He(I) and He(II) Photoelectron Spectra of Methyltin Chlorides

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He(I) and He(II) excited photoelectron spectra of the methyltin chlorides $Sn(CH_3)_3Cl$ and $Sn(CH_3)_2Cl_2$ are reported. On the basis of the variation of relative-intensity patterns on passing from He(I) to He(II) excitation, a reassignment of the spectra is suggested.

THE electronic structures of methyltin chlorides have been studied previously by He(I) photoelectron (p.e.) spectroscopy.[1,2] However, ambiguities remain in the assignment of the spectra. For instance, the band system having the lowest ionization energy (i.e.) in the He(I) p.e. spectrum of $Sn(CH_3)_3Cl$ [1] was assigned to ionization of molecular orbitals (m.o.s) of dominant Cl ($3p$–π) and Sn–Cl (σ) character. However, the observed ionization energies (9.88 and 1.16 eV respectively) † are much lower than in spectra of a wide range of closely related molecules.[3-5] Problems also arise when considering the He(I) p.e. spectrum of $Sn(CH_3)_2Cl_2$ where a single band was assigned [2] to four distinct chlorine lone-pair combinations; in the He(I) spectrum of $SnCl_2$, lone pairs give rise to at least three well separated bands.[5]

Variations in relative band intensities observed on switching from He(I) to He(II) excitation can provide crucial guidance on the assignment of p.e. spectra of molecules containing chlorine atoms because of the low cross section of chlorine $3p$ atomic orbitals [6] under He(II) irradiation. Moreover, He(II) radiation probes more deeply into electronic molecular subshells than is possible using He(I) radiation, and, in the case of tin compounds, may reveal additional structure related to ionization of the inner metal $4d$ subshell. As a consequence we felt that there was sufficient reason to re-examine the p.e. spectra of dimethyl- and trimethyl-tin chlorides using both He(I) and He(II) excitation.

EXPERIMENTAL

Commercial samples (Alfa-Ventron) were used in spectroscopic investigations after purification by sublimation *in vacuo*.

Spectra were measured on a Perkin-Elmer PS 18 spectrometer modified for He(II) measurements by inclusion of a hollow-cathode discharge lamp giving a high photon flux at He(II) wavelengths (Helectros Developments). Spectra were calibrated by reference to peaks due to admixed inert gases and to the He $1s$ self-ionization. Intensities were evaluated directly from raw spectra using both 'cut-and-weigh' techniques and a 310 Dupont curve resolver; errors in estimated band areas may be of the order of 10%. Intensities were corrected to allow for the decrease in analyser transmittance with electron kinetic energy. Pertinent experimental data are collected in Tables 1 and 2.

RESULTS

The low-ionization-energy region of the p.e. spectrum of $Sn(CH_3)_3Cl$ (Figure 1) contains two well resolved bands, labelled a and b in the Figure. Band a shows an incipient splitting into two components. The higher-energy region consists of a broad band (labelled d) whose general appearance resembles that of bands present in the same region of the p.e. spectra of other molecules containing methyl groups. This band shows a prominent shoulder (labelled x) to higher ionization energy.

TABLE 1

Ionization energy and relative intensity data for dimethyltin dichloride. M.o.s are filled up to $2b_2$

Band label	I.e./eV	Intensity		Assignment
		He(I)	He(II)	
a	10.43	0.2	0.8	$2b_2$
b	11.31	1.0	1.0	$2b_1 + 1a_2 + 1b_2$
c	12.16	1.1	1.4	$1b_1 + 3a_1$
d	14.30	2.4	5.4	σ(C–H) + σ(Sn–C)
x	15.93			
e	22.16		2.8	C $2s$
f	25.02 [a] (32.59) [b]		1.4 [c]	${}^2D_{\frac{5}{2}}$
f′	26.04 [a] (33.61) [b]			${}^2D_{\frac{3}{2}}$

[a] He(II) β satellite bands. [b] Expected positions of main He(II) α bands. [c] Values normalized to the intensity of the f′ band.

TABLE 2

Ionization energy and relative intensity data for trimethyltin chloride. M.o.s are filled up to $2e$

Band label	I.e./eV	Intensity		Assignment
		He(I)	He(II)	
a	(9.90) 10.11	0.5	1.2	$2e$
b	11.31	1.0	1.0	$1e$
d	13.80	2.5	5.2	σ(C–H) + σ(Sn–C)
x	15.24			
e	21.50		2.44	C $2s$
f	24.05 [a] (31.62) [b]		1.5 [c]	${}^2D_{\frac{5}{2}}$
f′	25.09 [a] (32.66) [b]		1.0	${}^2D_{\frac{3}{2}}$

[a-c] See footnotes to Table 1.

