

# Electrochemical oxidation of cyclic polysilanes

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Dedicated to the memory of my first Ph.D. student, Dr. Baruch Zinger, who was killed on December 2, 2001, at the age of 51

## Abstract

During the past decade, the electrochemical properties of cyclic polysilane derivatives, namely [Me<sub>2</sub>Si]<sub>3</sub> (**I**), [*t*-Bu(Me)Si]<sub>4</sub> (**IIa**), [Et<sub>2</sub>Si]<sub>4</sub> (**IIb**), [(*n*-Pr)<sub>2</sub>Si]<sub>5</sub> (**IIIa**), [Et<sub>2</sub>Si]<sub>5</sub> (**IIIb**), [Me<sub>2</sub>Si]<sub>6</sub> (**IVa**), [Et<sub>2</sub>Si]<sub>6</sub> (**IVb**), [Et<sub>2</sub>Si]<sub>7</sub> (**V**), [Me<sub>2</sub>Si]<sub>8</sub> (**VI**), and [Me<sub>2</sub>Si]<sub>9</sub> (**VII**), have been explored in our laboratory. Various parameters have been investigated, such as anodic peak potentials, the effect of anode material, nature of supporting electrolyte, atmosphere under which electrolyses were conducted, extent of electricity consumption, solvent, ring size, applied potential, and more. It has been found that the type of products emerged from electrolysis was highly sensitive to the nature of electrolyte. Thus, in the presence of BF<sub>4</sub><sup>-</sup> salts, cyclic polysilanes underwent ring opening followed by Si–Si bond cleavage to afford linear silanes with F [one or two (major)], H or OH moieties at the terminal positions. In the presence of ClO<sub>4</sub><sup>-</sup> salts, mostly cyclic siloxanes with different number of oxygen atoms were formed, in addition to linear ones, in some cases. The origin of oxygen atoms in the oxygen insertion process was postulated to stem from both ClO<sub>4</sub><sup>-</sup> anions and molecular oxygen. Both mechanisms are discussed. In the presence of non-oxidizing electrolytes, such as HSO<sub>4</sub><sup>-</sup> and acetate salts, mostly mono- and dihydroxy linear polysiloxanes and polysilanes, respectively, were generated. When CF<sub>3</sub>COO<sup>-</sup> (TFA) salt was utilized under “oxygen-free” and “water-free” conditions, in the dry box, the reaction became quite selective since the major products were cyclic siloxanes containing only one oxygen atom each. The source of oxygen is assumed to originate from the TFA electrolyte, and a plausible mechanism is suggested. The net effect of ring size was studied with cyclic silanes bearing the same substituents (**IIb**, **IIIb**, **IVb**, and **V**). Each derivative afforded a distinctive major five- or six-membered siloxane, containing either one or two oxygen atoms. In addition, whereas **IIb** and **IIIb** gave products with retention of the original number of silicon atoms, **IVb** and **V** gave also cyclic siloxanes with a loss of 1–3 Si atoms, due to fragmentation.

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## 1. Introduction

Cyclic peralkylpolysilanes (R<sub>2</sub>Si)<sub>*n*</sub> exhibit unique electronic, physical and chemical properties, which distinguish them from saturated cycloalkanes [1]. In fact, in some ways the properties of the cyclic polysilanes resemble those of polyunsaturated or aromatic hydrocarbons. For example, they show strong absorption bands in the UV–Vis; form charge-transfer complexes with π-acceptors [2], and undergo reduction to form electron-delocalized anion-radicals [3]. Some of the

cyclopolysilanes can also be oxidized to cation-radicals, which have been observed by ESR spectroscopy [4]. Their ESR spectra indicate that the unpaired electron is fully delocalized over the ring.

Cyclic peralkylsilanes are generally quite stable at ordinary temperatures. The various syntheses of cyclopolysilanes with different ring size and different patterns of substitution are known [5]. They could involve over 40 silicon atoms. However, the largest polysilane ring isolated and characterized by X-ray determination is Si<sub>16</sub>Me<sub>32</sub> [6].

Before shedding light on the outcome of the electrochemical oxidation of cyclic polysilanes, it would be of interest to describe briefly what is known about the chemical oxidation of polysilicon compounds in general.

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For example, the oxidation of disilanes ( $R_3SiSiR_3$ ) to form disiloxanes ( $R_3SiOSiR_3$ ), by a wide range of oxidizing agents, is a well-known reaction in organosilicon chemistry [7,8]. Later this reaction was extended to the oxidation of the Si–Si bonds of polysilanes [8–10] and cyclic polysilanes [7,11–13]. It has been shown that the siloxane products may result from the sequential insertion of oxygen atoms into the Si–Si bonds of the polysilanes. Furthermore, it was found that, generally, providing there is no ring strain [13], the oxygen in the ring activates adjacent silicon–silicon bonds towards oxidation relative to those that are not bonded to oxygen [7,9].

Two groups [14] determined the oxidation potentials of some cyclic peralkylsilanes by cyclic voltammetry (CV). In general, these compounds display at least two anodic waves separated by 0.2–0.4 V. The first oxidation potential is from 1.1 to 1.4 V and the second one is from 1.4 to 1.9 V (vs. SCE). It has been found that the first oxidation peak potentials depend both upon ring size and on the nature of substituents on silicon. The oxidation potentials increase going from three- to four- to higher-membered rings, with the lowest potential of all found for the highly strained compound  $[(t-Bu)_2Si]_3$ . In the dimethyl and diethyl series there is little difference between potentials for five-, six- and seven-membered rings, but in the two-rotane series, the five-membered rings undergo oxidation at lower potentials than the six-membered rings. Permethylcyclosilanes  $(Me_2Si)_n$  with  $n > 9$  show significantly lower oxidation potentials than for  $n = 5–9$ .

In general, there is a good correlation between the oxidation potentials and the electronic absorption energies which similarly increase with increasing ring size from  $n = 3$  to 6, and then decrease above  $n = 9$ . Ionization potentials were determined only for a few cyclic silanes, but those, which are known, are consistent with the values obtained. For example,  $Si_4$  rings show lower ionization potentials than  $Si_5$  and  $Si_6$  [15]. As the ring size decreases below six silicon atoms, the constraints on the Si–Si–Si bond angles evidently increase the energy of the highest occupied Si–Si  $\sigma$ -orbitals, as suggested earlier [16].

The present work surveys the results of electrochemical investigation of cyclic polysilanes which differ in both ring size and substitution (Scheme 1), and which has been carried out in our laboratory, in non-aqueous media and under various experimental conditions, by means of CV and controlled potential electrolysis (CPE).

