CHEMISTRY LETTERS, pp. 1683-1686, 1985. © 1985 The Chemical Society of Japan

ELECTROCHEMICAL BEHAVIORS OF CYCLOPOLYSILANES. OXIDATION POTENTIALS VIA CYCLIC VOLTAMMETRY

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The anodic peak potentials for a series of cyclopolysilanes, $[R^1R^2Si]_n$ (n=3-7), lowered with decreasing ring size and were found to be parallel to the lowest transition energies determined by the UV absorptions. In the anodic oxidation these cyclopolysilanes undergo the initial one electron transfer reaction to give a cation radical which leads to the formation of an acyclic α,ω-radical cation followed by the second electron transfer to give the corresponding di-cation.

Previously, Allred and co-worker have reported on the cathodic reduction of linear chloropermethylpolysilanes by cyclic voltammetry (CV) and also on the polarographic oxidation of permethylpolysilanes, and they discussed the effect of the chain length of these polysilanes on the ionization potentials.[1,2] However, no reports have appeared on the study of the electrochemical behaviors of cyclic polysilanes. Recently, we were able to obtain various peralkylcyclopolysilanes and their physical and chemical properties have been investigated.[3] In connection with the photospectroscopic properties for a series of cyclopolysilanes, $[R^1R^2Si]_n$ (n=2-7),[3c,3e,4] we now wish to report on the electrochemical behaviors for these cyclopolysilanes by the CV method.

Table 1 lists, together with the lowest absorption bands in the UV spectra,[3c,3e] the first anodic peak potentials which were determined via the cyclic voltammetry for cyclopolysilanes (see Ref. 5).[6] The oxidation potentials for the series of cyclopolysilanes fall in the range of +0.4—+1.5 and +0.7—+1.7 V vs. SCE

Table 1. The anodic peak potentials, Epa, and the lowest transition aborptions for cyclopolysilanes[7)]

Compound	Epa (V vs. SCE)[a)]		λ_{max}/nm[d)]
	CH_3CN[b,c)]	CH_2Cl_2	
$[(Bu^tCH_2)_2Si]_3$	+0.44	+0.72	310sh
$[Bu^tMeSi]_4$	+0.94		300
$[Pr^i{}_2Si]_4$	+1.00	+1.24	290sh
$[Bu^i{}_2Si]_4$	+1.02	+1.12	290sh
$[Bu^s{}_2Si]_4$	+1.10	+1.23	290sh
$[Bu^tPrSi]_4$	+1.04		294
$[Et_2Si]_5$	+1.48		265sh
$[PrMeSi]_5$	+1.32		270sh
$[Bu^iMeSi]_5$	+1.34		275
$[Pr_2Si]_5$	+1.42	+1.45	260
$[Bu_2Si]_5$	+1.40	+1.30	262
$[Bu^i{}_2Si]_5$	+1.36	+1.38	260sh
$[Me_2Si]_6$	+1.45	+1.65	258sh
$[PrMeSi]_6$	+1.22		257sh
$[Pr_2Si]_7$	+1.40	+1.40	242

a) The first anodic peak potential; scan rate, 250 mV/s; see also Ref. 6.
b) Solvent used. c) Due to poor solubility a saturated solution was used.
d) In cyclohexane; see Refs. 3c and 3e.

in CH_3CN and CH_2Cl_2, respectively, and also showed a lowering with decreasing ring size ($7 \approx 6 \approx 5 > 4 > 3$), the trend being in a sharp contrast to that observed in polarographic oxidations for linear permethylpolysilanes.[2)] The anodic peak potentials (O_1) showed a strong dependence on the ring size, but not on the bulk of the substituents on silicon. It also showed a parallelism to the trend in the lowest transition energies by going to smaller rings. The decreasing trend in the oxidation potentials could be interpreted in terms of the increasing ring strain energies in smaller cyclopolysilanes, such as 3- and 4-membered ones, since the ionization potentials reflect the energy levels (HOMO) of the ground states of molecules,[8)] as shown by the red shifts of the lowest transition absorption bands. Especially, it is worthwhile to note that the oxidation potential of hexaneopentylcyclotrisilane, $[(Bu^tCH_2)_2Si]_3$, shows an unusually low value[9)] compared with those of other rings and the value for this compound (0.44 V in CH_3CN) is much smaller than those for the carbon analogues, cyclopropane derivatives (2.05—2.5 V in CH_3CN via a controlled potential electrolysis) reported by Shono and co-worker.[10)] These facts suggest that the compound is remarkably strained and highly active toward electron-transfer-induced reactions, as evidenced by the longest absorption band (λ_{max} 680 nm(sh); CH_2Cl_2) in the $(CN)_2C=C(CN)_2/Si_3$ CT-complex compared with the corresponding CT-bands of the other cyclopolysilane complexes.[3e)]

