July, 1985] © 1985 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 58, 2149—2150 (1985) 2149

A Correlation of Electrochemical Oxidation and Ionization Potentials of Group 4B Dimetals

Kunio MOCHIDA,* Atsuko ITANI, Michiyo YOKOYAMA, Tohru TSUCHIYA,† Shelby D. WORLEY,*,†† and Jay K. KOCHI†††
Department of Chemistry, Faculty of Sciences, Gakushuin University, 1-5-1 Mejiro, Tokyo 171
†*National Chemistry Laboratory for Industry, 1-1 Higashi, Yatabe, Ibaraki 305*
††*Department of Chemistry, Auburn University, Alabama 36849, USA*
†††*Department of Chemistry, University of Houston, University Park, Houston, TX 77004, USA*

(Received March 15, 1985)

Synopsis. Correlations of ionization potentials and electrochemical oxidation potentials for group 4B dimetals were obtained.

The reactivity of the metal-metal bond of group 4B dimetals has received considerable interest in comparison with that of carbon-carbon double bond.[1,2] As electron-rich species, metal-metal bonds of group 4B dimetals are subject to cleavage by acids, halogens, metal complexes, and other electrophiles.[1] Since group 4B dimetals have rather low ionization potentials, electron-transfer process in solutions are also possible in which the rate is limited by the ionization potentials of organometals and the electron affinity of electrophiles.[3] In order to predict rates of reactions and the products for such processes, the most fundamental data are the ionization or oxidation potentials of organometals. However, there is only a paper on a correlation of organic oxidation and ionization potentials for group 4B metals.[4] Here we describe such a correlation for group 4B dimetals.

$$R_3M\text{-}M'R_3 \longrightarrow R_3M\text{-}M'R_3^{+\cdot} + e \qquad (1)$$
$$(M,\ M' = Si,\ Ge,\ Sn)$$

Results and Discussion

The anodic oxidation of group 4B dimetals was examined in acetonitrile solutions with tetraethylammonium perchlorate as a supporting electrolyte and a glassy carbon anode. The reference electrode was Ag/AgCl in acetonitrile. The anodic oxidation of each of the group 4B dimetals was found to be irreversible, suggesting that the dimetal cation radical is unstable. Equation (2) represents a probable mode of decomposition.[5]

$$R_3M\text{-}M'R_3^{+\cdot} \longrightarrow R_3M\cdot + {}^{+}M'R_3 \qquad (2)$$

Peak potentials (E_p) of group 4B dimetals are listed in Table 1. Since each of these oxidative processes is irreversible, the observed potentials shifted to more positive values relative to E°. However, the potentials listed in Table 1 reflect the relative ease of removal of a single electron from the group 4B dimetals examined in this study.

In order to determine if there is a correlation between the anodic oxidation of group 4B dimetals in solution and their ionization potentials, He (I) photoelectron spectra of group 4B dimetals were also examined.

The vapor-phase photoelectron spectra (PES) of some group 4B dimetals have been previously reported by several research groups.[6-8] The lowest-energy band is associated with ionization from the metal-metal σ bonding orbital. Semiempirical calculations for the group 4B dimetals show that a highest occupied molecular orbital (HOMO) is highly localized at the central metal-metal bond ($4a_{1g}$)[6,7] The lowest-energy bands of group 4B dimetals measured in this work are also listed in Table 1.

The threshold or adiabatic ionization energy of the lowest-energy band decreases in the order: Si-Si> Si-Ge>Ge-Ge>Si-Sn>Ge-Sn>Sn-Sn in accord with the metal-metal ionic bond dissociation energy.[9]

The vertical ionization potential correspond to the Frank-Condon transition of the ionic state. Electron detachment from group 4B dimetals in Eq. 1 under these conditions shows a relationship to the electrochemical oxidation potentials in acetonitrile solution as shown in Fig. 1.[4,10]

The plots in Fig. 1 fit the equations $E_p = 0.91\ (IP) - 6.08$ for permethyl derivatives and $E_p = 0.78\ (IP) - 4.82$ for perethyl derivatives. The correlation coefficents for the plots are 0.96 and 0.88, respective-

