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Journal of Organometallic Chemistry 613 (2000) 170–176

Electrochemical oxygenation of diorganyldichlorosilanes: a novel route to generation of diorganylsilanones

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Received 1 March 2000; received in revised form 28 June 2000

Abstract

Interaction of diorganyldichlorosilanes R_2SiCl_2 (R = Me, Et, Ph) with superoxide or peroxide anions, produced in situ by electroreduction of molecular oxygen, provides short-living diorganylsilanones $R_2Si{=}O$. The latter undergo cyclization to give lower perorganylcyclosiloxanes $(R_2SiO)_n$, $n = 3$ or 4 and then insert to the molecules of these primary products to form higher cyclic oligomers. When the process is carried out in the presence of a reagent-trap for silanones (hexamethyldisiloxane, hexamethylcyclotrisiloxane), the products of insertion of diorganylsilanones into the molecule-traps ($Me_3Si(OSiR_2)_nOSiMe_3$ with $n \geq 1$, and $(Me_2SiO)_3(R_2SiO)_m$ with $m \geq 1$, respectively) were obtained. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Diorganylsilanones; Dialkyldichlorosilanes; Diaryldichlorosilanes; Superoxide anion; Electrosynthesis

1. Introduction

Silanones, very labile compounds of silicon, are key intermediates in the reactions of silicon organic compounds containing a Si–O siloxane bond [1–10]. As individual compounds, diorganylsilanones $R_2Si{=}O$ were only observed in a Ne or Ar matrix when their IR spectra were registered [4–6,8]. These compounds are of great theoretical (as compounds of a three-coordinated silicon with a double bond silicon–element) and practical (as precursors of various siloxane structures) interest as well.

Reactions in which the formation of diorganylsilanones is practically undoubted, are processes of thermal (400–800°C) [11–20] or photochemical [1–10,21–23] destruction of many silicon organic compounds containing the Si–O bond. During recent years, Voronkov developed a conception, according to which silanones are generally produced as a result of a geminal cleavage (the α-elimination) of organic compounds containing a Si(OR)X group [9,10,24] as depicted by the following scheme:

$$>Si(OR)X \rightarrow >Si{=}O + RX \qquad (1)$$

Many low-energetic processes, involving silanones as intermediates, occur according to this scheme at reasonably low temperatures [9,10]. In particular, there are reactions of diorganyldichlorosilanes with DMSO [24–27], with metal oxides [24], with salts of several oxygen-containing acids [28], and also the hydrolysis of R_2SiCl_2 under specific conditions [29]. In these reactions, the formation of diorganylsilanones was proven by using 'traps' (specific reagents able to intercept silanones), e.g. hexamethyldisiloxane. Diorganylsilanones have also been shown to be intermediate products in the reactions of oxidation of silenes and silylenes by some oxygen-containing compounds (DMSO, ketones, epoxydes) [3,30–32], as well as during the photolysis of linear [33] and cyclic perorganyloligosilanes [34] in DMSO. Corresponding silanones were formed in a matrix by the oxidation of hydrosilanes of the formula $Me_{4-n}SiH_n$ ($n = 2$, 4) with either oxygen or ozone at 10–15 K [35–38].

The intermediacy of $Cl_2Si{=}O$ was used to explain the formation of linear and cyclic perchlorosiloxanes in the reaction of $SiCl_4$ with oxygen at 1000°C [39]. The formation of diorganylsilanones was reported during

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PII: S0022-328X(00)00464-2

the thermal decomposition of silylperoxydes $R^1R^2(H)SiOOR^3$ [40], although later the mechanism of this reaction was explained without involving diorganylsilanones [41].

It is to be noted that owing to their extremely high reactivity, diorganylsilanones cannot be observed directly neither in gas phase nor in solutions, so their assistance in various processes of organosilicon compounds is usually inferred retrosynthetically from the formation of the products of their autocyclization or the products of the insertion of $R_2Si{=}O$ intermediates into the molecules of special reagent-traps.

