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THEORY AND APPLICATION OF PHOTOELECTRON SPECTROSCOPY

XVI*. PHOTOELECTRON SPECTROSCOPY AND MOLECULAR CONFORMATIONS: Ge–C AND Sn–C HYPERCONJUGATION AND THE CONFORMATION OF ALLYLGERMANES AND -STANNANES

A. SCHWEIG, U. WEIDNER
Fachbereich Physikalische Chemie der Universität, D-3550 Marburg/Lahn, Biegenstrasse 12 (Germany)
and G. MANUEL
Laboratoire des Organométalliques, Université Paul Sabatier, F-31 Toulouse, 118, route de Narbonne (France)

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SUMMARY

The photoelectron spectra of vinyl- and allylgermanes and -stannanes have been investigated. The conformations of allylgermanes and allylstannanes are shown to be determined by Ge–C and Sn–C hyperconjugation. The hyperconjugative ability of the C–M(M=Si, C, Ge and Sn) bonding MO's with the ethylene π-MO is explained by simple perturbation theory. This result represents a new and independent confirmation of the hyperconjugative interaction mechanism.

INTRODUCTION

In preceding publications[1–4] we developed a new application of photoelectron (PE) spectroscopy to study molecular conformations. We showed that allyltrimethylsilane (VI) exists in conformation (A), due to a strong hyperconjugative interaction between the CH_2–Si bonding MO and the adjacent ethylene π system[1]. Using the PE spectra of tetraethylgermane (VII), triethylvinylgermane (VIII), triethylallylgermane (IX), tetra-n-butylstannane (X), tri-n-butylvinylstannane (XI) and tri-n-butylallylstannane (XII) we have extended our investigations[1–4] to Ge–C[5,6] and Sn–C[5,7] hyperconjugation (σ–π interaction) with ethylene. We obtain the first evidence in the case of (IX) and (XII) for the conformations (B) and (C), and account for the differences in the strengths of Si–C[1,4,5,8], C–C[4,9], Ge–C and Sn–C hyperconjugations with ethylene.

RESULTS AND DISCUSSION

Fig. 1 shows the PE spectra of (VII) to (XII), and Fig. 2 the correlation dia-

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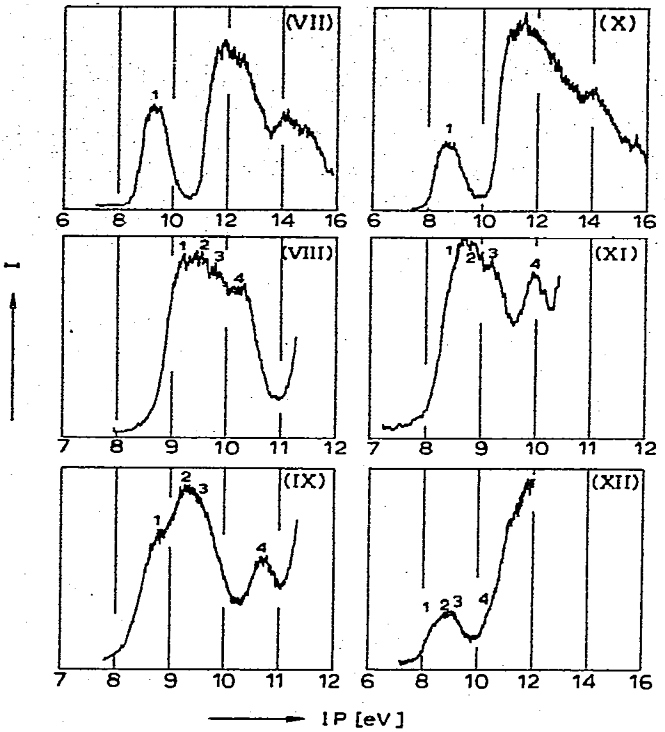
* For Part XV see ref. 16.



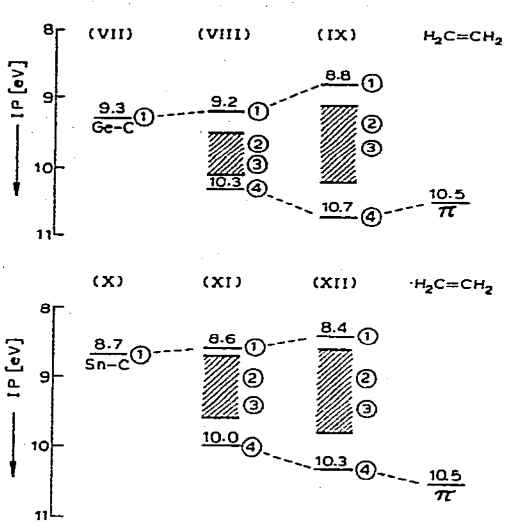


Fig. 1. Photoelectron spectra* of tetraethylgermane (VII), triethylvinylgermane (VIII), triethylallylgermane (IX), tetra-n-butylstannane (X), tri-n-butylvinylstannane (XI), and tri-n-butylallylstannane (XII).

