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The effect of ring-size on the electrochemical oxidation of perethylcyclopolysilanes [$(Et_2Si)_n$][☆]

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Abstract

For evaluating the net ring-size effect on the electrochemical properties of cyclic polysilanes, four perethylpolysilanes, namely octaethylcyclotetrasilane $(Et_2Si)_4$ (**I**), decaethylcyclopentasilane $(Et_2Si)_5$ (**II**), dodecaethylcyclohexasilane $(Et_2Si)_6$ (**III**) and tetradecaethylcycloheptasilane $(Et_2Si)_7$ (**IV**), were studied by cyclic voltammetry and controlled potential electrolysis. In addition, the effects of the nature of electrolyte, amount of electricity consumption and anode material on the electrolysis outcome was demonstrated for compound **II**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cyclic polysilanes; Electrochemical oxidation; Ring-size effect

1. Introduction

Peralkylpolysilanes are of special interest because they exhibit unique electronic, physical and chemical properties [1]. In particular, cyclic polysilanes mimic the behavior of aromatic hydrocarbons, by having electronic transitions in the UV–vis region, forming anion- and cation-radicals upon respective reduction and oxidation, in which the odd electron is distributed over the ring, forming charge-transfer complexes with π-acceptors, and exhibit substituent effects. A recent review describes the synthesis, structure, chemical reactions and photolysis of cyclic polysilanes [2].

Chemical oxidation of cyclic polysilanes by organic peracids [3,4] lead to the formation of cyclic siloxanes, due to the sequential insertion of oxygen atoms into the Si–Si bonds of the cyclic polysilanes. Their reactivity is determined by various factors, such as ring size, the nature of the substituents attached to the silicon, steric hindrance and the nature of the heteroatoms included in the ring.

Peralkyl derivatives of polysilanes undergo irreversible electrochemical oxidation, with oxidation potentials which are linearly related to first ionization energies [5]. Also, the oxidation potentials decrease with increasing chain length, and are correlated with UV spectra and with Sandorfy calculations [6].

Earlier papers from our laboratory [7–9] described the outcome of preparative scale electrolyses of different cyclic polysilanes (Si_3–Si_9), with different substituents (Me, Et, Pr, *t*-Bu and aryl). In the presence of tetraalkylammonium tetrafluoroborate salts they underwent ring opening followed by further Si–Si bond cleavage and reaction with BF_4^-, forming α,ω-difluorosilanes, F–$(SiR_2)_n$–F, as the major products [7]. However, their anodic oxidation in the presence of other electrolytes which do not contain fluorinated anions (ClO_4, HSO_4^-, AcO^-), led to both oxygen insertion and ring-opening processes to form mainly cyclic and linear siloxanes [8]. In the case of small rings [9], the anodic oxidation of $[t\text{-Bu(Me)Si}]_4$ led to oxygen insertion process and gave cyclic siloxanes as the major

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[☆] Dedicated to the memory of the late Professor Rokuro Okawara.

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products, whereas $(Mes_2Si)_3$ underwent ring opening followed by further 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).

Since all cyclic polysilanes studied previously contained different substituents, the net effect of ring-size on their electrochemical behavior is not well understood. To shed some light on this particular issue, the present paper reports on the electrochemical oxidation of four different ring-size perethylcyclopolysilanes, namely octaethylcyclotetrasilane $(Et_2Si)_4$ (**I**), decaethylcyclopentasilane $(Et_2Si)_5$ (**II**), dodecaethylcyclohexasilane $(Et_2Si)_6$ (**V**) and tetradecaethylcycloheptasilane $(Et_2Si)_7$ (**VI**), which all share in common the same alkyl substituent (an ethyl group). In addition, the effects of the nature of electrolyte, anode material and electricity consumption is reported for **II**, as a representative example.

2. Experimental details

2.1. Chemicals

Perethylcyclopolysilanes **I**–**IV** were synthesized according to published methods [14]. Tetrabutylammonium perchlorate ($TBA + ClO_4^-$, from Aldrich), tetrabutylammonium hydrogen sulfate ($TBA + HSO_4^-$, from Fluka) and tetraethylammonium tetrafluoroborate ($TEA + BF_4^-$, from Aldrich), were used as supporting electrolytes without further purification. Analytical grade CH_2Cl_2 and CH_3CN (distilled from CaH_2 and P_2O_5, respectively).

