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AN X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF VOLATILE TIN COMPOUNDS*

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ABSTRACT

Core-level X-ray photoelectron spectra of fifteen compounds of tin have been measured in the gas phase. The compounds include various organo and halo compounds as well as tin(IV) nitrate and $Sn\{N[Si(CH_3)_3]_2\}_2$. The tin binding energies span a range of 4.4 eV and are well correlated by the "transition-state" point-charge potential model equation using atomic charges calculated by the CHELEQ electronegativity equalization method. As expected, the empirically determined parameter k for tin is smaller than the k values obtained in previous work for carbon, silicon, and germanium. For $Sn(NO_3)_4$ and $Sn\{N[Si(CH_3)_3]_2\}_2$, the bonding can be described as a weighted average of several resonance structures. In these cases the binding energy data were used in conjunction with the CHELEQ method to determine the resonance structure weightings.

INTRODUCTION

The measurement of core-electron binding energies by X-ray photoelectron spectroscopy can provide useful information about the bonding and charge distribution in molecules.[1] Although a wide variety of compounds of the first and second-row elements have been studied, less attention has been focused on the heavier elements. Most of the previous XPS investigations of compounds of heavy elements have been carried out using solid samples. The difficulties encountered with solids - sample charging, proper referencing, surface impurities, and sample decomposition - complicate the interpretation of the data. In this work we have studied 15 tin compounds by X-ray photoelectron spectroscopy. Unlike previous XPS studies of tin,[2-6] all the compounds were examined in the gas phase. We have attempted to investigate as wide a range of binding energy shifts as possible, because it has been suggested[5] that for a heavy element such as tin, the core electrons may be relatively insensitive to changes in chemical environment.

EXPERIMENTAL

Materials. Stannane was prepared by the reduction of $SnCl_4$;[7] its purity was checked by a vapor pressure measurement at -83.6°. Trimethyltin iodide was prepared from $(CH_3)_3SnCl$ by treating the latter with a dilute basic solution, producing $(CH_3)_3SnOH$; the $(CH_3)_3SnOH$ was isolated and treated with an HI(aq)/Et_2O mixture. The $(CH_3)_3SnI$ was separated by fractional condensation on a vacuum line; its melting point of 4° agreed well with the literature value,[8] 3.4°. Trimethyltinmanganese pentacarbonyl was prepared by the method of Bichler et al.;[9] the melting point was 29 - 29.5° (lit., 29.5°). Tin(IV) nitrate was prepared by a method similar to that of Addison and Simpson;[10] after vacuum sublimation at 40°, its infrared spectrum agreed with the literature.[10] Bis[N,N-bis(trimethylsilyl)amino]tin(II) was kindly provided by Prof. M. F. Lappert. The preparation of $Sn\{N[Si(CH_3)_3]_2\}_2$ is described by Lappert and co-workers.[11] Tin tetrachloride was obtained from J. T. Baker Chemical Co. and was distilled prior to use. The remaining compounds listed in Table 1 were purchased from Orion Chemical Co. and were used without further purification.

X-Ray Photoelectron Spectra. The spectra were obtained with the Berkeley iron-free, double-focusing magnetic spectrometer. Magnesium K_α X-rays, with an energy of 1253.6 eV, were used as the photoionizing radiation. The sample pressure was maintained at 30-40 μ during the experiments. Argon gas at a partial pressure of 20-30 μ was simultaneously leaked into the sample chamber so that each spectrum could be referenced against the Ar $2p_{3/2}$ line (248.45 eV). The binding energies were determined by least-squares fitting the experimental data to Lorentzian lineshapes. Unless noted otherwise, all binding energies were found to be reproducible to ± 0.05 eV.

RESULTS AND DISCUSSION

The experimental binding energies are given in Table 1. For many compounds the Sn $3d_{3/2}$ line was measured as well as the Sn $3d_{5/2}$ line. The energy difference between the two lines of the multiplet was found to be nearly constant throughout the series of compounds. The average splitting for ten compounds was 8.47 eV, with a standard deviation of 0.04 eV. Morgan and Van Wazer[6] found the Sn $3d_{3/2}$ - $3d_{5/2}$ splitting to be 8.4 ± 0.1 eV for 11 tin compounds.

