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Electrochemical behaviour of three- to nine-membered cyclic polysilanes

Z.-R. ZHANG*, J. Y. BECKER

Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84120, Israel

R. WEST

Department of Chemistry, University of Wisconsin, Madison, WI 53706, USA

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The electrochemical behaviour of cyclic polysilanes, namely, hexamesitylcyclotrisilane $(Mes_2Si)_3$ (**I**), 1,2,3,4-tetra-*tert*-butyltetramethyl-cyclotetrasilane $[t\text{-Bu(Me)Si}]_4$ (**II**), decaethylcyclopentasilane $(Et_2Si)_5$ (**III**), decapropylcyclopentasilane $(Pr_2Si)_5$ (**IV**), dodecamethylcyclohexasilane $(Me_2Si)_6$ (**V**), tetradecaethylcycloheptasilane $(Et_2Si)_7$ (**VI**), hexadecamethylcyclooctasilane $(Me_2Si)_8$ (**VII**) and octadecamethylcyclononasilane $(Me_2Si)_9$ (**VIII**), have been studied by cyclic voltammetry and preparative scale electrolysis. The effects of electrolyte, ring size and nature of substitutes both on oxidation peak potential and upon reactivity as well as style of product are discussed.

Keywords: *Cyclic polysilanes, cyclic siloxanes, electrochemical oxidation*

1. Introduction

Peralkylpolysilanes have attracted interest because they exhibit potential applications in photoconducting and charge-transporting materials [1]. They show unique electronic, physical and chemical properties which distinguish these compounds from saturated catenates of carbon [2]. In particular, cyclic polysilanes resemble in their behaviour aromatic hydrocarbons, in that they have electronic transitions in the u.v.–vis. region, form anion radicals upon reduction and cation radicals upon oxidation, in which the odd electron is distributed over the ring, form charge-transfer complexes with π-acceptors, and exhibit substituent effects. The synthesis, structure, chemical reactions and photolysis of cyclic polysilanes are described in a recent review by West [3].

It has been found that cyclic polysilanes can be oxidized by organic peracids [4, 5] to form siloxanes, which may result from the sequential insertion of oxygen atoms into the Si–Si bonds of the cyclic polysilanes. Ring size, nature of the substituents attached to the silicon, steric factors and nature of the heteroatoms included in the ring, are the main factors determining the reactivity. Also, it was found that the initially inserted oxygen atom in the ring activates adjacent Si–Si bonds towards further insertion of oxygen atoms [4]. Furthermore, a well-known reaction of cyclosilanes is photochemical extrusion of a silylene fragment, R_2Si, yielding a ring-contracted product. In recent years this reaction has developed importance as a method for synthesis of disilenes, $R_2Si = SiR_2$ [6]. For example, $(Mes_2Si)_3$ undergoes photolysis to $Mes_2Si = SiMes_2$ and the silylene Mes_2Si; the latter dimerizes to produce more disilene.

Study of alkyl derivatives of group 14 elements has shown that these compounds undergo irreversible oxidation, with oxidation potentials which are linearly related to first ionization energies [7]. A series of linear permethylsilanes, $Me(SiMe_2)_nMe$ where $n = 2$ to 6, was studied by Boberski and Allred, who found that the oxidation potentials decrease with increasing chain length, and are correlated with u.v. spectra and with Sandorfly C calculations [8].

There is fairly limited information in the literature on the electrochemical behaviour of cyclic polysilanes. Earlier papers from our laboratory [9, 10] described the preparative scale electrolyses of medium size cyclic polysilanes, namely five-, six- and seven-membered rings, under various experimental conditions. The preparative scale electrolyses of cyclic peralkylsilanes in the presence of tetraalkylammonium tetrafluoroborate salts underwent ring opening followed by further Si–Si bond cleavage and reaction with BF_4^-, forming α, ω-difluorosilanes, $F\text{–}(SiR_2)_n\text{–}F$, as the major products [9]. However, their anodic oxidation in the presence of other electrolytes (ClO_4, HSO_4^-, AcO^-) which do not contain fluorinated anions, led to both oxygen insertion and ring-opening processes to form mainly cyclic and linear siloxanes [10]. In more recent work we reported the electrochemical oxidation of cyclic polysilanes to small rings $[t\text{-Bu(Me)Si}]_4$ and $(Mes_2Si)_3$ [11]. The anodic oxidation of the former led to oxygen insertion process and gave cyclic siloxanes as the major products, and the latter underwent ring opening followed by further

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* Author to whom correspondence should be addressed.

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Si–Si bond cleavage and a reaction with the electrolyte to generate mostly linear products of type: X–$(Mes_2Si)_n$–Y ($n = 1, 2$; X, Y = mesityl, H, OH or F).

Our objective here is to present our further understanding of electrochemical behaviour of cyclic polysilanes. Two techniques, cyclic voltammetry and controlled potential electrolysis, are used in this work. The effects of structure on the electrochemical behaviour of cyclic polysilane are discussed.