Fig. 2. Correlation diagrams of the highest occupied MO's in tetraethylgermane (VII), triethylvinylgermane (VIII) and triethylallylgermane (IX) and in tetra-n-butyl-stannane (X), tri-n-butylvinylstannane (XI), and tri-n-butylallylstannane (XII). The numbers printed above the levels are vertical ionization potentials [eV]. The shaded areas correspond to not well resolved ionization ranges in the spectra shown in Fig. 1. Intensity measurements, as well as analogy with the silicon compounds (V) and (VI)[1,4], suggest that two Ge–C ionizations occur in this range.

grams of the highest occupied molecular orbitals (MO's) of these compounds. The midpoint of the Ge–C ionisation in (VII) is observed at 9.3 eV, the π ionization in ethylene is found at 10.51 eV[10]. The π-MO (10.3 eV) and the antibonding Ge–C π combination (9.2 eV) (*cf.* representation of this combination) do not significantly change in (VIII).

CMe_4 (I)	$CH_2{=}CH{-}CMe_3$ (II)	$CH_2{=}CH{-}CH_2{-}CMe_3$ (III)
$SiMe_4$ (IV)	$CH_2{=}CH{-}SiMe_3$ (V)	$CH_2{=}CH{-}CH_2{-}SiMe_3$ (VI)

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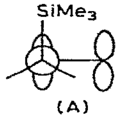
* The He-I (584 Å) photoelectron spectra were measured on a PS-16 photoelectron spectrometer from Perkin-Elmer, Beaconsfield, England.

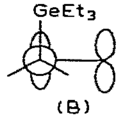
$GeEt_4$ (VII) $CH_2{=}CH{-}GeEt_3$ (VIII) $CH_2{=}CH{-}CH_2{-}GeEt_3$ (IX)

$SnBu_4$ (X) $CH_2{=}CH{-}SnBu_3$ (XI) $CH_2{=}CH{-}CH_2{-}SnBu_3$ (XII)

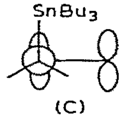
In (IX) the π-MO (10.7 eV) is stabilized (thus its ionization can be seen in the PE spectrum as the well resolved band 4), and one MO in the Ge–C ionization range (8.8 eV) is destabilized by 0.4 eV (thus the corresponding PE band can be clearly recognized as the shoulder 1). We obtain similar results in the case of the tin compounds (X) to (XII). Due to the already high lying Sn–C MO's [8.7 eV in (X)] in (XI), the π-MO (10.0 eV) can be observed as the separate band (4). For the same reason this band moves almost wholly under the σ ionization range (shoulder 4) in (XII).



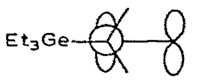
(A)



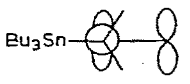
(B)



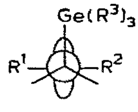
(C)



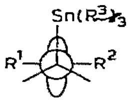
(D)



(E)

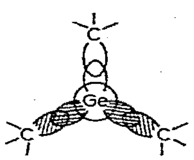


(F)



(G)

The above analysis shows one Ge–C and Sn–C MO in (IX) and (XII) to be raised as compared to those in (VIII) and (XI), and the π-MO to be lowered in both cases. The results are only consistent with conformations (B) and (C), for which, contrary to (D) and (E), the observed splitting would be expected, because of hyperconjugation between the Ge–C and Sn–C bonding MO's and the π-MO. In full agreement with this interpretation are recent ESR-spectroscopic results for β-germylalkyl- and β-stannylalkyl radicals[11,12] which show that these radicals also prefer conformations (F) and (G) in which hyperconjugation is possible.



The interaction between two MO's [in our case between the ethylene π-MO and the C–M(M=Si, C, Ge and Sn)] MO's is inversely proportional to their energy difference. Comparing columns 3 (energy difference between the interacting MO's) and 6 (HOMO, highest occupied MO, destabilization by hyperconjugation) of

TABLE 1

COMPARISON OF HOMO DESTABILIZATIONS WITH MO ENERGY DIFFERENCES

R_4M $M=$	IP^a (eV)	Energy diff.^{b} (eV)	$R_3MCH_2CH=CH_2$ $M=$	IP^a (eV)	HOMO destab.^{c} (eV)
Si (IV)	10.5^d	0.0	Si (VI)	9.0^e	1.5
	10.6^f	0.1			
C (I)	11.3^g	0.8	C (III)	9.6^e	0.9
	11.4^f	0.9			
Ge (VII)	9.3	1.2	Ge (IX)	8.8	0.5
Sn (X)	8.7	1.8	Sn (XII)	8.4	0.3

[a] Vertical ionization potentials. [b] Energy differences between the π-MO in ethylene (10.5 eV[10]) and the C–M bonding MOs. [c] HOMO destabilizations of the allyl compounds. [d] Ref. 13. [e] Ref. 4. [f] Ref. 14. [g] Ref. 15.

Table 1, we note that the effects of the substituents CH_2–$SiMe_3$, CH_2–CMe_3, CH_2–$GeEt_3$, and CH_2–$SnBu_3$ on the π system of ethylene follow this rule. This result independently confirms the postulated hyperconjugative interaction mechanism.

ACKNOWLEDGEMENTS

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