Journal of Organometallic Chemistry, 149 (1978) 289—295

STUDY OF THE ELECTRONIC STRUCTURE OF SOME ALKYLTIN DERIVATIVES BY MEANS OF UV PHOTOELECTRON SPECTROSCOPY

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(Received October 21st, 1977)

Summary

He(I) photoelectron spectra (UPS) provide data on the orbital energy levels in the valence shells of the following compounds: R_3SnOR (R = methyl), $R_3Sn(acac)$ (R = methyl, ethyl, acac = acetylacetonate), R_2SnCl_2 (R = methyl, n-butyl), $R_2Sn(acac)_2$ (R = methyl, n-butyl, acac = acetylacetonate), $R_2Sn(Tacac)_2$ (R = methyl, Tacac = trifluoroacetylacetonate). The results are discussed in the light of comparisons with the UPS spectra of simple tin compounds and of the β-diketonates of other metals.

Introduction

The electronic structures of some organotin compounds have previously been studied by UV photoelectron spectroscopy (UPS) [1—6]. In connection with studies of the UPS spectra of β-diketonates of transition metals [7—9], we have extended our investigation to some β-diketonates of alkyl-non-transition metals such as thallium(III) [10] and tin(IV) dialkyl and trialkyl derivatives. The aim is to characterize the bonding between the metal and the alkyl group, and to confirm the behaviour of β-diketones as ligands, which usually display UPS spectra with a band sequence similar and easily recognizable in all compounds studied up to now [7—14]. To obtain a better interpretation of the spectra of the dialkyl- and trialkyltin β-diketonates, we have also studied the corresponding dialkyltin dichlorides and trialkyltin alkoxides. Relative orderings of the energy levels of molecular orbitals in the valence shell of all these compounds could thus be deduced.

Results and discussion

The He(I) photoelectron spectra are shown in Fig. 1 and 2 and the ionization energies (*IE*) are listed in Tables 1 and 2.

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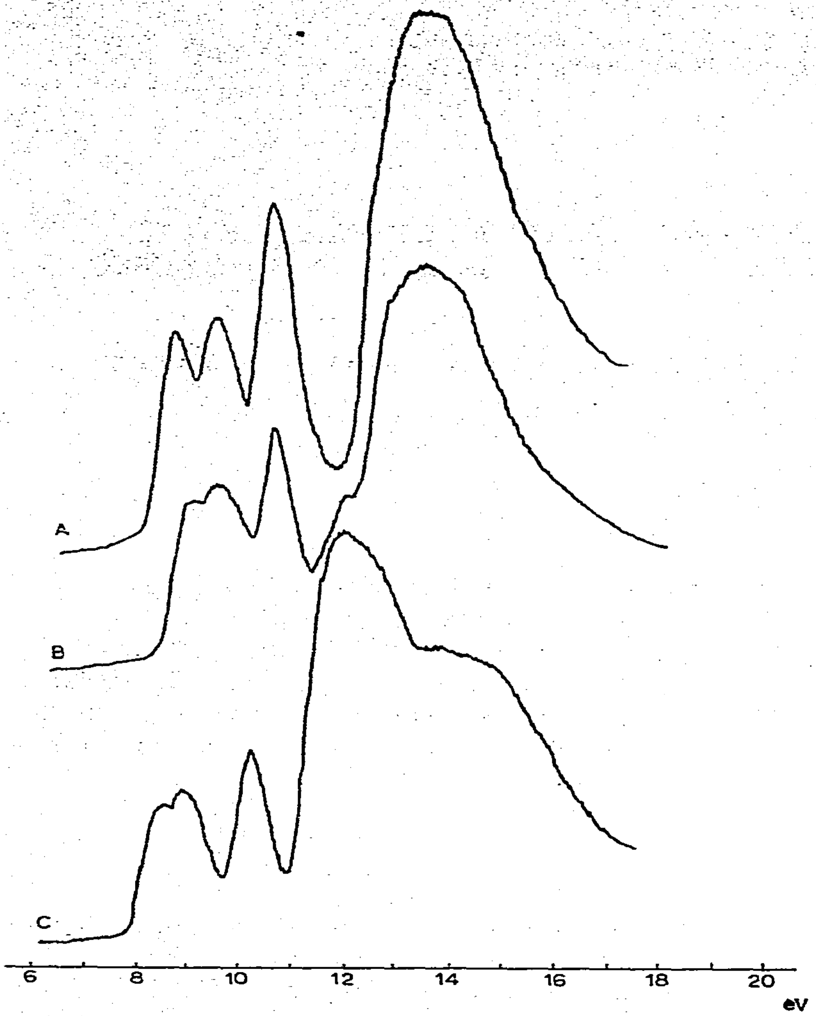

Fig. 1. He(I) photoelectron spectra of $(CH_3)_3SnOCH_3$ (A), $(CH_3)_3Sn(acac)$ (B), and $(C_2H_5)_3Sn(acac)$ (C).