2.2. Electrochemical measurements

Cyclic voltammetric experiments were performed using a conventional three-electrode cell under nitrogen atmosphere. The working electrode was a platinum disk electrode (ca. 1 mm diam.). A quasi-reference electrode (Ag/AgCl) was used. The auxiliary electrode studied in these was a Pt electrode. The concentration of perethylcyclopolysilane was 0.5–1 mmol l^{-1}, while that of the supporting electrolyte was 0.1 mol l^{-1}. 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 perethylcyclopolysilane dissolved in about 25 ml of solvent/electrolyte solution. For electrochemical measurements, Princeton Applied Research (PAR) potentiostat Model 173, PAR Universal Programmer Model 175 and Yokogawa XY-recorder Model 3068, were employed.

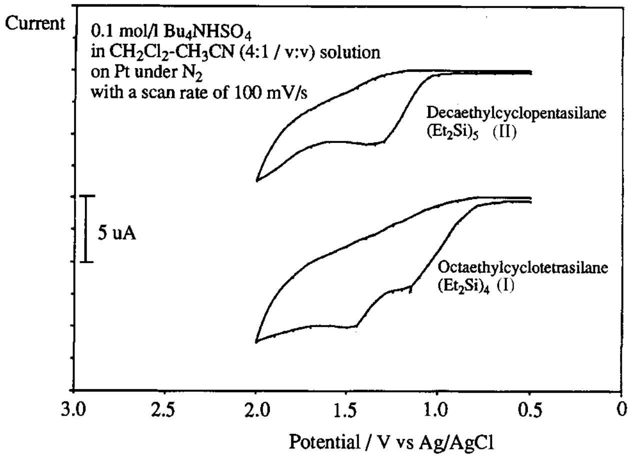


Fig. 1. Representative cyclic voltammograms.

Electrolyses were conducted under nitrogen atmosphere at controlled potential of 0.95–1.20 V (vs Ag wire), on Pt foil or graphite anode. 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 GC-MS 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 (GC-MS) was used also.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 1 shows representative cyclic voltammograms for **I** and **II**, which are recorded in 0.1 mol l^{-1} $TBA + HSO_4^-$–CH_2Cl_2–CH_3CN (4:1/v:v) on Pt. The results for compounds **I**–**IV** are summarized in Table 1. While only one irreversible oxidation wave is observed for perethylcyclopolysilane **II**, **III** and **IV**, the cyclic polysilane **I** exhibits two irreversible oxidation waves with a potential difference between them of about 300 mV. It is noteworthy that there is a little difference only in the

Table 1
Anodic peak potentials of perethylcyclopolysilanes[a]

I	II	III	IV
1.15	1.35	1.40	1.40

[a] Anodic peak potentials are in V vs Ag | AgCI reference electrode; working electrode: Pt; electrolyte: $TBA+HSO_4^-$; solvent CH_2Cl_2–CH_3CN (4:1/v:v); under N_2 atmosphere.

Table 2
The effect of structure on electrochemical oxidation[a] of perethylcyclopolysilanes

Products[c]	Yield (%)[b]				MS (EI)
	I ACP (V)	II	III	IV	
	0.95	1.2	1.2	1.2	
Starting material	–	45	–	–	
$[Et_2Si]_4O$ (**1**)	87	3	23	22	360(M^+), 331(100%), 303, 273
$[Et_2Si]_4O_2$ (**2**)	9	10	60	67	376(M^+), 347(100%), 289, 87
$[Et_2Si]_5O$ (**3**)	–	38	8	6	446(M^+), 417, 115, 87(100%)
$[Et_2Si]_5O_3$ (**4**)	–	4	–	–	478(M^+), 449, 172(100%), 87
$[Et_2Si]_4O_3$ (**5**)	–	–	4	5	392(M^+), 363(100%), 335, 87
$[Et_2Si]_4O_4$ (**6**)	–	–	5	–	408(M^+), 379(100%), 351

[a] Electrolyses were conducted under N_2 on Pt; applied controlled potentials (ACP) are in V vs Ag quasi-reversible reference electrode; electrolyte solution: CH_2Cl_2–CH_3CN (4:1/v:v) solution containing 0.1 mol l^{-1} $TBA+HSO_4^-$; electricity consumption stopped at 1.2 F mol^{-1} arbitrarily in order to compare the electrochemical reactivity of cyclopolysilanes.