2. Experimental details

2.1. *Chemicals*

The related cyclic polysilanes: hexamesitylcyclotrisilane $(Mes_2Si)_3$ (**I**), 1,2,3,4-tetra-*tert*-butyltetramethylcyclotetrasilane [*t*-Bu(Me)Si]$_4$ (**II**), decaethylcyclopentasilane $(Et_2Si)_5$ (**III**), decapropylcyclopentasilane $(Pr_2Si)_5$ (**IV**), dodecamethylcyclohexasilane $(Me_2Si)_6$ (**V**), tetradecaethylcycloheptasilane $(Et_2Si)_7$ (**VI**), hexadecamethylcyclooctasilane $(Me_2Si)_8$ (**VII**) and octadecamethylcyclononasilane $(Me_2Si)_9$ (**VIII**) were synthesized according to the usual methods [3]. Tetraethylammonium perchlorate (TEAP, from Southwestern Analytical Chemicals), tetrabutylammonium hydrogensulfate ($TBA^+HSO_4^-$, from Fluka), potassium acetate (from British Drug House) and tetraethylammonium tetrafluoroborate ($TEA^+BF_4^-$, from Adrich Chemical Company) were used as supporting electrolytes without further purification. HPLC grade CH_2Cl_2, CH_3CN and CH_3COOH [distilled from CaH_2, P_2O_5 and $(CH_3CO)_2O$, respectively], were used in all electrochemical experiments.

2.2. *Electrochemical measurements*

Cyclic voltammetric experiments were performed using a conventional three-electrode cell. The working electrode was a platinum disc electrode (~1 mm diam.). A quasi-reference electrode (Ag/AgCl) was used. The auxiliary electrode in these studies was a Pt electrode. The concentration of cyclic polysilane was 0.5–1 mmol dm^{-3}, while that of the supporting electrolyte was 0.1 mol dm^{-3}. An H-type two-compartment cell equipped with medium glass frit as a membrane was used for preparative electrolysis. The anode compartment contained a polished silver wire quasi-reference electrode, immersed in electrolyte solution in a glass cylinder with a fine glass frit at its end. Typically, the anodic compartment contained 0.05–0.1 mmol of cyclic polysilane dissolved in 25 ml of solvent–electrolyte solution. For electrochemical measurements, a PAR potentiostat (model 173), a PAR universal programmer (model 175) and a Yokogawa XY-recorder (model 3068) were employed.

Electrolyses were conducted at controlled potential of 0.65–1.30 V vs Ag wire, on Pt foil. The workup involved stripping of the solvent followed by water addition and extraction of the product mixture into diethyl ether, in which the electrolytes used were insoluble. In general, the mixture of products obtained after phase separation, drying over $MgSO_4$, filtration and evaporation, was submitted to GCMS and HRMS analyses. A Finnigan 4020 Quadrupole mass spectrometer was used for routine mass spectral measurements, and a high resolution Fison VG AutoSpec for high resolution measurements (HRMS), coupled with HP 5890 series II gas chromatograph (GCMS).

3. Results and discussion

3.1. *Cyclic voltmmetry*

Figure 1 shows the representative cyclic voltammograms which are recorded in 0.1 mol dm^{-3} $TBA^+HSO_4^-$–CH_2Cl_2–CH_3CN (4 : 1 v/v) on Pt. Two irreversible oxidation waves are observed for cyclic polysilane **II** (curve 1: wave A and B). Curve 2 represents the cyclic voltammogram of product [*t*-Bu(Me)Si]$_4$O (**1**), which is formed by electrochemical oxidation of cyclic polysilane **II**. It is clear that the product **1** shows one irreversible wave (B′) at the potential which is just the second oxidation peak potential of **II**. This indicates that the second oxidation peak of **II** belongs to the oxidation of [*t*-Bu(Me)Si]$_4$O(**1**) which is formed at the first oxidation wave of **II**.

Anodic peak potentials of **II** in different electrolyte solutions are listed in Table 1. First, it is noteworthy that in the presence of ClO_4^- the first oxidation wave is significantly lower compared to all other electrolytes studied. Presumably this anion stabilizes the transition state of the intermediate forms by the initial

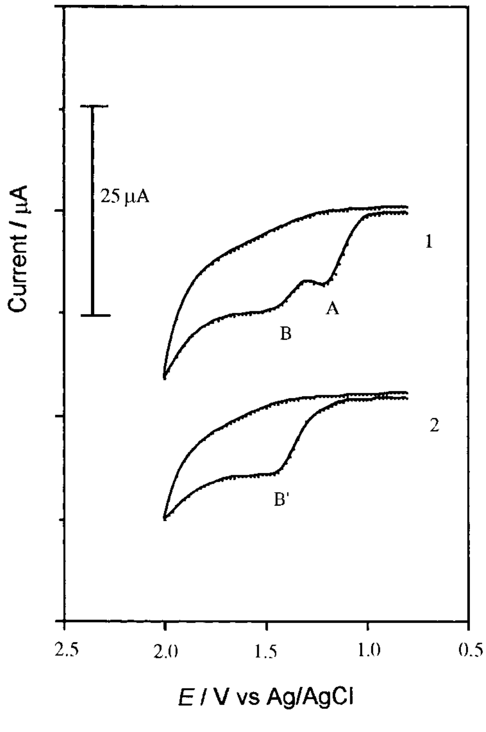


Fig. 1. Representative cyclic voltammograms. (1) Cyclic polysilane $(t\text{-}BuMeSi)_4$; (2) Product $(t\text{-}BuMeSi)_4O$; electrolyte solution: 0.1 mol dm^{-3} $TBAHSO_4$–CH_2C_{12}–CH_3CN (4 : 1 v/v).