Also listed in Table 1 are the differences in energy between the Sn $3d_{5/2}$ and Sn $4d_{5/2}$ levels. These ΔE_B values cluster about an average difference of 460.90 eV with a standard deviation of 0.08 eV. Previous work[6] on tin compounds showed a similar consistency in chemical shifts between different core levels.

Several other core level binding energies we measured include Br $3d_{5/2}$ [$SnBr_4$, 76.01 eV; $(CH_3)_3SnBr$, 74.81 eV], I $3d_{5/2}$ [SnI_4, 626.25 eV; $(CH_3)_3SnI$, 625.33 eV], Mn $2p_{3/2}$ [$(CH_3)_3SnMn(CO)_5$, 646.84 eV], N 1s [$Sn(NO_3)_4$, 414.56 eV; $Sn\{N[Si(CH_3)_3]_2\}_2$, 402.01 eV], O 1s [$Sn(NO_3)_4$, 540.51 eV], Si 2p [$Sn\{N[Si(CH_3)_3]_2\}_2$, 105.97 eV].

CHELEQ Charge Correlations. The point-charge potential model has often been used to correlate core-electron binding energies with estimated atomic charges. The simple form of the potential equation

TABLE 1

EXPERIMENTAL BINDING ENERGIES

Compound	E_B(eV)			ΔE_B(eV)
	Sn $3d_{5/2}$	C 1s	Cl $2p_{3/2}$	(Sn $3d_{5/2}$ - Sn $4d_{5/2}$)
SnH_4	492.74			460.97
$Sn(CH_3)_4$	491.38	289.47		461.03
$Sn_2(CH_3)_6$	491.01	289.27		460.96
$(CH_3)_3SnCl$	492.27	289.92	204.43	460.85
$(CH_3)_2SnCl_2$	493.21	290.42	204.96	460.84
CH_3SnCl_3	494.06	290.98	205.52	460.92
$SnCl_4$	494.92		206.19	460.85
$SnBr_4$	494.46			460.93
SnI_4	493.75			
$(CH_3)_3SnBr$	492.23	289.89		460.78
$(CH_3)_3SnI$	492.02	289.81		460.80
$(C_4H_9)_3SnOCH_3$	491.31			
$(CH_3)_3SnMn(CO)_5$	491.16			461.01
$Sn(NO_3)_4$	495.36			
$Sn\{N[Si(CH_3)_3]_2\}_2$	491.93	289.36[a]		

[a] Uncertainty in binding energy ± 0.07 eV.

$$E_B = kQ + V + \ell, \tag{1}$$

in which Q and V correspond to ground state molecules, can be modified by including a relaxation energy correction

$$E_B = kQ + V + \ell + E_R. \tag{2}$$

This correction, when evaluated by the "transition state" method of estimating relaxation energies, leads to significantly improved correlations.[12]

We have correlated the Sn $3d_{5/2}$ binding energies of 12 compounds with atomic charges calculated by the CHELEQ electronegativity equalization method[12,13] using the relaxation-corrected potential equation. The k and ℓ values were determined to be 14.77 and 493.57, respectively, by a least-squares fit of the experimental binding energy data to equation 2. These values were then used to obtain calculated values of the binding energies. Table 2 lists the ground-state CHELEQ charges on the tin atoms, the calculated tin binding energies, and their deviations from the experimental values. Figure 1 shows a plot of experimental versus calculated tin binding energies. The standard deviation of the correlation is 0.44 eV, and the correlation coefficient is 0.974.