[b] Yields reported are relative and estimated by GLC.

[c] High resolution MS results: found (calc.) for **1** ($C_{16}H_{41}OSi_4$): 361.2339 (361.2309); **2** ($C_{16}H_{41}O_2Si_4$): 377.2250 (377.2258); **3** ($C_{20}H_{51}Osi_5$) 447.2891 (447.2879); **4** ($C_{20}H_{51}O_3Si_5$) 479.2797 (479.2777); **5** ($C_{16}H_{41}O_3Si_4$) 393.2245 (393.2207); **6** ($C_{16}H_{41}O_4Si_4$) 409.2168 (409.2156).

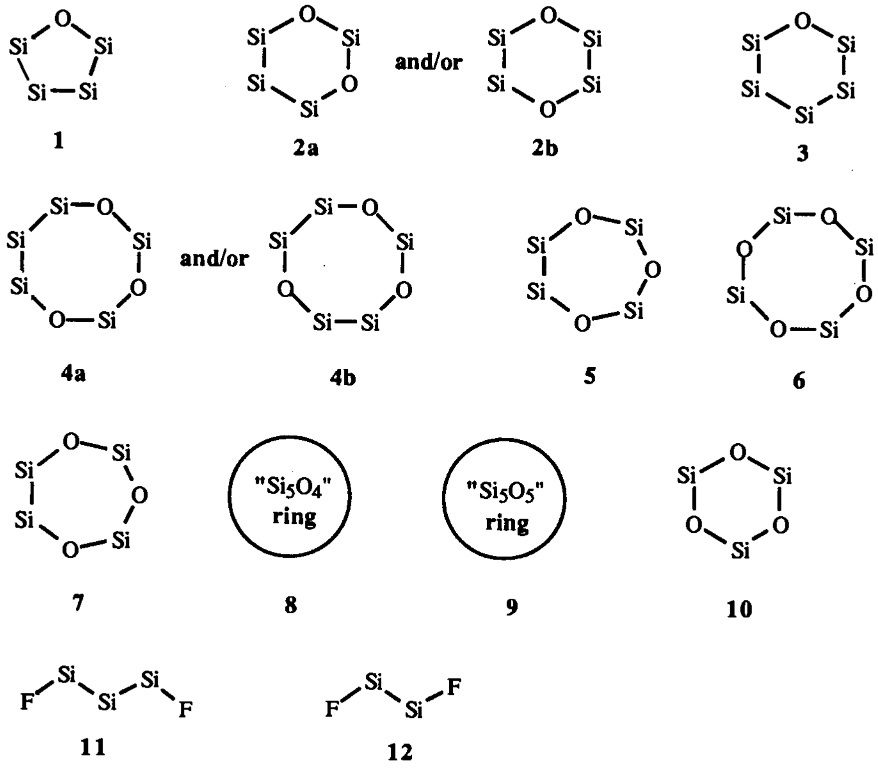
oxidation potentials of the five-, six- and seven-membered rings. However, the first oxidation wave of four-membered ring (**I**) is significantly lower compared with all other perethylcyclopolysilanes studied, presumably due to its ring strain. This kind of behavior is predicted from UV–Vis absorption bands. In general, the oxidation potentials are well correlated with electronic absorption energies. However, unlike linear permethylpolysilanes, for which the oxidation potentials decreased and the lowest energy electronic absorption bands moved to longer wavelengths as the chain length increases [2,6], cyclic polysilanes with small and medium size rings showed an opposite trend for their UV absorption bands: a bathochromic shift was observed as the ring size decreases [2]. 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 [10,11]. Rings from Si_7 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 the oxidation potentials decrease significantly, indicating destabilization of the HOMO. This is consistent with the increase in Si–Si bond length [12]. 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.