TABLE 1. OXIDATION AND IONIZATION POTENTIALS OF GROUP 4B DIMETALS

Compound	IP/eV[a]	E_p/V[b]
$Me_3SiSiMe_3$	8.68, 8.69[c]	1.76
$Me_3SiMe_2SiSiMe_3$	8.19[c], 9.14[c]	1.40, 1.76
$Me_3SiGeMe_3$	8.62	1.76
$Me_3GeGeMe_3$	8.60, 8.60[d]	1.70
$Me_3SiSnMe_3$	8.39, 8.32[d]	1.60
$Me_3GeSnMe_3$	8.36, 8.33[d]	1.44
$Me_3SnSnMe_3$	8.20, 8.20[d]	1.28
$Et_3SiSiEt_3$	8.39	1.76
$Et_3SiGeEt_3$	8.24	1.70
$Et_3GeGeEt_3$	8.33	1.48
$Et_3SiSnEt_3$	8.10	1.56
$Et_3GeSnEt_3$	8.05	1.40
$Et_3SnSnEt_3$	7.82	1.24

a) IP is associated with the metal-metal orbitals (vertical IP). b) In acetonitrile solution at 20 °C with glassy carbon anode. c) Ref. 6. d) Ref. 7.

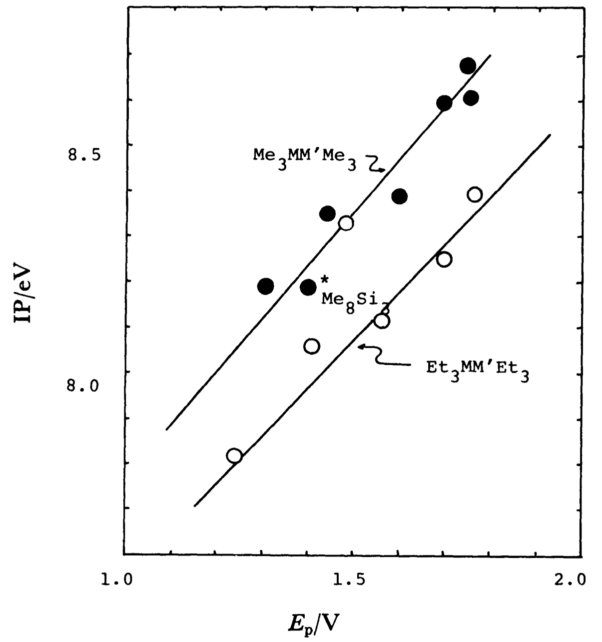

Fig. 1. Relationship between oxidation and ionization potentials of group 4B dimetals.

ly. Each slope is less than unity. It should be realized that these relations result from unstability of dimetal cation radicals and incursion of specific surface effects and solvations. Since the initially formed dimetal cation radicals may decay more rapidly than the time required for the measurement, E_p is a kinetic parameter for the overall oxidation process. The dimetal cation radicals will be strong acids stabilized by hydrogen bonding to the basic solvent, acetonitrile. This solvation will, of course, lower the E_p. These effects should be variable between permethyl derivatives and perethyl derivatives.

This correlation between anodic oxidation of group 4B dimetals in solution and their gas phase ionization potentials should provide interesting criteria for evaluating electron transfer processes involving group 4B dimetals.

Experimental

Materials. $Me_3SiSiMe_3$, bp 112 °C,[13] $Me_3SiMe_2SiSiMe_3$, bp 112 °C/106 mmHg,[14] $Me_3SiGeMe_3$, bp 122 °C,[15] $Me_3GeGeMe_3$, bp 136 °C,[16] $Me_3SiSnMe_3$, bp 144 °C,[17] $Me_3GeSnMe_3$, bp 154 °C,[17] $Me_3SnSnMe_3$, bp 182 °C,[18] $Et_3SiSiEt_3$, bp 100 °C/5.0 mmHg,[19] $Et_3SiGeEt_3$, bp 87 °C/3.0 mmHg,[20] $Et_3GeGeEt_3$, bp 73 °C/0.7 mmHg,[21] $Et_3SiSnEt_3$, bp 77 °C/0.7 mmHg,[22] $Et_3GeSnEt_3$, bp 120 °C/6 mmHg,[23] and $Et_3SnSnEt_3$, bp 160 °C/23 mmHg (1 mmHg=133.322 Pa),[24] were prepared according to the cited literatures.

