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Short communication

UV PHOTOELECTRON SPECTRA OF GROUP IV ALKYL HYDRIDES

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We have had occasion to measure the photoelectron spectra of some heavy group IV alkyls and alkyl hydrides. Although the ionization potentials serve primarily as a body of information which is useful in investigating trends in reactivity for processes involving electron transfer [1], they also provide a pleasing example of the simplicity with which the language of molecular orbital theory can be used to explain trends in the energies and nature of the radical cation states of a series of chemically related molecules [2]

EXPERIMENTAL

Tin tetrachloride was obtained as a commercial sample from M and T Chemical Co , Inc. Germanium and silicon tetrachlorides as well as ethyltrichlorogermane were obtained from the Alfa Division, Ventron Corporation. The symmetrical tetraethyl derivatives of tin, germanium and silicon were prepared from the metal tetrachlorides by reaction with ethyl magnesium bromide A typical example is. 70 g (0 27 mol) tin(IV) chloride was added dropwise to EtMgBr (1.5 mol) in ether under a nitrogen atmosphere. The mixture was refluxed for 4 h after the addition was completed, and hydrolyzed with dilute (0.1 M) aqueous HCl After repeated extractions with ether, the combined ethereal layer was finally washed with saturated $NaHCO_3$ and dried over $CaCl_2$ Distillation following the removal of solvent yielded Et_4Sn, b.p. 84°C/11 mm [3].

The trialkyltin hydrides R_3MH were prepared from the corresponding trialkyltin chlorides by reduction with lithium aluminum hydride or deuteride

[3, 4] The trialkyltin chlorides were obtained by disproportionation of the tetraalkyltin with tin(IV) chloride (0 33 mol) by heating to reflux followed by vacuum distillation [3]. The tetraalkyltin compounds were prepared from tin(IV) chloride and the appropriate Grignard reagent using a standard procedure Et_3SnH, b p. 70°C/50 mm [3]; n-Bu_3SnH, b.p 86°C/1 mm [3], Me_3SnH, b p. 60°C/[illegible]5 mm [3], i-Pr_3SnH, b.p 84°C/15 mm [3], and Ph_3SnH, b p 170°C/1 mm [3] The germanium analogs were prepared by a similar procedure Et_3GeH, b p 125°C/75 mm [4], and n-Bu_3GeH, b p 124°C/20 mm [4]. Triethylsilane, b.p. 110°C/75 mm [5] was also prepared by this procedure

Diethylgermane was prepared by the reduction of diethyldichlorogermane (10 g, 49.6 mmol) with lithium aluminum hydride (11 g, 45 mmol) in di-n-butyl ether, b p 77°C Diethyldichlorogermane was prepared from tetraethylgermane (10 g, 53 mmol) and acetyl chloride (9.4 g, 120 mmol) in the presence of aluminum chloride (16 g, 120 mmol).

Ethylgermane was prepared from the reaction of ethyltrichlorogermane with lithium aluminum hydride in diglyme [6]

The photoelectron spectrometer used in these studies has been described previously [7]. A xenon—argon gas mixture was used as an internal standard for each spectrum.

RESULTS AND DISCUSSION

As each group IV atom studied has an ionization potential much lower than carbon [8], the bands associated with the interaction of this atom with alkyl or hydrogen substituents will appear at lower ionization potential than the bands associated with the rest of the σ structure. Thus, as the HOMO structure is of primary interest, only the three molecular orbitals resulting from the interaction of the p orbitals of the central atom with the carbon $2p$ or hydrogen $1s$ orbitals of the four α atoms of the ligands will be discussed For four identical α atoms (local symmetry T_d) [9] one expects to observe a single band resulting from the ionization of a triply degenerate molecular orbital. For three atoms of one type, one of another type (local symmetry C_{3v}), two bands are expected of relative intensity 1 2 resulting from the ionization of an a_1-type orbital and an e-type orbital, respectively Finally, for two atoms of each type (local symmetry C_{2v}), three bands are expected of relative intensity 1 1 1 resulting from the ionization of b_2, a_1 and b_1-type orbitals. This analysis is summarized in Table 1.