Trialkyltin alkoxides

We measured the UPS spectra both of the trimethyltin methoxide and of the triethyltin ethoxide: they are very similar in shape, although a detailed comparison is difficult by the poor reproducibility of the spectra for the latter compound

TABLE 1

VERTICAL IONIZATION ENERGY DATA (eV) FOR TRIALKYLTIN COMPOUNDS [a] (shoulders in parentheses)

Compound	Ionization energies (eV)		
$(CH_3)_3SnOCH_3$	8.86	9.66	10.70
$(CH_3)_3Sn(acac)$	9.14	9.64	10.72 (12.12)
$(C_2H_5)_3Sn(acac)$	8.51	8.93	10.26

[a] acac = acetylacetonate.

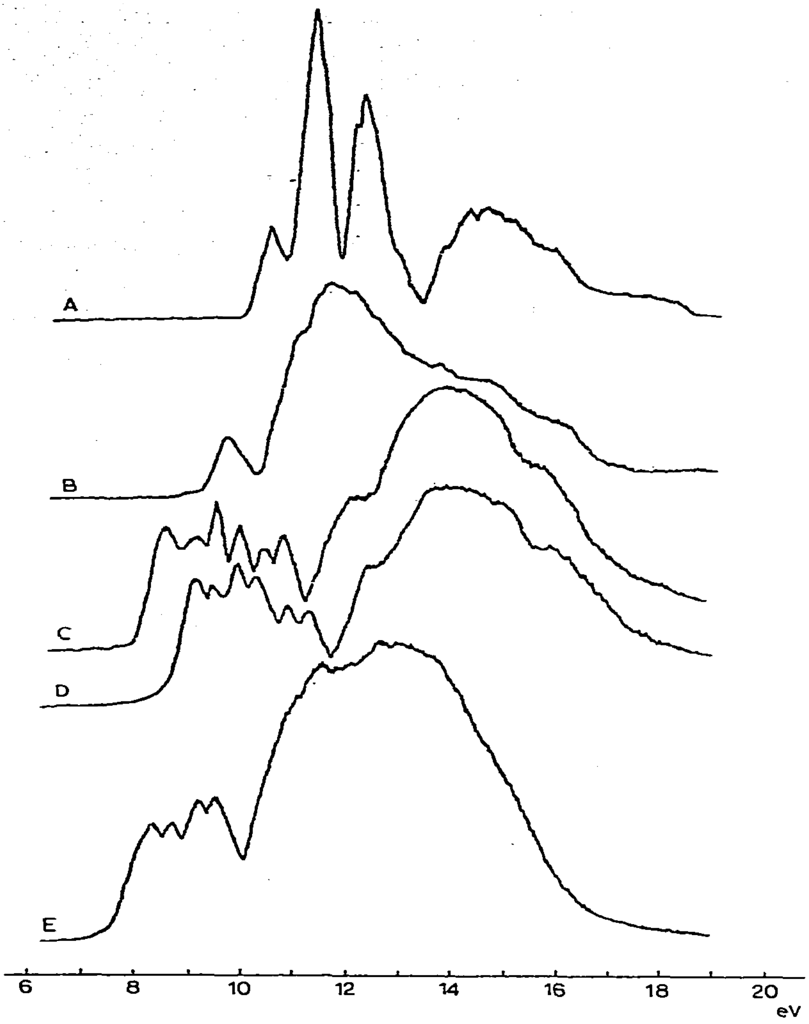

Fig. 2. He(I) photoelectron spectra of $(CH_3)_2SnCl_2$ (A), $(C_4H_9)_2SnCl_2$ (B), $(CH_3)_2Sn(acac)_2$ (C), $(CH_3)_2$-$Sn(Tacac)_2$ (D), and $(C_4H_9)_2Sn(acac)_2$ (E).

