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PROPERTIES OF LONG-CHAIN PERMETHYLPOLYSILANES

W.G. BOBERSKI and A.L. ALLRED*
Department of Chemistry, Northwestern University, Evanston, Illinois 60201 (U.S.A.)
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Summary

Permethylpolysilanes, including $Me(SiMe_2)_{18}Me$, $Me(SiMe_2)_{24}Me$ and lower homologs, were investigated by UV spectroscopy, cyclic voltammetry, and a.c. polarography. Solubilities in common solvents and reactions with potassium were investigated. Evidence is presented for the formation of the unstable species, $(CH_3)_3Si(NCCH_3)_n^+$, from the electrochemical oxidation of $(CH_3)_3SiSi(CH_3)_3$ in acetonitrile.

Introduction

The preparation of two new permethylpolysilanes, permethyloctadecasilane and permethyltetracosasilane, was reported recently [1]. Properties of the lower homologs of this series have been discussed in earlier reviews [2-5] and in recent publications [6-17]. Investigated properties include ultraviolet [6-10], photoelectron [11] and NMR [12] spectra, ionization potentials [13], melting point variation with increasing chain length [14], extensive cleavage of silicon—silicon bonds upon UV irradiation [15], and the formation of weak charge transfer complexes of linear permethylpolysilanes with tetracyanoethylene [16,17].

To provide further information about the physical and chemical properties of the permethylpolysilanes, we have examined the ultraviolet spectra and solubilities in common solvents of the long chain compounds. Also, the shorter chain members of the series were investigated by a.c. polarography and cyclic voltammetry and by observing their reactions with a potassium mirror.

Experimental

ESR spectra were obtained on a Varian Associates Model E-4 spectrometer over the temperature range −80° to −20°. Permethylpolysilanes were reduced by allowing tetrahydrofuran or dimethoxyethane solutions of the polysilanes to contact potassium mirrors in vacuo at —60°. Electrolytic reductions were attempted in tetrahydrofuran or tetrahydrofuran/ethyl ether solutions from —50° to —90°. A PAR 373 potentiostat operating at a constant potential of —4.00 V, platinum electrodes and tetra-n-butylammonium perchlorate as the supporting electrolyte were employed.

Cyclic voltammetry and a.c. polarography were carried out in acetonitrile solution using equipment described elsewhere [18]. The working, counter, and reference electrodes were platinum, platinum, and saturated calomel electrodes, respectively. Cyclic voltammograms were obtained at 25° with a sweep frequency of 0.05 Hz for ca. 0.01 *M* solutions with tetra-n-butylammonium perchlorate as the supporting electrolyte.

Ultraviolet spectra were recorded in cyclohexane solution with a Cary 14 spectrometer in 1 cm cells.

Solubilities were determined by placing a weighed sample in a tube calibrated by volume and measuring the amount of solvent required to give a saturated solution at 25°.

The permethylpolysilanes were synthesized by reported procedures [1,19]

Results and discussion

Ultraviolet spectra

The UV absorption maxima and molar absorptivities of the long chain polysilanes are listed in Table 1.

Hückel theory predicts [20] that for a chain of n silicon atoms the resulting j molecular orbitals will have energies given by:

$$E_j = \alpha_{Si} + (\beta_{SiSi})2\cos\frac{j\pi}{n+1}$$

$$j = 1,2,3\ldots n$$

The energies of the lowest energy UV transitions of the shorter permethylpolysilanes have been correlated [10,21,22] with the results of simple HMO calculations. The curves in Fig. 1 show the change in $2\cos(j\pi/n{+}1)$ as a function of chain length for $j = 1$ and $j = 2$. The points represent energies corresponding to the maxima of the first and second transition energies of the various permethylpolysilanes. This treatment is consistent with excitation to vacant delocalized orbitals of electrons from silicon-σ orbitals which are either of constant energy or effectively delocalized with energy dependent upon chain length. While the experimental and calculated values of the first transition obviously are similar in Fig. 1, an appropriate change of either of the ordinate scales would lead to the experimental points for the second, but not the first, transition being on the theoretical curve. Thus, the two plots of $2\cos(j\pi/n{+}1)$ as a function of transition energy are both linear.