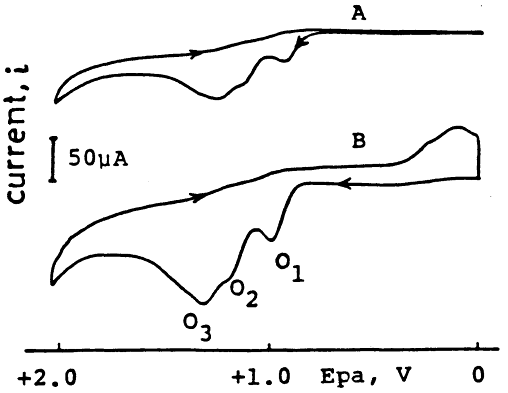
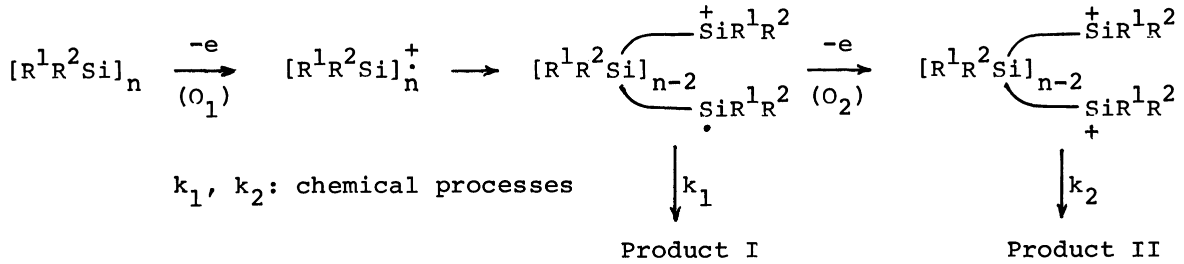


Fig. 1. Cyclic voltammograms of $[Pr^i{}_2Si]_4$ in CH_3CN solution; scan rate, A: 50 mV/s; B: 250 mV/s.

In the single sweep cyclic voltammograms for the series of cyclopolysilanes, at least two or more anodic waves were observed, but no corresponding cathodic waves appeared on the reverse scan in the range of 0—+2.0 V even at a fast scan rate (500 mV/s). Thus these phenomena clearly indicate that the electrochemical oxidation (O_1) of all the cyclopolysilanes is irreversible process. As a typical example, the voltammograms for octaisopropylcyclotetrasilane, $[Pr^i{}_2Si]_4$, were shown in Fig. 1. The cathodic wave appearing at ca. +0.1 V in the scan rate of 250 mV/s could not be detected when the scanning was clipped at +1.1 V after the first oxidation wave and also when a slow scanning rate (50 mV/s; Fig. 1A) was applied. It is likely from these observations that the cathodic peak is attributable to a reduction wave of species evolved from the reactive intermediate produced via the electrochemical oxidation of the cyclopolysilane. Therefore, the electrochemical behaviors of the cyclopolysilanes can be explained by Scheme 1, in which the first anodic wave (O_1) corresponds to the first one electron removal from the cyclosilanes, giving a radical cation which in turn undergoes a Si-Si bond



Scheme 1.

cleavage to form a reactive intermediate, α,ω-radical cation, and then the corresponding di-cation by the subsequent electron transfer (probably O_2).[11) The fact that the oxidation potentials for 3- and 4-membered rings in CH_3CN are slightly lower than those in CH_2Cl_2 might be explained by the solvation effect on the ionic structure during the oxidation process, as has been shown previously.[2)

Finally, it should be emphasized that the oxidation potentials obtained by the present study for a series of cyclopolysilanes provide quite significant informations about the fundamental properties such as the Si-Si bonding nature, ring strain energy and electron donating nature for the cyclic systems. Further study along this line is currently under way.

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(Received August 27, 1985)