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ULTRAVIOLET PHOTOELECTRON SPECTRA OF GROUP IV HEXAMETHYL DERIVATIVES CONTAINING A METAL—METAL BOND

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Summary

The He(I) photoelectron spectra of some organometallic compounds of general formula $(CH_3)_3M—M'(CH_3)_3$ ($M = M' = C$, Si, Ge, and Sn) are presented and assigned by comparison with those of simple related molecules and with the aid of CNDO/2 calculations. The HOMO is highly localized at the central metal—metal bond, and its energy is linearly related to the $M'—M^+$ ionic bond dissociation energy.

Introduction

The organometallic compounds of Group IV elements have been extensively studied by ultraviolet He(I) (UPS) and X-ray (XPS) photoelectron spectroscopy. These investigations have mainly concentrated on derivatives containing

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M—H, M—C, M—O, M—S and M—Hal bonds (M = C, Si, Ge, Sn and Pb) [1,2]. Organometallic compounds of the type $Me_3M—M'Me_3$ have not been studied by UPS except for $Me_3Si—SiMe_3$ [3]. Lappert et al. [4] have reported the mass spectra, ionization and appearance potentials for the above mentioned series. Thermodynamic data for the neutral and ionic species were also calculated and various trends discussed.

In this paper we present the UPS spectra of hexamethyl-ethane (I), -disilane (II), -digermane (III), -ditin (IV) as well as trimethylsilyl- (V) and trimethylgermyl-trimethyltin (VI). The aim of the work was to study the characteristics of metal—metal and metal—carbon bonds by means of UPS.

Experimental

Materials

The samples of I, III, V and VI were prepared by standard methods according to the following equations [5—8]:

$$2(CH_3)_3C—Cl + 2\ Li \xrightarrow[36^\circ C,\ Ar]{pentane} (CH_3)_3C—C(CH_3)_3 + 2\ LiCl \qquad (1)$$

$$2(CH_3)Ge—Cl + 2\ K \xrightarrow[64^\circ C,\ Ar]{HMPT} (CH_3)_3Ge—Ge(CH_3)_3 + 2\ LiCl \qquad (2)$$

$$(CH_3)_3SnLi + (CH_3)_3XCl \xrightarrow[0^\circ C,\ Ar]{THF} (CH_3)_3Sn—X(CH_3)_3 \qquad (3)$$

X = Si, Ge

Compounds II and IV were commercially available.

Spectra

The UPS spectra were recorded on a Perkin-Elmer PS18 photoelectron spectrometer and calibrated against Ar and Xe lines. The He(I) resonance line (584 Å, 21.22 eV) served as the ionization source. The accuracy of the ionization energy (IE) values is estimated to be ±0.05 eV for well resolved bands and ±0.1 eV in the other cases and for all the bands of III. The sample of III contained some impurities which could not be eliminated by distillation, but the data can be regarded with confidence since both the general appearance of the spectrum and the IE data agree with expectation.

Calculations

CNDO/2 semiempirical molecular orbital calculations [9] with an *spd* basis set and based on electron diffraction parameters [10,11] were carried out to confirm the assignment of the UPS spectra of $Me_3C—CMe_3$ and $Me_3Si—SiMe_3$.

Results and discussion

The UPS spectra are shown in Fig. 1. The experimental vertical IE's and the values of the three highest occupied MO's calculated by the CNDO/2 method for I and II are summarized in Table 2 together with the designated symmetry and the principal contributions to the MO's. In Table 2 are listed the experi-

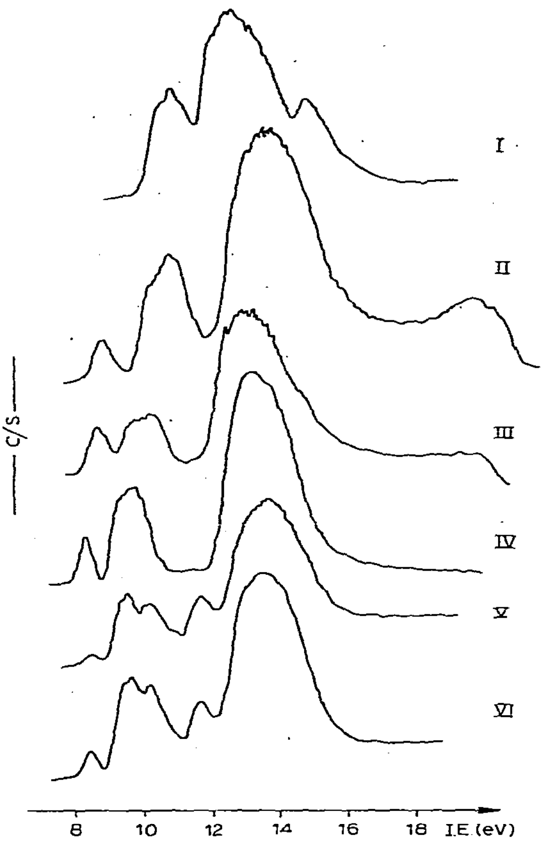

Fig. 1. He(I) photoelectron spectra of $Me_3M—M'Me_3$ derivatives. I—IV: M = M' = C, Si, Ge and Sn; V: M = Sn, M' = Si; VI: M = Sn, M' = Ge.

