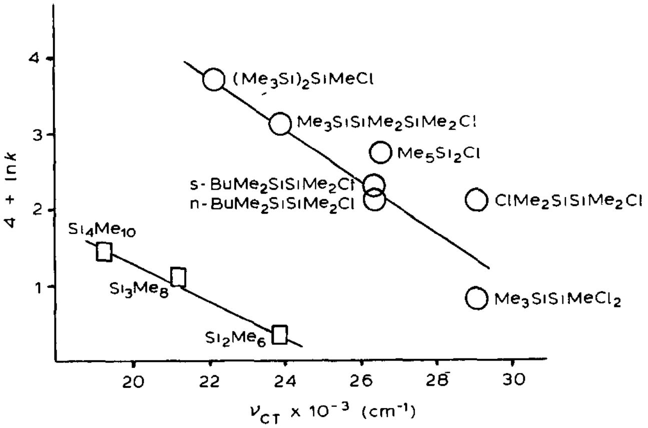
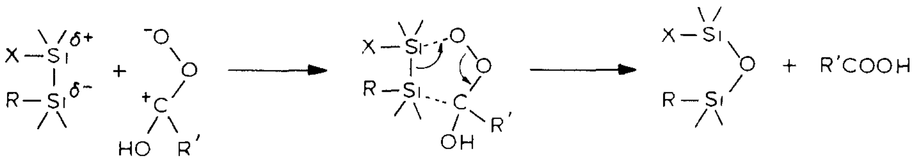


Fig. 8. Relationship between the logarithm of the rate constant for the oxidation of organochloropolysilanes (○) and permethylated-polysilanes (□) with peroxybenzoic acid and the charge-transfer frequency of the polysilane–TCE-complex.

molecule. Perhaps this fact may be explained by the Kwart mechanism proposed for olefin epoxidation [19], which has recently gained considerable support [55]. The interaction with the disilane may be represented as a 1,3-bipolar cycloaddition with participation of the Si–Si bond [18]:



The presence of X substituents (Cl or OR) results in a positive charge at the silicon atom in the fragment $\geqslant\mathrm{Si}^{\delta+}{-}\mathrm{X}^{\delta-}$, which may promote coordination of the silicon atom with the nucleophilic center of the peroxy acid. From the other side, donor-substituents R will enhance the nucleophilic ability of the other silicon atom, which coordinates with the electrophilic center of the peroxy acid.

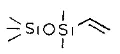
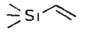
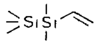
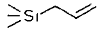
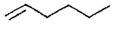
There are few data at the present time on the oxidation of substituted polysilanes, therefore it is impossible to suggest an adequately reasonable oxidation mechanism or to give preference to one of the mechanisms cited above, taken from the chemistry of carbon.

Dixon et al. reported recently on the oxidation of vinyl- and allyl-pentamethyldisilanes with *m*-chloroperoxybenzoic acid [56]. The results obtained enable one to compare the relative reactivities towards oxidation of adjacent and isolated C=C and Si–Si bonds, as well as to estimate their mutual influence. The data represented in Table 5 show that the introduction of a silicon atom into an unsaturated compound exercises a deactivating influence upon the ability of the C=C bond towards oxidation. The C=C bond in pentamethylvinyldisilane, judging from the products, is oxidized more readily than the Si–Si bond, whereas these bonds in allylpentamethyldisilane are oxidized at comparable rates.

The regularities observed in the change of oxidation reaction rate may be explained in terms of the inductive effect of the $\mathrm{Me_3SiOSiMe_2}$–, $\mathrm{Me_3Si}$–, $\mathrm{Me_5Si_2}$–, $\mathrm{Me_3SiCH_2}$–, and $\mathrm{CH_3CH_2CH_2}$– groups, as well as d_π–p_π and σ,π-conjugation effects [57–61]. It is known [57] that the $\mathrm{R_3Si}$– group in vinylsilanes, $\mathrm{R_3SiCH{=}CH_2}$, exhibits an acceptor-conjugative effect consisting of the shift of the π-electron density of the C–C double bond to the silicon atom. In contrast, in allyltrimethylsi-

TABLE 5

RELATIVE RATE OF OXIDATION OF C=C BONDS WITH *m*-CHLOROPEROXYBENZOIC ACID [56]

Olefin	Relative rate
	1
	2.1
	5.6
	13.0
	29.0

lane, the $-CH{=}CH_2$ fragment is enriched in electron density by the σ,π-conjugation mechanism. Therefore allyltrimethylsilane is oxidized more readily than trimethylvinylsilane. A pentamethyldisilanyl group joined to an ethylene bond may take part in 2 oppositely directed conjugation effects with the C–C double bond. The first effect (acceptor) involves d_π–p_π interaction, and the second effect (donor) involves σ,π-conjugation with participation of the easily-polarized Si–Si bond. From the data reported in ref. 57, the second effect dominates; that is, the Me_5Si_2 group shows an overall donor effect. As distinct from this, the Me_3SiCH_2 group exhibits only σ,π-conjugation and therefore shows a better donor ability than the Me_5Si_2 group. This is why $Me_5Si_2CH{=}CH_2$ is oxidized more readily than $Me_3SiCH{=}CH_2$, but more slowly than $Me_3SiCH_2CH{=}CH_2$.