Our preliminary results suggested that diorganylsilanones were probably generated in the reaction of diorganyldichlorosilanes with reduced forms of oxygen formed by the cathodic reduction of molecular oxygen [42].

$$O_2 \xrightarrow{\text{electroreduction}} [O] \xrightarrow[-2Cl^-]{R_2SiCl_2} R_2Si{=}O \quad (2)$$

Pursuing this study, we demonstrated the feasibility of the electrochemical generation of diorganylsilanones and found optimal conditions for this process.

2. Results and discussion

We assumed that the formation of diorganylsilanones might occur in the reaction of diorganyldichlorosilanes with nucleophilic forms of oxygen–superoxide or peroxide anions, according to formal reaction (2). In a solution, molecular oxygen does not react with chlorosilanes. However, the reduced forms of oxygen, being stronger nucleophiles than oxygen itself, can react in nucleophilic substitution reactions to cleave a Si–Cl bond. Both these forms of oxygen are easily produced during the cathodic reduction of O_2 in an appropriate aprotic solvent (DMSO, CH_3CN). The reduction involves two reversible one-electron steps:

$$O_2 \underset{-0.75\text{ V}}{\overset{+e}{\rightleftarrows}} O_2^{-\bullet} \underset{-2\text{ V vs. SCE}}{\overset{+e}{\rightleftarrows}} O_2^{2-} \quad (3)$$

The transfer of the first electron results in a superoxide anion O_2^- which, at a more negative potential, can accept one more electron to give a peroxide anion O_2^{2-} [43–45]. The first step of the reduction of oxygen occurs at substantially less negative potentials than the reduction of chlorosilanes [46] and therefore can be effected in the presence of the latter.

In contrast to voltammetric experiments, when for each reduction step there is a distinct rising signal with a span of 80–100 mV, in large-scale reduction of oxygen on macroelectrodes a usual voltammogram is no longer observed, and a continuous rising current having no distinct half-wave or peak potential is found instead. In addition, when the electrolyses were set at the potentials determined voltammetrically (−0.5 to −1.2 V versus Ag/0.1 M $AgNO_3$), it was impossible to achieve any significant reduction rate of O_2; under these conditions, a real increase of Faradaic current was only observed at potentials lower than −3 V. The effective (applied) potential which assured a perceptible rate of reduction ($I = 30$–90 mA), was even lower, about −3.6 to −3.9 V versus Ag/0.1 M $AgNO_3$. However, the real potential of the working electrode was substantially less negative since no disilane products (which should have been produced from the reduction of chlorosilanes at about −2.5 to −3.2 V) were detected after the electrolysis. The reason for this discrepancy in the behavior of the system in voltammetric and large-scale experiments is the high resistance of the solution. Indeed, much higher current of the electrolysis, and hence larger *iR* drop, makes the real potential of the cathode remarkably less negative than the applied potential. The value of experimentally observed current depends on the applied potential and the oxygen blow-through rate. Since at low potentials O_2 is the only reducible component and its supply rate was maintained constant in the course of the electrolysis, the current practically did not change at any given potential. This allowed us to carry out the electrolyses both in potentiostatic and galvanostatic modes (an average applied current $I = 100$ mA at the electrodes used and blow-through rate 10 ml min^{-1}, or with the potential ranging from −3.5 to −3.7 V), the latter being technically simpler. Given the above mentioned features, along with the fact that the electrochemical properties of the system change as the catholyte saturates with O_2, potentiostatic experiments were not conclusive for distinguishing between electrogenerated forms of reduced oxygen.

The cathodic reduction of oxygen in a system Me_2SiCl_2–THF–Bu_4NBF_4 0.01 M, in an electrochemical cell with separated cathodic and anodic compartments, results in the formation of permethyloligocyclosiloxanes of low molecular mass $(Me_2SiO)_n$ ($n = 3$, 4) in the catholyte. The concentration of these products first increases as the amount of passed electricity increases, and then drops slightly (Fig. 1).