*Table 1. Anodic peak potentials of **II** in different electrolyte solutions**

Electrolyte (0.1 M)	*Solvent* (v/v)	$E^1_{p_{ox}}$ /V†	$E^2_{p_{ox}}$ /V†
$TEA^+ClO_4^-$	CH_2Cl_2–CH_3CN (4:1)	1.05	1.4
$TBA^+HSO_4^-$	CH_2Cl_2–CH_3CN (4:1)	1.25	1.5
$TEA^+BF_4^-$	CH_2Cl_2–CH_3CN (4:1)	1.15	1.5
KOAc	CH_2Cl_2–CH_3CN–AcOH (4:1:1)	1.20	–

* All peaks are irreversible; concentration of **II**: 0.5–1.0 mmol dm^{-3}; working electrode: Pt.

† With respect to Ag/AgCl.

anodic oxidation step, more than the other ones do. Second, in the presence of $TEA^+ClO_4^-$, $TBA^+HSO_4^-$ and $TEA^+BF_4^-$, two waves are detected with potential difference of about 300 mV; whereas in the presence of KOAc, only one irreversible wave is observed. The reason for the absence of the second oxidation peak is not so clear. In fact, the nature of the supporting electrolyte on electrochemical reactivity at the electrode surface is believed to be important but is not nearly so well understood [12a].

Relationship between the first oxidation potentials and the structures of cyclic polysilanes is shown in Fig. 2. The first oxidation potentials for cyclosilanes depend both upon ring size and on the nature of substitutes on silicon. The oxidation potentials increase going from three- to four- and higher membered rings, with the lowest potential (0.80 V vs Ag/AgCl) of all tested for the highly strained compound, $(Mes_2Si)_3$ (**I**). However, there is little difference between oxidation potentials for five-, six-, seven- and eight-membered rings. Furthermore, it is noteworthy that the oxidation potential decreases going from eight- to nine-membered rings.

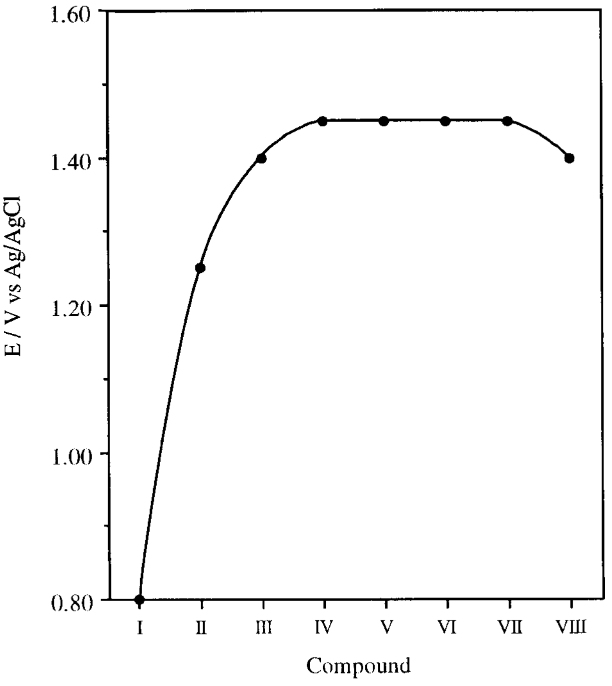


Fig. 2. Effects of structures of cyclic polysilanes on anodic peak potentials. Electrolyte solution: 0.1 mol dm^{-3} $TBAHSO_4$–CH_2C_{12}–CH_3CN (4 : 1 v/v); concentration of cyclic polysilanes: 1 mmol dm^{-3}; working electrode: Pt.

In general, the oxidation potentials are well correlated with electronic absorption energies. For example, for the linear permethylpolysilanes, the oxidation potentials decreased and the lowest energy electronic absorption bands moved to longer wavelengths as the chain length increases [3, 8]. The cyclic polysilanes with small and medium size rings, however, showed an opposite trend for their u.v. absorption bands, a bathochromic shift was observed as the ring size decreases. The u.v. absorption moved to longer wavelengths with increasing ring size for larger rings (containing more than eight silicon atoms) [3]. The electronic spectra of cyclic polysilanes actually consist of a series of overlapping absorptions. The low energy bands, including the HOMO to LUMO transition, have small absorptivity, while the higher energy transitions are more highly permitted. The relative energies of the HOMOs in cyclic polysilanes can be estimated from oxidation potentials [12b, 13]. Rings from Si_8 to Si_5 have approximately equal oxidation potentials, so the bathochromic shift with decreasing ring size is mainly due to stabilization of the LUMO. Going from Si_5 to Si_4 and Si_3 the oxidation potentials decrease significantly, indicating destabilization of the HOMO. This is consistent with the increases in Si–Si bond length [14]. Quantitatively, it has been found that about half of the decrease in the σ–σ^* excitation energy going from Si_5 to Si_4 rings could be accounted for in the increased energy of HOMO, due to ring strain and lengthened Si–Si bonds in the Si_4 ring. For Si_3 ring, where ring strain is much more severe, about 75% of the bathochromic shift, compared with Si_5 ring, was attributable to destabilization of HOMO [3]. The remainder of the decrease in excitation energy must be due to progressive stabilization of the LUMO, as ring size decreases from Si_5 to Si_3. It has been suggested that stabilization of the LUMO may result because the smaller ring is more nearly planar; this would imply that the LUMO is made up of out-of plane *p* orbitals on the silicon atoms [12, 15], which can overlap best in planar ring.