Molecules with Resonance. In order to use the CHELEQ method to calculate atomic charges, one must write a single valence-bond structure for the molecule - either a simple structure or a resonance hybrid. The corresponding bond orders and formal charges are then used in conjunction with orbital electronegativities to calculate atomic charges. In the case of the compounds $Sn(NO_3)_4$, $Sn\{N[Si(CH_3)_3]_2\}_2$,

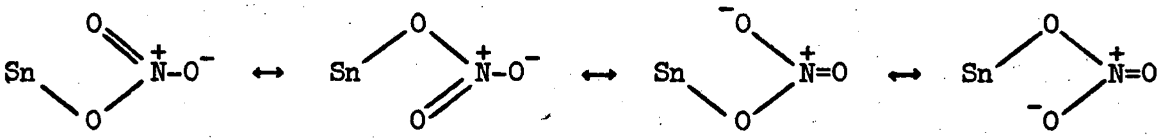
TABLE 2

CALCULATED TIN CHARGES AND BINDING ENERGIES

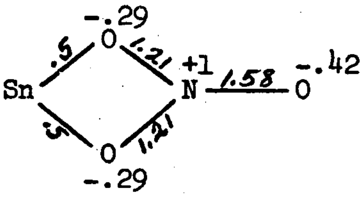
Compound	$Q_{CHELEQ}(Sn)$	E_B(calc), eV	E_B(calc) - E_B(expt), eV
$SnCl_4$	0.403	494.85	-0.07
$SnBr_4$	0.332	494.18	-0.28
CH_3SnCl_3	0.299	494.02	-0.04
SnI_4	0.231	493.38	-0.37
$(CH_3)_2SnCl_2$	0.195	493.20	-0.01
$(C_4H_9)_3SnOCH_3$	0.130	492.39	1.08
$(CH_3)_3SnCl$	0.091	492.37	0.10
$(CH_3)_3SnBr$	0.074	492.21	-0.02
$(CH_3)_3SnI$	0.049	492.01	-0.01
SnH_4	-0.087	491.92	-0.82
$Sn(CH_3)_4$	-0.013	491.54	0.16
$Sn_2(CH_3)_6$	-0.010	491.28	0.27

and $(CH_3)_3SnMn(CO)_5$, various resonance structures can be written, and there is no a priori way to weight these structures. Hence these three compounds were not included in the binding energy-charge correlation.

In tin(IV) nitrate the tin atom is coordinated to 8 oxygen atoms; the nitrate ligands are bonded to tin in a bidentate fashion.[14] If we assume that the tin atom conforms to the octet rule, we can describe the bonding between the tin atom and a given nitrate group in terms of the following valence bond resonance structures:



Using the CHELEQ charge-estimation method in conjunction with the transition-state point-charge potential model, we have found that the experimental tin, nitrogen, and oxygen binding energies are best predicted using the resonance hybrid structure



The numbers next to the bonds are average bond orders; the numbers next to the atoms are average formal charges. The values of Q_{CHELEQ}, E_B(calc), and E_B(calc) - E_B(expt) for tin, nitrogen and oxygen, corresponding to this bonding model, are given in Table 3. We believe the E_B(calc) values for the oxygen atoms are high because of unaccounted

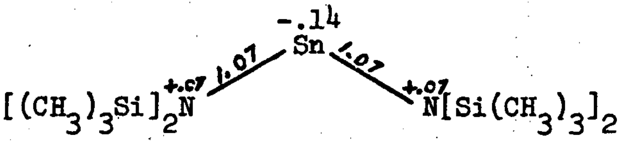
TABLE 3

CHELEQ CALCULATIONS FOR $Sn(NO_3)_4$ AND $Sn\{N[Si(CH_3)_3]_2\}_2$

		Q_{CHELEQ}	E_B(calc,eV)	E_B(calc) - E_B(expt)(eV)
$Sn(NO_3)_4$	Sn	0.435	495.37	0.01
	N	0.404	414.92	0.36
	O coordinating	-0.162	541.65	1.14
	O terminal	-0.188	542.13	1.62
$Sn\{N[Si(CH_3)_3]_2\}_2$	Sn	0.047	491.87	-0.06
	N	-0.212	400.61	-1.40
	Si	0.108	106.73	0.76

for "resonance" relaxation energy. The fact that we obtained the best fit by assigning a higher bond order to the terminal N-O bond than to the other two N-O bonds is consistent with the fact that the terminal bond is 0.11 Å shorter than the other bonds.[14]

We have used the CHELEQ method, in a manner similar to that used for $Sn(NO_3)_4$, to determine a suitable resonance hybrid structure for the tin(II) amide, $Sn\{N[Si(CH_3)_3]_2\}_2$. This molecule is believed to be a monomeric species in the gas phase.[11,15] We found that the following hybrid structure



gave the best overall agreement between the experimental and calculated binding energies. It should be noted that the tin atom in this structure is 1.72 electrons short of an octet configuration. The numerical data are given in Table 3.