3.2. Controlled potential electrolysis

3.2.1. Comparison of anodic oxidation of different perethylcyclopolysilanes

The results obtained by the electrochemical oxidation of a series of perethylcyclopolysilanes with different ring sizes (**I**–**IV**), in CH_2Cl_2–CH_3CN (4:1 v/v) solution containing 0.1 mol l^{-1} $TBA+HSO_4^-$, on platinum foil, under N_2 atmosphere, are summarized in Table 2. Electrolyses were arbitrary terminated after electricity consumption of about 1–1.2 F mol^{-1}, when for all compounds but one, no starting material was left. The structural formula of emerged products **1**–**6** are described in Scheme 1. The second column in Table 2 describes the product outcome from the electrochemical oxidation of $(Et_2Si)_4$ (**I**). Apparently the reaction is quite selective, affording two products (**1** and **2**), five- and six-membered cyclic siloxanes, with four silicon atoms and one and two oxygen atoms in their skeleton, respectively. The major product **1** is obtained in 87% yield. Both products stem from ring expansion due to oxygen insertion. It is noteworthy that **2** has two isomers (**2a** and **2b**, Scheme 1), however, no attempt was made to characterize the actual isomer(s) obtained. In general, the **2a** isomer is favorable because it was found that the initially inserted oxygen atom in the ring activates adjacent Si–Si bonds towards further insertion of oxygen atoms [3].

The third column (Table 2) describes the results obtained by $(Et_2Si)_5$ (**II**). Surprisingly, after electricity consumption of 1.2 F mol^{-1} only 55% of the starting material was consumed. The product mixture contained four products (**1**–**4**), all cyclic siloxanes, five- to eight-membered rings. The major product (38%) is **3** (which involves five silicon atoms and one oxygen atom). All



Scheme 1.

products maintained the same number of silicon atoms as in the parent compound except for **1** which lost one silicon atom. However, cyclic siloxanes **1** and **4** were minor products and formed in 3 and 4% yield, respectively. Again, it is noteworthy that **4** could have two isomers (**4a** and **4b**, Scheme 1) but no effort was done to characterize the actual isomer obtained, although we prefer **4a** for the reasons explained above.

Electrolyses of **III** and **V** afford similar spectra of products (the fourth and fifth columns, Table 2), although no starting material is left this time. Both cyclic polysilanes undergo oxygen insertion and give cyclic siloxanes **1**–**3** that were discussed previously, in addition to small amounts of a seven-membered product **5**, and an eight-membered **6** (obtained from **III** only). In both cases, the major product is the six-membered **2**, involving two oxygen atoms in its skeleton.

Based on the above described results obtained by preparative electrolysis of perethylcyclopolysilanes **I**–**IV**, some interesting observations could be deduced, as follows:

(a) Cyclic siloxanes are formed exclusively (no linear products were detected).

(b) The formation of five- (from **I**) and six-membered (from **II**–**IV**) siloxanes, with one or two oxygen atoms inserted, is preferred. These were the major products.

(c) For **I** and **II**, ring expansion by one oxygen atom insertion is predominant. No products due to Si–Si bond cleavage are observed.

(d) The major pathway for **III** and **IV** involves ring chopping followed by two oxygen atoms insertion, at least. It seems that the larger the ring size in the parent cyclosilane, the higher the number of oxygen atoms inserted in the products.

(e) The highest selectivity in terms of the number of products obtained was shown by **I** which yielded two products only, while all other cyclic polysilanes afforded four to five products each. It seems that for the cyclic polysilanes with the same substituent, the product selectivity depends on the size of ring, with smaller rings favoring higher product selectivity. Clearly, the lower selectivity could stem from the Si–Si bond cleavage process. In fact, no cleavage product is formed by the four-membered ring **I**. However, electrochemical oxidation of the five-membered ring **II** gives about 24% (with respect to the total products yield) of cleavage products, whereas all products from the six- and seven-membered rings (**III** and **IV**) are due to a ring cleavage process.