## 2. Experimental

Experimental details related to CV measurements, CPE, electrochemical cells and equipment, glove box

and chemicals, are described in Refs. [17,19,20,22,24,25]. Prof. Robert West, from the University of Wisconsin, Madison, WI, donated all the cyclic polysilanes listed in Scheme 1.

## 3. Results and discussion

### 3.1. Cyclic voltammetry

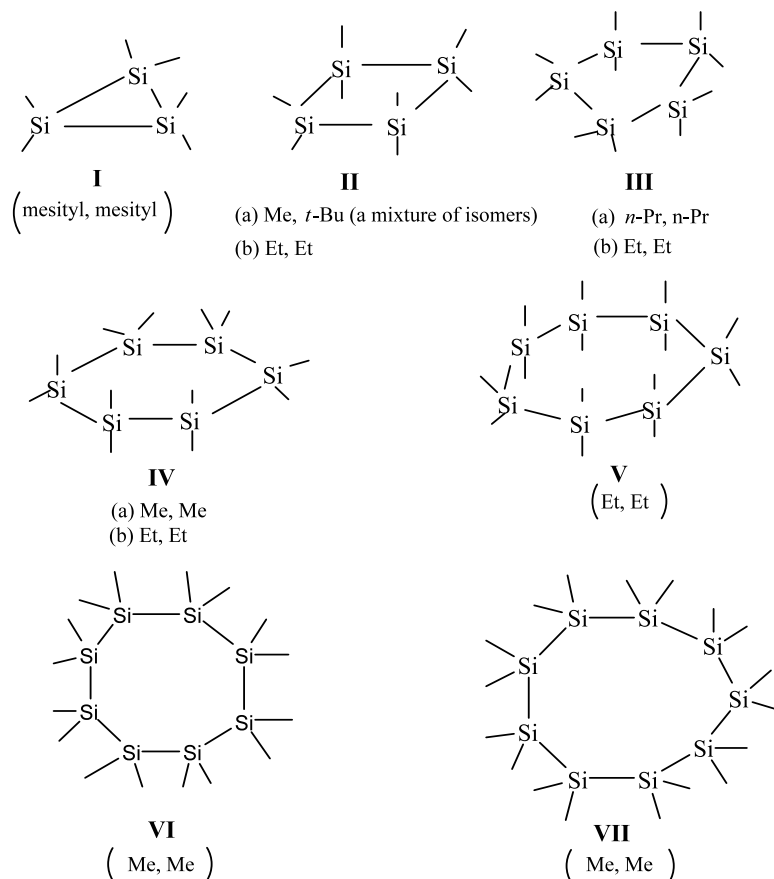
Cyclic voltammograms were recorded in a 4:1 mixture of dichloromethane–acetonitrile to allow dissolution of all substrates. The results are summarized in Table 1. Each of the derivatives studied showed at least one irreversible oxidation wave. As expected, the cyclic derivatives with the highest ring-tension showed lower oxidation potential, namely 0.7 and 1.0 V (vs. Ag/AgCl reference electrode) for the three- and four-membered rings, respectively, compared with all other rings with no or negligible strain (about  $\sim 1.4$  V).

### 3.2. Preparative electrolysis by CPE

Electrolysis of the listed compounds in Scheme 1 was investigated under various electrolytic conditions. The effects of ring size, nature of supporting electrolyte, solvent, atmosphere, applied potential, electricity consumption and anode material, have been investigated. Since we have found that the outcome of electrolysis was mainly dependent on the nature of electrolyte, the survey will be classified by the electrolyte employed, as follows:

#### 3.2.1. Electrolysis in the presence of $BF_4^-$

Earlier results [17] of preparative electrochemical oxidation of two cyclic peralkylsilanes, dodecamethylcyclohexasilane (**IIIa**) and deca-*n*-propylcyclopentasilane (**IVa**) in  $CH_2Cl_2$ – $CH_3CN$  (4:1)–0.1 M  $Et_4NBF_4$  showed that both derivatives undergo ring-opening, followed by further Si–Si oxidative fragmentation and reaction with  $BF_4^-$  to form  $\alpha,\omega$ -difluorosilanes,  $F-(SiR_2)_n-F$ , as the major products. The respective total yield of products was  $\sim 50$  and  $\sim 75\%$  (the rest was unreacted starting material), after consuming  $2.5 F mol^{-1}$ . This observation implies that once the ring is opened, the anodic fragmentation competes favorably with the oxidation of the starting material. It is noteworthy that in this electrolytic process,  $BF_4^-$  ion plays a role of a very mild fluorinating agent. In comparison,  $\alpha,\omega$ -dichloro- and dibromopermethylpolysilanes were prepared chemically by utilizing bromine and chlorine, respectively [18]. Later [19], the anodic oxidation was extended to other cyclic peralkylsilanes, **I** and **IIa**. The results are summarized in Table 2. As could be observed, three main types of linear fluoro-silanes have been generated:

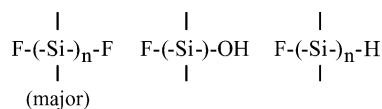


Scheme 1. Cyclic polysilanes that have been investigated electrochemically.

Table 1

Anodic peak potentials (vs. Ag/AgCl reference electrode) of cyclic polysilanes in 0.1 M Et<sub>4</sub>NClO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>CN (4:1, v:v) solutions on Pt working electrode

Cyclic polysilane	$E_{p_{ox}^1}$ (irreversible)	$E_{p_{ox}^2}$ (irreversible)
<b>I</b>	0.70	–
<b>IIa</b>	1.05	1.40
<b>IIb</b>	1.15	1.45
<b>IIIa</b>	1.45	–
<b>IIIb</b>	1.35	–
<b>IVa</b>	1.40	–
<b>IVb</b>	1.40	–
<b>Va</b>	1.40	1.65
<b>Vb</b>	1.40	–
<b>VI</b>	1.40	–
<b>VII</b>	1.40	–



With regard to the chain length of the final product, no obvious trend was observed. For instance, the major difluoro product from **IIIa** contains two silicon atoms, that from **IVa** four silicon atoms, and that from **IIa**, also contains four silicon atoms, without further Si–Si bond

breaking. It is noteworthy that (Mes<sub>2</sub>Si)<sub>3</sub> (**I**) afforded few other products which stem from aryl migration, forming Mes<sub>3</sub>SiF as the major product, whereas **IIa** yielded a cyclic siloxane, (*t*-Bu(Me)Si)<sub>4</sub>O, in addition to two  $\alpha,\omega$ -difluoro linear products.

