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Photoelectron Spectra and Electronic Structures of Antimony(III) Halides

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The photoelectron spectra of $SbCl_3$, $SbBr_3$ and SbI_3 are reported and discussed in terms of their molecular orbital structures.

Recent advances in the chemical application of the ^{121}Sb Mössbauer Effect have resulted in an increasing number of studies into the bonding properties of antimony in its compounds.[1] The information obtainable by this technique is relevant only to the solid state and therefore supplementary studies on antimony compounds in the vapour phase are useful in contributing to the overall picture.

One attractive feature of photoelectron spectroscopy is the direct elucidation of all or part of molecular valence level electronic structures thereby providing information on chemical bonding characteristics. The technique also yields data in terms which permit evaluations as to the effectiveness of the various theoretical procedures.

We report here the results of a He(I) photoelectron spectroscopic investigation into the bonding properties of vapour phase antimony(III) chloride, bromide, and iodide.

EXPERIMENTAL

$SbCl_3$ (E. Merck, Darmstadt, W. Germany) and $SbBr_3$ and SbI_3, prepared by the slow addition of stoichiometric quantities of the halogen to a suspension of powdered Sb in refluxing anhydrous benzene, were purified by sublimation *in vacuo* (0.05 Torr) at 60, 80 and 100 °C, respectively.

The photoelectron spectra were recorded on a Perkin-Elmer model PS-16 spectrometer. The temperatures of the samples at which the data were collected were 25, 50 and 115 °C for $SbCl_3$, $SbBr_3$ and SbI_3, respectively.

RESULTS AND DISCUSSION

The vapour phase molecular structures of the SbX_3 series (X = Cl, Br or I) are pyramidal[2] with point group C_{3v}. A simple chemical bonding picture may be given in terms of localised bonds between Sb and X with a lone-pair orbital occupying the apical position on Sb. An alternative model which lends itself better to more detailed bonding discussions is similar to that provided by the molecular orbital description of Cox *et al.*[3] for PCl_3 and PBr_3 in which the twenty-six valence electrons are distributed over nine different valence levels.

There are six X "lone-pair" group orbitals (irreducible representations a_1; a_2; e; e) which are non-degenerate because of the non-spherically symmetric X environments. Factors influencing energy separation include (i) interhalogen repulsions as a result of through-space interactions of orbitals of the same symmetry; (ii) the π-type interaction between the (X_3) a_1 symmetry group orbital and the Sb lone-pair a_1 orbital; and (iii) π-backbonding with empty acceptor $5d$ orbitals on Sb. The significance of the latter effect in second, third and fourth row main group elements has been the subject of some controversy. It should be noted that any $(p \rightarrow d)\pi$-backbonding in these pyramidal molecules is intertwined with the σ-interactions. In C_{3v} symmetry, as pointed out previously,[4] clear-cut distinctions between σ- and

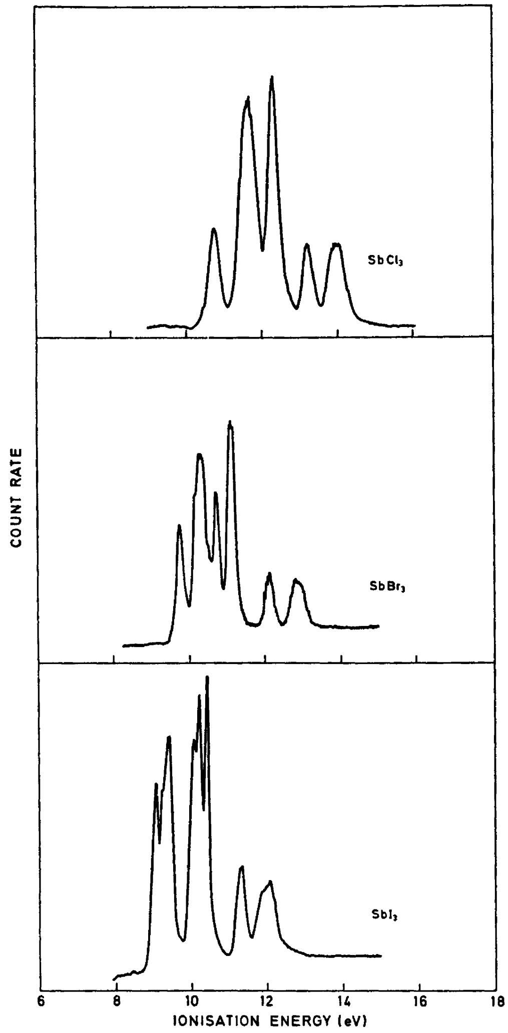

Fig. 1. Photoelectron spectra of $SbCl_3$, $SbBr_3$ and SbI_3.