The vertical ionization potentials of interest for the compounds R_x-MH_{4-x}($x = 1$—4, M = Si, Ge, Sn) are summarized in Table 2 In Fig 1 the spectra for the series $(C_2H_5)_xGeH_{4-x}$ for $x = 1$—4 are shown. The number of bands lying below 12 eV and the relative areas of these bands are in accord with the expectations summarized in Table 1 A line correlation between bands of similar character is shown in Fig 2 in which the known

TABLE 1
HIGHEST OCCUPIED MOLECULAR ORBITALS FOR R_xMH_{4-x}

Compound	Symmetry (local, M—C bonds only)	Orbital
R_4M	T_d	t_2 (MC_4)
R_3MH	C_{3v}	e (MC_3), a_1 (MH)
R_2MH_2	C_{2v}	b_2 (MC_2), a_1 (H_2MC_2), b_1 (MH_2)
RMH_3	C_{3v}	a_1 (MC), e (MH_3)
MH_4	T_d	t_2 (MH_4)

TABLE 2
LOWEST IONIZATION POTENTIALS OF GROUP IV ALKYL HYDRIDES

Compound	Vertical IP (eV)		
	Band 1	Band 2	Band 3
$(C_2H_5)_4Si$	9 8		
$(C_2H_5)_4Ge$	9 4		
$(C_2H_5)_4Sn$	9 0		
$(C_2H_5)_3SiH$	9 9	10 7	
$(i\text{-}C_3H_7)_3SiH$	9 5	10 4	
$(C_2H_5)_3GeH$	9 6	10 5	
$(CH_3)_3SnH$	9 9	10 6	
$(C_2H_5)_3SnH$	9 1	10 0	
$(i\text{-}C_3H_7)_3SnH$	8 6	9 7	
$(n\text{-}C_4H_9)_3SnH$	8 8	9 8	
$(C_2H_5)_2GeH_2$	9 8	10 5	11 1
$(C_2H_5)GeH_3$	10 4	11 6	

ionization potential of GeH_4 [10] is included for completeness. A smooth decrease in ionization potential with increasing number of ethyl groups is observed for both the Ge—C and Ge—H bands

The relative area of the bands at low ionization potential with respect to the intense band centered at about 12 3 eV is also consistent with the above assignment. The latter band results from the ionization of the molecular orbitals associated with the C—C and C—H interactions of the ethyl groups

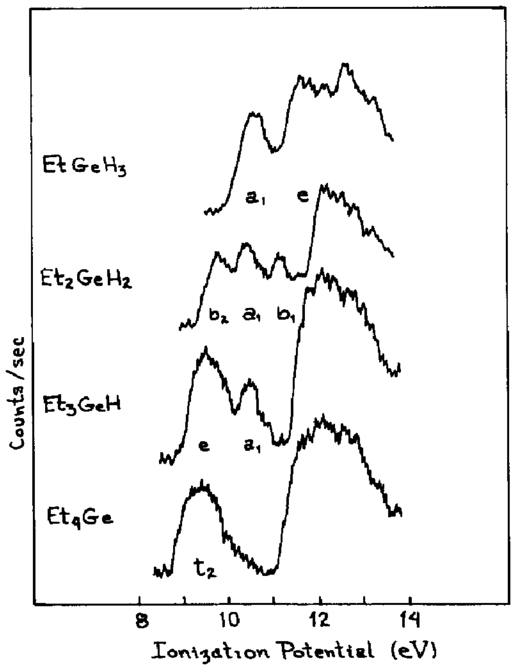

Fig 1 The He(I) photoelectron spectra of $(C_2H_5)_xGeH_{4-x}$

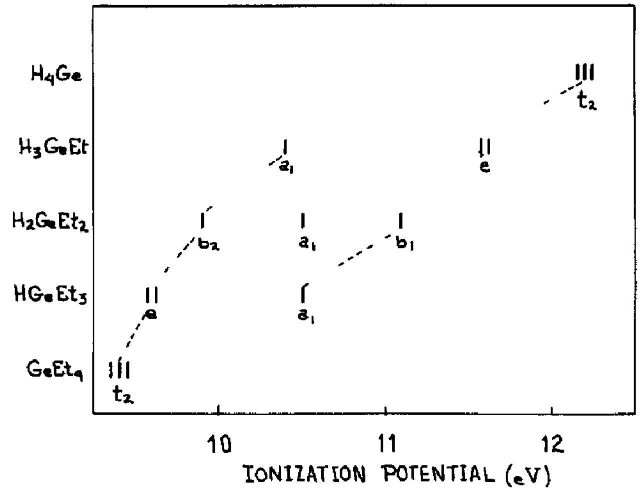

Fig 2 Correlation of the Ge—C and Ge—H ionizations in $(C_2H_5)_xGeH_{4-x}$ The ionization potential of GeH_4 is taken from ref 10

