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The Coordination Behavior of Acyclic Phosphites; a UV Photoelectron Spectroscopic Study

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Phosphite esters are employed extensively as ligands and, as such, are of great importance to the coordination chemist [1].

In a previous publication [2] the UV photoelectron spectrum (UPS) of the simplest phosphite, $(CH_3O)_3P$, was interpreted by analogy with that of $[(CH_3)_2N]_3P$. Like the latter compound, $(CH_3O)_3P$ exhibits four bands, I_1–I_4 (Figure 1), at low ionization energy (IE). Assuming a C_s skeletal symmetry for $(CH_3O)_3P$, peaks I_1 and I_3 were attributed to ionization of the oxygen lone pair molecular orbitals (MO's) while peaks I_2 and I_4 were assigned to mixed oxygen/phosphorus lone pair ionizations.

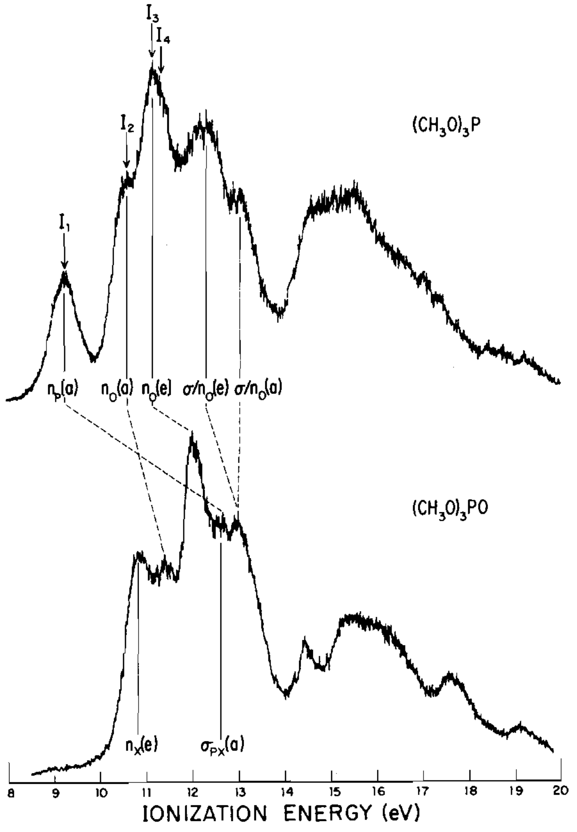

Figure 1. He(I) photoelectron spectra and assignments for $(CH_3O)_3P$ and $(CH_3O)_3PO$.

Our UPS studies have now been extended to a wider range of acyclic phosphites, $(CH_3O)_3As$, and to a variety of simple adducts of $(CH_3O)_3P$. Collectively, the data indicate that in acyclic phosphites the first ionization is due to electron ejection from the phosphorus lone pair MO.

In an electron diffraction study of $(CH_3O)_3P$ [3], it was impossible to delineate the precise ground state conformation. However, the most likely structures involved either C_3 or C_s skeletal symmetry. Assuming the C_3 model for $(CH_3O)_3P$, the lowest IE peak is assigned to the phosphorus lone pair MO, $n_P(a)$. On the basis of relative intensities the next three peaks are attributed to the ionization of the oxygen $2p_x$ (orthogonal to P–O–C framework) lone pair MO's, n_o, of symmetries a and e, respectively, the splitting of the latter being caused by the Jahn–Teller effect. The next two peaks arise from ionization of σ/n_o MO's. These MO's are formed by the overlap of an oxygen $2p_z$ orbital with P–O and C–O σ-bonding orbitals [4]. Combinations of the σ/n_o MO's, which retain some oxygen lone pair character, transform as a and e in C_3 symmetry; however, their energy sequencing is reversed compared to that of the n_o lone pair combinations.

In a UPS study [5] of the coordination of $(CH_3)_3P$ to oxygen or sulfur atoms it was demonstrated that the phosphorus lone pair MO, n_P, is stabilized by ~3–4 eV as it becomes the dative $P \rightarrow X$ sigma bond, σ_{PX}. Stabilization of other MO's occurred concomitantly because of charge redistributions within the adducts; however, these changes were overwhelmed by the shift of the phosphorus lone pair MO. Clearly, the first UPS peak of $(CH_3O)_3P$ corresponds to ionization of the $n_P(a)$ MO because it is shifted significantly more than any other peak in the spectrum when coordination to X takes place (see Figure 1 for X = O).

Each of the acceptors features a doubly degenerate lone pair MO, $n_X(e)$, at low IE and a singly degenerate MO, $n_X(a)$, comprising largely s-character, at appreciably higher IE. The acceptor $n_X(e)$ lone pair MO replaces the phosphorus lone pair MO as the lowest IE peak when coordination to $(CH_3O)_3P$ occurs.

The deduction that the first UPS peak of $(CH_3O)_3P$ corresponds to ionization of the phosphorus lone pair MO is confirmed by comparing the spectral data for $(CH_3O)_3P$ and $(CH_3O)_3As$ (Table I). Note that the first ionization for $(CH_3O)_3As$ occurs at higher energy than that of $(CH_3O)_3P$, but that the second and third ionizations occur at lower energy. These trends are anticipated because previous studies of related phosphines and arsines [6] have shown that although arsenic is less electronegative than phosphorus, the IE's of As lone pairs are larger than those of P lone pairs. This effect arises because of the smaller bond angles in arsines which, in turn, causes greater s character in the arsenic lone pair.

In a recent UPS study of aminophosphines [7] an attempt was made to assign the low IE bands by assuming that the nitrogen lone pair ionizations would be more sensitive to substituent changes than those of the phosphorus lone pairs. Our data for $(CH_3O)_3P$, $(CH_3CH_2O)_3P$, and $(CF_3CH_2O)_3P$ show that this approach is not valid generally since the changes in the phosphorus and oxygen lone pair IE's are essentially uniform.

Finally, we note that UPS data cannot be used to distinguish between the C_3 and C_s structures for $(CH_3O)_3P$ since the spectrum could be assigned on the basis of either geometry.

Acknowledgments

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TABLE I. UPS Data[a] and Assignments for Acyclic Phosphites, $(CH_3O)_3As$, and $(CH_3O)_3PX$; X = O, S, Se.

Compound	Phosphites and $(CH_3O)_3As$				
	$n_P(a)$ or $n_{As}(a)$	$n_O(a)$	$n_O(e)$	$\sigma/n_O(e)$	$\sigma/n_O(a)$
$(CH_3O)_3P$	9.22	10.54	11.11 11.3	12.3	13.0
$(CH_3O)_3As$	9.73	10.30	10.58 10.9	11.6	11.8
$(CH_3CH_2O)_3P$	8.92	10.23	10.80 11.0	11.8	–[b]
$(CF_3CH_2O)_3P$	10.37	11.71	12.3 12.5	13.2	13.9
	Adducts of $(CH_3O)_3P$				
	$n_X(e)$	$n_O(a)$	$n_O(e)$	$\sigma_{PX}(a)$	$\sigma/n_O(a + e)$
$(CH_3O)_3PO$	10.82	11.36	11.9 12.1	12.4	12.9
$(CH_3O)_3PS$	9.16	11.15	11.56 11.8	12.0	12.7
$(CH_3O)_3PSe$	8.67	10.93	11.5	–[b]	–[b]

[a]Vertical IE's in eV. [b]Overlapping peaks.

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