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AND GERMANIUM

Winfield B. Perry and William L. Jolly

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THE USE OF X-RAY PHOTOELECTRON  
SPECTROSCOPY TO ASSESS d ORBITAL  
PARTICIPATION IN COMPOUNDS OF SILICON  
AND GERMANIUM

WINFIELD B. PERRY and WILLIAM L. JOLLY

Department of Chemistry, University of California, and  
Inorganic Materials Research Division,  
Lawrence Berkeley Laboratory, Berkeley, California 94720

ABSTRACT

Chemical shifts in core binding energies have been determined for analogous gaseous compounds of carbon, silicon and germanium. These data, in conjunction with the atomic charge potential model and both CNDO/2 and electronegativity parameter charges, indicate that the silicon and germanium atoms in these compounds, except for  $\text{SiH}_4$  and  $\text{GeH}_4$ , have unexpectedly negative charges. The results are consistent with the existence of significant  $p\pi-d\pi$  bonding in these compounds.

We have determined core electron binding energies for some analogous gaseous compounds of carbon, silicon and germanium with the hope that the data could be used to determine the relative importance of p -d bonding in these compounds. Argon was introduced as a standard reference with each sample; the spectra were obtained with the Berkeley magnetic-focussing spectrometer [1,2]. The carbon, silicon and germanium binding energies, presented in Table 1, were calculated from the observed chemical shifts from the argon  $2p_{3/2}$  peak (248.457 eV).

It is reasonable to assume that the participation of d orbitals in the bonding of the compounds not containing silicon or germanium is negligible. We would expect that, if the valence shell d orbitals of silicon or germanium were significantly occupied in a compound of either of these elements, both the effective charge and the core binding energy of the silicon or germanium atom would be smaller (more negative) than predicted on the basis of the nonparticipation of these orbitals. To correlate binding energies and atomic charges, we shall use the following relation, based on the electrostatic potential model [3],

$$E_B = kQ + V + \ell \quad (1)$$

In this equation,  $E_B$  is the relative core binding energy in eV, Q is the charge of the ionizing atom, V is the coulomb potential energy of an electron at the hypothetical vacated site of that atom in the midst of the other atoms of the molecule, k is a constant which can be evaluated either empirically or theoretically, and  $\ell$  is an empirical constant

Table 1

## Core Binding Energies for Compounds of Carbon, Silicon and Germanium

Molecule	Binding energy, eV		
	M=C (1s)	M=Si (2p <sub>3/2</sub> )	M=Ge (3p <sub>3/2</sub> )
M(CH <sub>3</sub> ) <sub>4</sub>	290.32	105.83	120.55
MH <sub>3</sub> CH <sub>3</sub>	290.58	---	122.64
MH <sub>4</sub>	290.74	107.09	123.69
MH <sub>3</sub> Br	291.95	107.96	123.38
(MH <sub>3</sub> ) <sub>2</sub> O	292.14	107.68	---
MH <sub>3</sub> Cl	292.31	107.98	123.78
MCl <sub>4</sub>	296.23	110.25	124.17
MF <sub>4</sub>	301.68	111.54	128.91

whose value depends on the choice of reference compound. The energy  $V$  is calculated from the relation  $V = \sum (q/r)$ , in which  $q$  is the charge on an atom,  $r$  is its distance from the ionizing atom, and the sum is carried out over all the atoms except the ionizing atom. We have chosen the hydrides  $\text{CH}_4$ ,  $\text{SiH}_4$ , and  $\text{GeH}_4$  as the reference compounds; i.e.,  $E_B = 0$  for these compounds. We have used two methods for estimating atomic charges: the CNDO/2 molecular orbital method [4] and a relatively simple method based on electronegativity parameters [5]. In neither of these methods did we make any provision for the use of d orbitals.

Plots of  $E_B - V$  vs.  $Q$  for the carbon compounds, using the CNDO/2 and electronegativity parameter methods, gave straight lines with standard deviations of 0.67 and 0.35 eV, respectively, and  $k$  values of 24.6 and 24.8, respectively. A theoretical value of  $k$  (i.e.,  $dE_B/dQ$ ) for carbon can be calculated from the first and second ionization potentials of carbon and nitrogen, using the principle of equivalent cores [6]. By representing the energies of the ions by the quadratic expressions  $E_C = a_C Q^2 + b_C Q$  and  $E_N = a_N Q^2 + b_N Q$ , we find that the value of  $k$  for carbon,  $k_C$ , can be represented by the following expression

$$k_C = 2a_N + b_N - b_C \quad (2)$$

By evaluating this expression and the corresponding expressions for silicon and germanium, we obtain  $k_C = 15.79$ ,  $k_{\text{Si}} = 10.35$ , and  $k_{\text{Ge}} = 9.55$ .