(f) The fact that no starting material was left from **I**, **III** and **IV**, and as much as 45% from **II**, may suggest that the former three compounds have higher electrochemical reactivity than **II**, 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 [2]. For instance, the cyclic pentamer is also the most stable ring in the perphenyl

Table 3
Electrochemical oxidation[a] of **II** under N_2

Products[c]	Yield (%)[b]					MS (EI)
	A	B	C	D	E	
II	13	–	7	–	–	
$[Et_2Si]_4O_2$ (**2**)	20	24	49	3	–	376(M^+), 347(100%), 289, 87
$[Et_2Si]_5O$ (**3**)	55	39	26	–	–	446(M^+), 417, 115, 87(100%)
$[Et_2Si]_5O_3$(**4**)	–	–	–	10	–	478(M^+), 449, 172(100%), 87
$[Et_2Si]_4O_3$ (**5**)	4	6	16	38	–	392(M^+), 363(100%), 335, 87
$[Et_2Si]_4O_4$ (**6**)	–	–	–	6	–	408(M^+), 379(100%), 351
$[Et_2Si]_5O_2$(**7**)	8	30	2	7	–	462(M^+), 433(100%), 291, 275
$[Et_2Si]_5O_4$ (**8**)	–	–	–	7	–	494(M^+), 465(100%), 379, 87
$[Et_2Si]_5O_5$(**9**)	–	–	–	2	–	510(M^+), 481, 337, 115(100%), 87
$[Et_2Si]_3O_3$ (**10**)	–	–	–	24	13	306(M^+), 277(100%), 221
$[Et_2Si]_3F_2$ (**11**)	–	–	–	–	42	296(M^+), 277, 172, 87(100%)
$[Et_2Si]_2F_2$ (**12**)	–	–	–	–	45	210(M^+), 191, 172, 87(100%)

[a] Applied controlled potentials (ACP) are in V vs Ag quasi-reversible reference electrode; [**II**] = 2–4 mM; electrolyte solution: CH_2Cl_2–CH_3CN (4:1/v:v) solution containing 0.1 mol l^{-1} electrolyte.

[b] Yields reported are relative and estimated by GLC. A electrolyte: $TBA+HSO_4^-$; ACP = 1.2; electricity consumption: 2.5 F mol^{-1}; working electrode: Pt. B electrolyte: $TBA+HSO_4^-$; ACP = 1.2; electricity consumption: 4.0 F mol^{-1}; working electrode: Pt. C electrolyte: $TBA+HSO_4^-$; ACP = 1.2; electricity consumption: 4.0 F mol^{-1}; working electrode: graphite. D electrolyte: $TBA+ClO_4^-$; ACP = 1.05; electricity consumption: 2.5 F mol^{-1}; working electrode: Pt; the cyclic voltammogram exhibits two irreversible oxidation peaks at 1.25 and 1.6 V. E electrolyte: $TEA+BF_4^-$; ACP = 1.05; electricity consumption: 2.5 F mol^{-1}; working electrode: Pt; the cyclic voltammogram exhibits two irreversible oxidation peaks at 1.25 and 1.6 V.

[c] High resolution MS results: found (calc.) for **7** ($C_{20}H_{51}O_2Si_5$): 463.2819 (463.2828); **8** ($C_{20}H_{51}O_4Si_5$): 495.2708 (495.2726); **9** ($C_{20}H_{51}O_5Si_5$): 511.2683 (511.2675); **10** ($C_{12}H_{31}O_3Si_3$): 307.1641 (307.1637); **11** ($C_{12}H_{31}F_2Si_3$): 297.1741 (297.1750); **12** ($C_8H_{21}F_2Si_2$): 211.1185 (211.1180).