and correlates with the $1e_g$ and $3a_{1g}$ ionizations of ethane [11]. The intensity of this band will be proportional to the number of ethyl substituents If the ratio of the band area for the Ge—C and Ge—H ionizations to the area of the 12 3-eV band is corrected for the relative number of ethyl groups, the numbers in the fourth column of Table 3 are obtained Within the precision

TABLE 3
BAND AREA RATIOS FOR Et_xGeH_{4-x} (x = 1—4)

	$a = \Sigma\, C_{2p}/Ge_{4p}$ [a]	$b = A_{GeC,\, GeH}/A_{CC,\, CH}$	$a \cdot b$
Et_4Ge	4	0.26	1.0
Et_3GeH	3	0.38	1.1
Et_2GeH_2	2	0.47	0.9
$EtGeH_3$	1	0.88	0.9

[a] Using ethane as a model compound, three ionizations are expected in the 12.3-eV, CC, CH band per ethyl group

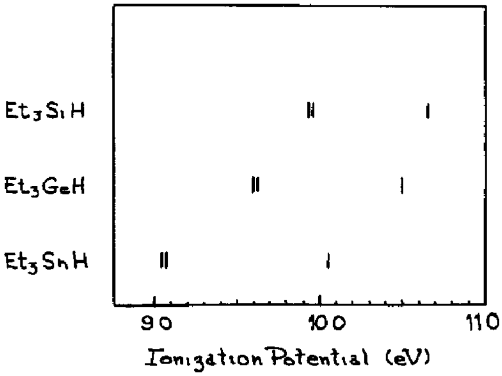

Fig 3 Correlation of the M—C and M—H ionizations in $(C_2H_5)_3MH$

of measurement, the ratios are constant through the series. The fact that the ratio is about 1 indicates that the ionization cross-sections for germanium and carbon are approximately the same. The ratios observed for $(C_2H_5)_3SiH$ and $(C_2H_5)_3SnH$ are 1.2 and 0.9, respectively.

Other trends in the data in Table 2 support this assignment. In Fig. 3 the ionization potentials of the e and a_1 bands for $(C_2H_5)_3MH$ are shown for M = Si, Ge and Sn. The decrease in ionization potential along the series parallels the decrease observed for the t_2 bands of $(C_2H_5)_4M$, demonstrating substantial M character. On the other hand, in the series R_3SnH for R = CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9 (Fig. 4) the ionization potential of the M—C band decreases as the size of the R group increases The trend parallels that observed previously for HgR_2 compounds, as might be expected in view of the fact that in both cases the band in question involves the ionization of an orbital with M p and C $2p$ character.

Others have used the photoelectron spectra of tetrahedral group IV compounds to comment on the role of d orbital participation in bonding [12]

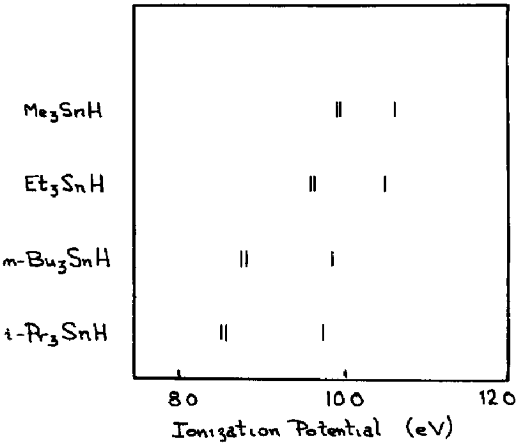

Fig 4 Correlation of the Sn—C and Sn—H ionizations in R_3SnH

The spectra of the halides have been interpreted in terms of significant halogen lone pair—central atom *d*—π interactions [13] but others have disputed this conclusion [14, 15]. In the case of the compounds examined here any *d* orbital participation would be of a hyperconjugative nature and would in any case not affect the energies of the three highest-occupied molecular orbitals discussed here

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