3.2. *Preparative scale electrolyses*

*3.2.1. Anodic oxidation four-membered cyclic polysilane **II**.* The electrochemical oxidation of **II** is investigated in different conditions, as summarized in Table 2. The results show that when $TBA^+HSO_4^-$ is used as the electrolyte (column A), the cyclic polysilane derivative **II** undergoes oxygen insertion exclusively and the electrochemical oxidation is quite selective because it give only one cyclic siloxane, **1** (involves only one oxygen atom), in quantitative yield. This product remains predominant (90.3%) also when $TBA^+HSO_4^-$ is replaced by KOAc (column B). However, in the latter case, the reaction mixture is not able to consume more than 1.5 F mol^{-1} of

*Table 2. Anodic oxidation of **II** on Pt*[a]

Products[b]	*F* mol^{-1}:	Yield/%[c] *A* 2.4	*B* 1.5[d]	*C* 2.4	*D* 1.9[d]	*E* 1.2	*F* 3.1	*G* 4.0	Mass spectrum (*EI*)
I		–	4.9	–	–	33.0	–	–	
[*t*-Bu(Me)Si]$_4$O (**1**)		100[e]	90.3	30.0	35.9	65.5	97.2	–	416 (M$^+$), 359, 303, 133, 73(100%)
[*t*-Bu(Me)Si]$_4$O$_2$ (**2**)		–	–	62.5	–	–	2.8	51.7	432 (M$^+$), 375, 319, 73(100%)
[*t*-Bu(Me)Si]$_4$O$_3$ (**3**)		–	–	–	–	–	–	43.8	448 (M$^+$), 391(100%), 207, 73
[*t*-Bu(Me)Si]$_3$O$_3$ (**4**)		–	–	7.5	–	–	–	4.5	348 (M$^+$), 291, 249, 207(100%)
F[*t*-Bu(Me)Si]$_4$F (**5**)		–	–	–	59.8[f]	–	–	–	438 (M$^+$), 423, 419, 381, 319, 73(100%)
F[(*t*-Bu(Me)Si)$_4$O]F (**6**)		–	–	–	4.3	–	–	–	454 (M$^+$), 397, 335, 293, 73(100%)

[a] All applied controlled potentials (ACP) in electrolyses are vs Ag quasi-reversible reference electrode. Initial concentration of **II**: 2–4 mM.

[b] Measurements of molecular weights of major products are satisfactory: **1**, found 416.2804 (calculated for $C_{20}H_{48}OSi_4$ 416.2782); **2**, found 432.2687 (calculated for $C_{20}H_{48}O_2Si_4$ 432.2731); **3**, found 448.2693 (calculated for $C_{20}H_{48}O_3Si_4$ 448.2680).

[c] Mass of the product mixture after electrolysis and work-up are 80–88% of the mass of [*t*-BuMeSi]$_4$ before electrolysis. Yields reported are relative and estimated by GLC.

[d] Electrolyses are terminated when current reached the background level.

[e] This product is submitted for elemental analysis and i.r.: Found: C 57.36%, H 11.33% (calculated: C 57.61%, H 11.60%) i.r.: 3043.48, 2930.43, 2843.48, 1260.87 and three typical absorptions for 'Si–O' bond: 1005.83, 964.56, 929.85 cm^{-1}.

[f] High resolution MS results of this product are as follow: M$^+$–CH$_3$, found: 423.2553 (calculated for $C_{19}H_{45}F_2Si_4$ 423.2566); M$^+$–F, found: 419.2805 (calculated for $C_{20}H_{48}FSi_4$ 419.2817); M$^+$–Bu^t, found: 381.2110 (calculated for $C_{16}H_{39}F_2Si_4$ 381.2097).

A, E and F: 0.1 M TBA$^+$HSO$_4^-$–CH$_2$Cl$_2$–CH$_3$CN (4 : 1 v/v); ACP = 1.05 V.

B: 0.1 M KOAc–CH$_2$Cl$_2$–CH$_3$CN–AcOH (4 : 1 : 1 v/v); ACP = 1.05 V.

C and G: 0.1 M TEA$^+$ClO$_4^-$–CH$_2$Cl$_2$–CH$_3$CN (4 : 1 v/v); ACP = 0.90 V.