The schematic mechanistic diagram outlined in Scheme 2 could explain the formation of the variety of linear silicon products mentioned in Table 2. The electrogenerated cation radical (cyclic/linear) undergoes different follow-up reaction pathways, in parallel or consecutively (e.g., with BF<sub>4</sub><sup>–</sup>, hydrogen atom abstraction from solvent and/or electrolyte, further anodic oxidation of a radical intermediate, anodic fragmentation. The latter could take place almost at any stage, after forming the cation radical).

### 3.2.2. Electrolysis in the presence of ClO<sub>4</sub><sup>–</sup>

We have found that the nature of products is highly dependant on the electrolyte used and amount of electricity consumed. When the electrolyte was replaced [20] with a non-fluorinated one, e.g. Et<sub>4</sub>NClO<sub>4</sub>, the course of the reaction changed dramatically, yielding mostly cyclic siloxanes, depending on the experimental conditions.

Anodic oxidation of **IIa** on Pt at 0.9 V, under air and after consuming 2.4 F mol<sup>–1</sup>, led to the formation of

Table 2  
Product distribution from anodic oxidation<sup>a</sup> of **I**, **IIa–IVa**

$(R_2Si)_n$	F-(R <sub>2</sub> Si) <sub>n</sub> -F (%) <sup>b</sup>						Other products (%)
	n = 1	n = 2	n = 3	n = 4	n = 5	n = 6	
<b>I</b>	15						Mes <sub>2</sub> SiH <sub>2</sub> (5), Mes <sub>3</sub> SiOH (7), Mes <sub>3</sub> SiF (21), H[Mes <sub>2</sub> Si]F (13), F[Mes <sub>2</sub> Si][F <sub>2</sub> Si]Mes (6)
<b>IIa</b>	60						F[( <i>t</i> -Bu(Me)Si) <sub>4</sub> O]F (4), ( <i>t</i> -Bu(Me)Si) <sub>4</sub> O (36)
<b>IIIa</b>	1	54	30	10	–	–	F-( <i>n</i> -Pr <sub>2</sub> Si) <sub>3</sub> -OH, F-( <i>n</i> -Pr <sub>2</sub> Si) <sub>3</sub> -H, H-( <i>n</i> -Pr <sub>2</sub> Si) <sub>3</sub> -OH, F-( <i>n</i> -Pr <sub>2</sub> Si) <sub>5</sub> -OH
<b>IVa</b>	5	27	12	49	2	1	F-(Me <sub>2</sub> Si) <sub>2</sub> -OH, F-(Me <sub>2</sub> Si) <sub>3</sub> -OH, F-(Me <sub>2</sub> Si) <sub>5</sub> -OH, F-(Me <sub>2</sub> Si) <sub>5</sub> -H

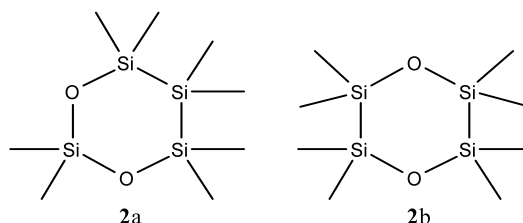
<sup>a</sup> CPE was conducted at the onset of the anodic peak potential (1.25 V vs. Ag/AgCl) in an 'H'-type divided cell, on Pt anode, in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>CN (4:1)-0.1 M Et<sub>4</sub>NBF<sub>4</sub>; [substrate] = 12–14 mM.

<sup>b</sup> Based on GLC.

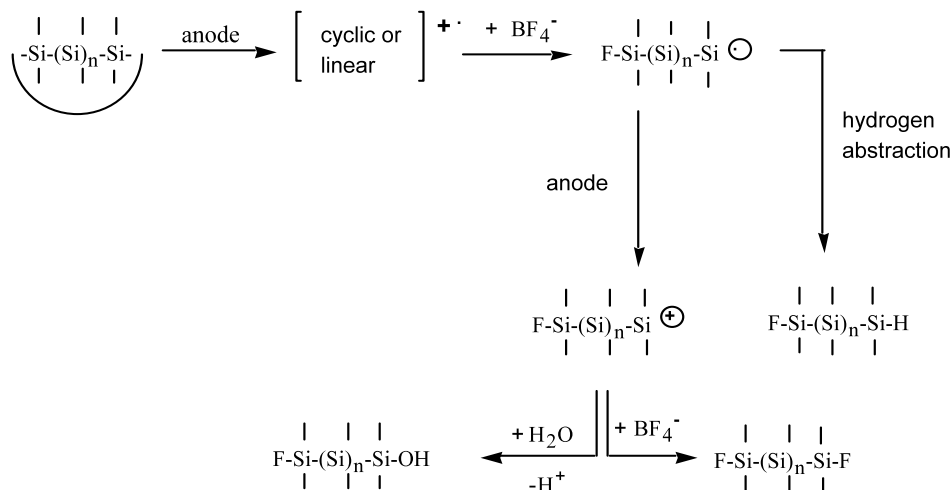
three products: **1** (30%), **2** (63%) and **4** (7%) (Scheme 3), leaving no unreacted starting material [19]. When the electricity consumption increased to 4 F mol<sup>-1</sup>, the three products were **2** (52%), **3** (44%) and **4** (4%). Under argon atmosphere, the reaction became more selective and already after passing 1.2 F mol<sup>-1</sup>, only **1** was formed in 94% yield. Upon increasing the electricity consumption to 2.4 and 3 F mol<sup>-1</sup>, more oxygenated products (**2–4**) were formed at the expense of **1**. When the potential was raised from 0.9 V to the onset (1.25 V) of its second anodic wave, an additional product, richer with oxygen, **5** (2–3%), was obtained with electricity consumption of 2.4 F mol<sup>-1</sup> and higher.