TABLE I

ORBITAL STRUCTURE, EXPERIMENTAL AND THEORETICAL IONIZATION ENERGIES (eV) FOR $Me_3C—CMe_3$ (UPPER ROW) AND $Me_3Si—SiMe_3$ (LOWER ROW) [a]

Species	Character	Composition (%)			Energy (eV)	
		$C_c(Si_c)$	C_p	H	Exp	CNDO/2
$4a_{1g}$	X—X	48.8	20.6	30.6	10.3	13.6
		65.7	27.0	7.3	8.7	10.8
$4e_g$	X—C_p	26.2	50.6	23.2	{10.7 11.0	13.9
	(C_p—H)	8.9	58.3	32.8	{10.2 10.7	13.5
$4e_u$	C_p—H	19.2	43.5	37.3		16.1
		12.4	59.0	28.6	{10.2 10.7	13.45

[a] $C_c(Si_c)$ and C_p denote central and peripheral atoms, respectively.

TABLE II

IONIZATION ENERGY DATA (eV) FOR THE $MeM—M'Me_3$ DERIVATIVES

M—M'	M—M'(a_1)	$C_3M(e)$	$C_3M'(e)$	$C_3M(a_1)$
Ge—Ge	8.6	9.7 10.2		
Sn—Sn	8.20	9.2 9.6		
Sn—Si	8.32	9.42	10.1	11.65
Sn—Ge	8.33	9.5	10.15	11.63

mental IE data for III—VI in the low energy part of the spectra. The outermost orbitals are depicted schematically in Fig. 2.

The spectra of II, III and IV are very similar, each showing three bands of increasing intensity and at similar IE values. They differ, however, in some respects from that of the carbon analog I.

As each Group IV atom studied has an IE much lower than carbon (the atomic IE's are: 11.26 (C), 8.15 (Si), 7.88 (Ge) and 7.34 (Sn) eV), the band associated with the M—M orbital ($4a_{1g}$) will appear at lower IE than the bands

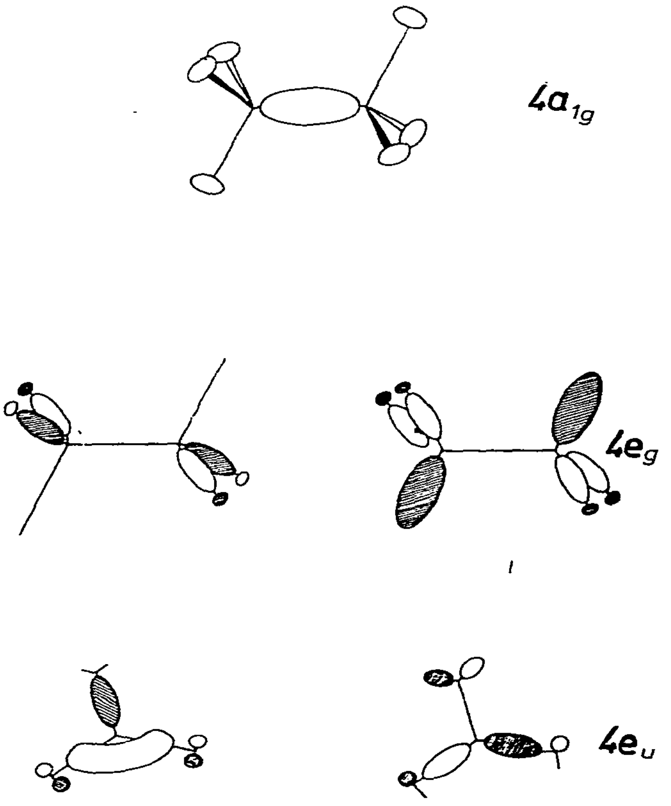

Fig. 2. Schematic plot of highest occupied canonical molecular obitals in $Me_3M—MMe_3$ molecules (M = C, Si). Note that the $4e_u$ orbitals are seen from a direction parallel to the M—M axis.

associated with the interaction of this atom with the methyl substituents ($4e_g$ and $4e_u$ MO's) which, in turn, will have lower IE's than the bands associated with the rest of the σ structure. This assignment is in agreement with the following facts. The IE of the first band (including that of I) is close in energy and linearly related to the first IE of the central atom. The same is true when the energy of the centre of the second band is plotted against the C_3M MO of e symmetry (the HOMO) of the Me_3MH series [12—15]. Finally, the broad, intense band between 12 and 15—15.5 eV in the spectra of II—IV can be confidently assigned to ionization from MO's localized at the CH_3 groups, on the basis of the assignments reported for closely related compounds [12—17]. The broadening of this band for smaller M results from increase in the through-space interactions between the CH_3 groups [17]. The relative intensities of the three bands supports the proposed assignment. The narrow energy gap between the $4e_g$ and $4e_u$ orbitals, (see calculations in Table 1) together with the possible effect of Jahn-Teller distortion explain the broadness of the second band. The valence MO ordering and the presence of Jahn-Teller forces in the ion is in agreement with the spectrum of disilane [18].