Pronounced variations in relative band intensities are observed on switching from He(I) to He(II) excitation. In particular, bands a and b have similar intensities in the He(II) spectrum, whereas b is markedly the stronger in the He(I) spectrum. Moreover, the He(II) spectrum contains structure beyond 20 eV which is necessarily absent from the He(I) spectrum. This consists of a broad band (labelled e) and two low-intensity features (f and f′) centred around the He $1s$ self-ionization peak.‡

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† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

‡ To prevent contamination of the lamp by sample vapours, a relatively high helium pressure was maintained in the discharge region. Under these circumstances it is difficult to suppress the helium self-ionization peak.

The general appearance of the p.e. spectra of $Sn(CH_3)_2Cl_2$ (Figure 2) resembles those of $Sn(CH_3)_3Cl$. The only pronounced differences are in the low-ionization-energy region where two strong bands (labelled b and c) appear in the He(I) spectrum instead of the single band (b); they become much weaker in the He(II) spectrum. Two low-intensity bands are again present in the region of the spectrum close to the helium self-ionization peak, but they are shifted to higher ionization energy than their counterparts in the He(II) spectrum of $Sn(CH_3)_3Cl$.

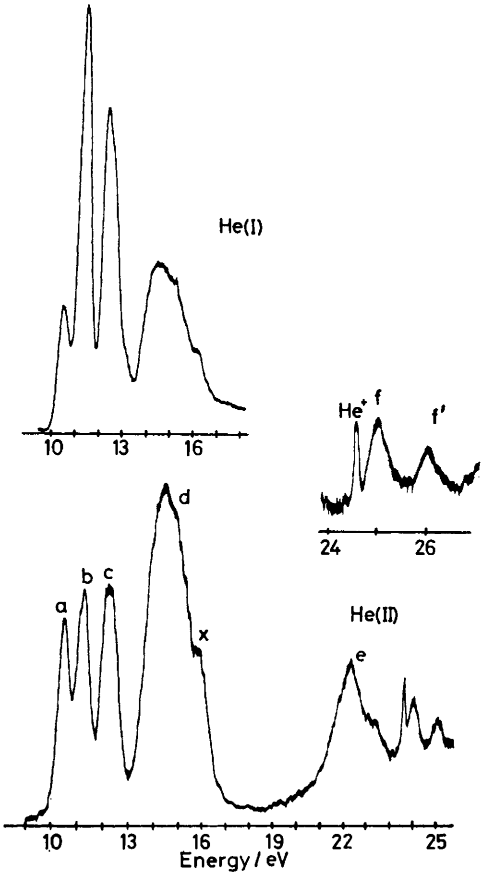

FIGURE 1 P.e. spectra of dimethyltin dichloride. Close-up of the 4*d* region of the He(II) spectrum

DISCUSSION

Our discussion of the p.e. spectra is based on a correlation between measured ionization energies and the ordering of molecular-orbital (m.o.) eigenvalues derived from a qualitative localized-orbital description of the electronic structure of the molecules of interest. *Ab initio* ΔSCF calculations indicate that differential-relaxation effects may lead to differences between the ordering of orbital energies and energies of corresponding ionic states in transition-metal complexes,[7-9] but orbital-rescaling effects should be of less importance in the valence shell of methyltin halides. The 4*d* shell of tin undoubtedly has a large relaxation energy, but this ' inner ' metal subshell is essentially core-like and sensitive to the molecular environment only *via* electrostatic ligand-field perturbation.[10]

Localized orbitals [11] used as bases for construction of

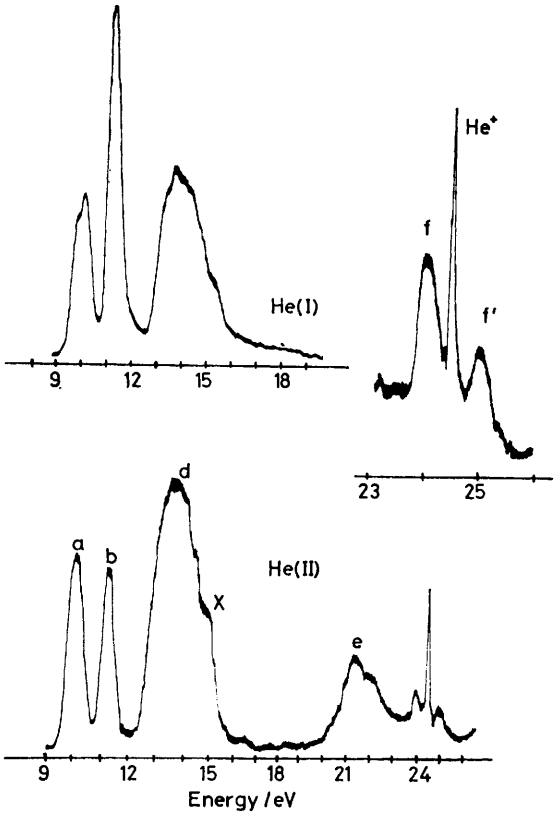

FIGURE 2 P.e. spectra of trimethyltin chloride. Close-up of the 4*d* region of the He(II) spectrum

