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ELECTROCHEMICAL REDUCTION OF CHLOROPERMETHYLPOLYSILANES

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Summary

Investigations of several chloropermethylpolysilanes by a.c. polarography and cyclic voltammetry indicate increasing interaction between chlorine and the polysilane chain as the chain length increases. The reduction potentials for 1-chloropermethylpolysilanes are in all cases, including the hexasilanes, less negative than those for the corresponding α, ω-dichloropermethylpolysilanes. The cathodic EC processes for chloropermethylpolysilanes involve the formation of permethylpolysilyl hydrides.

Introduction

Few studies of the electrochemical behavior of chloroorganosilanes have been reported. Dessy, Kitching and Chivers [1] published results of reductions of triphenylchlorosilane and diphenyldichlorosilane. Tyurin, Flerov and Goncharuk [2] have given reduction potentials of trimethylchlorosilane and dimethyldichlorosilane.

Recently, [3,4] evidence was presented for greater donation of electrons from chlorine to polysilane orbitals as chain length increases. The current study was undertaken for the purpose of examining the electrochemical behavior of chloropermethylpolysilanes. Points of particular interest were: (1) the effect of chain length on reduction potential, (2) the comparison of reduction potentials of monochloropermethylpolysilanes and the corresponding α, ω-dichloropermethylpolysilanes, and (3) the products of reduction of chloropermethylpolysilanes.

Experimental

Cyclic voltammograms were obtained in acetonitrile containing 0.1 *M* tetrabutylammonium perchlorate. The working electrode was a short platinum wire, the counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode. A Hewlett—Packard Model 202A function generator supplied the triangular wave, and a Princeton Applied Research Model 373 potentiostat monitored the current. The voltammograms were recorded on Tektronix Model 502A oscilloscope or a Houston Instrument Model 2000 recorder. The cyclic voltammograms presented herein were run at a sweep frequency of 0.05 Hz unless otherwise indicated.

A.c. polarograms were also obtained with platinum, platinum, and s.c.e. electrodes in acetonitrile solution. A small amplitude sine wave, supplied by the function generator, was superimposed on the output of a linear ramp generator and applied to the cell by means of the potentiostat. Compensation for *iR* drop was accomplished by the method of Brown, Smith and Booman [5]. Current was monitored with an Ithaco Model 353 phase-lock amplifier.

Controlled potential electrolyses were carried out with the above potentiostat.

Compounds were synthesized by published procedures [3,6].

Results

Reduction potentials as determined by a.c. polarography for chloropermethylpolysilanes are given in Table 1. The trends in observed potentials are: (1) the monochloropermethylpolysilanes are reduced at less negative potentials than the corresponding α, ω-dichloropermethylpolysilanes, and (2) the reduction potentials are less negative for longer chains.

Representative cyclic voltammograms are presented in Figs. 1 and 2. The magnitude of the reoxidation current (peak B) relative to the magnitude of the reduction current (peak A) is a measure of the rate of the reaction coupled to the electrode process. The ratios of reoxidation currents to reduction currents are given in Table 1. The reductions are (1) less reversible with increasing chain length and (2) less reversible for monochloropermethylpolysilanes than for the corresponding α, ω-dichloropermethylpolysilanes.

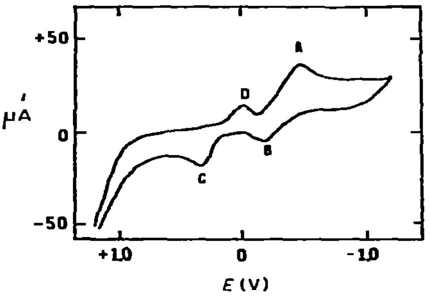
Peaks C and D are not present in an initial cyclic scan starting from zero and going to positive potentials. Peaks C and D for the chloropermethylpolysilanes occur at similar potentials to the peaks observed in the cyclic voltammogram of triethylsilane (Fig. 3). Analogous cyclic voltammograms are exhibited by triphenylchlorosilane. The electrochemical reduction of triphenylchlorosilane to triphenylsilane has been reported [1], and our cyclic voltam-