UV spectra and ionization potentials of the polysilanes have been correlated [9,13] also with the results of calculations by the Sandorfy C molecular orbital method [23]. In this method, the resonance integral β' for two orbitals on each $SiMe_2$ group in addition to the resonance integral β for orbitals on contiguous silicons are considered. In the present work, various β'/β ratios were

TABLE 1

UV SPECTRA OF LONG-CHAIN PERMETHYLPOLYSILANES

Compound	λ_{max}(nm)	Molar absorptivity × 10^{-4}
$Me(SiMe_2)_{12}Me$	285	4.30
	264	4.35
	221 (sh)	
$Me(SiMe_2)_{18}Me$	291	4.43
	270	3.98
	225 (sh)	
$Me(SiMe_2)_{24}Me$	293^a	4.55
	228	2.78
	210	2.80

[a] First and second transitions not resolved.

tested. For $\beta' = 0.6\,\beta$, calculated differences in energy of the highest occupied (σ) molecular orbital and the lowest, as well as the second lowest, unoccupied molecular orbitals are shown by the curves in Fig. 2. The experimental points in Fig. 2, as in Fig. 1, are close to the curves. For the earlier suggested [13] relationship, $\beta' = 0.346\,\beta$, analogously calculated curves can be fitted almost as well with present experimental data.

From the linear variation of β as a function of $\bar{\nu}$ for all chains longer than disilane, the value of β_{Si-Si} is 2.73 eV by the simple HMO method for the first transition, in agreement with earlier results [10,21], and 2.33 eV by the Sandorfy C method for the first transition and for the second transition treated separately.

For the first transitions of $Me(SiMe_2)_{18}Me$ and $Me(SiMe_2)_{24}Me$, the experimental points are well onto the upper asymptotic portion of the curves in

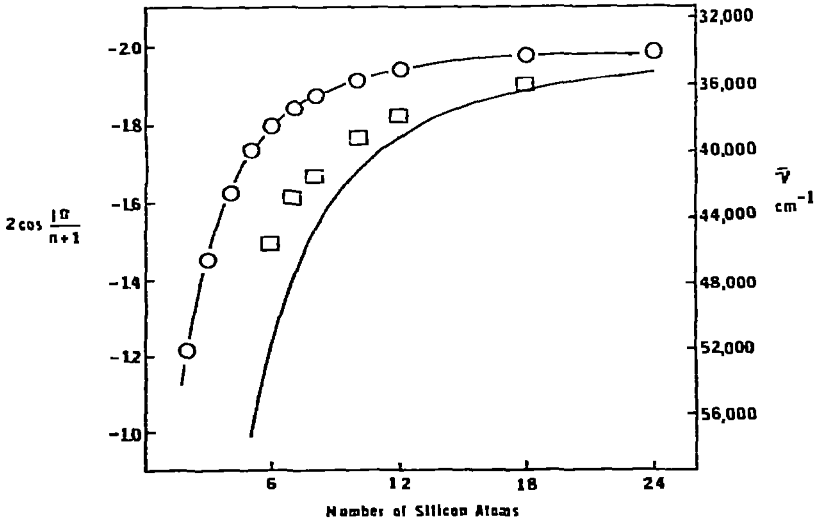

Fig. 1. Calculated (HMO) curves for energies and observed transition frequencies as a function of chain length. First transition: o, second transition: □. UV data from refs. 1 and 21.