The bonding in $(CH_3)_3SnMn(CO)_5$ is relatively complicated because of π back bonding to the CO ligands and the possibility of fractional σ bonding to the CO ligands. In the absence of adequate binding energy data for other manganese carbonyl derivatives, any attempted weighting of resonance structures in $(CH_3)_3SnMn(CO)_5$ would be too ambiguous to permit meaningful conclusions. We can note, however, that the Sn $3d_{5/2}$ binding energy for this compound is almost as low as that for $Sn_2(CH_3)_6$, suggesting that the $Sn(CH_3)_3$ and $Mn(CO)_5$ groups have similar electron-withdrawing abilities.

<u>The Magnitude of k</u>. In previous studies of tin compounds, very

small ranges of binding energies have been observed. For example, Grutsch, Zeller, and Fehlner[5] have investigated 35 solid compounds ranging from $PtCl(SnCl_3)[(C_6H_5)_3As]_2$ to SnF_4 and found only a 1.8 eV range in tin binding energies. Morgan and Van Wazer[6] measured a 1.3 eV chemical shift between $(C_6H_5)_4Sn$ and $(C_6H_5CH_2)_2SnCl_2$. Swartz et al.[4] observed a chemical shift range of only 0.7 eV for a number of tetraethylammonium hexahalostannates. In this work, the range of tin $3d_{5/2}$ binding energies extends from 491.01 eV for hexamethylditin to 495.36 eV for $Sn(NO_3)_4$, a range of 4.35 eV. The shifts that we observed can be shown to be of a reasonable magnitude. According to a simple atomic shell model, the constant k can be equated to the reciprocal of the covalent radius of the atom in question.[16] Much more accurate k values can be calculated by a method involving atomic ionization potentials and the equivalent-cores approximation.[17,18]

$$k \simeq I_2(B) - I_1(A) \qquad (3)$$

In equation 3, A and B represent successive elements in the periodic table. In making comparisons between empirical and theoretical k values, it is best to compare the ratios of k values for different elements. Such comparisons can be made in Table 4. The empirical, CHELEQ-based values are very similar to the estimated values. Since atomic relaxation is accounted for in the equivalent-core method for estimating k (Eq 3), the better agreement found with these values might have been anticipated.

ACKNOWLEDGMENT

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TABLE 4

EMPIRICAL AND THEORETICAL RATIOS OF k VALUES

	CHELEQ (empirical)	$1/r_{cov}$ [a]	Eqn 3 [b]
k_C/k_C	1.00	1.00	1.00
k_{Si}/k_C	0.58 [c]	0.65	0.63
k_{Ge}/k_C	0.53 [c]	0.63	0.59
k_{Sn}/k_C	0.49	0.55	0.50

[a] Covalent radii taken from A. F. Wells, Structural Inorganic Chemistry, Oxford University Press, Fair Lawn, N.J., 1962.

[b] Ionization potentials used in Eqn 3 taken from C. E. Moore, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., No. 34 (1970).

[c] From ref. 17.

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Figure 1. Plot of E_B(expt) vs. E_B(calc) for tin $3d_{5/2}$ binding energies for the following compounds: (1) $Sn_2(CH_3)_6$, (2) $(C_4H_9)_3SnOCH_3$, (3) $Sn(CH_3)_4$, (4) $(CH_3)_3SnI$, (5) $(CH_3)_3SnBr$, (6) $(CH_3)_3SnCl$, (7) SnH_4, (8) $(CH_3)_2SnCl_2$, (9) SnI_4, (10) CH_3SnCl_3, (11) $SnBr_4$, (12) $SnCl_4$.

