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# He I Photoelectron Spectra of Permethylated Polygermanes

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Photoelectron spectra of permethylated linear germanes display isolated bands in the 7.70-8.60 eV region, which are readily assigned to ionizations from the germanium framework.

Organometals, particularly those with metal-metal σ bonds, are excellent electron donors. As electron-rich species, they are subject to cleavage by various organic electrophiles as well as transition metal complexes.[1)] Since group 14 element catenates have rather low ionization potentials, electron-transfer mechanisms are also possible in which the rate is limited by the ability of the group 14 element catenates to transfer an electron to an electrophile acting as an electron acceptor. While the electron-donor properties of silicon-silicon σ bonds have been amply investigated by both chemical and physical methods,[2,3)] those of germanium-germanium σ bonds have not been reported except for hexamethyldigermane and hexaethyldigermane.[4-6)] We herein describe the first report on ionization potentials (IP's) of permethylated linear polygermanes, $Me(Me_2Ge)_nMe$ (n=2-5), obtained by photoelectron spectroscopy.

Figure 1 shows the He I (584 A, 21.22 eV) photoelectron spectra of gaseous $Me_4Ge$ and linear permethylated polygermanes $Me(Me_2Ge)_nMe$ (n=2-4) measured by a transmission-corrected electron spectrometer.[7)] For $Me_4Ge$, three bands labeled A-C have been attributed to emissions from relevant molecular orbitals;[8)] band A is due to the $7t_2$ orbital having GeC bonding character; band B is due to the $1t_1$, 2e, and $6t_2$ orbitals, all of which are CH bonding; weak band C is due to the $6a_1$ orbital having Ge 4s character. Owing to the Jahn-Teller distortion upon ionization, band A is split into three subbands and appears considerably broadened.

The spectrum of $Me(Me_2Ge)_2Me$ exhibits a new band at the lower IP re-

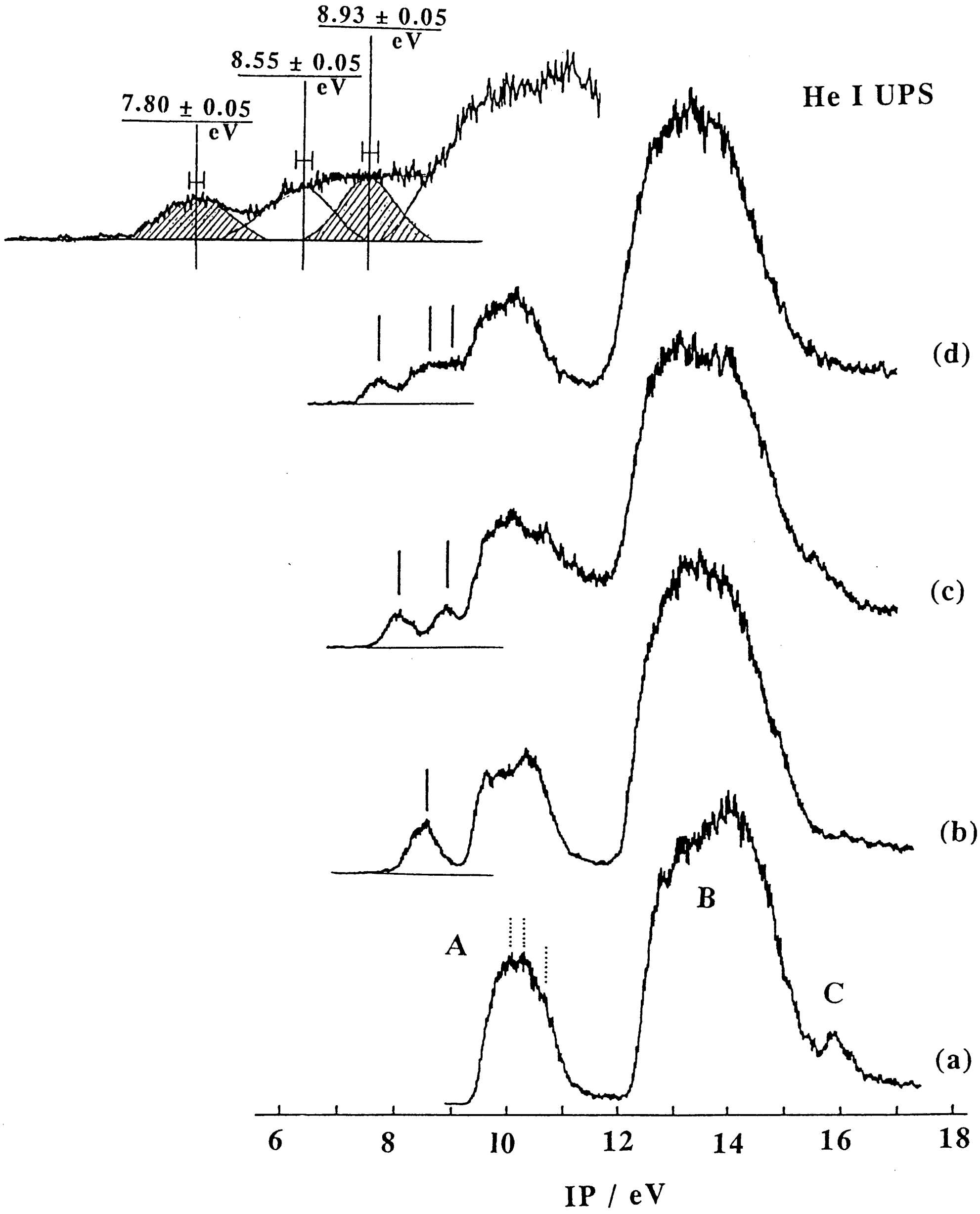

Fig. 1. PES of $Me_4Ge$ (a), $Me_3GeGeMe_3$ (b), $Me(Me_2Ge)_3Me$ (c), and $Me(Me_2Ge)_4Me$ (d).