D: 0.1 M TEA$^+$BF$_4^-$–CH$_2$Cl$_2$–CH$_3$CN (4 : 1 v/v); ACP = 0.95 V.

electricity, and the reaction is not so complete because a small amount of starting material is left (~5%). Column C describes the results obtained by anodic oxidation of **II** in CH$_2$Cl$_2$–CH$_3$CN solution containing 0.1 mol dm^{-3} tetraethylammonium perchlorate. In this case, the cyclic polysilane derivative **II** undergoes oxygen insertion exclusively, affording cyclic siloxanes **1** and **2** (involve one and two oxygen atoms, respectively) as the major products, along with a small amount of decomposition product **4** (involves three oxygen atoms). Upon comparing the results described in column A with those in column C, a possible conclusion could be deducted, that ClO$_4^-$ promotes the oxygen insertion reaction. A plausible mechanism describing the involvement of the perchlorate anion was discussed previously [10].

The results of the electrochemical oxidation of **II** on platinum, in CH$_2$Cl$_2$–CH$_3$CN (4 : 1 v/v) and in the presence of fluorinated anion (0.1 mol dm^{-3} TEA$^+$BF$_4^-$), is shown in column D. Both oxygen insertion and ring-opening processes take place to provide the cyclic siloxane **1** and linear difluoropolysilane **5** as the major products, in 35.9% and 59.8% yields, respectively. In addition, another linear product, a difluoropolysiloxane **6**, is observed in 4.3% yield. It seems that the ring-opening process competes favourably with the oxygen insertion process, in the presence of BF$_4^-$ salt.

The effect of electricity consumed on the distribution of products is also investigated. Upon comparing the results obtained by electrochemical oxidation of **II** in the presence of TBA$^+$HSO$_4^-$, with different electricity consumption (column A, E and F), one observes that the electrochemical oxidation of **II** give cyclic siloxane, **1** (involves only one oxygen atom), as the major products. However, when only 1.2 F mol^{-1} are passed, the reaction is not complete because there is some starting material left (33%); when 3.1 F mol^{-1} are allowed to pass, besides major product **1** (involves only one oxygen atom; ~97%), the product with a higher oxygen content in the siloxane ring, **2** (involves two oxygen atoms), is also formed in about 3% yield. It can be concluded that electrochemical oxidation of **II** with a higher electricity consumption leads to products with a higher oxygen content in the siloxane rings. This result is reminiscent of the outcome from the anodic oxidation of the cyclic peralkylsilane [(*n*-Pr)$_2$Si]$_5$ which showed similar behaviour at different electricity consumption [10]. This conclusion becomes more clear when electrochemical oxidation is conducted in the presence of tetraethylammonium perchlorate (by comparing between the column C and G). It can be observed that when 2.4 F mol^{-1} are passed, the major products are five- and six-membered siloxanes **1** and **2**, which involve insertion of one and two oxygen atoms, respectively. However, when 4.0 F mol^{-1} are allowed to pass, no cyclic siloxane **1** is observed and the major products become cyclic siloxanes **2** and **3** (a seven-membered ring), in about equal ratio, which involve insertion of two and three oxygen atoms, respectively.

3.2.2. Comparison of anodic oxidation of different cyclic polysilanes. The results obtained by electrochemical oxidations of a series of cyclic polysilanes with different ring size and different substituents on silicon atom, in CH$_2$Cl$_2$–CH$_3$CN (4 : 1 v/v) solution containing 0.1 mol dm^{-3} TBA$^+$HSO$_4^-$, on platinum foil, are summarized in Table 3. Apparently, the

Table 3. Distribution of products of anodic oxidation of cyclic polysilanes[a]