The formation of $(Me_2SiO)_n$ indicates that the interaction of the reduced forms of oxygen with dimethyldichlorosilane involves the intermediate formation of dimethylsilanone. The latter undergoes cyclization to $(Me_2SiO)_3$ and $(Me_2SiO)_4$, and then, as the concentration of these products increases by the end of the electrolysis, the silanone inserts into their Si–O bonds resulting in higher permethylcyclosiloxanes $(Me_2SiO)_n$, $n \geq 5$. The beginning of the process can be presented as follows:

$$O_2 \xrightarrow{+e} O_2^{-\bullet} \xrightarrow{+e} O_2^{2-} \quad (4)$$

$$O_2^{2-} + Me_2SiCl_2 \rightarrow [Me_2Si(O_2)Cl_2]^{2-} \quad (5)$$

In the case if superoxide anion radical acts as the oxygenating reagent, the process leading to the intermediate silanone must include an additional redox step (homogeneous or at the cathode). Then, the reaction schema must be completed by equations:

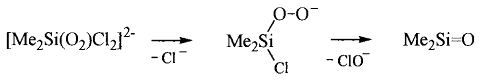
$$O_2^{-\bullet} + Me_2SiCl_2 \rightarrow [Me_2Si(O_2)Cl_2]^{-\bullet} \quad (6)$$

$$[Me_2Si(O_2)Cl_2]^{-\bullet} \xrightarrow{+e} [Me_2Si(O_2)Cl_2]^{2-} \quad (7)$$

or

$$[Me_2Si(O_2)Cl_2]^{-\bullet} \xrightarrow[-Cl^-]{+e} [Me_2Si(O_2)Cl_2]^{-} \quad (8)$$

The place of the second redox step in the total reaction scheme is hard to determine. Indeed, wherever it intervenes, either right after the addition of $O_2^{-\bullet}$ to Me_2SiCl_2 (Eq. (7)) or after the thus formed $[Me_2Si(O_2)Cl_2]^{-\bullet}$ intermediate has lost the first Cl^- anion (Eq. (8)), the overall stochiometry of the process will be the same. Since the potential of the working electrode is not really known, for the reasons discussed above, it is impossible to discriminate between these reaction pathways.



$$[Me_2Si(O_2)Cl_2]^{2-} \xrightarrow[-Cl^-]{} Me_2Si(O\text{-}O^-)Cl \xrightarrow[-ClO^-]{} Me_2Si{=}O \quad (9)$$

$$n\mathrm{Me_2Si{=}O} \rightarrow (\mathrm{Me_2SiO})_n \xrightarrow{m\mathrm{Me_2Si{=}O}} (\mathrm{Me_2SiO})_{n+m}$$

$$n = 3,\ 4;\ m > 1 \quad (10)$$

The nucleophilic attack of superoxide or peroxide anion on Me_2SiCl_2 is thought to proceed via a pentacoodinated transition state.

Towards the end of the electrolysis, a substantial amount of higher permethylcyclosiloxanes $(Me_2SiO)_{n+m}$ ($n + m \geq 5$) was accumulated in the catholyte. Since the hydrolysis of Me_2SiCl_2 by residual water in the solution could, in principle, account for the formation of permethylcyclosiloxanes, the interaction of Me_2SiCl_2 with O_2 was studied under similar conditions but without passing the current. In contrast to what was observed during the electrolysis, it was shown that the formation of cyclic permethylsiloxanes did not occur (Fig. 1). This fact corroborates the formation of these permethylcyclosiloxanes from the electrogenerated $Me_2Si{=}O$. One of the characteristic primary transformations of diorganylsilanones is their cyclooligomerization to $(R_2SiO)_3$. The formation of hexaorganylcyclotrisiloxanes is often considered as a forcible argument for the assistance of diorganylsilanones as intermediates in a given reaction [9,10,24]. For identification of diorganylsilanones, the reaction of their insertion into the M–X bonds (M = Si, Ge, C; X = O, Cl, H etc) is often used [3,9,10,24,47].