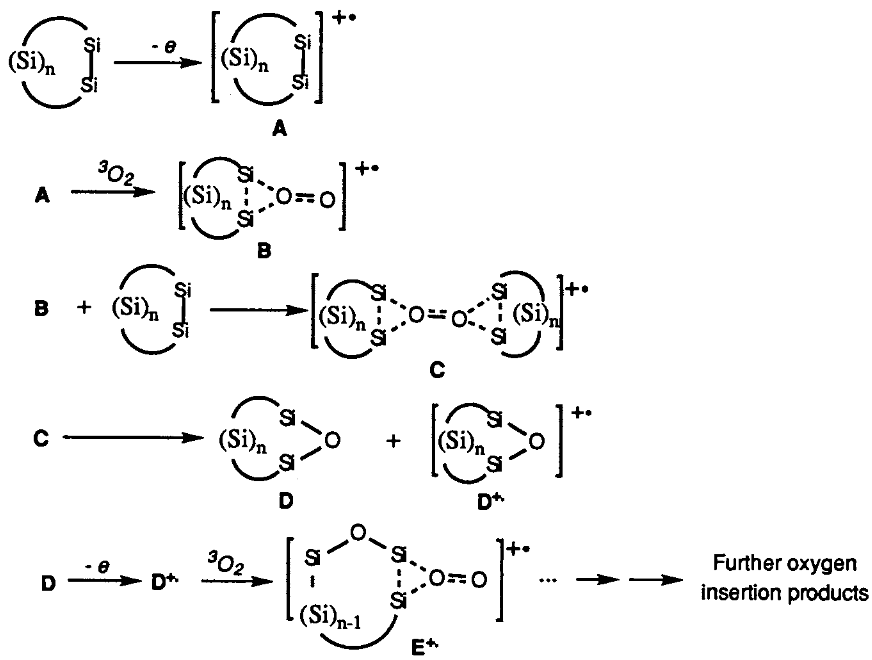
series [13]. Attempts to produce the equilibrium mixture of $(Et_2Si)_n$ rings by stirring **I** in THF in the presence of K or Na/K, led to fast rates of redistribution. The observed composition at equilibrium was 96% **II**, 2% **I** and 2% **III** at 30°C [14], indicating that the five-membered ring is the most stable one for the ethyl substituted series. Apparently, decreasing the ring size in cyclic polysilanes from five to four introduces ring tension, and as a consequence, destablization of the Si–Si bond [15].

An alternative explanation by which one of the products which is formed from **II** competes favorably with the oxidation of the parent compound is ruled out on the basis that in that case one would expect **III** and **IV** to show the same behavior, because they all share similar products. Instead, the latter two derivatives afford products containing higher number of oxygen atoms.

3.2.2. The effects of electricity consumption and anode material

Cyclic polysilane $(Et_2Si)_5$ (**II**) was chosen as the representative example from this series on which various effects were investigated. Columns A and B in Table 3 describe the product outcome from its electrochemical oxidation, in the presence of $TBA + HSO_4^-$, with 2.5 and 4 F mol^{-1} of electricity consumption, respectively. Evidently, the starting material was still left even after consumption of 2.5 F mol^{-1}. Upon increasing the electricity consumption to 4 F mol^{-1}, all starting material is consumed. Furthermore, the yield of the formerly major product (**3**) decreases, while the yield of a higher oxygen contaminated product (**7**) increases. This result is reminiscent of the outcome from the anodic oxidation of the cyclic peralkylsilanes $[(n\text{-Pr})_2Si]_5$ and $[t\text{-Bu(Me)Si}]_4$ which showed similar behavior at different electricity consumption [8,9]. It is noteworthy that the ratio of Si_4/Si_5 products for 4.0 F mol^{-1} electricity consumption is slightly higher (0.43) than that for 2.5 F mol^{-1} electricity consumption (0.38). This shows that the Si–Si bond cleavage becomes a competitive process with increased electricity consumption.

The effect of anode material on the reaction pathway is described in column C, in which a graphite was used instead of Pt anode (column B). It seems that on graphite the conversion of **II** to products is incomplete even after 4 F mol^{-1} of electricity were consumed, since 7% of it remained unreacted at the end of electrolysis. Furthermore, the ratio of Si_4/Si_5 products in column C is reversed from 0.43 on Pt to 2.32 on graphite. These results indicate that the anode material has a marked effect on the products distribution. Apparently, there is a large difference in the actual current density on the two anode surfaces, which causes to a different concentration gradient near the electrode surface. As a consequence, the distribution of the products is changed [16].



Scheme 2.

3.2.3. *The effect of supporting electrolyte*

The electrochemical oxidation of **II** was investigated in the presence of three different electrolyte solutions, leaving all other conditions the same. Let us compare the results presented in columns A, D and E (Table 3). Column D describes the results obtained with tetrabutylammonium perchlorate. Evidently the reaction is less selective compared with the results in column C, since eight cyclic siloxanes (**2**, **4**–**10**) were formed instead of four. However, all of them are cyclic siloxanes. Among the eight products there are two with large size rings: nine-membered (**8**) and ten-membered (**9**). In addition, the major products (**5** and **10**) are now the ones containing three oxygen atoms rather than one (as in **2**).