Reactions of peralkylated- and chloro-polysilanes with peroxybenzoic acid are not accompanied by oxidative cleavage of the Si–C bond. However, R_3SiCl (R = alkyl, aryl) in the presence of bases, reacts with peroxy acids, forming (acyl)alkoxysilanes [62]. Kumada et al. [63] reported recently on the oxidation of Si–C bonds in organofluorosilanes. All of the Si–C bonds in these compounds are cleaved by *m*-chloroperoxybenzoic acid in dimethylformamide, to give the corresponding alcohols in high yield.

The proposed mechanism involves formation of an intermediate with a hexacoordinated silicon atom in which organic group, due to the high polarity of the Si–C bond, migrates from the silicon atom to the oxygen atom of the *m*-chloroperoxybenzoic acid.

V. Oxidation of cyclic organopolysilanes with peroxybenzoic acid

There is fairly limited information in the literature on the reactions of cyclic organopolysilanes with peroxy acids. However, the main factors determining the reactivity of these compounds in oxidation reactions are: ring size, the substituents attached to the silicon, steric factors and the nature of the heteroatoms included in the ring.

It is believed that the reactions with peroxybenzoic acid proceed by an electrophilic oxidation mechanism similar to that of olefin epoxidation [3–5,16,64].

The considerable ring strain in cyclotetrasilanes leads to the high sensitivity of these compounds to oxidizing agents, in contrast to the analogous five–six-membered cyclic compounds [65,66]. 1,2,3,4-Tetra-t-butyltetramethylcyclotetrasilane obtained by Biernbaum and West [67] appeared to be stable to oxygen. The authors explained this as due to the influence of the bulky t-butyl-substituents blocking the silicon atoms from reagent action.

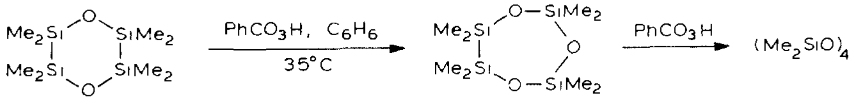
All four Si–Si bonds are oxidized with *m*-chloroperoxybenzoic acid, but at different rates [64].

$$(\text{t-BuMeSi})_4 \xrightarrow{k_1} (\text{t-BuMeSi})_4O \xrightarrow{k_2} (\text{t-BuMeSi})_4O_2 \xrightarrow{k_3} (\text{t-BuMeSi})_4O_3 \xrightarrow{k_4} (\text{t-BuMeSiO})_4 \qquad (39)$$

This reaction is rigorously stereospecific. The oxygen in the ring activates adjacent Si–Si bonds towards oxidation, but the dominating factor is the ring strain, which is why $k_1 > k_2 > k_3$; the Si–Si bond situated between *cis*-substituents is oxidized most easily. The product with three oxidized Si–Si bonds, $(t\text{-BuMeSi})_4O_3$, does not accumulate in the reaction mixture because it is readily oxidized to the tetrasiloxane (i.e. $k_4 \gg k_3$).

Six-membered cyclic compounds, containing from one to six silicon–silicon bonds in the molecule are mostly inert to oxygen [18,68–72]. For example, dodecamethylcyclohexasilane is practically unoxidized with atmospheric oxygen and by 30% hydrogen peroxide [73]. The reaction of this compound with peroxybenzoic acid, carried out in benzene at 35 °C, leads to the formation of a mixture of siloxane products [74]. It is found that the oxidation reaction constant for the first Si–Si bond in dodecamethylcyclohexasilane is ~ 0.16 l mol^{-1} min^{-1}, which is greater than twice the oxidation rate of an Si–Si bond in linear decamethyltetrasilane (Table 3) [74].

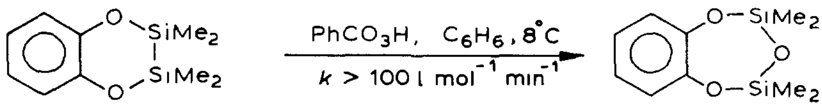
A sharp increase of the oxidation rate of an Si–Si bond occurs when the two oxygen atoms in a six-membered ring are arranged symmetrically between two Si–Si bonds (eq. 40). Octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane reacts with peroxybenzoic acid 60 times faster than permethylated cyclohexasilane. The reaction begins with the oxidation of one Si–Si bond and represents a consecutive-parallel process. The rate constant values for the first and second stages of the process are 9.3 and 1.3 l mol^{-1} min^{-1}, respectively [74].



(16)

(40)

Consequently, in the compound **16** the first Si–Si bond is oxidized more easily than the second one. The Si–Si bond in 5,6-benzo-2,2,3,3-tetramethyl-1,4-dioxa-2,3-disilacyclohexane, **17**, shows higher reactivity to oxidation [74]. This compound is sensitive to atmospheric oxygen. Reaction of the compound **17** with peroxybenzoic acid proceeds at a considerable higher rate than that of compound **18**.



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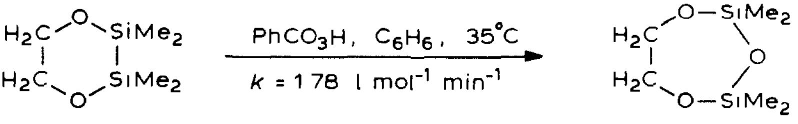

(18)

The results obtained on the oxidation of six-membered silane rings with peroxybenzoic acid demonstrate the activating action of adjacent oxygen atoms and of the π-system of an aromatic ring upon reacting Si–Si bond.

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