To demonstrate the electrogeneration of dimethylsilanone by the formation of the products of its insertion into the Si–O bonds, we carried out an electrolysis of oxygen in the system Me_2SiCl_2–$Me_3SiOSiMe_3$. Hexamethyldisiloxane (HMDS) is traditionally used as a reagent-trap for diorganylsilanones [9,10,24,48]. In addition, HMDS is both chemically and electrochemically inactive under the conditions of the electrolyses, therefore its only possible reaction can be the interaction with the intermediary formed dimethylsilanone. When reducing oxygen in the system Me_2SiCl_2–HMDS in a two-compartment cell, the concentration of hexamethyldisiloxane diminishes linearly with the amount of electricity passed (Fig. 2a). At the same time, linear permethyloligosiloxanes $Me_3Si(OSiMe)_nOSiMe_3$ ($n = 1$, 2) appear in the solution; the concentration of these products increases in the course of the electrolysis.

These results can be rationalized as the dimethylsilanone was formed in this system during the electroreduction and then inserted into the Si–O bond of

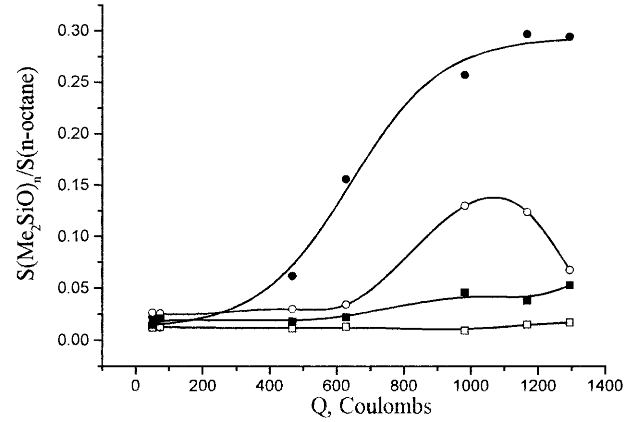


Fig. 1. Variation of the content of low-mass permethyloligocyclosiloxanes (the ratio of GC peak areas of a product and the standard) as a function of the amount of electricity during the electroreduction of O_2 in the system Me_2SiCl_2–THF–Bu_4NBF_4: ● $(Me_2SiO)_3$, ○ $(Me_2SiO)_4$. Variation of the content of permethyloligocyclosiloxanes in the experiment with no current applied: ■ $(Me_2SiO)_3$, □ $(Me_2SiO)_4$.

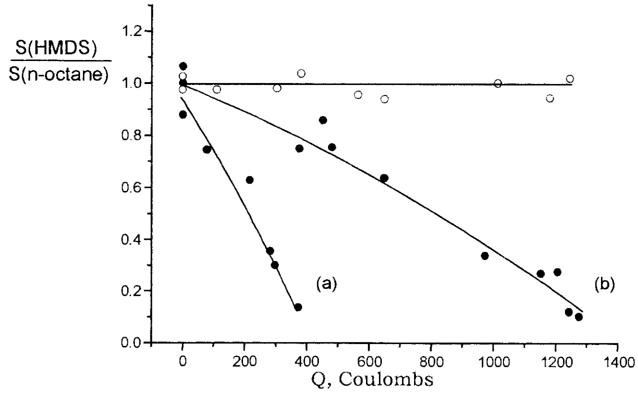


Fig. 2. Variation of the concentration of hexamethyldisiloxane plotted against the amount of electricity passed during the reduction of oxygen: ○ Electrolysis of O_2 in the absence of Me_2SiCl_2. ● electrolyses of O_2 when Me_2SiCl_2 is present in the solution: (a) in a separated (two-compartment) cell, (b) in an undivided cell with a sacrificial Al anode.