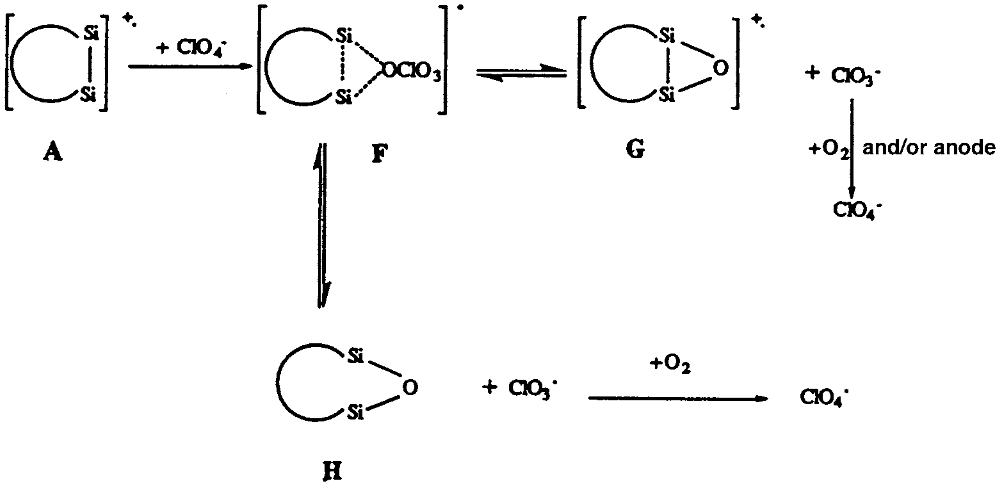
Column E (Table 3) describes the results obtained in the presence of the third electrolyte studied, tetrabutylammonium tetrafluoroborate. Both oxygen insertion and ring-opening processes take place to provide a cyclic siloxane **10** (13%) and two linear difluoropolysilanes, **11** and **12**, as the major products (42 and 45% yield, respectively). The fact that the ratio of (**11** + **12**)/**10** is high (6.7/1) suggests that the ring-opening process competes much more favorably with the oxygen insertion process, in the presence of BF_4^- salt.

3.3. *Mechanism*

It has been suggested that the chemical oxidation of cyclic polysilanes with peracids proceeds by an electrophilic oxidation process [3]. In the anodic oxidation process, the initial step involves an electron uptake from the cyclic polysilane to generate a cadon radical, which is an electrophile. Therefore, one has to look for a nucleophile to react with the cation-radical. In spite of the fact chat all electrochemical oxidation experiments were carried out under nitrogen atmosphere, all products (except for the ones obtained in the presence of BF_4^-) were cyclic siloxanes, containing one to three oxygen atoms in their skeletons. As to the origin of the oxygen atoms in the products, different reaction pathways could be suggested. It seems chat a plausible mechanism could involve molecular oxygen (contaminated in the electrolyte solution or diffused from air) insertion into the Si–Si bond. Scheme 2 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 may couple with a neutral cyclic silane molecule to form **C**. The latter decomposes to a final product **D** and its cation-radical $\mathbf{D}^{+\bullet}$, which could also be generated by direct electrochemical oxidation of the siloxane **D**. Further oxygen insertion and Si–Si bond cleavage steps could take place via intermediate $\mathbf{E}^{+\bullet}$.

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 orefins [17,18], dienes [19] and acetylenes [20].