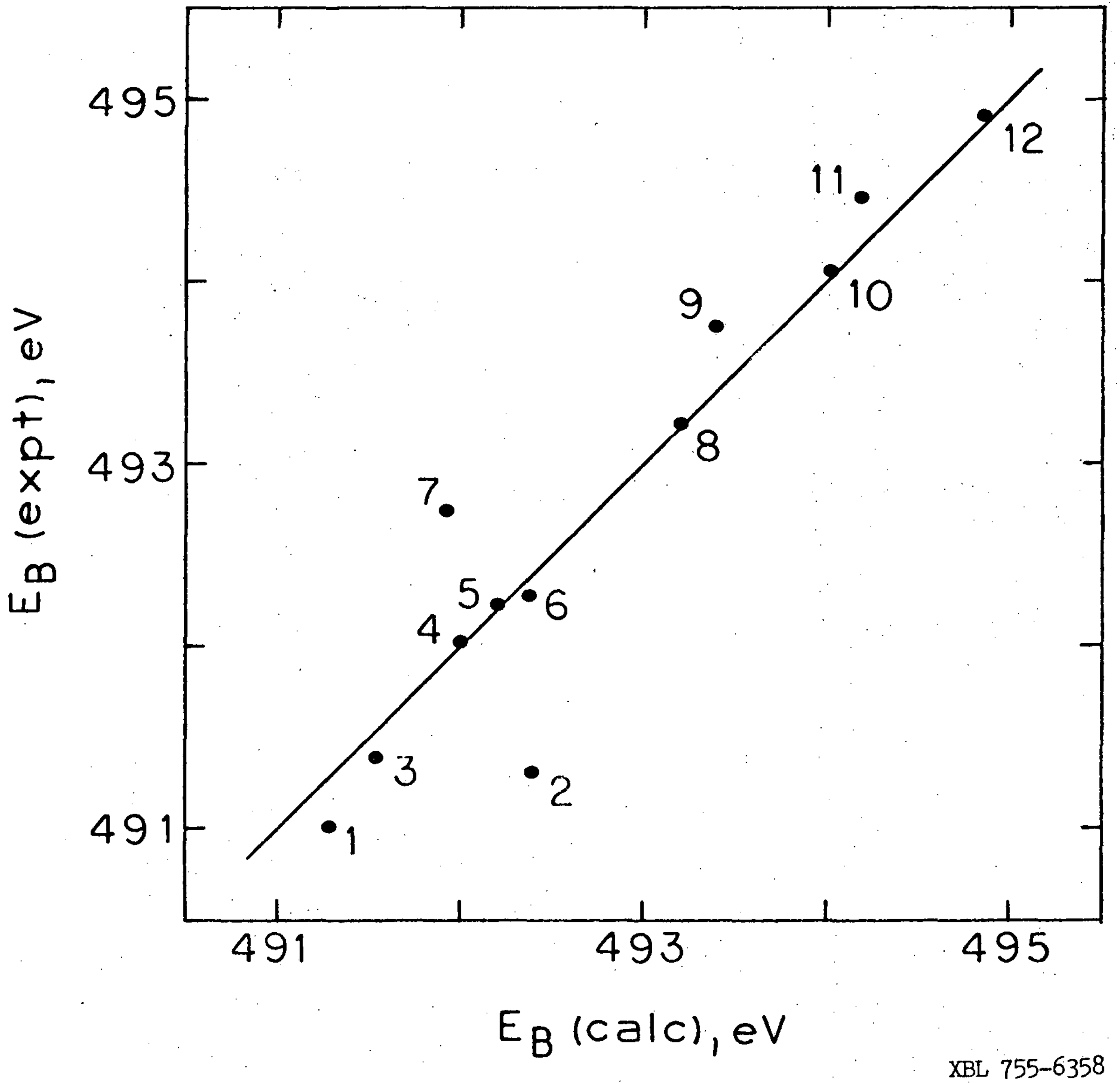

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Fig. 1.

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