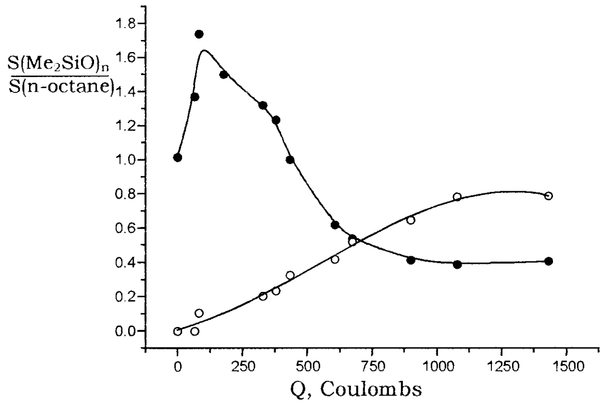


Fig. 3. The content of permethylcyclosiloxanes in the electrolyte as a function of the amount of electricity passed during the electrolysis of O_2 in the system Me_2SiCl_2–$(Me_2SiO)_3$. ● $(Me_2SiO)_3$, ○ $(Me_2SiO)_4$.

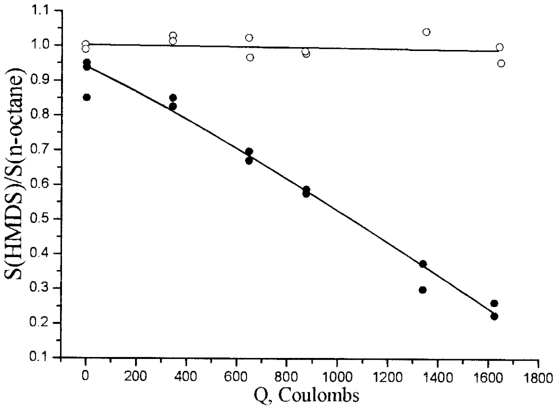


Fig. 4. Variation of the relative content of HMDS in the catholyte with the amount of electricity passed during the reduction of oxygen in an undivided cell: ● in the presence of Ph_2SiCl_2, ○ without Ph_2SiCl_2.

hexamethyldisiloxane to give linear permethyloligosiloxanes [24,28,48,49].

$$n\mathrm{Me_2Si{=}O} + \mathrm{Me_3SiOSiMe_3} \rightarrow \mathrm{Me_3Si(OSiMe_2)}_n\mathrm{OSiMe_3}\ \ n = 1,\ 2 \qquad (11)$$

When reducing oxygen in the presence of HMDS alone, without Me_2SiCl_2, i.e under the conditions precluding the formation of dimethylsilanone, the amount of HMDS does not change in the course of the electrolysis (Fig. 2). This proves that HMDS does not react with the reduced forms of oxygen so its consumption during the electrolysis of O_2 in a system containing Me_2SiCl_2 occurs exclusively in the reaction with dimethylsilanone.

Similar results were obtained when carrying the electrolyses out in an undivided cell, in this case a coupled anodic process is dissolution of an Al electrode (Fig. 2b). However, under these conditions, the consumption of HMDS and the formation of low-mass linear permethyloligosiloxanes (with $n = 1, 2$) could also result from the splitting the Si–O bond of HMDS by aluminium chlorides formed in the anodic reaction. The cleavage of HMDS by halogenides of Al [47], In and Ga [24,49,50] is known to occur rather easily. Therefore, in spite of the very mild conditions of the electrolyses, a possibility that this reaction could intervene cannot be ruled out. To check this assumption, the electrolysis of a solution of Me_2SiCl_2 and HMDS in THF was carried out in an undivided cell fitted with an Al anode but without bubbling oxygen through the catholyte. During this electrolysis, the metal of the anode dissolved but neither a decrease of the HMDS content in the solution nor the formation of insertion products, and hence, no generation of dimethylsilanone, was observed.

Under similar conditions, the use of hexamethylcyclotrisiloxane $(Me_2SiO)_3$ as a reagent-trap for silanones also corroborates the formation of dimethylsilanone in the process. During the electrolysis, the concentration of hexamethylcyclotrisiloxane in the electrolyte was shown to be inversely proportional to the amount of electricity passed. At the same time, a product of insertion of the intermediate dimethylsilanone into the molecule of $(Me_2SiO)_3$, octamethylcyclotetrasiloxane $(Me_2SiO)_4$, appeared in the solution, its concentration increased as the amount of electricity increased (Fig. 3).