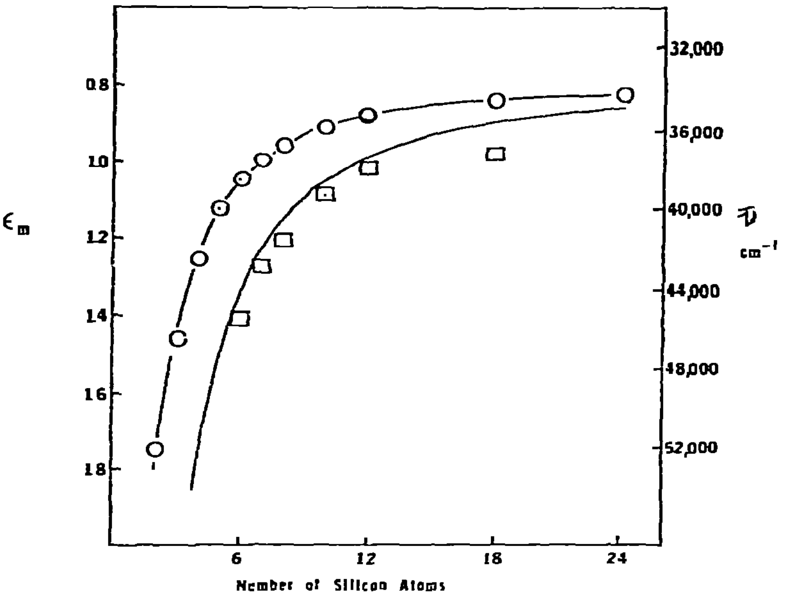

Fig. 2. Calculated (Sandorfy C) curves for energy differences and observed transition frequencies as a function of chain length.

Figs. 1 and 2 and thus close to the transition energy expected for an infinitely long permethylpolysilane chain. The predicted minimum energy of the first transition is 33,740 cm^{-1} from Fig. 1 and 33,800 cm^{-1} from Fig. 2.

Although the LUMO presumably is mostly of π character in the simple HMO model and an antibonding σ orbital in the Sandorfy C model, the present UV data cannot be used alone to choose between these models as shown by the good agreement in both Fig. 1 and Fig. 2.

Electrochemistry of permethylpolysilanes

Oxidation potentials as determined by a.c. polarography for several permethylpolysilanes are given in Table 2. Electrochemical data for the longer chain permethylpolysilanes are not available owing to their low solubilities in acetonitrile. The cyclic voltammograms for hexamethyldisilane and octamethyltrisilane are shown in Figs. 3 and 4, respectively. The cyclic voltammograms of Me(SiMe$_2$)$_n$Me where n is 4, 5 [18] or 6 differred qualitatively from that in

TABLE 2

LOWEST OXIDATION POTENTIALS OF PERMETHYLPOLYSILANES

Compound	$E_{ac}{}^{a}$
Me(SiMe$_2$)$_2$Me	1.880 ± 0.005
Me(SiMe$_2$)$_3$Me	1.520
Me(SiMe$_2$)$_4$Me	1.330
Me(SiMe$_2$)$_5$Me	1.180
Me(SiMe$_2$)$_6$Me	1.075

^{a}Reference: SCE.

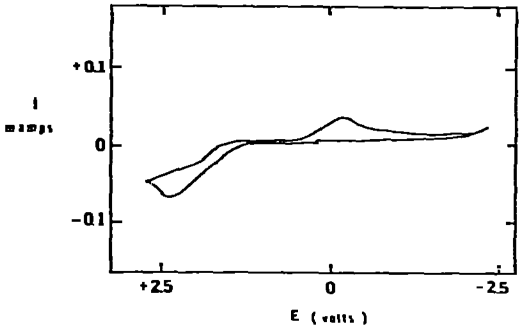

Fig. 3. Cyclic voltammogram of $Me(SiMe_2)_2Me$.

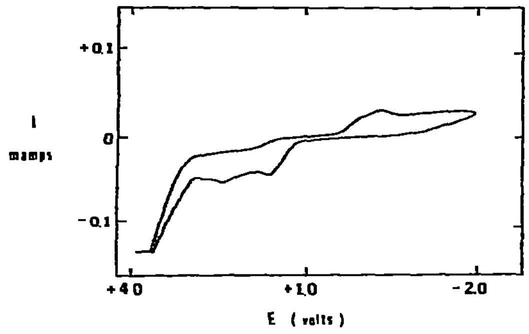

Fig. 4. Cyclic voltammogram of $Me(SiMe_2)_3Me$ (second and subsequent sweeps).

Fig. 4 by having additional ill-defined oxidative waves in the +1.5 to +3.5 V range and differently shaped reductive waves at ca. +0.1 V.

The oxidation potentials, E_{ac}, of permethylpolysilanes vary almost linearly with the energies of the highest occupied molecular orbitals as determined by the Sandorfy C treatment (Fig. 5). Ionization potentials which have been measured [11] by photoelectron spectroscopy for $Me(SiMe_2)_nMe$, where $n = 2$, 3 and 4, also increase linearly with the energies of these orbitals as calculated by the Sandorfy C method.