From the above details, it seems obvious that the four-membered derivative **IIa** undergoes an exclusive oxygen insertion, affording only cyclic siloxanes **1–5** (**4** is a decomposition product due to fragmentation). It is noteworthy that product **2** may involve two structural isomers (**2a** and **2b**). Our preference of **2a** stems from previous observations that the initially inserted oxygen atom in the ring activates adjacent Si–Si bonds towards further insertion of oxygen atoms [21]. Furthermore, the IR pattern of **2a** isomer strongly supports the presence of an 'Si–O–Si–O–Si' bonding sequence rather than of an exclusive 'Si–Si–O–Si–Si' functionality (which exists

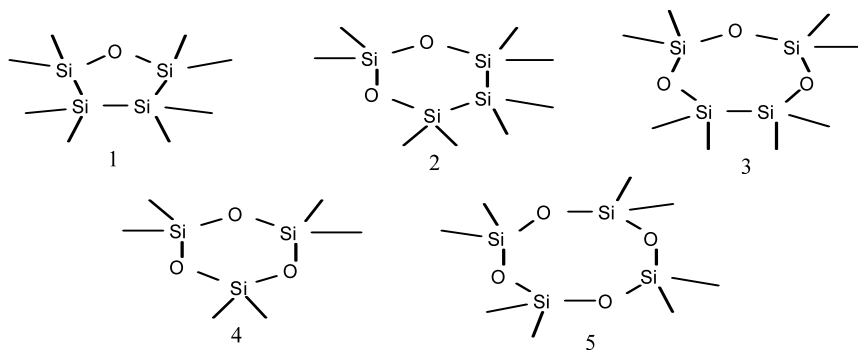
in **2b**). Typical absorption bands for the "Si–O" bond were found in the IR spectrum of siloxanes. Cyclic siloxane **1** exhibits three bands at 930, 965 and 1006 cm<sup>-1</sup>. Siloxanes with higher oxygen content afford additional absorption bands at higher frequencies. For instance, cyclic siloxanes **2** (with two oxygen atoms) and **3** (with three oxygen atoms) give additional bands at 1034 and 1058 cm<sup>-1</sup>, respectively [19].



It has been also found that the spectrum of products is strongly dependant on the atmosphere under which the electrolysis takes place (e.g., oxygen vs. nitrogen or argon), and the nature of anode material (graphite, platinum). As an example, the anodic oxidation of **IIIa** at graphite gave [22] only cyclic siloxanes, seven of them (**6–13**, excluding **7**), with no distinct preference, and with 32% of unreacted starting material left, after consuming 4 F mol<sup>-1</sup>. Under the same experimental



Scheme 2. Mechanism for formation of products in the presence of BF<sub>4</sub><sup>-</sup> electrolyte.



Scheme 3. Products from anodic oxidation of **IIa** in the presence of  $\text{Et}_4\text{NClO}_4$  in  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{CN}$  (4:1, v/v). Each Si atom is attached to Me and *t*-Bu groups.

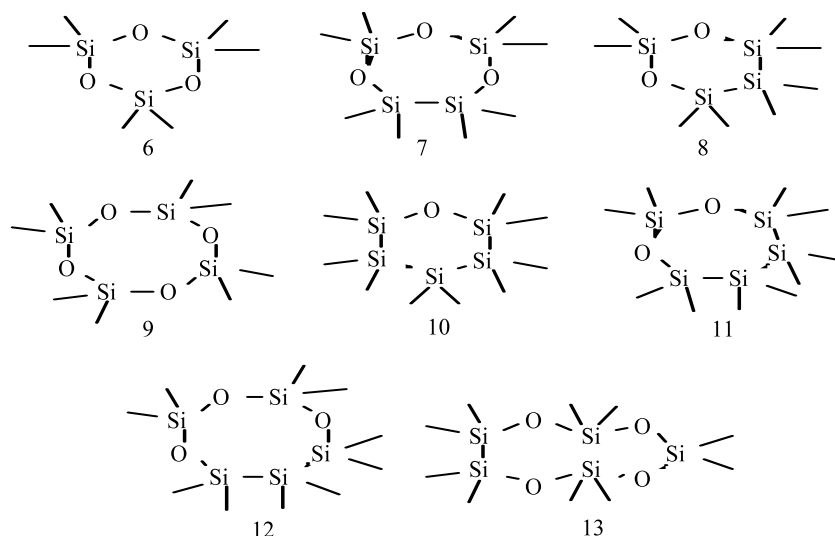
conditions, on Pt, no starting material was left, but two linear siloxanes  $[(n\text{-Pr})_2(n\text{-Pr})_2\text{Si}]_4\text{O}_2$  and  $(n\text{-Pr})_2[(n\text{-Pr})_2\text{Si}]_4\text{O}_3$  were obtained in addition to four cyclic ones, where **9** was the major product [20]. Apparently, the electrochemical oxidation on Pt is more efficient and sometimes even more selective than on graphite. One explanation could be based on the existence of a large difference in the actual current density on the two different anodes, causing a different concentration gradient near the electrode surface, and as a consequence, the nature and distribution of product could change. Upon decreasing the electricity consumption from 4 to  $2.2 \text{ F mol}^{-1}$  [20], under air, at Pt, six cyclic siloxanes (**6–11**) were formed exclusively, but 20% of the starting material remained unchanged. Scheme 4 describes the products (**6–13**) obtained from the CPE of **IIIa**.

The fact that siloxanes are formed from **IIIa** at various oxidation levels, while still unreacted **IIIa** remains, indicates that the former are oxidized easier than **IIIa**. This is a well-established phenomenon for both cyclic and linear polysilanes. The observed [23]

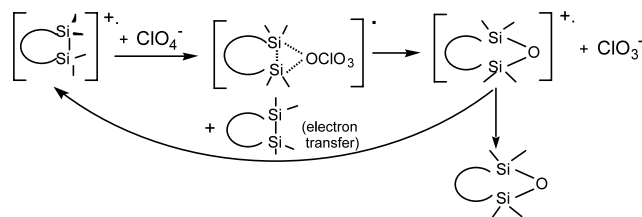
acceleration of the consecutive oxidation steps compared to the initial oxidation of the parent silane derivative, could stem from a  $n, \sigma$ -conjugation between the oxygen lone-pair and the Si–Si single bond, or intramolecular co-ordination due to interaction between the oxygen lone-pair and a vacant d-orbital of the silicon atom.

Surprisingly, siloxanes were formed from **IIIa** also under nitrogen atmosphere, eight cyclic ones (**6–13**) and a linear one  $[(n\text{-Pr})_2(n\text{-Pr})_2\text{Si}]_4\text{O}_4$  [20]. In comparison to nitrogen, the reaction became much more selective under argon atmosphere [22], because only three products were formed {**6**, **9** and  $\text{MeCONH}[(n\text{-Pr})_2\text{Si}]_5(\text{CH}_2\text{CN})$  which involves two molecules of the solvent acetonitrile in 13, 41 and 40% yield, respectively}, but still, two of them were highly oxygenated. Therefore, it was suggested that the perchlorate anion could play a role as an oxidizing agent, as outlined schematically in Scheme 5, for insertion of an oxygen atom.