		Yield/%[b]								
Products	*Cyclic polysilanes:* *ACP*:	*I* *0.65*	*II* *1.05*	*III* *1.25*	*IV* *1.25*	*V* *1.30*	*VI* *1.25*	*VII* *1.30*	*VIII* *1.25*	*Mass spectrum* (*EI*)
Starting material		–	–	26.1	20.3	87.6	–	84.7	87.5	
Mes_3SiH (**7**)		45.8								386(M^+), 267(100%), 149, 119
$(HO)[Mes_2Si]_2(OH)$ (**8**)		12.6								566(M^+), 329, 283, 267, 165(100%), 120
$Mes_2Si(OH)_2$ (**9**)		9.1								300(M^+), 283, 181(100%), 119
$Mes[Mes_2Si]_2H$ (**10**)		4.9								652(M^+), 385, 295, 267(100%), 119
Mes_2SiH_2 (**11**)		4.5								268(M^+), 149(100%), 119
Mes_3SiOH (**12**)		2.9								402(M^+), 385, 283(100%), 163, 119
$[t\text{-}Bu(Me)Si]_4O$ (**1**)			100							416(M^+), 359, 303, 133, 73(100%)
$[Pr_2Si]_5O$ (**13**)					44.3					586(M^+), 543, 115, 73(100%)
$[Pr_2Si]_5O_2$ (**14**)					4.0					602(M^+), 559, 228(100%), 186
$[Pr_2Si]_4O_2$ (**15**)					3.4					488(M^+), 445, 289, 117(100%)
$[Pr_2Si]_4O_3$ (**16**)					7.8					504(M^+), 461(100%), 419
$[Pr_2Si]_4O_4$ (**17**)					3.8					520(M^+), 477(100%), 196, 175
$[Pr_2Si]_3O_3$ (**18**)					15.1					390(M^+), 347, 305, 263(100%)
$[Me_2Si]_6O$ (**19**)						4.8		–	1.0	364(M^+), 349, 291, 116, 73(100%)
$[Me_2Si]_6O_3$ (**20**)						1.8		–	–	396(M^+), 381, 323, 116, 73(100%)
$[Me_2Si]_5O$ (**21**)						–		1.8	1.1	306(M^+), 291, 233, 73(100%)
$[Me_2Si]_5O_2$ (**22**)						4.0		1.9	2.3	322(M^+), 307, 249, 116, 73(100%)
$[Me_2Si]_5O_3$ (**23**)						1.8		6.1	1.6	338(M^+), 323, 265, 116(100%), 73
$[Me_2Si]_5O_4$ (**24**)						–		1.4	–	354(M^+), 339, 281, 73(100%)
$[Me_2Si]_4O$ (**25**)						–		1.0	–	264(M^+), 249, 205(100%), 73
$[Et_2Si]_5O$ (**26**)				18.9			–			446(M^+), 417(100%), 331
$[Et_2Si]_5O_2$ (**27**)				6.7			–			462(M^+), 433(100%), 347, 172
$[Et_2Si]_4O$ (**28**)				5.7			–			360(M^+), 331(100%), 273
$[Et_2Si]_4O_2$ (**29**)				21.0			–			376(M^+), 347(100%), 319, 290
$[Et_2Si]_4O_3$ (**30**)				14.5			35.4			392(M^+), 363(100%), 335, 87
$[Et_2Si]_4O_4$ (**31**)				3.6			22.3			408(M^+), 379(100%), 351
$[Et_2Si]_3O_3$ (**32**)				3.5			26.1			306(M^+), 277(100%), 249, 221

[a] All applied controlled potentials (ACP) in electrolyses are vs Ag quasi-reversible reference electrode. Initial concentration of cyclic polysilanes: 2–4 mM. All electrolyses are conducted in 0.1 mol dm^{-3} $TBA^+HSO_4^-$–CH_2Cl_2–CH_3CN on Pt. Electricity consumed: 2.4 F mol^{-1}.

[b] Yields reported are relative and estimated by GLC. With respect to **I** and **VI**, the fact that gas chromatograph also show some compound which is from solvent leads to the decrease of total yields.

general outcome stems from ring opening of cyclic polysilane $(Mes_2Si)_3$ (**I**) followed by fragmentation, affording linear products, exclusively, containing one or two silicon atoms in their skeleton (the first column). Product **7**, which contains one silicon atom and involves a migration of a mesityl group, is formed as the major one (~46%). Its analog (**10**), with two silicon atoms, is detected only in ~5% yield. The rest of the products contain mostly one (**12**) or two (**8**, **9**) hydroxy groups, with a small amount of Mes_2SiH_2 (**11**). No starting material is detected.

The third column describes the product outcome from the electrochemical oxidation of cyclic polysilane $(Et_2Si)_5$ (**III**). The cyclic polysilane derivative **III** undergoes oxygen insertion and gives seven cyclic siloxane products, containing three to five silicon atoms and one to four oxygen atoms in their skeleton. Cyclic polysiloxane **26**, **29** and **30** is formed in about 19%, 21% and 15% yield, respectively. Other four products, **27**, **28**, **31** and **32**, are detected in relative low yields. There are about 26% of starting materials left.

The result obtained by the electrochemical oxidation of $(Pr_2Si)_5$ (**IV**) is shown as the fourth column. Two six-membered cyclic polysiloxanes, **13** (involves five silicon atoms and one oxygen atom) and **18** (involves three silicon atoms and three oxygen atoms), are formed as the major products, in 44% and 15% yield, respectively. Seven-membered rings **14** and **16**, eight-membered ring **17** and other six-membered ring **15** are also formed in about 3% to 8% yields. About 20% of starting material is left.

In the dimethyl series, similar spectra of products are obtained by electrolyses of cyclic polysilanes, **V**, **VII** and **VIII**, involving six-, eight- and nine-membered rings (the fifth, seventh and eighth columns). These cyclic polysilanes undergo oxygen insertion and give seven cyclic siloxanes: **19**, **20**, **21**, **22**, **23**, **24** and **25**, containing four to six silicon atoms and one to four oxygen atoms in their skeleton. However, the reactions are very limited because there are a lot of starting materials (more than 85%) left.

Electrochemical oxidation of cyclic polysilane $(Et_2Si)_7$ (**VI**) leads to the formations of six- to eight-membered cyclic polysiloxanes (**26**, **27** and **28**) with almost average yields. These cyclic siloxanes contain three or four silicon atoms and oxygen atoms in their skeleton. No starting material is detected.