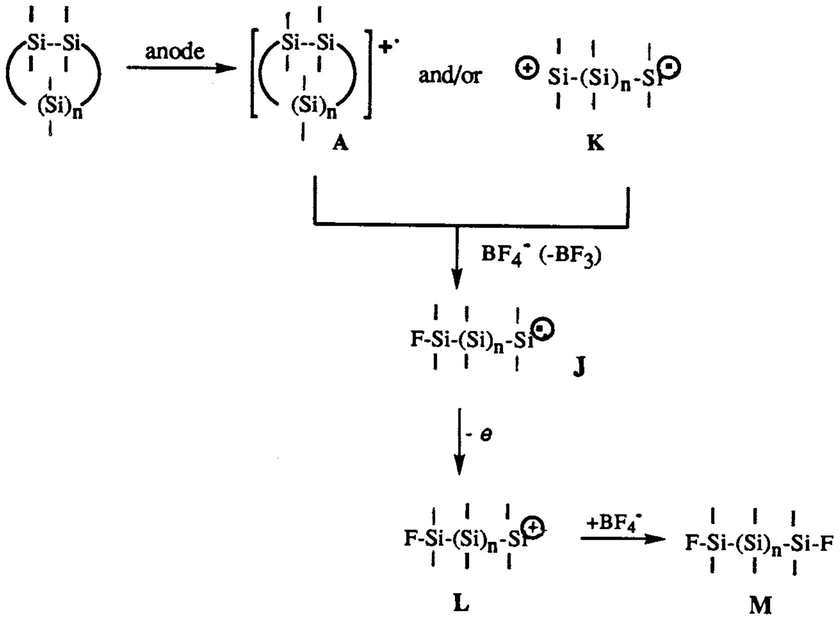
When TBA + ClO^- is used as the electrolyte (column D, Table 3), the spectrum of products was significantly different from that obtained in the presence of TBA + HSO_4^- (column A). Not only were more



Scheme 3.

types of cyclic siloxanes formed, but also more oxygen-contaminated products were produced. Therefore, one cannot rule out the possibility that the perchlorate anion could also promote the oxygen insertion reaction. A plausible mechanism describing the involvement of the perchlorate anion is shown in Scheme 3. The electrogenerated cation-radical **A** coordinates with the perchlorate anion to afford the intermediate **F**. The latter could be in an unfavorable equilibrium with **G** and the chlorate anion (or with **H** and the chlorate radical). As long as the chlorate species is not reoxidized to the corresponding perchlorate, the further oxidation of siloxanes is inhibited.

We have found that in the presence of BF_4^-, the ring-opening process competes favorably with the oxygen insertion process. Scheme 4 describes a mechanism which involves the participation of the fluoroborate anion. 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 (**J**), or alternatively, undergo ring opening to generate a linear cation-radical (**K**) which could then form the same entity, **J**. The latter intermediate could undergo further oxidation to form the cation **L**, which may then react with BF_4^- to yield the α,ω-difluorosilane **M**. This compound could undergo further oxidative cleavage to give the products F–Si–$(Si)_{n-m}$–Si–F.



Scheme 4.

4. Conclusion

This work investigated the net effect of ring-size on the electrochemical properties of a series of cyclic perethylpolysilanes, by both cyclic voltammetry and preparative scale electrolysis. In general, perethylcyclopolysilanes show one irreversible oxidation wave, except for the four-membered derivative which exhibits a second irreversible wave. The first oxidation peak potentials depend upon the ring size of the cyclosilanes. While there is a little difference among the oxidation potentials of the five-, six-, and seven-membered rings (**II**, **III** and **IV**), that of the four-membered ring (**I**) is significantly lower compared with all other derivatives studied, due to ring tension.

When a non-fluorinated electrolyte is used, the electrochemical oxidation of perethylcyclopolysilanes leads to the exclusive formation of cyclic siloxanes, due to oxygen insertion. The formation of five- and six-membered cyclic siloxanes was favorable. No linear siloxanes were observed. Generally, molecular oxygen is responsible for the insertion reaction of oxygen into the Si–Si bond. However, when ClO_4^- salt is the electrolyte, this particular anion could be associated with the oxygen insertion process, as well. In the presence of BF_4^- anion the spectrum of products changes dramatically; both ring-opening and oxygen insertion processes take place, the former being predominant.

Among the cyclic polysilanes studied, the four-, six- and seven-membered rings (**I**, **III** and **IV**) show a higher electrochemical reactivity, compared with the five-membered ring (**III**). Also, the larger the size of the ring, the higher the degree of Si–Si bond cleavage and the higher the number of oxygen atoms in the products. The product selectivity depends on both the size of the ring (the smaller the ring the higher the product selectivity) and the amount of electricity consumption (for the same ring-size, a higher selectivity is obtained at lower F mol^{-1} values).

Acknowledgements

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