Bonding in Phosphorus Trifluoride and Phosphorus Oxyfluoride. An *ab initio* SCF–LCAO–MO Study

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Summary The importance of *d*-orbital participation and of π-back-donation in phosphorus oxyfluoride is discussed through the results of *ab initio* SCF–MO calculations.

THE bonding ability of phosphorus trifluoride PF_3 is well known in the chemistry of transition-metal complexes. The simplest adduct of this molecule is the phosphorus oxyfluoride molecule PF_3O. The nature of the P–O bond in PF_3O has been a matter of speculation for many years, a much debated question being the importance of phosphorus 3*d* orbitals in the bonding. The short P–O bond length in F_3PO has been ascribed to strong d_π–p_π bonding, but some doubt has been raised recently by the fact that the NO bond in F_3NO is also short enough to qualify it as a double bond.[1] In phosphoryl molecules Y_3PO, several properties vary considerably as the Y group is varied, indicating significant changes in the P–O bond character. The effects of changing the substituents Y on the P–O bond have already been investigated through semi-empirical calculations.[2] The limits of the variation seem to correspond respectively to the molecules $P(CH_3)_3O$ and PF_3O. A description of the bonding in the PH_3O molecule has already been given by one of us[3] and we report here the results of *ab initio* SCF–LCAO–MO calculations for the molecules PF_3 and PF_3O.

We used a basis set of twelve *s* and nine *p* Gaussian functions on phosphorus,[4] ten *s* and six *p* functions on oxygen and fluorine.[5] To these orbitals a double set of *d* functions (exponents 0·8 and 0·2) on P has also been added.

Calculations have been performed with the following geometries: P–F bond length 1·57 Å (experimental value in PF_3[6]) and P–O bond length 1·45 Å (experimental value in OPF_3[7]). We used the same value of 97·8° (experimental value in PF_3[6]) for the FPF angle in both molecules.

The results are summarized in the Table. For the sake of comparison, we have also included part of the results obtained previously for the PH_3 and PH_3O molecules.†[3] The participation of the *d* orbitals to the bonding should be analysed first. From the Table, it is apparent that this participation is much more important in PF_3O than in PF_3. The *d* orbital population[8] is slightly negative in PF_3 (not much significance should be attached to this small negative value) but rises to 0·5 in PF_3O. A similar trend has been observed in the phosphine and phosphine oxide molecules[3] with a *d* orbital population in PH_3O of 0·36, less than in PF_3O. The 3*d* population in PF_3O is of the $3d_\pi$ type (the $3d_\sigma$ population being slightly negative‡). Bassett *et al.* have reported 3*d* populations of, respectively, 0·66 and 1·32 in the molecules PF_3 and PF_3O.[9] These values are probably overestimated due to the use of an unbalanced basis set, with the *d* orbitals being used partly to remedy the incompleteness of the *s,p* basis set[10] (the calculations reported in ref. 9 are of the "single-ζ" type while the ones presented here are of the "double-ζ" quality). The *d* orbital participation is also apparent from the overlap populations. The contribution of phosphorus 3*d* orbitals to the overlap population for the P–O bond in PF_3O is 0·228 (the corresponding value in PH_3O was 0·272). The contribution of

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† Calculation for the PH_3 and PH_3O molecules included only one set of *d* functions on P, so that the results are not strictly comparable to the ones for PF_3 and PF_3O. However, we feel that the comparison is meaningful at least for the main trends.

‡ Strictly speaking, the notation σ and π is valid only for linear and planar molecules. However it has become customary to extend this notation to molecules of any geometry. In this paper, the σ and π notation refers to the ternary axis of the molecules.

phosphorus 3*d* orbital to the P–F overlap population is smaller, being 0·143 in PF_3 and 0·079 in PF_3O.