The anodic oxidation of **IVa** afforded four cyclic siloxanes only (in 17, 28, 9 and 13% yields) (Scheme 6),



Scheme 4. Structural formula of cyclic siloxanes products (all substituents attached to the silicon atoms are *n*- $\text{C}_3\text{H}_7$  groups).



Scheme 5. Mechanism for formation of products in the presence of  $\text{ClO}_4^-$ .

at Pt anode [22], leaving 21% of unreacting starting material. However, on graphite anode, only product **18** was obtained after passing  $4 \text{ F mol}^{-1}$ , but in 8% yield (the rest, 90%, was starting material).

As to the anodic oxidation of **V** at graphite anode, it also gave only cyclic siloxanes in the presence of  $\text{Et}_4\text{NClO}_4$ , but no starting material was left after consuming  $4 \text{ F mol}^{-1}$  of electricity. It was found that the products contained four or five silicon atoms in each ring and the reaction under air was more selective (four products:  $(\text{Et}_2\text{Si})_4\text{O}_2$  (**19**, 7%);  $(\text{Et}_2\text{Si})_4\text{O}_3$  (**20**, 38%);  $(\text{Et}_2\text{Si})_4\text{O}_4$  (**21**, 34%); and  $(\text{Et}_2\text{Si})_5\text{O}_4$  (**22**, 5%)) than under argon (six products: **19–21** and  $(\text{Et}_2\text{Si})_5\text{O}$  (**23**),  $(\text{Et}_2\text{Si})_5\text{O}_2$  (**24**), and  $(\text{Et}_2\text{Si})_5\text{O}_5$  (**25**)), but with higher content of oxygen atoms.

### 3.2.3. Electrolysis in the presence of $\text{HSO}_4^-$ and $\text{AcO}^-$

In order to examine more closely the source of oxygen in the insertion process during the anodic oxidation of cyclic polysilanes, the use of non-oxidizing electrolytes was utilized. Therefore,  $\text{HSO}_4^-$  and  $\text{CH}_3\text{COO}^-$  were employed as electrolytes instead of  $\text{ClO}_4^-$  salts. In the case of the three-membered ring **I**, neither cyclic nor linear siloxanes were formed, and the detected products in the presence of  $\text{Bu}_4\text{NHSO}_4$  (at 0.65 V) on Pt, under air, were:  $\text{Mes}_3\text{SiH}$  (**26**),  $(\text{HO})[\text{Mes}_2\text{Si}]_2(\text{OH})$  (**27**),  $\text{Mes}_2\text{Si}(\text{OH})_2$  (**28**),  $\text{Mes}[\text{Mes}_2\text{Si}]_2\text{H}$  (**29**),  $\text{Mes}_2\text{SiH}_2$  (**30**) and  $\text{Mes}_3\text{SiOH}$  (**31**), **26** being the major product, with 46% yield.

The results obtained from the anodic oxidation of **IIa** were significantly different compared with those of **I**, even though the experimental conditions remained un-

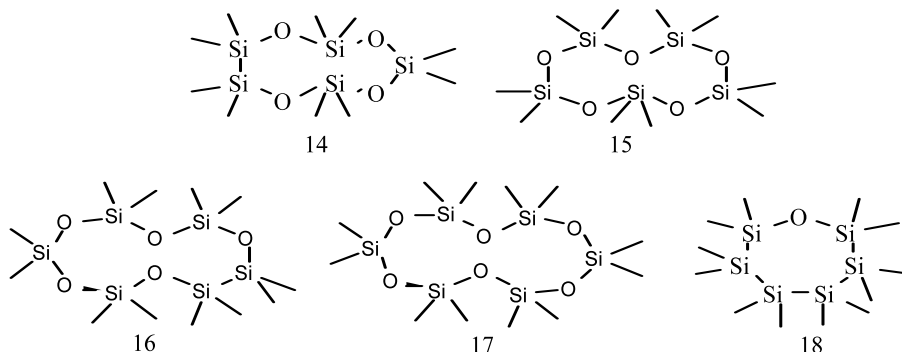
changed. Not only no linear products were generated, but surprisingly, oxygen insertion took place to yield two cyclic siloxanes, **1** and **2**, as the sole products. This observation may hint that the source of oxygen could stem also from air. Table 3 includes products distribution and yields.

A similar trend of oxygenation took place also when **IIIa** was oxidized in the presence of acetate salt, under air, yielding cyclic siloxanes (e.g. **6** and **8**), linear siloxanes  $\{(\text{HO})_2[(n\text{-Pr})_2\text{Si}]_2\text{O}$  (**32**) and  $(\text{AcO})(\text{CH}_2\text{CN})[(n\text{-Pr})_2\text{Si}]_4\text{O}_2$  (**33**)}, and mono- and dihydroxypolysilanes,  $(\text{HO})(n\text{-Pr})[(n\text{-Pr})_2\text{Si}]_4$  (**34**) and  $(\text{HO})_2[(n\text{-Pr})_2\text{Si}]_3$  (**35**), respectively [20]. When electrolysis was conducted under nitrogen atmosphere, the amount of siloxanes was diminished and the yield of unreacted starting material increased from 0 to 35%. Again, this outcome strengthens the hypothesis that molecular oxygen could be involved in the oxygen insertion process (Scheme 7).

This is in analogy to the chemical reactions found between triplet oxygen and radical cations of alkenes [24] and alkynes [25].

When  $\text{TEAHSO}_4$  electrolyte was used, also under air, there was a difference only in the nature of linear products obtained compared to the results with acetate salts. No hydroxysilanes were detected, but instead, two additional dihydroxysiloxanes were observed:  $(\text{HO})_2[(n\text{-Pr})_2\text{Si}]_3\text{O}$  (**36**) and  $(\text{HO})_2[(n\text{-Pr})_2\text{Si}]_3\text{O}_2$  (**37**) [22].

We disfavor the possibility that the source of oxygen in the oxygen insertion process stems from water, because when electrolysis was conducted under dry air atmosphere, the extent of oxygen in the products was considerably higher than that obtained under dry inert atmosphere, using the same electrolyte and solvents mixture. In addition, in most cases, the reaction was less selective in terms of number of products containing oxygen atoms. This trend could be also observed in the following paragraph that describes the results from **V**. However, having said that, one cannot entirely rule out the involvement of water, even to a low extent, unless labeling experiments will be carried out.



Scheme 6. Products obtained from **IVa** (all substituents are methyl groups).



