UV Photoelectron Spectra of Peralkylated Catenates of Group 4B Elements (Silicon, Germanium, and Tin)

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Synopsis. The low-energy photoelectron spectra (PES) of twelve peralkylated catenates of group 4B elements (silicon, germanium, and tin) were recorded. The trends in the energies and the nature of the metal-metal and metal-carbon bonds are discussed.

In connection with predicting rates of the reactions and the products for processes involving electron transfer, UV photoelectron spectra (PES) of the organometals, particularly of group 4B metals, have received considerable attention.1) These PES studies have mainly focussed on the metal–carbon,2–8) metal–hydrogen,9–15) and metal–halogen bonds16–24) of the group 4B metals. However, there are a few reports on PES of the metal–metal bonds of the group 4B metals.25–29) Compounds which contain metal–metal bonds have attracted increasing interest in comparison with those of carbon–carbon double bonds.30,31) The carbon–carbon double bonds have, of course, already been very extensively studied by PES.32) Here we present the PES of twelve peralkylated catenates of group 4B elements, $R_3M-M'R_3$ (R=Me, Et; M, M′=Si, Ge, Sn) to explain trends in the energies and the nature of metal–metal and metal–carbon bonds.

Results and Discussion

Although the PES of permethylated and perethylated catenates of group 4B elements (silicon, germanium, and tin) are slightly different from the spectrum of carbon analogue, 2,2,4-trimethylpentane,28) these spectra show similar patterns, each exhibiting three bands of increasing intensity. The vertical ionization potentials corresponding to the highest three occupied orbitals are summarized in Table 1, together with the designated symmetry and the principal contributions to MO's.28) The highest occupied molecular orbital (HOMO), which is of principal concern to us, is associated with ionization from M–M′ σ bonding orbital (a_1), while the next two bands correspond to M–C and/or M′–C bonding orbitals (e).

The bands corresponding to M–M′ σ bonding orbital ionization of a series of kindred catenates of group 4B elements will appear at lower ionization potentials than the bands corresponding to the interaction of this 4B atom with the methyl or ethyl group, since each group 4B atom studied has an ionization potential much lower than carbon. The first ionization potentials of a series of kindred catenates of group 4B elements shown in Table 1 are essentially the same as those of the parent metal (C, 11.26; Si, 8.15; Ge, 7.88; Sn, 7.34 eV),33) indicating that electrons ionized are localized relatively at the M–M′ bonds. The first ionization potential of a series of peralkylated catenates of group 4B elements decreases generally in order: Si–Si>Si–Ge>Ge–Ge>Si–Sn>Sn–Sn in accord with the M–M′ ionic bond dissociation energy. The internal consistency of the data is illustrated in Fig. 1 by a comparison of the ionization potentials of the permethylated derivatives with the perethylated analogues.

Table 1. Ionization potentials (eV) of group 4B dimetals

Compound	M–M′ (a_1)	C–M (e)	C–M′ (e)
$\mathrm{Me_3SiSiMe_3}$	8.68	10.23, 10.67	
$\mathrm{Me_3SiGeMe_3}$	8.62	9.91	10.50
$\mathrm{Me_3GeGeMe_3}$	8.60	9.87, 10.40	
$\mathrm{Me_3SiSnMe_3}$	8.39	9.71	10.41
$\mathrm{Me_3GeSnMe_3}$	8.36	9.65	10.09
$\mathrm{Me_3SnSnMe_3}$	8.20	9.26, 9.62	
$\mathrm{Et_3SiSiEt_3}$	8.39	9.40, 9.78	
$\mathrm{Et_3SiGeEt_3}$[a]	8.24	b)	9.75
$\mathrm{Et_3GeGeEt_3}$	8.33	9.14, 9.53	
$\mathrm{Et_3SiSnEt_3}$	8.10	8.90	9.70
$\mathrm{Et_3GeSnEt_3}$	8.05	8.79	9.29
$\mathrm{Et_3SnSnEt_3}$	7.82	8.49, 8.87	

a) The PES resolution was rather poor due to the complexity of the compounds under study. b) This band was not resolved from leading edge of the 9.75 eV band.