TABLE 1

ELECTROCHEMICAL DATA FOR CHLOROPERMETHYLPOLYSILANES

Compound	E_r (volts) [a]	Current ratio [b]
$Me(SiMe_2)_3Cl$	-0.400 ± 0.005	0.67 ± 0.05
$Cl(SiMe_2)_3Cl$	-0.500	0.83
$Me(SiMe_2)_4Cl$	-0.358	0.46
$Cl(SiMe_2)_4Cl$	-0.470	0.83
$Me(SiMe_2)_5Cl$	-0.236	0.22
$Cl(SiMe_2)_6Cl$	-0.430	0.29

[a] Potentials vs. saturated calomel electrode as determined by a.c. polarography. [b] Ratio of maximum oxidation current (i_B) to maximum reduction current (i_A) as determined from cyclic voltammograms for which the scan range and frequency were 2.5 V and 0.05 Hz, respectively.



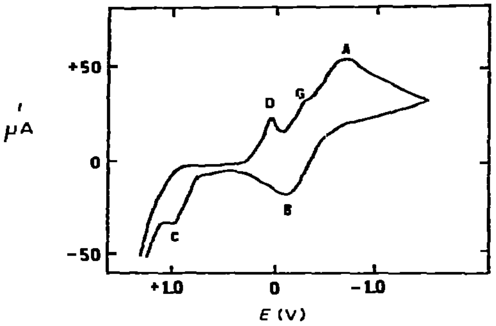


Fig. 1. Cyclic voltammogram (second cycle) of $Me(SiMe_2)_4Cl$.

Fig. 2. Cyclic voltammogram (second cycle) of $Cl(SiMe_2)_4Cl$.

mogram of triphenylsilane contains peaks corresponding to C and D. In the cyclic voltammograms of these compounds, the sum of the integrated currents for waves B and C is equal to or less than that of wave A. As the time for scanning from wave A to wave B increases, wave B becomes smaller and wave C becomes larger.

For trimethylchlorosilane, wave B is small on the first scan with a fresh platinum electrode but grows with repeated scans (Fig. 4). In the steady state for trimethylchlorosilane, but not for the polymethylchlorosilanes, wave B is almost as large as wave A.

For the second and subsequent sweeps, the cyclic voltammogram of each α, ω-dichloropermethylpolysilane shows a small wave, G in Fig. 2, at a less negative potential than the potential of peak A. These additional waves may be due to either $H(SiMe_2)_n Cl$ or $Cl(SiMe_2)_{2n} Cl$ which could be formed by the coupling of $Cl(SiMe_2)_n{}^\bullet$ radicals.

Anodic peaks are exhibited above +1.0 V for each of the chloropermethylpolysilanes. Peaks in this potential region arise from oxidation of the silicon chains [7] as well as silicon—chlorine groups. The cyclic voltammogram of permethylpentasilane (Fig. 5) shows similar peaks. Analysis of electrolyzed solutions of permethylpolysilanes by ultraviolet spectroscopy shows silicon—silicon bond cleavage.

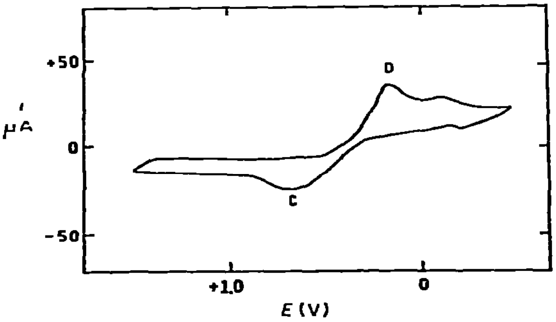


Fig. 3. Cyclic voltammogram of Et_3SiH.