Table 3  
Anodic oxidation of **IIa** on Pt in different electrolyte solutions<sup>a</sup>

Products	Yield (%) <sup>b</sup>			
	TBAHSO <sub>4</sub> , 2.4 (F mol <sup>-1</sup> )	TEAHSO <sub>4</sub> , 2.3 (F mol <sup>-1</sup> )	KOAc <sup>c</sup> , 1.5 (F mol <sup>-1</sup> )	TBAOAc, 0.6 <sup>d</sup> (F mol <sup>-1</sup> )
[ <i>t</i> -Bu(Me)Si] <sub>4</sub> O ( <b>1</b> )	100 <sup>c</sup>	86	90	15
[ <i>t</i> -Bu(Me)Si] <sub>4</sub> O <sub>2</sub> ( <b>2</b> )	–	7	–	–
<b>IIa</b>	–	–	5	85

<sup>a</sup> Under air, in CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>CN (4:1, v/v).

<sup>b</sup> The mass of the product mixture after electrolysis and work-up was 80–88% of the mass of [*t*-BuMeSi]<sub>4</sub> before electrolysis. Yields reported are relative and estimated by GLC.

<sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>CN–AcOH (4:1:1, v/v).

<sup>d</sup> No further charge could be passed. This behavior could stem from the very hygroscopic nature of the electrolyte.

Table 4 describes the results obtained from the electrochemical oxidation of **V** in the presence of KOAc, under air and argon. It is shown in column A that the products obtained under air are cyclic siloxanes **19**, **20**, **23**, and **38–39**, involving five-, six- and seven-membered rings, as well as a linear siloxane **40**, containing two hydroxyl groups at the terminal positions. The major products are **39** and **40**. However, when the oxidation was carried out under argon (column B), the oxygen-insertion products do no longer predominate, and instead, four additional linear products **41–44**, which contain OH, Et, Me, AcO or H at their terminal positions, were detected. The origin of the methyl group, which was found in **43**, could stem from Kolbe-type electrolysis of the acetate anion. Although it seems that by replacing the acetate anion with HSO<sub>4</sub><sup>-</sup> the reaction becomes more selective (four products; compare column C with A), only about half of the substrate was electrolyzed. However, a sole and new linear product was formed as the major one, the dihydroxysiloxane, **45**. It is noteworthy that in the presence of acetate anion, the sole linear product was the dihydroxysilane, **40**. By comparing columns A with C one could conclude that HSO<sub>4</sub><sup>-</sup> promotes the formation of products with higher oxygen content than those obtained in the presence of acetate anion.

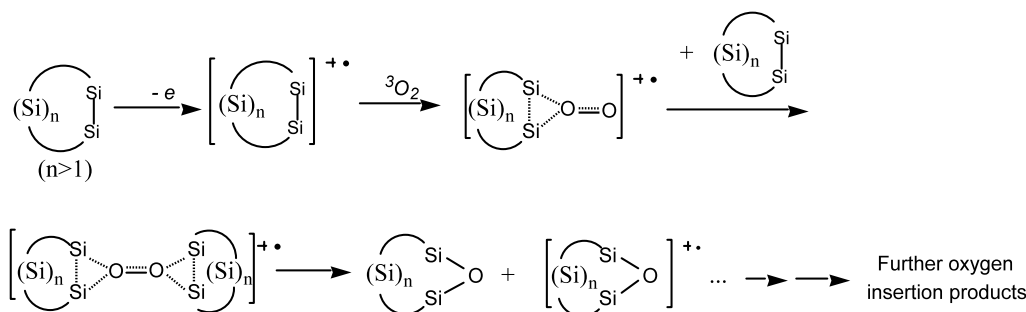
Table 4  
Results from anodic oxidation of **V** on graphite<sup>a</sup>

Product	Yield (%) <sup>b</sup>		
	A	B	C
<b>V</b>	–	–	44
<i>Cyclic</i>			
(Et <sub>2</sub> Si) <sub>4</sub> O <sub>2</sub> ( <b>19</b> )	8	5	7
(Et <sub>2</sub> Si) <sub>4</sub> O <sub>3</sub> ( <b>20</b> )	4	5	7
(Et <sub>2</sub> Si) <sub>4</sub> O <sub>4</sub> ( <b>21</b> )	–	–	4
(Et <sub>2</sub> Si) <sub>5</sub> O ( <b>23</b> )	7	7	–
(Et <sub>2</sub> Si) <sub>5</sub> O <sub>2</sub> ( <b>24</b> )	–	14	–
(Et <sub>2</sub> Si) <sub>3</sub> O <sub>2</sub> ( <b>38</b> )	5	–	–
(Et <sub>2</sub> Si) <sub>4</sub> O ( <b>39</b> )	37	–	–
<i>Linear</i>			
(HO) <sub>2</sub> (Et <sub>2</sub> Si) <sub>3</sub> ( <b>40</b> )	16	–	–
(HO) <sub>2</sub> (Et <sub>2</sub> Si) <sub>5</sub> O <sub>2</sub> ( <b>41</b> )	–	6	–
Et(Et <sub>2</sub> Si) <sub>4</sub> (OH) ( <b>42</b> )	–	16	–
Me(Et <sub>2</sub> Si) <sub>5</sub> H ( <b>43</b> )	–	20	–
Et(AcO)(Et <sub>2</sub> Si) <sub>3</sub> O ( <b>44</b> )	–	13	–
(HO) <sub>2</sub> (Et <sub>2</sub> Si) <sub>3</sub> O <sub>2</sub> ( <b>45</b> )	–	–	25

A: 0.1 M KOAc–4:1:1 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN/HOAc; ACP, 1.2 V; The CV of **V** exhibits one irreversible oxidation peak at 1.4 V; A, under air. B: As in “A”, but under Ar. C: 0.1 M TEAHSO<sub>4</sub>–4:1 CH<sub>3</sub>OH–CH<sub>2</sub>Cl<sub>2</sub>, under air, on graphite. ACP, 1.1 V. The CV of **V** exhibits one irreversible oxidation peak at 1.3 V.

<sup>a</sup> The mass of the product mixture after electrolysis and work-up was 60–90% of the mass of **I** before electrolysis. Electricity consumption: 4 F mol<sup>-1</sup>.

<sup>b</sup> This column represents relative yields as determined by GLC.



Scheme 7. Mechanism of oxygen insertion in the presence of O<sub>2</sub>.

