Ab Initio SCF–MO Calculations of the Bonding in Phosphorus Trichloride and Phosphorus Oxychloride

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Summary The bonding in PCl_3 and $POCl_3$ is described by *ab initio* SCF–MO calculations and the results compared with the experimental photoelectron spectra.

THE method of co-ordination of phosphines is a subject of continuing interest. The simple borane and oxide adducts of phosphine and trifluorophosphine have been investigated by *ab initio* SCF–MO calculations,[1-3] but no theoretical investigation of chloro-derivatives of phosphorus, and their mode of co-ordination has been reported. We here present the results of *ab initio* SCF–MO calculations on PCl_3 and the simple oxide $POCl_3$, and compare the experimental vertical ionization potentials, measured by photoelectron spectroscopy, with the calculated energies of the valence electrons.

The basis orbitals consisted of a minimal basis of Slater-type orbitals with best atom exponents,[4] augmented by five phosphorus 3*d*-orbitals of exponent 1·8, close to the optimum value (1·77) calculated for PF_3.[5] No 3*d* functions were included on the chlorine atoms, as such functions are mainly important in the bonding of later second-row elements when their valency is increased from its natural value.[5] For computational ease each member of this basis was expanded in a linear combination of three Gaussian-type functions, the expansion coefficients and orbital exponents being determined by a least-squares procedure.[6,7] The calculations were performed using the ATMOL system on the Manchester University ATLAS computer.

The experimental geometry for $POCl_3$ was used,[8] and to economize on computer time, the P–Cl bond length and

ClPCl angle in PCl_3 were taken to be the same as in the oxide.

TABLE 1

Bonding in PCl_3 *and* $POCl_3$

Atomic populations

		PCl_3	$POCl_3$
Phosphorus	$3s$	1·69	1·19
	$3p(a_1)$	1·32	0·76
	$3p$ (e)	1·46	1·78
	$3d$ (a_1)	0·07	0·16
	$3d$ (e)	0·42	0·91
Atomic charge		+0·10	+0·25
Chlorine	$3s$	1·91	1·91
	$3p$	5·14	5·12
Atomic charge		−0·03	−0·01
Oxygen	$2s$		1·86
	$2p$		4·35
Atomic charge			−0·21

Phosphorus–oxygen overlap populations

Phosphorus orbital	Oxygen orbital	
$3s$	$2s$	−0·139
$3s$	$2p_\sigma$	0·256
$3p_\pi$	$2p_\pi$	0·378
$3p_\sigma$	$2s$	−0·092
$3p_\sigma$	$2p_\sigma$	0·292
$3d_\pi$	$2p_\pi$	0·414
$3d_\sigma$	$2s$	0·039
$3d_\sigma$	$2p_\sigma$	0·054

TABLE 2

Calculated and experimental vertical ionization potentials (ev)

PCl_3			$POCl_3$		
Orbital symmetry	Calc. I.P.	Expt. I.P.	Orbital symmetry	Calc. I.P.	Expt. I.P.
$11a_1$	9·20	10·52	$11e$	11·50	12·13
$2a_2$	11·52	11·71	$2a_2$	11·92	12·52
$10e$	11·74	12·01	$10e$	12·35	13·18
$9e$	12·83	12·97	$13a_1$	12·86	13·63
$10a_1$	14·78	14·24	$9e$	13·53	13·99
$8e$	15·39	15·22	$12a_1$	15·54	15·54
$9a_1$	20·19	18·85	$8e$	16·65	16·63
			$11a_1$	20·05	19·48

In Table 1 the orbital populations for the two molecules obtained by a Mulliken analysis, and the contributions to the P–O overlap population in $POCl_3$ are shown. In PCl_3, the P–Cl bonds are predicted to be only slightly polar with a formal charge of +0·10 on the phosphorus atom, in contrast to PF_3, where the phosphorus charge was calculated to be +1·02.[2] The $3d$ population, 0·49e, is rather smaller than the value calculated for PF_3 (0·66e), and is much smaller than the values found when the valency of the second-row atom is increased from its natural value.[5] The highest filled orbital in PCl_3, $11a_1$, has 47% phosphorus character, lower than that of the lone-pair orbital in PF_3.[9] Its orbital energy, −9·20 ev is *ca.* 3·5 ev higher than that of PF_3, which may be attributed to the smaller positive charge on the phosphorus atom in PCl_3. The next three orbitals, $2a_2$, $10e$ and $9e$ are predominantly of chlorine $3p$ character and non-bonding in nature, the $10a_1$, $8e$, and $9a_1$ contributing to the P–Cl bonds. The major changes in the orbital populations on formation of $POCl_3$ are a large decrease ($1{\cdot}06e$) in that of the phosphorus $3s$ and $3p_\sigma$ orbitals and a large increase ($0{\cdot}81e$) in that of the phosphorus $3p\pi$ and $3d\pi$ orbitals, resulting in an increase in the formal charge on the phosphorus atom to +0·25, the charge on the chlorine atoms being little affected. These charge migrations illustrate the σ-donor and π-acceptor properties of PCl_3, which are further shown in the contributions to the P–O bond overlap populations (Table 1). The major interactions involve the phosphorus $3s$ and $3p_\sigma$ orbitals with the oxygen $2p_\sigma$ orbital, and the phosphorus $3p_\pi$ and $3d_\pi$ orbitals with the oxygen $2p_\pi$ orbitals, the $3d_\pi$–$2p_\pi$ component being the largest. The highest filled orbital of $POCl_3$, $11e$, is calculated to be mainly non-bonding, with nearly equal oxygen $2p_\pi$ and chlorine $3p$ components. The major contributions to the $2a_2$, $10e$, $13a_1$, and $9e$ molecular orbitals are chlorine $3p$ orbitals (>70%), the $9e$ and $10e$ providing contributions to the phosphorus $3d_\pi$–oxygen $2p_\pi$ overlap population. The $12a_1$ orbital is the highest to have a significant phosphorus σ-component ($3p_\sigma$, 19%), and is strongly P–O bonding, so that it may be correlated with the "lone-pair" donor orbital ($11a_1$) in PCl_3. The $8e$ and $11a_1$ orbitals provide contributions to the P–Cl and P–O bonds.

There is good correlation between the measured vertical ionization potentials[10,11] and the negative of the calculated orbital energies (Table 2), showing that a minimal basis, expanded by the inclusion of $3d$ functions on the phosphorus atom gives a good description of the bonding.

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