gion in addition to the above-mentioned bands A-C. On going to $Me(Me_2Ge)_3Me$ and $Me(Me_2Ge)_4Me$, this band is split into two and three bands, respectively. Evidently, these bands are ascribed to electron removal from orbitals having GeGe bonding character ($\sigma_{GeGe}$), as in the cases of linear polysilanes[2)] and linear permethylated polysilanes.[2,4)] The vertical IP's of polygermanes are summarized in Table 1. In the Table the peak

Table 1. Vertical Ionization Potentials (eV) of Permethylated Polygermanes

| Compound | $\sigma_{GeGe}$ 1 | 2 | 3 |
|---|---|---|---|
| $Me_3GeGeMe_3$ | 8.57 ± 0.05 | | |
| $Me(Me_2Ge)_3Me$ | 8.15 ± 0.05 | 8.93 ± 0.05 | |
| $Me(Me_2Ge)_4Me$ | 7.80 ± 0.05 | 8.55 ± 0.05 | 8.93 ± 0.1 |

positions were determined by deconvolution of the spectrum and by referring Penning ionization electron spectrum.[9)] We also measured the photoelectron spectrum of $Me(Me_2Ge)_5Me$ (which is not shown in Figure 1 owing to the low signal/noise ratio) and assigned bands at IP ≈ 7.7, 8.5, and 9.2 eV to $\sigma_{GeGe}$ orbitals.[9)]

Figure 2 shows the energy diagram of the $\sigma_{GeGe}$ levels with increasing Ge chain length together with that of the $\sigma_{SiSi}$ levels of linear permethylated polysilanes.[2)] The splitting pattern shows a good corresponding between the Ge and Si compounds except for the fact the $\sigma_{GeGe}$ levels are shifted slightly to the lower IP side compared with $\sigma_{SiSi}$. This indicates that the σ bond-bond interaction in polygermanes resembles to that in polysilanes, in the sense of simplified model based on the linear combination of the bonding orbitals.[2)] This respect involving the case of cyclic polygermanes will be discussed

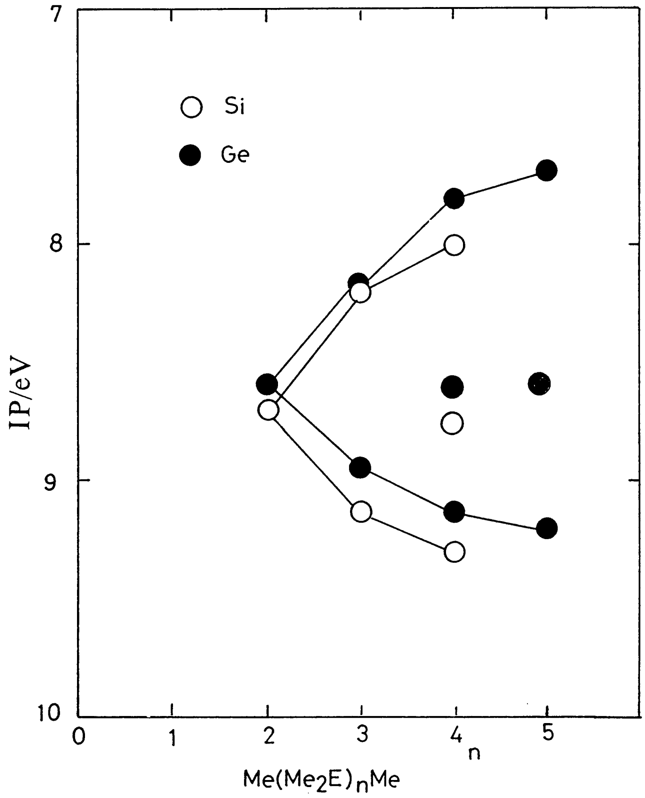

Fig. 2. Energy diagram of the $\sigma_{GeGe}$ ($\sigma_{SiSi}$) levels with increasing Ge(Si) chain length.

in more detailed elsewhere.

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References

1) J. K. Kochi, "Organometallic Mechanism and Catalysis," Academic Press, New York (1978).

2) For examples; H. Bock and W. Enssiin, Angew. Chem., 83, 435 (1971); H. Bock, W. Enssiin, F. Fehner, and R. Freund, J. Am. Chem. Soc., 98, 668 (1976).

3) For examples; V. F. Traven and R. West, J. Am. Chem. Soc., 95, 6824 (1973); H. Sakurai, M. Kira, and T. Uchida, ibid., 95, 6826 (1983).

4) C. G. Pitt, M. M. Bursey, and P. F. Rogerson, J. Am. Chem. Soc., 92, 519 (1970).

5) L. Szepes, T. Koranyi, G. N-Szabo, A. Modelli, and G. Distefano, J. Organomet. Chem., 217, 35 (1981).

6) K. Mochida, S. D. Worley, and J. K. Kochi, Bull. Chem. Soc. Jpn., 58, 3389 (1985).

7) Y. Harada, K. Ohno, and H. Mutoh, J. Chem. Phys., 79, 3251 (1983); S. Masuda and Y. Harada, ibid., 96, 2469 (1992).

8) M. Aoyama, S. Masuda, K. Ohno, Y. Harada, C. Y. Mok, H. H. Huang, and S. Y. Lee, J. Phys. Chem., 93, 1800 (1989), and references cited therein.

9) K. Mochida, S. Masuda, and Y. Harada, to be published.

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