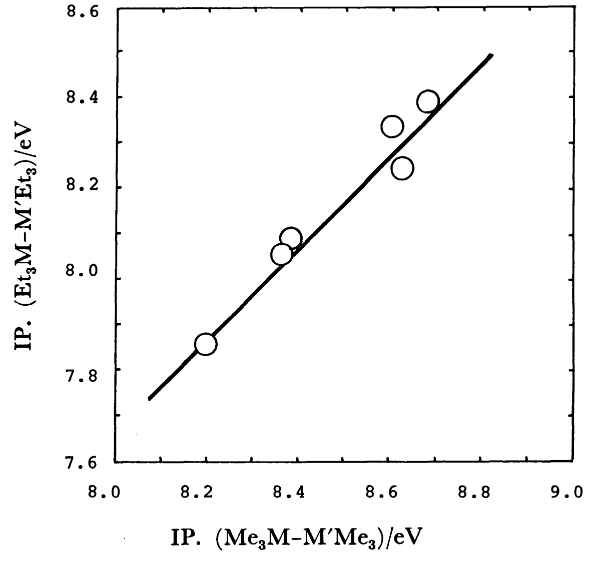

Fig. 1. First ionization potential of $\mathrm{Me_3M\text{-}M'Me_3}$ *vs.* the first ionization potential of $\mathrm{Et_3M\text{-}M'Et_3}$ (M, M′ = Si, Ge, Sn).

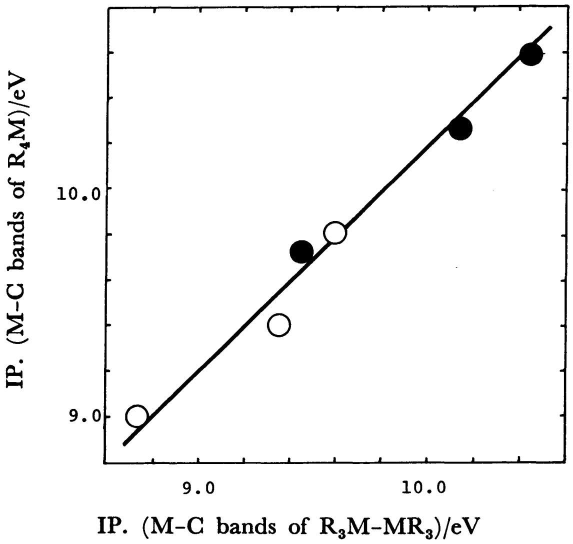

Fig. 2. The mean value of two bands of M-C bonding orbitals of R_3M–MR_3 *vs.* the first ionization potential of R_4M (M=Si, Ge, Sn); ●; permethylated derivatives, ○; perethylated derivatives.

Furthermore, the average of the next two bands corresponding to M-C bonding orbitals of kindred catenates of group 4B elements is close in energy and linearly related to the M-C σ bonding orbital (the HOMO) of R_4M (Si, 10.57, 9.8; Ge, 10.23, 9.4; Sn, 9.70, 9.0 eV for R=Me, Et).[2,15] The correlation of the average of bands corresponding to M-C bonding orbitals of kindred catenates of group 4B elements with M-C σ bonding orbitals (the HOMO) of R_4M is illustrated in Fig. 2. Figure 2 shows that interaction between the M-M bond and the M-C bond is weak.[25]

The ionization potentials of peralkylated catenates of group 4B elements in this study should provide interesting criteria for evaluating electron transfer processes involving catenates of group 4B elements.

Experimental

Peralkylated catenates of group 4B elements (silicon, germanium, and tin) and the photoelectron spectrometer used in these studies have been described previously.[34]

References

1) For example; J. K. Kochi, "Organometallic Mechanism and Catalysis," Academic Press, New York (1978), Part 3.

2) S. Evans, J. C. Green, P. J. Joachim, A. F. Orchard, D. W. Turner, and J. P. Maier, *J. Chem. Soc., Faraday Trans. 2*, **1972**, 905.

3) S. Cradock, E. A. V. Ebsworth, W. J. Savage, and R. A. Whiteford, *J. Chem. Soc., Faraday Trans. 2*, **68**, 934 (1972).

4) A. E. Jonas, G. K. Schweitzer, F. A. Grimm, and T. A. Carlson, *J. Electron Spectros.*, **1**, 29 (1972).