TABLE 2

VERTICAL IONIZATION ENERGY DATA (eV) FOR DIALKYLTIN COMPOUNDS [a] (shoulders in parentheses)

Compound	Ionization energies (eV)					
$(CH_3)_2SnCl_2$		10.42	11.35	(12.18)	12.38	14.56
$(C_4H_9)_2SnCl_2$		9.53				
$(CH_3)_2Sn(acac)_2$	8.51	9.06	9.33	9.77	10.27	10.54
$(CH_3)_2Sn(Tacac)_2$	8.96	9.17	9.75	10.08	10.71	11.21
$(C_4H_9)_2Sn(acac)_2$	8.31	8.69	9.24	9.49		

[a] acac = acetylacetonate; Tacac = trifluoroacetylacetonate.

because of its instability. Both compounds are known to be monomeric [15]. The spectra show three well resolved bands below ca. 12 eV, the first two being equal in intensity and the third one twice as intense: in $(CH_3)_3SnOCH_3$ they fall at 8.86, 9.66 and 10.70 eV. In this region we expect ionization of one π non-bonding electron pair of oxygen and of three σ-bonding electron pairs (one Sn—O and two Sn—C, the third Sn—C lying at higher *IE*). We thus assign the third band to ionization of the four σ(Sn—C) electrons, from intensity considerations and by comparison with the UPS spectrum of the trimethyltin chloride, studied by Flamini et al. [4], which has a similar spectrum and whose third band, at 11.33 eV, was assigned to ionization of σ(Sn—C) electrons. The shift to lower *IE* of this band in the methoxide may be explained by the smaller electronegativity of the O—CH_3 group with respect to the chlorine.

The assignment of the first two bands is not so easy because of uncertainty about the relative positions of the σ(Sn—O) and π(O) energy levels. Both 8.86 and 9.66 eV are unusually low values for the ionization of the oxygen lone pair, which falls e.g. at ~11 eV in CH_3OH [16]; on the other hand, in $(CH_3)_3$-SnCl [4] the ionization of σ(Sn—Cl) electrons (comparable, although not strictly so, the σ(Sn—O) is associated with the first band at 9.88 eV. By analogy, our assignment of the spectrum of $(CH_3)_3SnOCH_3$ relates the first band, at 8.86 eV, to the ionization of σ bonding Sn—O electrons and the second band, at 9.66 eV, to the oxygen lone pair, probably shifted to *IE* lower than usual by the presence of the $SnMe_3$ group.

Above 12 eV the spectrum shows a broad envelope of overlapping, poorly resolved bands, arising from ionizations of the remaining σ-bonding electrons.

Trialkyltin β-diketonates

Triethyltin acetylacetonate is known to be monomeric [15]; we have synthesized trimethyltin acetylacetonate for the first time, and found it also to be a monomer. The UPS spectra, very similar to each other, show three bands in the low *IE* region (<11 eV), the first two being close in energy and about equal in intensity, and the third higher in energy (ca. 1—1.5 eV) and more intense.

On comparing these spectra with dimethylthalliumacetylacetonate [10], we observe a similar shape in the low energy region, apart from small relative shifts of the bands. By analogy with the latter compound and with other β-diketonates [7—14], we assign the first band (at 9.14 eV in $(CH_3)_3Sn(acac)$, at 8.51 eV in $(C_2H_5)_3Sn(acac)$) to the π_3 orbital of acetylacetone and the second band (at 9.64 eV in $(CH_3)_3Sn(acac)$, at 8.93 eV in $(C_2H_5)_3Sn(acac)$) to the n^--Sn—O bonding orbital.

The third band (at 10.72 eV in $(CH_3)_3Sn(acac)$, at 10.26 eV in $(C_2H_5)_3Sn$-(acac)) probably arises from the ionization of two nearly degenerate σ bonding Sn—C pairs; the value of 10.72 eV in the trimethyl compound is practically equal to that one found for the analogous band in $(CH_3)_3SnOCH_3$. On passing from the trimethyl to the triethyl compound all the *IE*'s shift to lower values, consistent with the greater electron release by ethyl than by methyl.

The n^+-Sn—O bonding orbital appears to contribute to the broad envelope of bands beyond 11 eV, which arises also from the remaining σ(Sn—C) and other ligand orbitals. In $(CH_3)_3Sn(acac)$, this shoulder can be associated with the shoulder at 12.12 eV.

