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Electrochemical Properties and UV Spectra of Permethylpolygermanes

Mitsutoshi OKANO and Kunio MOCHIDA*
Department of Chemistry, Gakushuin University,
1-5-1 Mejiro, Toshima-ku, Tokyo 171

Cyclic voltammograms of $Me(GeMe_2)_nMe$ n=2-6 and $(GeMe_2)_6$ were recorded. The data showed that HOMO moves up more largely than LUMO moves down as the polygermane chain elongates. UV spectra were also measured. Examination of UV data and the oxidation potentials for $Me(GeMe_2)_6Me$ and $(GeMe_2)_6$ suggested that $(GeMe_2)_6$ is stabilized by 2.3 kcal mol^{-1}.

Polysilanes have been investigated by many workers for their interesting properties. Application of them for SiC precursors,1) in microlithography,2) as photoinitiators,3) and in reprography4) were proposed. Polygermanes are recently attracting attention for the same reason. While Boberski et al. reported on the electrochemical properties for polysilanes more than 10 years ago,5) no such data is reported on polygermanes. The purpose of the present paper is to provide some of the physical and chemical properties of polygermanes and to compare the data with those for polysilanes.

Permethylpolygermanes, $Me(GeMe_2)_nMe$;n=2-6, and permethyl cyclic polygermane, $(GeMe_2)_6$ were synthesized and identified in the conventional manner.

Electrochemical measurements were carried out in a three-electrode system. The working and counter electrodes were platinum wires, and the reference electrode was a silver wire. Polygermanes were dissolved by sonication in dry acetonitrile containing 0.1 mol dm^{-3} of tetrabutylammonium perchlorate (TBAP). Ferrocene (Fc) was also dissolved in the solution. The oxidation and reduction peaks were not affected by the addition of ferrocene. The oxidation-reduction peaks of Fc and ferricinium cation (Fc^+) were used as the reference redox system.6)

The cyclic voltammogram of $Me(GeMe_2)_3Me$ is shown in Fig. 1. The scan was started around 0 V vs. Fc/Fc^+. The peaks for the redox reaction of Fc/Fc^+ can not be recognized in Fig. 1 because the peaks are very small.

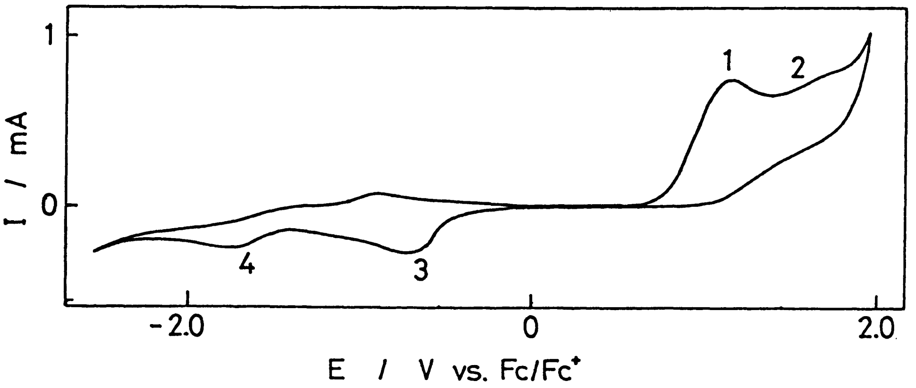

Fig. 1. Cyclic voltammogram for $Me(GeMe_2)_3Me$ in 0.1 mol dm^{-3} TBAP acetonitrile solution at the scan rate of 100 mV s^{-1}.

Table 1. Half peak potentials obtained by cyclic voltammetry in acetonitrile

Compound	$E_{p/2}$ / V vs. Fc/Fc^+	
	Peak 1[a]	Peak 3[a]
$Me(GeMe_2)_nMe$ n=2	1.28	-0.46
3	0.93	-0.56
4	0.72	-0.53
5	0.61	-0.48
6	0.53	-0.53
$(GeMe_2)_6$	0.66	-0.34
$Me(SiMe_2)_nMe$ n=2	1.36	-0.59
3	1.10	-0.58

a) The values may include errors ±0.03 V.

It has two oxidation peaks; Peak 1 and Peak 2. Peak 2 is ill defined. Peak 3 around -0.5 V vs. Fc/Fc^+ is the reduction wave for the intermediate species which are produced at Peak 1. When the electrode potential was reversed before the first oxidation peak, no reduction peak was observed there. With slower sweep rates, the ratio of the height of Peak 3 to that of Peak 1 decreased. The fact indicates the disappearance of the intermediate species. The three peaks were also reported for $Me(SiMe_2)_3Me$.[5] Peak 4 originates from oxygen or moisture which came into the electrolyte solution during the process of sonication. The process is necessary for dissolving polygermanes.