Although the absolute values of these  $k$ 's are probably of little significance when applied to atoms in compounds because of the arbitrariness

involved in apportioning charges among the atoms, we nevertheless believe that the relative values are fairly reliable. It is significant that the ratio of these  $k$  values,  $1 : 0.66 : 0.60$ , is very similar to the ratio of the corresponding reciprocals of the covalent radii,  $1 : 0.66 : 0.63$ . This proportionality of  $k$  and  $1/r_{\text{cov}}$  is expected on the basis of a simple valence shell model [7]. By use of the calculated ratios  $k_{\text{Si}}/k_{\text{C}}$  and  $k_{\text{Ge}}/k_{\text{C}}$  and the empirical  $k_{\text{C}}$  values obtained from the CNDO/2 and electronegativity parameter plots, we can calculate effective values of  $k_{\text{Si}}$  and  $k_{\text{Ge}}$  for use with these methods of estimating atomic charges. For the silicon compounds, we have used both methods of charge estimation; for the germanium compounds we have used only the electronegativity parameter method. The corresponding  $E_{\text{B}}$  values were calculated from equation 1. In Table 2 we have listed the deviations between the calculated and experimental  $E_{\text{B}}$  values,  $E_{\text{B}}(\text{calcd}) - E_{\text{B}}(\text{exptl})$ .

The participation of  $d$  orbitals would be expected to be minimal in the cases of the reference compounds  $\text{SiH}_4$  and  $\text{GeH}_4$  inasmuch as hydrogen atoms have no valence  $\pi$  orbitals. However, appreciable  $p\pi-d\pi$  bonding is conceivable in all the other compounds of silicon and germanium. The differences  $E_{\text{B}}(\text{calcd}) - E_{\text{B}}(\text{exptl})$  would be expected to be proportional to the extent of such bonding. From Table 2 we see that all the  $E_{\text{B}}(\text{calcd}) - E_{\text{B}}(\text{exptl})$  values are positive except for those of the reference compounds,  $\text{SiH}_4$  and  $\text{GeH}_4$ , and for three anomalous negative values obtained by the electronegativity parameter method. We have no good explanation for the negative values; they are probably due to deficiencies of the charge estimation method. (Only the negative value for  $\text{SiH}_3\text{Br}$  is of

Table 2

Experimental and calculated relative binding energies

Molecule	$E_B(\text{calcd}) - E_B(\text{exptl}), \text{eV}$	
	CNDO/2	E.-P. Method
$\text{Si}(\text{CH}_3)_4$	2.33	0.80
$\text{SiH}_4$	0.00	0.00
$(\text{SiH}_3)_2\text{O}$	0.98	-0.29
$\text{SiH}_3\text{Br}$	-----	-0.59
$\text{SiH}_3\text{Cl}$	0.91	0.01
$\text{SiCl}_4$	2.95	0.35
$\text{SiF}_4$	5.22	0.69
$\text{Ge}(\text{CH}_3)_4$		2.18
$\text{GeH}_3\text{CH}_3$		0.82
$\text{GeH}_3\text{Br}$		0.89
$\text{GeH}_4$		0.00
$\text{GeH}_3\text{Cl}$		0.74
$\text{GeCl}_4$		2.20
$\text{GeF}_4$		-0.17

sufficient magnitude to be worrisome; the other values are, within the uncertainty of the method, equal to zero.)

The data indicate relatively strong  $p\pi-d\pi$  bonding in the tetramethyl compounds (hyperconjugation) and the tetrachlorides of both silicon and germanium. It is noteworthy that although strong  $p\pi-d\pi$  bonding is indicated for  $\text{SiF}_4$ , essentially no such bonding is indicated for  $\text{GeF}_4$ . Perhaps the lack of such bonding in  $\text{GeF}_4$  is evidence of poor orbital overlap between the  $\text{Ge}4d$  and  $\text{F}2p$  orbitals.

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