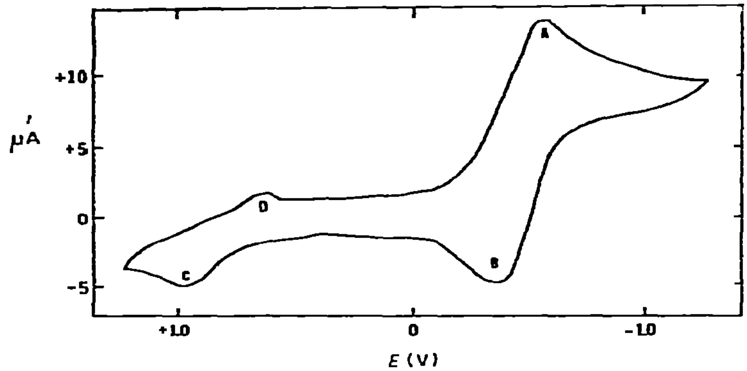


Fig. 4. Cyclic voltammogram of Me_3SiCl.

Discussion

Reduction potentials

The trends in reactivity of chloropermethylpolysilanes toward methylmagnesium iodide were discussed [3] in terms of the increasing extent of π-bonding between chlorine and vacant polysilane orbitals as the chain length increases. For the two chlorines of α, ω-dichloropermethylpolysilanes, there appears to be less π-bonding between each chlorine and vacant polysilane orbitals than in the case of the corresponding monochloropermethylpolysilanes. The trends in reduction potentials shown in Table 1 are consistent with these apparent variations in chlorine—silicon chain interactions. With increasing chain length, the less negative reduction potentials reflect greater ease of addition of electrons. It appears that the extent of π-bonding between chlorine and polysilane orbitals is the dominant factor in the trends of reduction potentials. For permethylpolysilanes, no reduction was observed prior to the solvent—electrolyte cut-off [7]. Transmission of the effect of one chlorine through a chain should decrease the extent of π-bonding between the second chlorine and the polysilane orbitals and apparently leads to a more negative reduction potential.

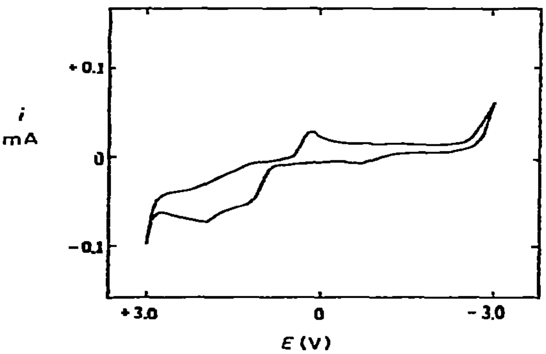


Fig. 5. Cyclic voltammogram (second cycle) of $Me(SiMe_2)_5Me$.

Of considerable interest is the observation that the difference in reduction potentials for monochloro and α, ω-dichloro derivatives increases with chain length.

Coupled reactions

The reduction of chloropermethylpolysilanes apparently proceeds through a radical intermediate:

$$Me(SiMe_2)_nCl + e^- \underset{B}{\overset{A}{\rightleftharpoons}} Me(SiMe_2)_nCl^- \rightarrow Me(SiMe_2)_n\cdot + Cl^- \qquad (1)$$

The radical can either dimerize or abstract hydrogen from the solvent:

$$2Me(SiMe_2)_n\cdot \rightarrow Me(SiMe_2)_{2n}Me \qquad (2)$$

$$Me(SiMe_2)_n\cdot + CH_3CN \rightarrow Me(SiMe_2)_nH + \cdot CH_2CN \qquad (3)$$

The permethylpolysilane resulting from dimerization is electrochemically oxidizable [7] but at more positive potentials than shown in Figs. 1,2, and 4. Silyl radicals are known [8] to dimerize very rapidly. Each $Me(SiMe_2)_nH$ species resembles triethylsilane and triphenylsilane by being easily and irreversibly electrochemically oxidized with a coupled chemical reaction giving a product, postulated [7] to be a silicenium ion, which can in turn be reduced at a positive potential relative to the s.c.e. electrode.

Acknowledgements

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