TABLE

		PF_3	PF_3O	PH_3[a]	PH_3O[a]
Total energy (a.u.)		−639·1546	−714·0301	−342·4382	−417·3168
Atomic populations					
P	3*s*	2·22[b]	1·32	1·54	1·20
	$3p\sigma$	0·97	0·81	1·67	0·74
	$3p\pi$	0·88	1·20	1·56	1·62
	$3d_\sigma$	−0·26	−0·08	0·06	0·14
	$3d_\pi$	0·20	0·58	0·03	0·22
	Total	14·02	13·83	14·87	13·92
O	2*s*		1·77		1·84
	$2p_\sigma$		1·25		1·34
	$2p_\pi$		3·28		3·50
	Total		8·31		8·72
F	2*s*	1·89	1·90		
	2*p*	5·43	5·39		
	Total	9·32	9·29		
Overlap populations					
P–O	(σ)		0·483		0·586
P–O	(π)		0·784		0·646
P–O	(Total)		1·266		1·232
3*s*	2*s*		0·171		−0·097
$3p_\sigma$	2*s*		−0·102		0·007
$3d_\sigma$	2*s*		−0·250		0·025
$3p_\pi$	$2p_\pi$		0·354		0·438
$3d_\pi$	$2p_\pi$		0·430		0·190
3*s*	$2p_\sigma$		0·309		0·239
$3p_\sigma$	$2p_\sigma$		0·307		0·343
$3d_\sigma$	$2p_\sigma$		0·048		0·057
P–F	(Total)	0·566	0·722		
3*s*	2*s*	−0·006	0·111		
3*p*	2*s*	0·071	0·015		
3*d*	2*s*	−0·054	−0·073		
3*p*	2*p*	0·372	0·329		
3*d*	2*p*	0·197	0·152		
3*s*	2*p*	−0·017	0·186		

[a] From ref. 3.

[b] Six *d* functions (XX, XY, XZ, YY, YZ, ZZ) have been used in this calculation. This amounts to introducing one additional 3*s* function which contributes a small negative population. When this is taken into account, the 3*s* atomic population should become less than or equal to 2.

The total overlap population for the P–O dative bonding in PF_3O is 1·266, which is very close to the value of 1·232 obtained for PH_3O.[3] There is an appreciable σ-bonding (with an overlap population of 0·483) between the 3*s* and $3p_\sigma$ orbitals of phosphorus and the $2p_\sigma$ orbital of oxygen. However, the most important contribution to the P–O bonding comes from the π-bonding between the $3p_\pi$ and $3d_\pi$ orbitals of phosphorus and the $2p_\pi$ orbitals of oxygen. This π-bonding appears to be larger in the PF_3O molecule than in the PH_3O molecule, the opposite being true of the σ-bonding This can be easily rationalized on the basis of the electronegativity difference between the hydrogen and fluorine atoms: in the PF_3 molecule, the phosphorus atom brings a large positive charge (+0·98 *versus* +0·13 in PH_3) which makes it a poorer donor of σ-electrons and a better acceptor for the π-electrons.

Some insight into the nature of the co-ordinate bonding is also given by an examination of the charge transfer. The formal charge of the phosphorus atom is +0·98 in PF_3 and +1·17 in PF_3O (the corresponding values were +0·13 in PH_3 and +1·08 in PH_3O). This small variation indicates that the amount of π-charge-transfer from the oxygen atom to the phosphorus atom in PF_3O is nearly equal to the amount of σ-charge-transfer from the phosphorus atom to the oxygen atom. This is substantiated by an examination of the orbital populations: the σ-charge-transfer from phosphorus to oxygen is 0·88 e and the π-charge-transfer from oxygen to phosphorus amounts to 0·70 e. It is noticeable that the σ-charge-transfer towards oxygen is more important in PH_3O, about 1·2 e, with a π-back-donation from the oxygen of about 0·5 e.[3] This difference in the amount of σ-charge-transfer is also rationalized on the basis of the electronegativity difference between hydrogen and fluorine and on the basis of the difference in the formal charge of phosphorus in PH_3 and PF_3. As a result, the phosphorus atom has nearly the same formal charge in PH_3O and PF_3O while the formal charge of the oxygen atom is much smaller in PF_3O (0·3 e) than in PH_3O (0·7 e).

There is very little change in the fluorine charge and orbital populations when going from PF_3 to PF_3O.

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[1] L. S. Bartell, L. S. Su, and H. Yow, *Inorg. Chem.*, 1970, **9**, 1903.
[2] E. L. Wagner, *J. Amer. Chem. Soc.*, 1963, **85**, 161.
[3] J. Demuynck and A. Veillard, *Chem. Comm.*, 1970, 873.
[4] A. Veillard, *Theor. Chim. Acta*, 1968, **12**, 405.
[5] S. Huzinaga, *J. Chem. Phys.*, 1965, **42**, 1293.
[6] Y. Morino, K. Kutchitsu, and T. Moritani, *Inorg. Chem.*, 1969, **8**, 867.
[7] Q. Williams, J. Sheridan, and W. Gordy, *J. Chem. Phys.*, 1952, **20**, 164.
[8] R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833.
[9] P. J. Bassett, D. R. Lloyd, I. H. Hillier, and V. R. Saunders, *Chem. Phys. Letters*, 1970, **6**, 253.
[10] B. Roos and P. Siegbahn, *Theor. Chim. Acta*, 1970, **17**, 199.