The cyclic voltammograms of linear permethylpolysilanes show oxidative waves in the region +1.2 to +3.0 V which have fast reactions coupled to the electrode processes. The UV spectrum of a solution of permethyltrisilane after electrolysis at +1.8 V shows a decrease in permethyltrisilane and appearance of permethylcyclopentasilane indicating that silicon—silicon bond cleavage occurs.

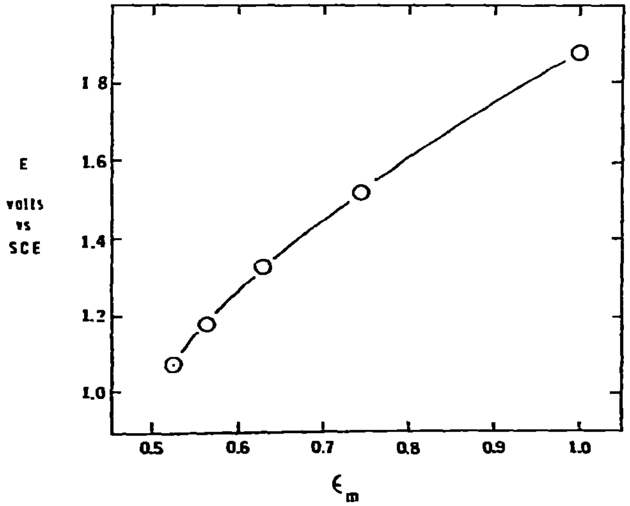

Fig. 5. Correlation of oxidation potentials with the energy of the highest occupied molecular orbital as calculated by the Sandorfy C method ($\beta' = 0.6\ \beta$).

The subsequent reduction sweep in each of the above cyclic voltammograms produces one or more processes in the +0.3 to −0.25 V range. These electrochemical processes also have fast coupled reactions. Tetramethylsilane was not electroactive.

For initial scans from +1.0 V to −2.5 V, no reduction of permethylpolysilanes is observable. The number, relative intensities and shape of the reductive waves in subsequent scans varied with chain length, temperature and sweep frequency.

For the oxidation of hexamethyldisilane, the number of electrons transferred is calculated to be 2.0 ± 0.3 from the Randles—Sevcik equation [24]. From this result, the reaction coupled to the oxidation of hexamethyldisilane is postulated to be:

$$Me_3SiSiMe_3 \xrightarrow[CH_3CN]{-2e} 2Me_3Si^+(NCCH_3)_n$$

The product from the oxidation of hexamethyldisilane was short-lived but at convenient scan rates gave a reduction wave at ~ −0.25 V. For an investigation of whether either $Me(NCMe)^+$ formed either during the oxidation process or during decomposition of $Me_3Si^+(NCCH_3)_n$ to Me_2Si:, the cyclic voltammogram of $Me(NCCH_3)^+$ was recorded. This species was prepared by addition of $MeOSO_2CF_3$ to acetonitrile [25]. The cyclic voltammogram shows a reduction at ca. −0.44 V and much greater stability of $Me(NCCH_3)^+$ than of the species produced in the electrolysis of hexamethyldisilane. Goodrich and Treichel [26] have reported isolation of salts containing the $Me(NCCH_3)^+$ cation. The relative magnitude of the −0.25 V wave, relative to the oxidative wave, decreases with decreasing scan rate. A plot of the reciprocal of the ratio of maximum current of the reductive wave to the maximum current of the oxidative wave as a function of elapsed time between oxidation and reduction (Fig. 6) establishes