Dialkyltin dichlorides

The spectrum of $(CH_3)_2SnCl_2$ shows four bands or band groups between 10 and 16 eV; in this region one expects the bands corresponding to the ionization of the following orbitals: the π-type lone-pairs orbitals of the chlorine atoms (four orbitals which cannot be degenerate because of the C_{2v}-symmetry of the molecule), two σ-bonding Sn—Cl orbitals, two σ-bonding Sn—C orbitals and four σ-bonding C—H orbitals (the remaining two σ(C—H) orbitals have a very low orbitals energy, giving rise to a broad band at higher *IE* (>16 eV)). The energies of the chlorines lone-pairs are probably very close, so that in the spectrum there is, at 11.3 eV, a single, very intense and relatively sharp band (in accord with the largely non-bonding character of the electrons involved in the ionization), arising from all four lone-pairs. This assignment is supported by the fact that in the spectrum of $SnCl_4$ the chlorine lone-pairs give rise to three bands with barycenter at about 12.4 eV, while in the spectrum of $(CH_3)_3$-SnCl [4] the corresponding band lies at 10.16 eV, consistent with the greater electron density on the chlorines in the latter compound induced by the three electron-releasing methyl groups. In our compound this band lies at an intermediate *IE*, in accord with the fact that the molecule has onyl two methyl groups bonded to Sn.

The band at 10.42 eV is much less intense (about one quarter) and is therefore associated to one only orbital, while the band at 12.38 eV has an intensity of approximately 1/2 with respect to the 11.35 eV band, and thus arises from the ionization of four electrons in two nearly degenerate orbitals (actually one can see a shoulder at 12.18 eV in the left side of the band). We thus attribute these bands to ionization of three σ-bonding orbitals (the fourth one contributing probably to the broad band peaked around at 14.56 eV), although it is not easy to sort out the contribution of the single atomic orbitals to the molecular orbitals involved in the ionization. Because of the low symmetry of the molecule, we expect a large mixing between σ(Sn—C), and σ(Sn—Cl), so that it is not correct to assign each band to a particular type of bond; however, the proposed assignment is supported by comparison with the spectrum of $(CH_3)_3SnCl$, discussed by Flamini et al. [4]. The latter spectrum shows a band at 9.88 eV which the authors assign to the ionization of an orbital of predominant σ(Sn—Cl) character; by analogy, we assign our band at 10.42 eV to a similar ionization, the increase of *IE* probably being due to the replacement of a methyl group by a chlorine atom. In this interpretation, we assume that the remaining σ(Sn—Cl) band lies at an *IE* at least 2 eV higher, probably contributing to the band at 12.38 eV; the other component of this band must be one of the two σ(Sn—C) bands, while the remaining σ(Sn—C) band is to be identified in the broad band at about 14.5 eV. It is interesting to note that the first band σ(Sn—C) in the spectrum of $(CH_3)_4Sn$ [2,3] lies at 9.70 eV, while the corresponding band in $(CH_3)_3SnCl$ is [4] at 11.33 eV; in $(CH_3)_2SnCl_2$ one observes a further shift to higher ionization energy (12.38 eV), consistent with the successive replacement of methyl groups by chlorine atoms.

The σ(C—H) orbitals (or at least four of them) probably contribute to the band at 14.56 eV: this band must therefore correspond to ionization of ten electrons, even if its measured intensity is lower than expected because of instrumental effects [17].

Less resolved is the appearance of the spectrum of the dibutyltin dichloride, which shows only one band at 9.53 eV before a broad envelope between 10 and 16 eV; the band at 9.53 eV corresponds to the band at 10.42 eV in the spectrum of dimethyltin dichloride, the shift towards lower *IE* being due to the greater electron-releasing power of the butyl groups with respect to the methyl groups.

The unresolved section above ca. 10 eV contains all the remaining bands (4 π chlorines lone-pairs, one with predominant character σ(Sn—Cl), two σ(Sn—C), many σ(C—H) and σ(C—C)), as indicated also by the much greater intensity with respect to the first band.

Dialkyltin bis-β-diketonates

The spectrum of dimethyltin bis(acetylacetonate) shows six rather well resolved bands of approximately equal intensity in the 8—11 eV region, followed by a broad envelope between 11 and 16 eV.