The non-linearity of the graphs in Fig. 3 indicates that several parallel processes involving dimethylsilanone occur in the system. (1) Insertion of $Me_2Si{=}O$ into the starting molecule $(Me_2SiO)_3$, affording $(Me_2SiO)_4$. (2) Interaction of $Me_2Si{=}O$ with $(Me_2SiO)_4$ thus appearing in the electrolyte, resulting in $(Me_2SiO)_5$. (3) Auto-cyclization of $Me_2Si{=}O$ to $(Me_2SiO)_3$, occurring, probably, via an intermediate $(Me_2SiO)_2$. Earlier it was reported that the rate of auto-cyclization of dimethylsilanone is less than the rate of its insertion into the Si–O bonds of siloxane traps [24], therefore the role of the last process seems to be less important compared to the first two. As seen from Fig. 3, the increase in the concentration of $(Me_2SiO)_4$ during the electrolysis is slightly inferior to the decrease of the amount of $(Me_2SiO)_3$. Apparently, it is caused by the reaction of $Me_2Si{=}O$ with $(Me_2SiO)_4$ which, in turn, can serve as a trap for dimethylsilanone.

The decrease of the content of HMDS and the formation of corresponding insertion products were also observed when reducing oxygen in the presence of other diorganyldichlorosilanes such as Et_2SiCl_2 and Ph_2SiCl_2 (Fig. 4).

When Ph_2SiCl_2 was used as a dichlorosilane, α,ω-bis(trimethylsiloxy)oligodiphenylsiloxanes formed in the process precipitated as white bulky flakes soluble in DMF and toluene. The conversion of HMDS is 70–90% in all cases.

$$\mathrm{Ph_2SiCl_2} + \mathrm{O_2^{2-}} \rightarrow \mathrm{Ph_2Si{=}O} + 2\mathrm{Cl^-} \qquad (12)$$

Table 1
The ratio of oxygen, reduced at the cathode, and HMDS consumed in the process of electrochemical oxygenation of R_2SiCl_2

R_2SiCl_2	Electrolysis mode	Amount of reduced O_2 ($n = 2$) (mmol)	Amount of reacted HMDS (mmol)	Ratio O_2/HMDS
Me_2SiCl_2	undivided cell	6.6	3.8	1.7
Me_2SiCl_2	divided cell	1.5	2.6	0.6
Et_2SiCl_2	undivided cell	8	3.0	2.6
Ph_2SiCl_2	undivided cell	4	2.5	1.6

$$n\,Ph_2Si{=}O + Me_3SiOSiMe_3 \rightarrow Me_3Si(OSiPh_2)_nOSiMe_3 \quad n = 1, 2 \qquad (13)$$

It seemed to us to be important to determine the role of oxygen in the electrochemical process, since both steps of its reduction are reversible and since the formation of the peroxide anion O_2^{2-} takes place at the potential about 0.2–0.7 V more positive than the reduction of used diorganyldichlorosilanes [46], an eventual possibility that O_2^{2-} might act as a redox-catalyst of the homogeneous reduction of chlorosilanes cannot be ruled out. Such processes, involving anion radicals of some aromatic compounds, are known [51,52] and occur at close potentials. To check this hypothesis, electrolysis of oxygen in a system Me_3SiCl–THF–Bu_4NBF_4 0.01 M was carried out. After the electrolysis was over, there were no traces of hexamethyldisilane $Me_3SiSiMe_3$ (the product of reduction of chlorotrimethylsilane) found in the electrolyte. This fact can be interpreted in two ways: first, due to a great affinity of oxygen to silicon and great Si–O bond strength, the peroxide anion does not act as a catalyst in this process but exclusively as a nucleophile; second, the potential of the formation of the peroxide anion has not been achieved so the actual electrogenerated species was the superoxide anion $O_2^{-\bullet}$ whose redox-potential is not negative enough to trigger an efficient homogeneous redox catalysis.