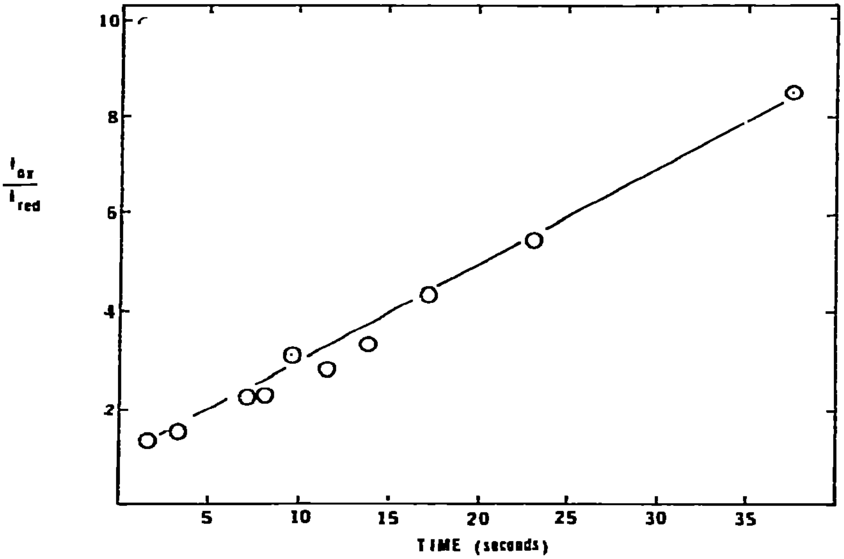

Fig. 6. Second-order kinetic plot of decomposition of $Me_3Si^+(NCCH_3)_n$.

that the decomposition of $Me_3Si^+(NCCH_3)_n$ takes place by a second-order process. The ratio of the reductive current to the oxidative current is independent of the initial concentration of hexamethyldisilane. Upon decreasing the temperature from +25° to —20°, the peak at —0.25 V decreases in magnitude and a second peak at ca. —1.0 V appears. The sum of the areas under these two peaks is about the same as the area of the —0.25 V peak at room temperature, if equal scan voltages and sweep frequencies are employed. It is conceivable that the peak at ca. —0.25 V is due to the reduction of $Me_3Si^+(NCCH_3)_{1(or\ 2)}$ and that the peak at ca. —1.0 V is due to the reduction of $Me_3Si^+(NCCH_3)_{2\ (or\ 1)}$. Another conceivable species which could be reduced at one of these potentials is the covalent compound $Me_3SiOClO_3$ which may be formed in a coupled chemical reaction involving the supporting electrolyte. The electrochemical oxidation of triphenylgermanium chloride (or bromide or iodide) has been shown [27] to give the germenium ion, $(C_6H_5)_3Ge^+$, which exists in solution as an ion pair with the ClO_4^- gegen ion. In the latter system, product isolation led to the covalent species, $(C_6H_5)_3GeOClO_3$. No oxidative wave was present in the cyclic voltammogram of hexamethyldisilane when methylene dichloride was the solvent.

Reactions with potassium

In either tetrahydrofuran or dimethoxyethane, permethylpolysilanes react with a potassium mirror at —60° to give a radical with the ESR spectrum comparable to that exhibited by $(SiMe_2)_5^{-\cdot}$. Carberry, West, and Glass [28] have reported this radical and found its formation during attempted alkali metal reductions of permethylcyclohexasilane. Bukhtiyarov, Solodovnikov, Nefedov and Shiryaev [29] have reported that the reduction of permethyltetrasilane by sodium/potassium alloy in dimethoxyethane gives the anion radical of permethyltetrasilane, but attempts in this laboratory to reproduce this result failed with only $(SiMe_2)_5^{-\cdot}$ being observed. Attempts to electrochemically prepare detectable anion radicals of the long chain (n = 12, 18, 24) polysilanes failed owing to the low solubility of these compounds in THF or THF/Et_2O from —50° to —90°.

TABLE 3

SOLUBILITY OF PERMETHYLPOLYSILANES

Solvent	$Me(SiMe_2)_nMe$ (mol/l)	
	n = 18	n = 24
Carbon tetrachloride	2.08×10^{-2}	8.63×10^{-3}
Cyclohexane	1.45×10^{-2}	4.06×10^{-3}
Benzene	1.03×10^{-2}	2.70×10^{-3}
Hexane	6.45×10^{-3}	1.30×10^{-3}
Tetrahydrofuran	8.13×10^{-3}	Insol.^{a}
Ethyl ether	8.82×10^{-4}	Insol.^{a}
Acetone	Insol.^{a}	Insol.^{a}
Ethanol	Insol.^{a}	Insol.^{a}

^{a}Less than 1×10^{-4} M.

Solubilities

Solubilities of permethyloctadecasilane and permethyltetracosasilane were determined in several common solvents, and data are presented in Table 3.

Acknowledgements

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