π-orbitals disappear as the σ- and π-orbitals with the same irreducible representation (a_1 and e) mix. Symmetry constrains one of the (X_3) group orbitals (a_2) to be truly non-bonding since none of the Sb valence orbitals possesses this representation. Consequently, the energy of this orbital should reflect the net relative electron density flow towards or away from the X atoms.

The photoelectron spectra of $SbCl_3$, $SbBr_3$ and SbI_3 are reproduced in Fig. 1 and their spectral assignments (Table 1) are based on considerations of line-intensities, spin-orbit coupling (for X = Br or I) and by comparisons with those already established for the C_{3v} molecules CHX_3 and PX_3 (X = Cl, or Br).[3,5,6] Only six of the nine levels are detected because the more strongly σ-bonding orbitals ($1a$, and $1e$) are too deep-seated having energies clearly in excess of -21 eV. This is consistent with these, together with the missing $2a_1$ level, possessing considerable *s*-character, the former from X and the latter from Sb. The Sb $5s$ and $5p_z$ orbitals being both of a_1 symmetry can mix and the $2a_1$ level would therefore represent a large degree of the total $5s$ contribution to the lone-pair. For all three compounds the four bands occurring at lowest ionisation energies are assigned to X lone-pair orbitals. In common with the other three-coordinate compounds PCl_3 and PBr_3 these parts of the spectra exhibit a reversal in the ordering of the two least tightly bound orbitals over that observed for the four-coordinate molecules CHX_3 and $SiHCl_3$,[7] the $4a_1$ levels in the former being destabilised with respect to the $1a_2$. This effect is consistent with a mixing-in of P or Sb lone-pair character with the a_1 orbitals on X thereby stabilising $3a_1$ (bonding) and destabilising $4a_1$ (antibonding). It is therefore difficult to accurately assess the extent of the major contribution to the range of X lone-pair energies *viz.* the effect of interhalogen repulsion.

For a series with a given X the range of ionisation energies of the a_2 group orbitals, although nonbonding (*vide supra*), must depend on changes in electronic shielding from the X nuclei and hence reflect electron density drifts towards or away from the halogen *via* the bonding interactions of the a_1 and e orbitals with those of the apical atom. The observed orders of decreasing a_2 orbital ionisation energies are $PCl_3 > CHCl_3 \sim SbCl_3$ and $PBr_3 > CHBr_3 > SbBr_3$. These are not as might be predicted from simple electronegativity differences alone.

Expansions of X lone-pair orbitals of a_1 symmetry through interactions with the Sb lone-pair and any $(p \rightarrow d)\pi$ back donations (a_1 and e symmetries) would contribute to the net shifts. However, the separations between the $3e$ or $4e$ levels and $1a_2$ in PX_3 and SbX_3 do not indicate any significant stabilisations which would be expected if back donation involving

Table 1. Vertical ionisation potentials (eV) and their orbital assignments.

Compound	$2a_1$	$3a_1$	$2e$	$3e$	$4e$	$1a_2$	$4a_1$
$CHCl_3$	19.8	16.96	15.99	12.85	12.01	11.48	11.91
$CHBr_3$	19.8	15.81	14.71	11.88 11.72	10.95 10.81	10.47	11.28
PCl_3	18.85	14.23	15.19	12.94	11.97	11.69	10.52
PBr_3	–	13.09	14.09	11.85	11.18 10.87	10.67	10.00
$SbCl_3$	–	13.20	13.98	12.28	11.62	11.50	10.73
$SbBr_3$	–	12.12	12.84	11.14	10.75 10.35	10.22	9.77
SbI_3	–	11.29	12.05 11.89	10.40 10.19	10.04 9.40	9.26	9.06
$SiHCl_3$	18.14	14.98	14.75	13.07	12.41	11.94	12.41

empty P 3*d* or Sb 5*d* orbitals was important. The bands designated $3a_1$ and $2e$ exhibit a more extensive orbital delocalisation due to bonding interactions. The $3a_1$ molecular orbital includes a contribution from the Sb lone-pair and its appearance is in accordance with the structural changes resulting from ionisation of an electron from this level.

Comparison of the molecular orbital description with the localised bond concept valence shell electron pair repulsion model[8] reveals that the lone-pair orbital on Sb is now explicitly described in terms of contributions from a number of a_1 symmetry molecular orbitals. The non-planarity of the molecules is hence mainly attributable to a balance between the bonding $3a_1$ and antibonding $4a_1$ orbitals together with the interhalogen interactions.

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