5) R. Boschi, M. F. Lappert, J. B. Pedley, W. Schmidt, and B. T. Wilkins, *J. Organomet. Chem.*, **50**, 69 (1973).

6) A. Schweig, U. Weidner, and G. Manual, *J. Organomet. Chem.*, **54**, 145 (1973).

7) A. Hosomi and T. G. Traylor, *J. Am. Chem. Soc.*, **97**, 3682 (1975).

8) C. L. Wong, K. Mochida, A. Gin, M. A. Weiner, and J. K. Kochi, *J. Org. Chem.*, **44**, 3979 (1979).

9) A. W. Potts and W. C. Price, *Proc. Roy. Soc., Ser. A*, **326**, 165 (1971).

10) W. B. Perry and W. L. Jolly, *Chem. Phys. Lett.*, **17**, 611 (1972).

11) S. Cradock and R. A. Whiteford, *J. Chem. Soc., Faraday Trans. 2*, **1972**, 281.

12) S. Cradock and R. A. Whiteford, *J. Chem. Soc., Faraday Trans. 2*, **1972**, 934.

13) L. Szepes, G. Náray-Szabó, F. P. Colonna, and G. Distefano, *J. Organomet. Chem.*, **117**, 141 (1976).

14) G. Distefano, S. Pignataro, L. Szepes, and J. Borossay, *J. Organomet. Chem.*, **104**, 173 (1976).

15) G. Beltram, T. P. Fehler, K. Mochida, and J. K. Kochi, *J. Electron Spectros.*, **18**, 153 (1980).

16) D. C. Frost, F. G. Herring, A. Katrib, R. A. N. McLean, J. E. Drake, and N. P. C. Westwood, *Can. J. Chem.*, **49**, 4033 (1971).

17) M. B. Hall, M. F. Guest, I. H. Hillier, D. R. Lloyd, A. F. Orchard, and A. W. Potts, *J. Electron Spectros.*, **1**, 497 (1973).

18) D. R. Lloyd and J. R. Robert, *J. Electron Spectros.*, **7**, 325 (1975).

19) C. Glidewell, *Inorg. Chim. Acta.*, **13**, L11 (1975).

20) A. Flamini, E. Semprini, F. Stefani, S. Sorriso, and G. Cardaci, *J. Chem. Soc., Dalton Trans*, **1976**, 731.

21) G. C. Stocco and A. F. Orchard, *Chim. Ind. (Milan)*, **59**, 122 (1977).

22) J. E. Drake, B. M. Glavincevski, and K. Gorzelska, *Can. J. Chem.*, **57**, 2278 (1979).

23) J. E. Drake, B. M. Glavincevski, and K. Gorzelska, *J. Electron Spectros.*, **17**, 73 (1979).

24) J. E. Drake, B. M. Glavincevski, and K. Gorzelska, *J. Electron Spectros.*, **16**, 331 (1979).

25) H. Bock and W. Ensslin, *Angew. Chem.*, **83**, 435 (1971).

26) C. G. Pitt, M. Bursey, and P. F. Rogerso, *J. Am. Chem. Soc.*, **92**, 519 (1970).

27) H. Bock, W. Ensslin, F. Feher, and R. Freund, *J. Am. Chem. Soc.*, **98**, 668 (1976).

28) L. Szepes, T. Korányi, G. Náray-Szabó, A. Modelli, and G. Distefano, *J. Organomet. Chem.*, **217**, 35 (1981).

29) H. Sakurai, M. Ichinose, M. Kira, and T. G. Traylor, *Chem. Lett.*, **1984**, 1383.

30) H. Sakurai, *Kagaku No Ryoiki*, **29**, 36 (1975).

31) R. West, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press (1982), Vol. 2, p. 365.

32) For example; D. W. Turner, C. Baker, A. D. Baker, and C. R. Brunde, "Molecular Photoelectron Spectroscopy," John Wiley & Sons, New York (1970).

33) C. E. Moore, National Bureau of Standards Circular 467, Vol. 3, U. S. Government Printing Office, Washington, D. C. (1958).

34) K. Mochida, A. Itani, M. Yokoyama, T. Tsuchiya, S. D. Worley, and J. K. Kochi, *Bull. Chem. Soc. Jpn*, **58**, 2149 (1985).