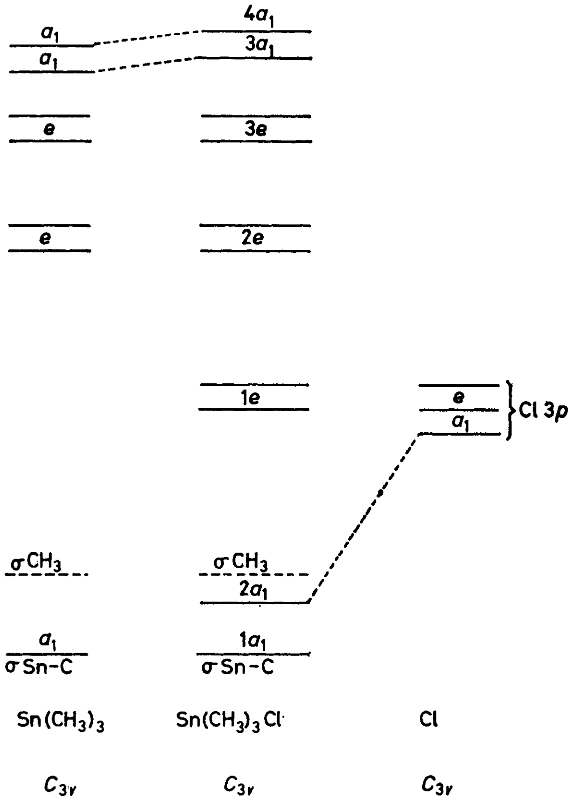

FIGURE 3 Qualitative m.o. scheme of dimethyltin dichloride

the m.o. diagrams shown in Figures 3 and 4 include (*i*) Sn–C σ bonds, (*ii*) Sn–Cl σ bonds, (*iii*) Cl lone pairs, and (*iv*) C–H bonding orbitals. We also include antibonding counterparts of the Sn–C bonds. The ordering of basis orbitals in our Figures is based in part on a consideration of ionization energies in related molecules such as $Cd(CH_3)_2$ and $SnCl_2$.[5,12] Interactions between basis orbitals clearly depend on both energy separations and group overlaps; in arriving at the ordering of m.o.s shown in our Figures we have been guided by our empirical assignments of the spectra which in turn depend largely on a consideration of He(II) intensity patterns (see below).

The assignments are given in Tables 1 and 2. For both spectra we propose that the first band (a) relates to ionization from a locally antisymmetric combination of Sn–C bonding orbitals, of *e* symmetry for $Sn(CH_3)_3Cl$ and of b_2 symmetry for $Sn(CH_3)_2Cl_2$. The incipient splitting in the spectrum of $Sn(CH_3)_3Cl$ we take to be due to vibronic Jahn–Teller distortion of the ^2E molecular ion produced by removing one electron from the two-electron molecular orbital. The remaining sharp features in the low i.e. region of the p.e. spectra are assigned to ionization from m.o.s largely chlorine lone pair in character, these local orbitals spanning the representations $b_1 + b_2 + a_1 + a_2$ for $Sn(CH_3)_2Cl_2$ and *e* for $Sn(CH_3)_3Cl$.