The amount of electricity, consumed in the process can also serve as an indication of the nature of the active form of oxygen taking part in the process. Assuming 100% current yield for the reduction of oxygen, a theoretical amount of O_2^{2-}, generated at the electrode, is determined by the ratio $m = Q/2F$, where m is the number of moles of oxygen, reduced at the electrode, 2 is the number of electrons per molecule of oxygen ($n = 1$ or 2 for the formation of $O_2^{-\bullet}$ or O_2^{2}, respectively), Q is the amount of electricity passed. The stochiometry of peroxide anions, formed during the electrolysis, and HMDS, consumed in the reaction, is presented in Table 1.

The ratio O_2:$Me_3SiOSiMe_3$, close to 0.5 for the reaction in the undivided cell, agrees with the stoichiometry of a formal scheme of the process:

$$O_2 + 2e \rightarrow O_2^{2-} \qquad (14)$$

$$O_2^{2-} + Me_2SiCl_2 \rightarrow Me_2Si{=}O + 2Cl^- + 0.5O_2 \qquad (15)$$

$$Me_2Si{=}O + Me_3SiOSiMe_3 \rightarrow Me_3SiOSiMe_2OSiMe_3 \qquad (16)$$

A deviation of this ratio from the theoretical value, especially important when the process is realized in an undivided mode, can be attributed to some by-processes both at the electrode (the reduction of protons resulting from the hydrolysis of diorganyldichlorosilanes by residual moisture, the reduction of products of anodic processes or a partial re-oxidation of the reduced forms of oxygen at the anode) and in the bulk of the solution.

Although the obtained data do not yet allow us to establish definitely the mechanism of the formation of diorganylsilanones during the electrochemical oxygenation of R_2SiCl_2, one can suppose that the reaction begins with the nucleophilic attack of either peroxide or superoxide anion on the Si atom in a diorganyldichlorosilane affording a transient penta-coordinated complex. The elimination of a chloride anion from this complex leads to a geminal chlorosilylperoxide anion which undergoes a cleavage [3] to give diorganylsilanone and to partially regenerate oxygen. Geminal cleavage of the intermediate $R_2Si(O)Cl$ is an essential step in this process. It can be illustrated by an experiment when a similar process was realized using chlorotrialkylsilanes (Me_3SiCl or $OctMe_2SiCl$), and neither the formation of silanones nor a decrease of the concentration of reagent-traps were observed.

To summarize, the obtained results unequivocally show that the interaction of the reduced forms of oxygen (superoxide or peroxide anions) with diorganyldichlorosilanes R_2SiCl_2 involves the formation of short-living diorganylsilanones $R_2Si{=}O$. The latter readily insert into the Si–O bond of a reagent-trap (hexamethyldisiloxane, hexamethylcyclotrisiloxane) or, in the absence of such a trap, undergo cyclization to form low-mass perorganylcyclosiloxanes $(R_2SiO)_n$ ($n = 3$, 4) and then insert into the molecules of these primary products. The electrochemical transformation of

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[3] As one of the referees of this paper pointed out, the geminal cleavage of the intermediate $Me_2Si(Cl)OR$ with $R = O^-$ can be accomplished either by homolytic fission of both the O–O and the Si–Cl bond or by heterolytic fission with formation of Cl^+ and O^{2-} but to establish the exact mechanism of the cleavage, this issue needs additional studies.

R_2SiCl_2 to $R_2Si{=}O$ and then to stable products occurs under very mild conditions and can be realized in both divided and undivided cells. All this allows us to believe this process to be a very promising method for the generation of diorganylsilanones. Further study in this direction is in progress.