In the first energy region (8—11 eV) we again expect, by comparison with UPS spectra of other known acetylacetonates [7—14], in order of increasing *IE*, the π_3 levels of the chelate rings, the Sn—O σ bonds, formed from n^-, at least one or both the Sn—O bonding orbitals, formed from n^+, and also ionization of one or both Sn—C σ bonds. We associate the first of such ionizations with the band at 12.4 eV in $(CH_3)_2SnCl_2$, while in $Sn(CH_3)_4$ there are two bands at 9.70 and 13.4 eV [2,3]. Obviously, as a consequence of the low molecular symmetry, all the above bands, particularly those of the σ bonds, are expected to be strongly mixed in the molecular orbitals. Taking into account, for simplicity, only the probable major contribution, by comparison with related substances, we propose the following assignment. The first two bands at 8.51 and 9.06 eV arise from ionization of the two components of the π_3 ligands level: such a splitting of 0.55 eV, although not very large, is non usual in non-transition metal β-diketonates. The bands at 9.33 and 9.77 eV are probably related to the two n^- orbitals; again, no splitting is usually observed between the two components of n^- level in non-transition metal β-diketonates (apart from the gallium(II) hexafluoroacetylacetonate, with a splitting of 0.34 eV) [11], the obvious reason being the lower symmetry of our compounds, with respect to the other β-diketonates till now studied by UPS.

The bands at 10.27 and 10.54 eV must account for the ionization of at least one of the n^+ and one of the σ(Sn—C) orbitals: the former is probably associated with n^+ and the latter with σ(Sn—C), given that the σ(Sn—C) band falls at 10.72 eV in $(CH_3)_3SnOCH_3$ and at 10.72 eV in $(CH_3)_3Sn(acac)$. The section beyond 11 eV contains many unresolved bands associated with some σ-bonding orbitals (the second σ(Sn—C), many σ(C—H) and σ(C—C) and with another combination (π_2) of the π-orbitals of the acetylacetone. Comparison of this spectrum with that of $(CH_3)_3Sn(acac)$ reveals some interesting features: all the ligand bands are shifted to lower *IE* on passing from the trimethyl to the dimethyl compound, whereas one would expect the opposite shift from electrostatic considerations. This effect is particularly pronounced for the n^+ band (which shifts from 12.12 eV in $(CH_3)_3Sn(acac)$ to 10.27 eV in $(CH_3)_2Sn(acac)_2$), suggesting a greater interaction of the tin with the ligand in the former compound, while in the latter compound such interaction is smaller, probably because of the presence of two strongly interacting chelated rings. This effect is confirmed by the splittings observed for all ligand ionization bands in $(CH_3)_2Sn(acac)_2$.

In the spectrum of $(CH_3)_2Sn(Tacac)_2$, all the bands are shifted towards higher *IE*'s with respect to $(CH_3)_2Sn(acac)_2$, but the shape and the sequence of the bands is approximately the same. The possible assignments are therefore analogous to those discussed for the dimethyltin bis(acetylacetonate), the increase in *IE*'s being attributable to the well-known fluorine effect.

The spectrum of dibutyltin bis(acetylacetonate) shows only four resolved bands in the low *IE* region, as expected because of the greater number of σ(C—H) and σ(C—C) bonding orbitals with respect to the dimethyl analogous; this broadens the envelope of unresolved bands, which in this compounds begins at ca. 10 eV, masking at least two bands which, in contrast, are visible in the spectrum of $(CH_3)_2Sn(acac)_2$. By analogy with the latter compound, we attribute the first two bands, at 8.31 and 8.69 eV, to the π_3 orbital, and the bands at 9.24 and 9.49 eV to the two components of the n^- orbital, the n^+ band (or bands) probably lying under the following envelope such as the σ(Sn—C) bonds.

Experimental

The dialkyltin dichlorides were obtained commercially. The trialkyltin alkoxides and the triethyltin acetylacetonate were synthesized by literature methods [15], as were dialkyltin β-diketonates [18]. The trimethyltin acetylacetonate was prepared by the method previously used for the triethyl analogue. All compounds were purified by sublimation in vacuo.

The spectra were recorded on a Perkin—Elmer PS-18 spectrometer, between 35 and 90°C, except that for $(CH_3)_2SnCl_2$, which was recorded at room temperature. Calibration was performed by introducing inert gases (Ar, Xe) into the sample chamber.

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