### 3.2.4. Electrolysis in the presence of $CF_3COONa$ (TFANa)

In our previous work we came to the conclusion that both perchlorate and molecular oxygen from air could play a role in the formation of cyclic and linear siloxanes, from cyclic polysilanes, by being the source of oxygen in the insertion process. Although we abandoned the role of water molecules, as explained in the previous section, it cannot be totally ruled out. Therefore, electrolysis of “Si<sub>3</sub>” through “Si<sub>9</sub>” cyclic polysilanes was conducted in the dry box [26], to eliminate oxygen and moisture, and in the presence of a known weak nucleophile,  $CF_3COO^-$  (TFA). The chosen media was 0.1 M TFANa–4:1:1  $CH_2Cl_2$ – $CH_3CN$ –TFA acid, and few drops of  $TFA_2O$ , to further eliminate any trace of water. Cyclic voltammograms of the cyclic polysilanes studied in this media indicate that all compounds, except for **I**, exhibit two irreversible oxidation waves, the first being 10–40 mV lower than what was observed in 0.1 M  $Et_4NClO_4/CH_2Cl_2$ – $CH_3CN$  (4:1, v:v) solution, also at Pt working electrode. The results of preparative electrolysis are summarized in Scheme 8.

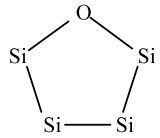
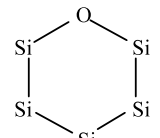
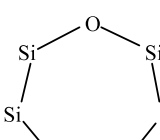
Derivative **I** could not be electrolyzed at all, while the remaining ones left 20–40% unreacted starting material after consuming 1–2.5 F mol<sup>-1</sup>, depending on the

substrate. Under these conditions, the reaction became quite selective, but surprisingly, even under the previously described strict conditions, all formed major products contain one oxygen atom as cyclic siloxanes, along with minor cyclic siloxanes with two oxygen atoms, at most. No linear siloxanes were detected.

Now the obvious question, which arises, is where the oxygen atoms in the products mentioned in Scheme 8 come from? A plausible mechanism is described in Scheme 9 and may shed light on this issue. It shows how two TFA anions participate in the mechanism by contributing one of their oxygen atoms, and leave as the corresponding anhydride,  $TFA_2O$ . In attempts to try to trap a diester intermediate,  $[(Si)_n(OCOCF_3)_2]$ , electrolysis was carried out in 0.1 M TFANa– $CH_3CN$ , with no TFA (in order to avoid acid catalysis hydrolysis of the diester), in the dry box. Evidently, electrolysis could not take place due to very low currents. This observation points to the important role that TFA acid plays in executing the electrolysis.

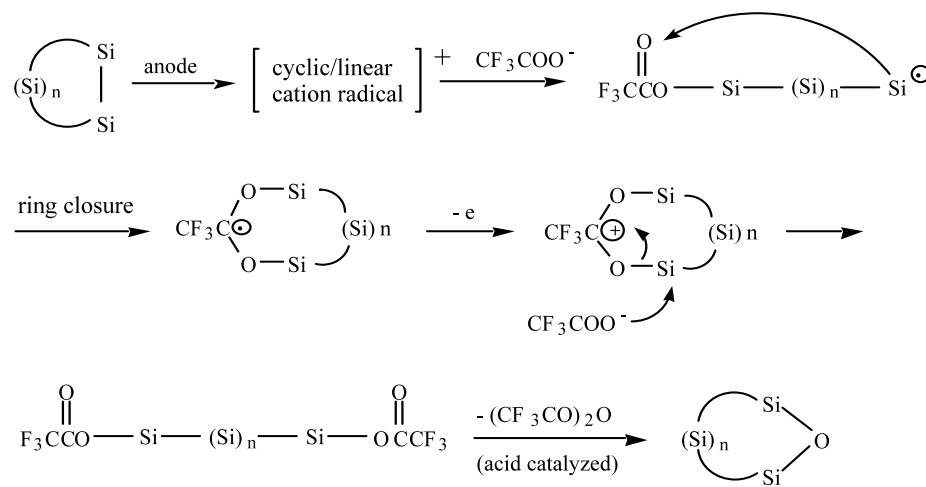
### 3.2.5. Electrolysis in the presence of $Ph_4B^-$ salts

After realizing the remarkable involvement of fluorine and oxygen atoms in the products, originating from the so called “naïve” electrolytes, it seemed quite logical to try out electrolytes which do not contain neither oxygen

Unreacted starting material	(%)/Fmol <sup>-1</sup>	Major products (%)
(Mes <sub>2</sub> Si) <sub>3</sub>	(100)/0	No reaction
[t-Bu(Me)Si] <sub>4</sub>	(25)/1.1	 (65)
(n-Pr <sub>2</sub> Si) <sub>5</sub>	(19)/1.2	 (55)
(Me <sub>2</sub> Si) <sub>6</sub>	(40)/2.5	 (56)
(Et <sub>2</sub> Si) <sub>7</sub>	(0)/2.5	$Si_4O$ ; $Si_4O_2$ $Si_5O$ ; $Si_5O_2$ } (75)
(Me <sub>2</sub> Si) <sub>8</sub>	(36)/2.5	} (Gave the same products) $Si_5O$ ; $Si_5O_2$ $Si_6O$ ; $Si_6O_2$ } (70)
(Me <sub>2</sub> Si) <sub>9</sub>	(23)/2.5	

Scheme 8.





Scheme 9.

nor fluorine atoms in their chemical structures. Consequently, we have chosen [27] the sodium and tetrabutylammonium salts of  $\text{Ph}_4\text{B}^-$ . Unfortunately, it turned out that  $\text{Ph}_4\text{B}^-$  anion competes favorably with the oxidation of the cyclic polysilanes **IIa** and **IIIa**. However, we did observe some silicon products that have not been fully characterized yet. According to HRMS, some of them contain fragments, which correspond to “ $\text{Ph}_2\text{B}(\text{SiR}_2)_n$ ” moieties. Our next attempts will be to utilize electrolytes that are more difficult to oxidize, such as  $(\text{C}_6\text{F}_5)_4\text{B}^-$  salts.