Based on the results obtained by preparative electrolyses of cyclic polysilanes, some interesting conclusions can be obtained. First, it is noticeable that no starting material is left for three-, four- and seven-membered cyclic polysilanes (**I**, **II** and **VI**), whereas there are 20% to 88% of starting materials left for five-, six-, eight- and nine-membered rings (**III**, **IV**, **V**, **VII** and **VIII**). This observation suggests that **I**, **II** and **VI** have higher electrochemical reactivity than **III**, **IV**, **V**, **VII** and **VIII**. Apparently, decreasing the ring size in cyclic polysilanes from five to four and three ring, introduces ring tension, and as a consequence, destabilization of the Si–Si bond [16]. In addition, compound **I** contains mesityl groups and compound **II** contains bulky *t*-butyl groups, therefore these cyclic polysilanes are highly strained [17]. Cyclic polysilane **VI** has higher electrochemical reactivity presumably because that five- or six-membered cyclic polysilanes (**III**, **IV** or **V**) resemble in their behaviour cycloalkanes, in that they are more stable than seven-membered ring.

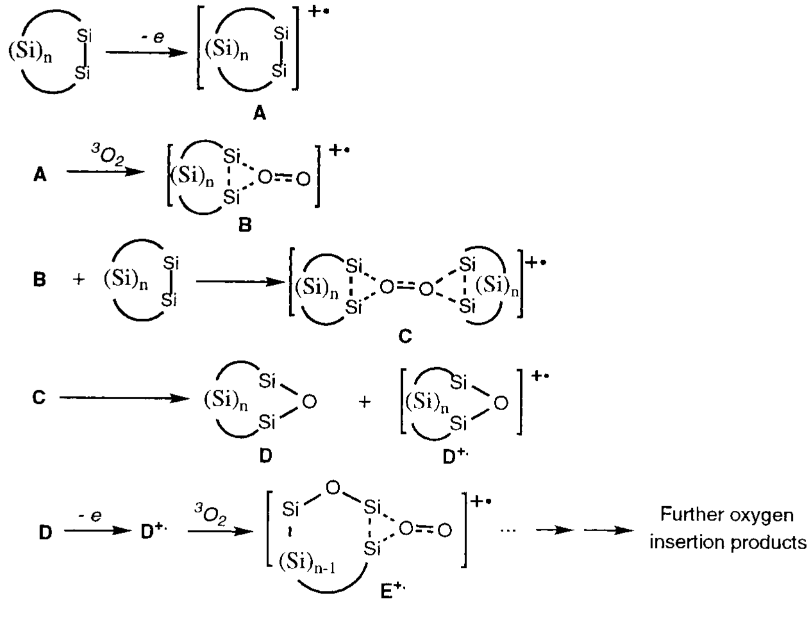
Second, by comparing the reactions of two five-membered rings (**III** and **IV**), it is noteworthy that the starting material left in the anodic oxidation of **IV** (~20%) is lower than **III** (~26%). This fact indicates that **IV** has a higher electrochemical reactivity than **III**, because cyclic polysilane **IV** contains larger substituents on silicon atoms in its skeleton upon comparing propyl and ethyl groups. As a consequence, it can be concluded that, for the cyclic polysilanes with a same ring size, the larger the substituent on silicon atom, the higher the electrochemical reactivity.

Furthermore, in the dimethyl series (**V**, **VII** and **VIII**), the fact which more than 85% of starting materials are left demonstrates the reactions are very limited. The reasons are not clear. However, it is known that six-membered cyclic silanes are most inert to oxygen [12]. Dodecamethylcyclohexasilane **V** was practically untouched by atmospheric oxygen or by 30% hydrogen peroxide [18]. The chemical oxidation of **V** by MCPBA underwent ring-insertion exclusively, but gave only 40% of a mixture of cyclic siloxanes after three days, leaving 60% of unreacted substrate [4].