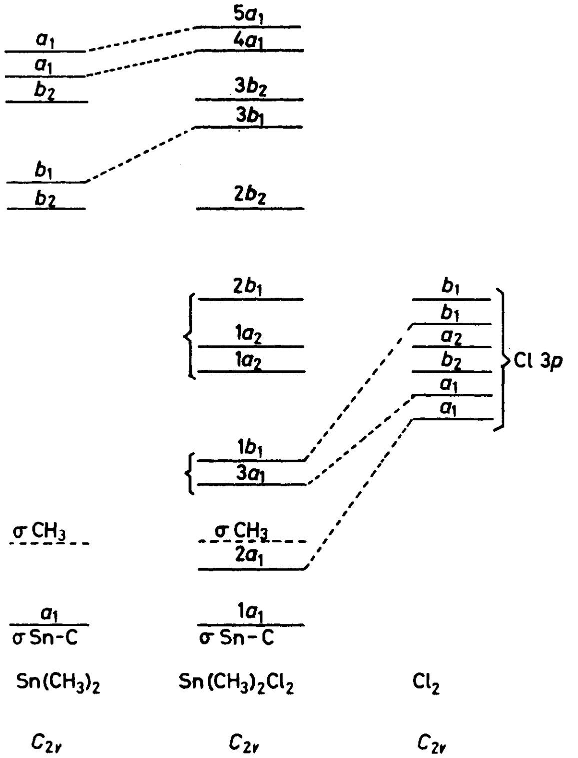

FIGURE 4 Qualitative m.o. scheme of trimethyltin chloride

This general view is supported by the observation that band b (and c in the case of the trimethyl compound) undergoes a pronounced decrease in intensity relative to that of band a on switching to He(II) excitation. This effect can be understood in terms of the increase in the cross-section ratio σ(C 2*p*) : σ(Cl 3*p*), behaviour related in turn to the low cross section for chlorine 3*p* atomic orbitals at He(II) wavelengths.[6]

The simple doublet structure observed in the 11—13 eV region of the p.e. spectrum of $Sn(CH_3)_2Cl_2$ is somewhat puzzling given that Cl 3*p*-based levels give rise to four distinct bands in the p.e. spectrum of $SnCl_2$. It must be remembered, however, that two types of interaction will determine the overall spread of chlorine 3*p* ionizations: first non-bonded Cl–Cl interactions and secondly interactions between the $(CH_3)_2Sn\!<$ and Cl_2 fragments.

The Cl–Sn–Cl angle is wider in the dimethyltin complex than in $SnCl_2$ itself,[13,14] which must certainly result in a reduced spread in energy of lone-pair orbitals. Moreover, interactions between the tin–methyl and tin–chlorine σ bonding levels within the a_1 manifold are likely to be more important than interactions involving the a_1 chlorine lone-pair levels. We arrive, then, at the m.o. scheme shown in Figure 4. Band b is taken to represent three distinct lone-pair ionizations ($b_1 + a_2 + b_2$) and band c a superposition of the remaining a_1 lone-pair combination and the out-of-phase b_1 Sn–Cl σ-bonding combination. The relatively higher intensity of band c in the He(II) spectrum (Table 2) can be understood in terms of the C 2*p* contribution to the $3a_1$ orbital. On the basis of earlier work [15] it seems clear that the broad band d must represent molecular orbitals localized mainly in the C–H framework; the relative lowering of the intensity of this band in He(II) spectra presumably reflects the H 1*s* contributions to the m.o.s, the atomic cross section for H 1*s* atomic orbitals being rather low at He(II) wavelengths.[16] Band d must also contain the a_1(σ Sn–Cl) and a_1(σ Sn–C) p.e. signals. Considerations of i.e.s of corresponding m.o.s measured in the p.e. spectra of $SnCl_4$ [4] and $Sn(CH_3)_4$ [15] suggests that the high-energy shoulder (X) present in both spectra represents the in-phase a_1(σ Sn–C) molecular orbital. The remaining ligand-based valence orbitals, of dominant C 2*s* atomic character, we associate with the broad band e.

Finally we turn to the low-intensity doublets (f and f′) in the high-ionization-energy region of the He(II) spectra. These features relate to the $^2D_{\frac{5}{2}}$ and $^2D_{\frac{3}{2}}$ final states produced by ionization of the tin 4*d* subshell, but are satellite peaks excited with He(II β) ($h\nu = 48.37$ eV) satellite radiation. The primary doublets excited by He(II α) ($h\nu = 40.81$ eV) radiation should appear in the 34—36 eV ionization-energy region, but are obscured by more intense He(I α) p.e. signals.

Similar He(II β) excited Sn 4*d* ionizations have been detected in He(II) spectra of $SnCl_2$, $SnBr_2$,[17] and $SnCl_4$.[18] The tin 4*d* ionization-energy data are discussed in detail elsewhere [18] and here we merely restrict ourselves to the comment that the Sn 4*d* half-widths found in the methyltin halides (*ca.* 0.35 eV) are markedly lower than in the tin dihalides (*ca.* 0.45 eV).[17] This indicates that the crystal field experienced by the tin atom is of pseudotetrahedral symmetry, line broadening due to the presence, in the crystal-field expansion, of a C_2^0 electric-field-gradient term being of minor importance.

Conclusion.—Our study of methyltin chlorides reinforces the view that combined He(I) and He(II) measurements may provide crucial guidance on the assignment of p.e. spectra of moderately complicated molecules containing elements whose valence orbitals have markedly different radial distribution.

[9/611 *Received*, 18*th April*, 1979]

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