A Localized Orbital Interpretation of ESCA Chemical Shifts on Phosphine Co-ordination

By M. BARBER, J. A. CONNOR, M. F. GUEST, I. H. HILLIER,* and V. R. SAUNDERS

(Department of Chemistry, The University, Manchester M13 9PL)

Summary Measured differences in the binding energies of the phosphorus and chlorine core electrons in PCl_3 and $POCl_3$ are interpreted in terms of the nature of the P–O bond using the results of localized orbital calculations

THE mode of co-ordination of phosphines is traditionally discussed qualitatively in terms of σ-donation from the phosphorus lone pair and π back-bonding into the phosphorus virtual d orbitals. Recent ab initio self-consistent field molecular orbital (SCF–MO) calculations have supported such interpretations.[1-3] We here show that measurements of the changes in the binding energies of the core electrons on co-ordination reflect the associated change in distribution of the valence electrons which may be interpreted in terms of localized orbitals obtained from ab initio SCF–MO calculations.

The binding energies of the phosphorus and chlorine $2p$ electrons in PCl_3 and $POCl_3$ were measured in the solid state using an A.E.I. ES100 photoelectron spectrometer, internal standards being used to overcome surface charging effects and non-linearity of the energy scale. In $POCl_3$ these binding energies are greater than those in PCl_3 by 2·5 eV for $P(2p)$, and by 0·9 eV for the $Cl(2p)$. We have previously reported ab initio SCF–MO calculations of the electronic structure of these two molecules in a minimal basis of Slater type orbitals augmented by phosphorus $3d$ functions.[4]

The change in core binding energies from these calculations, using Koopmans' theorem [2·2 eV for $P(2p)$, 0·5 eV for $Cl(2p)$] are in good agreement with the experimental values. To understand the origin of these shifts in chemical terms we have evaluated the change in the potential at the phosphorus and chlorine atoms on formation of the P–O bond, such an approximation having previously been found to yield chemical shifts in satisfactory agreement with Koopmans' theorem values.[5]

The chemical shifts calculated in this way [3·2 eV for $P(2p)$, 0·6 eV for $Cl(2p)$] are not appreciably worse than the Koopmans' theorem values when compared with the experimental measurements.

Localized orbitals were constructed from the calculated SCF–MOs for these molecules by the procedure due to Foster and Boys,[6] and their contributions to the potential at the phosphorus and chlorine atoms in the two molecules were evaluated. In both molecules there are three lone pairs on each chlorine atom, two of which are equivalent, and three P–Cl bonding pairs. The potential at the phosphorus atom due to these electrons is not appreciably different in the two molecules so that the P–Cl bond pairs and chlorine lone pairs do not contribute significantly to the phosphorus chemical shift. In PCl_3 there is a large negative potential at the phosphorus atom due to the phosphorus lone pair (approximately $sp^{0.5}$ hybridized), the centroid of

this orbital being 0·59 Å from the phosphorus atom. In POCl₃ there are three equivalent P–O 'banana' bonds, strongly polarized towards the oxygen atom, the centroid of each orbital being 1·17 Å from the phosphorus atom. These three P–O bonds result from the σ donation and π back-bonding discussed previously. The origin of the phosphorus chemical shift can be attributed mainly to the difference between the potential arising from the three P–O bonds, the oxygen lone pair and core in POCl₃, and that from the phosphorus lone pair in PCl₃.

The chlorine chemical shift is so small that the very small changes in the contribution of the P–Cl bonding electrons on oxide formation do not allow the origin of the shift to be interpreted as readily in terms of localized orbitals.

This study suggests that phosphorus ESCA chemical shifts which result from the co-ordination of phosphines may be directly interpreted in terms of the phosphine lone pair and the nature of the additional bonds which are formed. Thus quantitative information on the bonding in co-ordinated phosphines which are not susceptible to accurate calculations at present may be obtained from core binding energy measurements.

[1] J. Demuynck and A. Veillard, *Chem. Comm.*, 1970, 873.
[2] I. H. Hillier and V. R. Saunders, *J. Chem. Soc. (A)*, 1970, 2475.
[3] I. H. Hillier and V. R. Saunders, *J. Chem. Soc. (A)*, 1971, 664.
[4] I. H. Hillier and V. R. Saunders, *Chem. Comm.*, 1970, 1510.
[5] M. E. Schwartz, *Chem. Phys. Letters*, 1970, **6**, 631.
[6] J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, 1960, **32**, 300; S. F. Boys in 'Quantum Theory of Atoms, Molecules and the Solid State,' ed., P.-O. Löwdin, Academic Press, New York, 1966, p. 253. The alternative definition given by Boys in the second paper above has been used in the present work.