### 3.2.6. Effect of ring size

In order to study the *net* effect of the ring size on the spectrum and nature of electrolytic products, one must study cyclic polysilanes bearing the same substituents. Of the ones described in Scheme 1, only four derivatives, **IIb**, **IIIb**, **IVb** and **V**, contain ethyl groups. Their cyclic voltammetric data [28] are listed in Table 1, showing no

Table 5  
The effect of ring size on the electrochemical oxidation<sup>a</sup> of perethylcyclopolysilanes

Products	Yield (%) <sup>b</sup>			
	<b>IIb</b> , 0.95 <sup>c</sup>	<b>IIIb</b> , 1.2 <sup>c</sup>	<b>IVb</b> , 1.2 <sup>c</sup>	<b>V</b> , 1.2 <sup>c</sup>
Starting material	–	45	–	–
$[\text{Et}_2\text{Si}]_4\text{O}$ ( <b>46</b> )	87	3	23	22
$[\text{Et}_2\text{Si}]_4\text{O}_2$ ( <b>47</b> ) <sup>d</sup>	9	10	60	67
$[\text{Et}_2\text{Si}]_5\text{O}$ ( <b>48</b> )	–	38	8	6
$[\text{Et}_2\text{Si}]_5\text{O}_3$ ( <b>49</b> )	–	4	–	–
$[\text{Et}_2\text{Si}]_4\text{O}_3$ ( <b>50</b> )	–	–	4	5
$[\text{Et}_2\text{Si}]_4\text{O}_4$ ( <b>51</b> )	–	–	5	–

<sup>a</sup> Electricity consumption stopped at  $1.2 \text{ F mol}^{-1}$  arbitrarily in order to compare the electrochemical reactivity of cyclopolysilanes.

<sup>b</sup> Yields reported are relative and estimated by GLC.

<sup>c</sup> Applied controlled potentials are in volts vs. Ag quasi-reversible reference electrode.

<sup>d</sup> Could involve two isomers.

particular effect of the substituents on the anodic peak potentials, between rings of the same size. The outcomes of CPE experiments, at Pt, under nitrogen atmosphere and in  $0.1 \text{ M Bu}_4\text{NHSO}_4\text{--CH}_2\text{Cl}_2\text{--CH}_3\text{CN}$  (4:1, v:v), are summarized in Table 5. Except for **IIIb**, all other derivatives left no starting material after consuming  $\sim 1\text{--}1.2 \text{ F mol}^{-1}$ . Also, it seems that the reaction is most selective for **IIb**, affording only two products (**46** and **47**), the favorable one in 87% yield. Upon further examination of the results in Table 5, some interesting observations could be deduced, as follows:

- Cyclic siloxanes are formed exclusively (no linear products were detected).
- The formation of five- and six-membered siloxanes, with one or two oxygen atoms inserted, as major products, is preferred. The highest selectivity in terms of the number of products obtained is shown by **IIb**, which yields two products only, while all other cyclic polysilanes afford 4–5 products each. It seems that for the cyclic polysilanes bearing the same substituents, the product selectivity depends on the size of the ring, with smaller rings favoring higher product selectivity.
- For **IIb** and **IIIb**, ring expansion by one oxygen atom insertion, keeping the original number of silicon atoms, is predominant. However, the major pathway for **IVb** and **V** involves ring ‘chopping’ followed by two (at least) oxygen atoms insertion. It seems that the larger the ring size in the parent cyclopolysilane, the higher the number of oxygen atoms inserted in the products.
- The fact that no starting material is left from **IIb**, **IVb** and **V**, and as much as 45% from **IIIb**, may suggest that the former three compounds have higher electrochemical reactivity than **IIIb**, which is particularly stable in this series. In fact, it is known that ring stability in cyclic polysilanes

depends on the size of the organic groups which are appended [29]. For instance, the cyclic pentamer is also the most stable ring in the perphenyl series [30].

#### 4. Summary

It has been found that both the type and spectrum of products emerged from electrochemical oxidation of cyclic polysilanes, are highly sensitive to a variety of factors: nature of electrolyte, amount of molecular oxygen dissolved in solution, type of anode material, amount of electricity consumed, etc. By employing  $\text{BF}_4^-$  salts as the electrolytes, the electrochemical process undergoes ring opening exclusively, followed by further Si–Si bond cleavage to form  $\alpha,\omega$ -difluorosilanes,  $\text{F}-(\text{SiR}_2)_n-\text{F}$  as the major products.

It seems that perchlorate anions promote the formation of “oxygen-rich” cyclic siloxanes, whereas acetate anions and sulfate favor the formation of linear silanes and siloxanes (mostly with two hydroxyl groups at the terminal positions). Whenever methanol was used as a co-solvent (this issue was not discussed in this survey), the electrolysis of the substrate was either incomplete or did not take place at all. It seems that under these conditions the solvent methanol competes favorably with the oxidation of cyclic polysilanes. The use of acetonitrile or acetic acid as co-solvents with dichloromethane, led to the formation of additional linear products containing a ‘ $\text{CH}_3\text{COO}$ ’ or ‘ $\text{CH}_2\text{CN}$ ’ group (or both), at the terminal positions of the chain. Also, it was found that acetate anion promotes the formation of linear dihydroxysilanes and cyclic siloxanes (under air), whereas hydrogen sulfate anion favors the formation of dihydroxysiloxanes (and cyclic siloxanes), which are richer with oxygen contamination. As to the anode material, it appears that the oxidation on Pt was more efficient and more selective than on graphite. For comparison, it is noteworthy that six-membered cyclic silanes are most inert to oxygen. Dodecamethylcyclohexasilane **IVa** was untouched practically by atmospheric oxygen or by 30% hydrogen peroxide. However, its chemical oxidation by MCPBA underwent ring insertion exclusively, but gave only 40% of a mixture of cyclic siloxanes after 3 days, leaving 60% of unreacted substrate [31]. While the four-membered ring, **IIa** is inert to dioxygen and even to concentrated sulfuric acid [31], the octamethyl cyclic derivative,  $(\text{Me}_2\text{Si})_4$ , reacts rapidly with molecular oxygen [32].

Electrolysis in the presence of  $\text{CF}_3\text{COO}^-$  (TFA) salt in the dry box, under strict conditions of oxygen and moisture, led to high selectivity since the major products were cyclic siloxanes containing only one oxygen atom. It has been postulated that the origin of oxygen in this case stems from the TFA electrolyte.

The net effect of ring size, which was studied with cyclic siloxanes bearing the same substituents (ethyl groups) attached to the silicon atoms, afforded a distinctive major five- or six-membered siloxanes, containing either one or two oxygen atoms, from each cyclic polysilane studied in this series. In addition, the cyclic silanes with four- and five-membered rings, **IIIb** and **IIIb**, gave products with retention of the original number of silicon atoms, whereas the six- and seven-membered rings, **IVb** and **V**, underwent fragmentation to yield also cyclic siloxanes, but with a loss of 1–3 Si atoms.

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