Photoelectron spectra were obtained with a Perkin-Elmer PS-18 photoelectron spectrometer of Auburn University, using the He (I) resonance line at 21.22 eV as an excitation source. The spectra were calibrated with Ar and Xe as internal standards.

Electrochemical measurements were performed with Bioanalytical System Inc. CV-1B Cyclic Voltammetry Instrument under conditions similar to those described in previous works.[25] The values of E_p were measured in acetonitrile solution containing 0.1 M tetraethylammonium perchlorate (1 M=1 mol dm^{-3}) at 100 mV s^{-1}.

References

1) H. Sakurai, *Kagaku no Ryoiki*, **29**, 36 (1975).

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

3) J. K. Kochi, "Organometallic Mechanism and Catalysis," Academic Press, New York, (1978), part 3.

4) H. C. Gardner and J. K. Kochi, *J. Am. Chem. Soc.*, **97**, 1855 (1975).

5) Mass spectral craking patterns of the group 4B dimetals were examined. At an ionizing voltages of 20 eV, formation of group 4B centered radical in the series Me_3M-$M'Me_3$ (M, M'=Si, Ge, Sn) increased in order Si<Ge<Sn.

6) H. Bock and W. Enβlin, *Angew Chem.*, **83**, 435 (1971).

7) L. Szepes, T. Korányi, G. Nóray-Szabó, A. Modell, and G. D. Distefano, *J. Organomet. Chem.*, **217**, 35 (1981).

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

9) The first band of the PES of the group 4B dimetals showed a substantial difference between the adiabatic and vertical *IP* (*e.g.*, 0.75 eV for $Me_3SiSiMe_3$) indicate of a substantial change in geometry upon ionization.

10) A. similar relationship has been observed with hydrocarbons.[11,12]

11) M. Fleischmann and D. Pletcher, *Tetrahedron Lett.*, **1968**, 6255.

12) L. L. Miller, G. D. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, **37**, 916 (1972).

13) K. Oita and H. Gilman, *J. Org. Chem.*, **21**, 1009 (1956).

14) G. R. Wilson and G. A. Smith, *J. Org. Chem.*, **26**, 557 (1961).

15) C. Shaw, F. III; Allred, and L. Albert, *J. Organomet. Chem.*, **28**, 53 (1971).

16) M. P. Brown and G. W. A. Fowles, *J. Chem. Soc.*, **1958**, 2811.

17) H. Schumann and S. Ronecker, *Z. Naturforsch., B* **22**, 452 (1967).

18) T. Harada, *Bull. Chem. Soc. Jpn.*, **15**, 481 (1940).

19) M. G. Voronkov and J. I. Khudobin, *Zeitschrift für Chemie*, **26**, 930 (1956).

20) J. M. Shackelford, H. de Schmertzing, C. H. Henther, and H. Podall, *J. Org. Chem.*, **28**, 1700 (1963).

21) E. J. Bulten and J. G. Noltes, *J. Organomet. Chem.*, **11**, 22 (1968).

22) N. S. Vyazankin, G. A. Razuvaev, E. N. Gladyshev, and S. P. Korneva, *J. Organomet. Chem.*, **7**, 353 (1967).

23) N. S. Vyazankin, E. N. Gladyshev, S. P. Korneva, G. A. Razuvaev, and E. A. Arkhangel'skaya, *Zh. obshch. Khim.*, **38**, 1803 (1968).

24) W. P. Neuman and B. Schneider, *Angew. Chem.*, **76**, 891 (1964).

25) D. T. Sawyer, G. Chiericato, Jr., C. T. Angelis, E. J. Nanni, and T. Tsuchiya, *Anal. Chem.*, **54**, 1720 (1982).