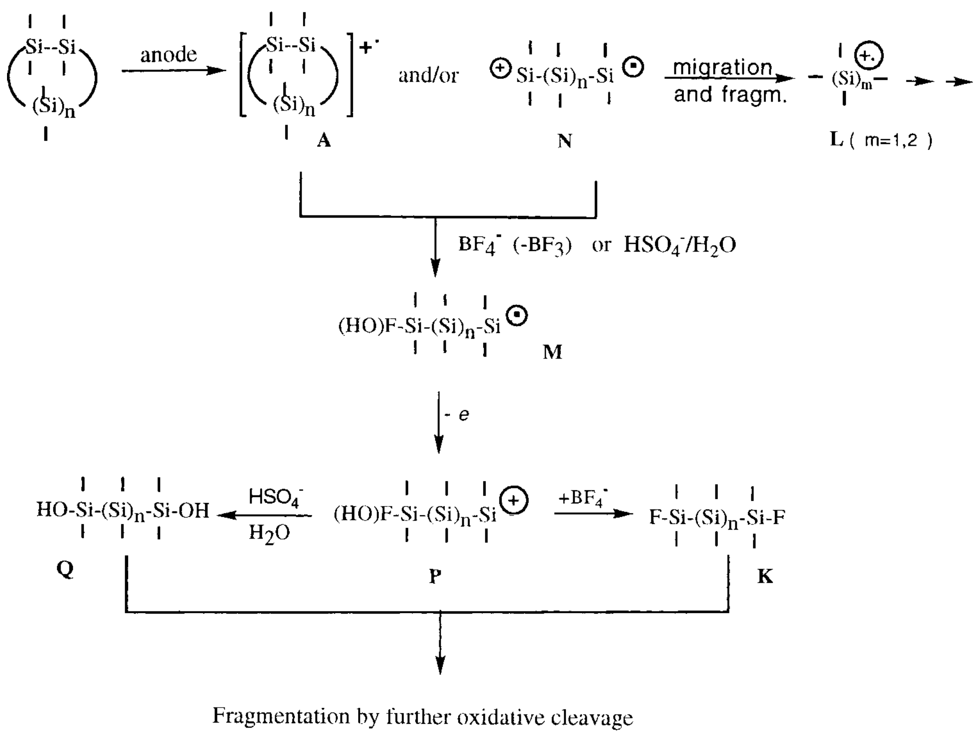
Finally, it is clear that, cyclic polysilane $(Mes_2Si)_3$ (**I**) undergoes ring opening process followed by fragmentation, leading linear products, exclusively. These results are in contrast to what is achieved by the anodic oxidation of **II**, which undergoes oxygen insertion process exclusively, affording only cyclic siloxanes, similar to the results obtained by the electrochemical oxidation of larger polysilane rings. The difference in the results between **I** and **II** could be explained by their difference in strain energy, which is evidenced by the relative ease of oxidation of **I** vs **II** (Fig. 2). Also, the calculated strain energy for $(H_2Si)_3$ and $(H_2Si)_4$ was found to be 167.5 and 70 kJ mol^{-1}, respectively [19]. Strain energies for alkylcyclosilanes have been estimated [20] to be 172 and 96 kJ mol^{-1}, respectively. These results are in sharp contrast to those for cycloalkane analogs, where the strain energies for $(CH_2)_3$ and $(CH_2)_4$ are nearly equal, ~113 kJ mol^{-1} [21]. Various theories [3] have been suggested to explain the striking difference in strain energy patterns between silicon and carbon compounds. The fact is that Si_4 rings possess low strain energies, and therefore more stable than their C_4 analogs. As a consequence, it is not surprising that the outcome of the anodic oxidation of **II** resembles that of Si_5–Si_9 rings rather than that of **I**.

3.3. *Mechanism*

To try to rationalize the formation of products outlined in Tables 2 and 3, several plausible pathways could be suggested. Scheme 1 describes the formation of cyclic siloxanes via consecutive steps of oxygen insertion into the Si–Si bonds of cyclic polysilanes. The initially formed cation-radical **A** reacts with molecular oxygen to generate intermediate **B**, which



Scheme 1



Scheme 2

may couple with a neutral cyclic silane molecule to form **C**. The latter decomposes to a final product **D** and its cation-radical $\mathbf{D}^{+\cdot}$, which could also be generated by direct electrochemical oxidation of the siloxane **D**. Further oxygen insertion step could take place via intermediate $\mathbf{E}^{+\cdot}$.

It is noteworthy that the suggested reaction between molecular oxygen and the electrochemically generated cation-radical species is in analogy to the chemical reaction found between oxygen and radical-cations of olefins [22, 23], dienes [24] and acetylenes [25].

As in our previous work [9], we again find that in the presence of BF_4^-, ring-opening process competes favourably with the oxygen insertion process (column D in Table 2). In Scheme 2, the initially formed unstable cyclic cation-radical (**A**) is a highly reactive intermediate which may undergo an attack by BF_4^- to form the radical (**M**), or alternatively, undergo ring opening to generate a linear cation-radical (**N**) which could then form the same entity, **M**. The latter intermediate could undergo further oxidation to form cation **P**, which may then react with BF_4^- to yield the α,ω-difluorosilane **K**. Similarly, intermediate **A** and/or **N** could react with HSO_4^-, followed by hydrolysis, to generate hydroxylated products (e.g., **Q**).

The formation of products which involve mesityl migration could take place through the intermediary of **L**.

4. Conclusion

In this work we have investigated the electrochemical behaviours of cyclic polysilanes by cyclic voltammetry and preparative scale electrolysis. Cyclic polysilanes show one or two irreversible oxidation waves. The first oxidation peak potentials depend upon the structures of the cyclosilanes. The oxidation potentials increase going from three- to four- and higher membered rings. However, there is little difference between oxidation potentials for five-, six-, seven- and eight-membered rings.

The electrochemical oxidation of four- to nine-membered cyclic polysilanes leads to oxygen insertion and gives cyclic siloxanes, exclusively. Generally, molecular oxygen is responsible for the insertion reaction of oxygen into the silicon–silicon bond. When ClO_4^- salt is present, this particular anion could be associated with the oxygen insertion process, as well. Whereas the electrolysis undergoes both ring-opening and oxygen insertion processes when BF_4^- salts are used. However, the smallest cyclic polysilane, three-membered ring **I**, undergoes an exclusive ring-opening followed by Si–Si bond cleavage, to form linear products containing one or two silicon atoms. Among all cyclic polysilanes, three- and four-membered rings (**I** and **II**) show a higher electrochemical reactivity, whereas those with methyl groups on silicon atoms (**V**, **VII** and **VIII**) have a lower reactivity. For the cyclic polysilanes with a same ring size, the larger the substituent on silicon atom, the higher the electrochemical reactivity (comparing five-membered rings **III** and **IV**).

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