The assignment of the spectrum of I is complicated by the lack of metal—metal and metal—carbon orbitals at high energy, and by the largest through-space interaction [17] among the various CH_3 groups. The first band in the isooctane spectrum, centered at 10.70 eV, shows a structure similar to that of the first band of ethane, which consists of three components. According to Murrel and Schmidt's assignment [12] the first of these at 12.1 eV is taken to be the $3a_{1g}$ MO, while the second and third components belong to the Jahn-Teller split $1e_g$ MO with a mean of 13.0 eV [12]. The Jahn-Teller splitting, 0.65 eV in ethane [19], decreases by increasing the size of the molecule to 0.4—0.45 eV in isobutane [12] and neopentane [20] and is expected to have a somewhat smaller value in our case. In isooctane the three components are symmetrically located at 10.3, 10.7 and 11.1 eV, which excludes the possibility that the first and the third components might be related to the $4e_g$ MO. The order of MO energies given by calculations: $4a_{1g} > 4e_g > 4e_u$ (see Table 1) is in agreement with the correlations made on the basis of the comparisons above.

We have found in a previous work [13] that CNDO/2 orbital energies correlate well with the experimental IE values of hydrocarbons and corresponding silicon derivatives. The regression equation does not change much when the data for $Me_3C—CMe_3$ and $Me_3Si—SiMe_3$, given in Table 1, are also included. ($IE_{exp} = aIE_{CNDO} + b$, with $a = 0.47$ and $b = 4.68$. The inclusion of the present data gives $a = 0.49$ and $b = 4.22$, with correlation coefficients of 0.94 and 0.95, respectively.)

The spectra of the mixed derivatives V and VI are very similar to each other and also resemble those of II—IV. There is no doubt that the first band can be assigned to ionization from the Sn—Si or the Sn—Ge bond on the basis of the IE's (8.32 and 8.33 eV, respectively) and the shape and relative intensities. The second band, partly split in two components, in both cases appears to arise from the weakly interacting C_3Sn and C_3M' (M' = Si, Ge) skeleton orbitals of e symmetry. A new band centered at about 11.6 eV is present in these spectra. This band is tentatively assigned to the C_3Sn a_1 orbital, and its appearance in the spectra is in agreement with the low IE value for the corresponding

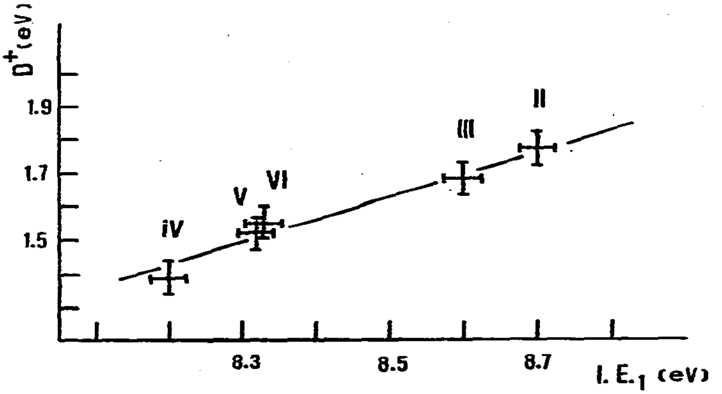

Fig. 3. Plot of D^+ (AP — IP) for the formation of the $[(CH_3)_3M]^+$ ion from Me_3M—$M'Me_3$ vs. IE_1 for II—VI. (The appropriate appearance and ionization potentials are taken from ref. 4).

MO in the spectrum of Me_3SnH [15], which gives a band with a peak at 10.6 eV. The intense band centered at about 13.5 eV becomes broader when one tin atom of IV is replaced by M′ (M′ = Si, Ge) in agreement with the variation noted for this band in the symmetric compounds.

Finally, it is important to note that, except for I, there is a satisfactory linear correlation between IE_1 and the ionic bond dissociation energy (AP — IP) for the formation of the $[(CH_3)_3M]^+$ ion as calculated from the data measured by Lappert et al. [4] (see Fig. 3). One possible explanation for the existence of such a correlation is as follows. The $4a_{1g}$ orbital has an M—M′ character which increases from 48.8 to 65.7% upon changing the central carbon atoms to silicon (see Table 1). It seems that this change can be extrapolated to the other members of the series by use of the M orbital energies, and that the $4a_{1g}$ canonical orbital of these molecules can be treated as an M—M′ "bond orbital". Thus ionization from this orbital causes a gradual bond weakening, that is a decrease of ionic bond dissociation energy, going down the series. The large deviation for I (AP — IP = 0.62 eV) may be due to the interplay of: i) the smaller localization of the HOMO in the central C—C bond, ii) the steric strain in this bond [4], and iii) the energy gain associated with the formation of the planar $[(CH_3)_3C]^+$ ion, while the other $[(CH_3)_3M]^+$ species are pyramidal [4,21].

Summarizing our results, we conclude that the highest occupied MO in the compounds of the type Me_3M—$M'Me_3$ (M, M′ = Group IV element) is highly concentrated at the central M—M′ bond.

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