3. Experimental

3.1. Instrumentation

Large-scale electrolyses were carried out using a potentiostat P-5827M. The working electrode (cathode) was a Pt gauze cylinder with an apparent area of 37 cm, the auxiliary electrode (anode) was a Pt (in a divided cell) or Al (in an undivided cell) wire. The reference electrode was Ag/0.1 M $AgNO_3$ in CH_3CN, separated from the working solution by an electrolytic bridge filled with 0.01 M Bu_4NBF_4 solution in THF. A 30 ml hermetic glass cell, equipped with a jacket for cooling the electrolyte with flowing water, was used; the anodic and the cathodic compartments of this cell were separated by a sintered glass diaphragm with medium porosity. Chromatographic analysis of the reaction mixture was carried out using a chromatograph Chrom-5 fitted with a thermo-conductivity detector and a column of 240×0.3 cm, filled with SE-30 (5%) on Inerton 0.125–0.160; the carrier gas was He. The sampler temperature was set at 230°C, the thermostat at 95°C, and detector at 150°C. As an internal standard, either *n*-octane or *n*-nonane was used, depending on the boiling points of the products of the electrolysis. Mass spectra were obtained using a MC-2040 spectrometer with the ionization energy 70 eV. NMR spectra were recorded using a Varian-100 or Bruker-250 spectrometer.

3.2. General procedure

Prior to the main electrolysis (before bubbling oxygen through the catholyte), pre-electrolysis of the solution of diorganyldichlorosilanes was carried out to reduce protons resulting from the hydrolysis of R_2SiCl_2 by traces of water. The pre-electrolysis was realized in a constant-current mode ($I = 50$ mA) until the evolution of bubbles of hydrogen at the cathode stopped; average duration of the pre-electrolysis was 1.5 h approximately.

In a typical experiment, the catholyte contained 10 mmol of R_2SiCl_2, 0.65 g (4 mmol) HMDS, 0.5 g (4 mmol) of octane, used as an internal standard for chromatography, and 2.64 g (7 mmol) Bu_4NBF_4 in 20 ml of THF. The electrolyses were carried out in galvanostatic mode maintaining the current at 20–50 mA (at the electrode given) and the flow of dry oxygen through the solution at 10 ml min^{-1}.

3.3. Chemicals

Analytical grade THF was additionally purified by passing through a column packed with activated neutral Al_2O_3, twice distilled from Na and then stocked under argon over 4A molecular sieves. The supporting electrolyte (Bu_4NBF_4, Aldrich) was kept in a vacuum desiccator over P_2O_5. Oxygen, dried by passing consecutively through H_2SO_4 (conc.), P_2O_5 and Al_2O_3, was bubbled into the solution through a porous glassy sprayer. Before using, diorganyldichlorosilanes were purified by distillation from Mg turnings, HMDS was distilled from Na. Linear and cyclic permethyloligosiloxanes (standards) were synthesized according to a described method [53].

Hexamethylcyclotrisiloxane. NMR ($CDCl_3$, TMS): 0.17 (s 18H). Mass, *m*/*e*: 207 ($M^+ - 15$, 100), 191 (15), 177 (5), 133 (10), 96 (15).

Octamethylcyclotetrasiloxane. NMR ($CDCl_3$, TMS): 0.14 (s 24H). Mass, *m*/*e*: 281 ($M^+ - 15$, 100), 265 (10), 249 (5), 207 (15), 191 (10), 133 (10), 73 (8).

Hexaethylcyclotrisiloxane. NMR ($CDCl_3$, TMS): 0.52 (quad 12H), 0.92 (t 18H). Mass, *m*/*e*: 277 ($M^+ - 29$, 100), 249 (88), 221 (72), 193 (30), 163 (30), 165 (28), 137 (30), 110 (28), 96 (20).

Octamethyltrisiloxane. NMR (CCl_4, TMS): 0.15 (s 18H), 0.19 (s 6H). Mass, *m*/*e*: 221 ($M^+ - 15$, 58), 205 (8), 147 (5), 133 (12), 103 (20), 73 (100), 59 (15).

Decamethyltetrasiloxane. NMR (CCl_4, TMS): 0.08 (s 18H), 0.03 (s 12H). Mass, *m*/*e*: 295 ($M^+ - 15$, 22), 221 (40), 147 (48), 73 (100).

Hexaphenylcyclotrisiloxane. NMR ($CDCl_3$, TMS): 7.58 (d 12H), 7.35 (m 18H). Mass, *m*/*e*: 594 (8, $M+$), 516 (15), 439 (100), 361 (30), 219 (45), 197 (30), 144 (30), 131 (40), 77 (35).

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