The half peak potentials ($E_{p/2}$) of Peak 1 and Peak 3 for the poly-

Table 2. Absorption maxima and molar absorptivity for the polygermanes and the polysilanes

	$Me(GeMe_2)_nMe$		$Me(SiMe_2)_nMe$[a]		$(GeMe_2)_n$		$(SiMe_2)_n$	
	λ_{max}/nm	ε	λ_{max}/nm	ε	λ_{max}/nm	ε	λ_{max}/nm	ε
2	193.7	16000	193.5	10800	-----	-----	-----	-----
3	217.5	8830	216.3	9020	-----	-----	-----	-----
4	232.5	16400	235.0	14700	-----	-----	-----	-----
5	245.5	20700	250.0	18400	-----	-----	272[b]	970[b]
6	222.0	26800	220.0	14000	235.0	3900	232[c]	5800[c]
	255.3	25000	260.0	21100	250.0	1600	255[c]	2000[c]

a) Data from Ref. 9. b) Data from Ref. 10. c) Data from Ref. 11.

germanes and polysilanes are listed in Table 1. The half peak potentials are listed because the former peaks, in some cases, were not clearly observable for the close presence of the ill-defined Peak 2. The half peak oxidation potentials for Peak 1 became less positive value as the germanium chains became longer. Peak 1's for hexamethyldisilane and octamethyltrisilanes were also measured under the same conditions. The oxidation potentials of polygermanes are less positive compared with those for the polysilanes of the same chain length. Thus, the polygermanes are more easily oxidized than the polysilanes. Considering the linearity between ionization potentials and electrochemical oxidation potentials,[7)] HOMO level of polygermanes should be higher than those of polysilanes.

All the reduction potentials for Peak 3's were seen between -0.3 V and -0.6 V vs. Fc/Fc^+. This means that all the intermediate species, produced by the oxidation of various polygermanes and polysilanes in Table 1, have the similar oxidizing power.

UV data measured in cyclohexane are listed in Table 2. Absorption maxima for $Me(GeMe_2)_nMe$;n=2,3 were located at the longer wave length compared with those for the corresponding polysilanes. However, those for n=4,5,6 were located at the shorter wave length. This is surprising because simply all n=2-6 polygermanes have been expected to have their λ_{max}'s at longer wavelength. The plot of longest absorption peaks against $E_{p/2}$'s makes a good line. These data look reasonable at this point of view.

LUMO levels can be discussed as follows. UV absorption data give the information of the energy difference between HOMO and LUMO. Comparison between λ_{max} for $Me(GeMe_2)_2Me$ and that for $Me(GeMe_2)_6Me$ indicates the approach of HOMO to LUMO by 1.54 eV in $Me(GeMe_2)_6Me$. Meanwhile, comparison between $E_{p/2}$'s (Peak 1) of the two compounds shows the difference of 0.75 V. The relation between the oxidation potentials and ionization potentials for the same compounds is expressed as E = k(IP) + c where E is oxidation potential (V) and IP is ionization potential (eV).[7] It is also known that k is less than 1. (For $Me(SiMe_2)_nMe$;n=2-6, k=0.81.) Thus, the value 0.75 eV means the raise of HOMO more than 0.75 eV. (Using k=0.81, it becomes 0.93 eV.) Finally, comparison of 1.54 eV with 0.75 eV (or 0.93 eV) reveals that the raise of HOMO is as large as the lowering of LUMO or more than that. For polysilanes, HOMO shifts more than LUMO does, as the chain elongates.[8]

Absorption maximum for $(GeMe_2)_6$ is located at 250.0 nm while that for $Me(GeMe_2)_6Me$ is located at 255.3 nm. The shift of 5.3 nm to the shorter wave length suggests us that the 6-membered ring is more stabilized than the linear polygermanes. The comparison of $E_{p/2}$'s for these two polygermanes also indicates that HOMO level is lowered in $(GeMe_2)_6$. HOMO level is lowered inspite of the fact that $(GeMe_2)_6$ has less number of electron donating methyl groups. The stabilization energy was estimated to be 2.3 kcal mol^{-1} by comparing the absorption maxima. The calculations were made according to the method which was used for the calculation of the strain energy.[12] Such estimation using the reported values for permethylpolysilanes gave the stabilization energy of 2.1 kcal mol^{-1}.

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References

1) S. Yajima, J. Hayashi, and M. Omori, Chem. Lett., 1975, 931.
2) G. C. Gobbi, W. W. Fleming, R. Sooriyakumaran, and R. D. Miller, J. Am. Chem. Soc., 108, 5624(1986).
3) A. R. Wolff and R. West, Appl. Organomet. Chem., 1, 7(1987).
4) M. Abkowitz, F. E. Knier, H. J. Yuh, R. J. Weagley, and M. Stolka, Solid State Commun., 62, 547(1987).
5) W. G. Boberski and A. L. Allred, J. Organomet. Chem., 86, 65(1975).
6) Recommendations on Reporting Electrode Potentials in Nonaqueous Solvents (Recommendation 1983) Pure Appl. Chem., 56, 461(1984).
7) K. Mochida, A. Itani, M. Yokoyama, T. Tsuchiya, S. Worley, and J. K. Kochi, Bull. Chem. Soc. Jpn., 58, 2149(1985).
8) H. Bock and W. Enslin, Angew. Chem., 83, 435(1971).
9) M. Kumada, M. Ishikawa, K. Yamamoto, and K. Tamao, "Yūki Keiso Kagoubutsu No Kagaku," Kagaku Dojin, Kyoto (1972).
10) E. Carberry and R. West, J. Organomet. Chem., 6, 582(1966).
11) H. Gilman and W. H. Atwell, J. Organomet. Chem., 4, 176(1964).
12) H. Watanabe, H. Shimoyama, T. Muraoka, T. Okawa, M. Kato, and Y. Nagai, Chem. Lett., 1987, 1057.

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