Valence-shell Photoionization Spectra of some Methyl Dihalogenophosphates

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He(I) photoelectron spectra of $PX_2O(OMe)$ (X = F, Cl, or Br), $PCl_2O(OEt)$, and $PCl_2(OMe)S$ are reported, and the peaks are assigned on the grounds of systematic comparisons throughout the investigated series, with the parent POX_3 (PSX_3) compounds, and with results from CNDO/2 calculations. Twelve out of the 19 (for the methyl compounds) valence orbitals can thus be identified, with characterizing contributions from specific bond orbitals or groups of bond orbitals, including (in approximate order of decreasing orbital energy) π_{PO} or π_{PS} $> \pi_X \sim \pi_{OMe} \sim \sigma_{CH}$ (higher levels) $\sim \sigma_{PO}$ or $\sigma_{PS} > \sigma_{PX} > \sigma_{CH}$ (lower levels) $\sim \sigma_{OC}$. Evidence is given for the inductive effect of halogens, and for some splitting and mixing effects related to the low symmetry of the investigated molecules.

ULTRAVIOLET photoelectron (p.e.) spectroscopy has been widely employed in the investigation of valence-shell orbital energies of many tetrahedral phosphorus compounds,[1-5] including phosphoryl halides POX_3 and their sulphur analogues,[6-8] where the relative simplicity of the spectra and high symmetry of the molecules allows a fairly detailed assignment of most of the relevant valence orbitals. We have made p.e. investigations of some *O*-methyl phosphates $PX_2O(OMe)$ (X = F, Cl, or Br) and $PCl_2(OMe)S$, with the aim of determining the effects of the lower symmetry with respect to POX_3 and PSX_3.

EXPERIMENTAL

Synthesis.—The compounds $PCl_2O(OMe)$, $PBr_2O(OMe)$, and $PCl_2(OMe)S$ were prepared from the corresponding (thio)phosphoryl halides and MeOH (1 : 1) and subsequent distillation, by the procedure described by Saunders *et al.*[9] for $PClO_2(OEt)$; the latter compound was also investigated for comparison. Methyl difluorophosphate was obtained from $PCl_2O(OMe)$ and NaF, again analogously to $PF_2O(OEt)$.[9] Elemental compositions and physical properties were in agreement with those reported by other workers who synthesized the substances by slightly different methods, *e.g.* $PCl_2O(OMe)$,[10-12] $PF_2O(OMe)$,[10] and $PCl_2(OMe)S$;[11-13] the vibrational spectrum of the latter compound was in better agreement with ref. 13 than 12, showing four well resolved CH stretching frequencies of CH_3 at 2 956, 2 899, 2 850, and 3 011 cm^{-1}. Methyl dibromophosphate formed colourless crystals, m.p. *ca.* 50 °C (b.p. 86—88 °C, 18 Torr) † which are very unstable, turning brown on decomposition with HBr evolution.

P.e. Spectra: Instrumentation.—Spectra were run on a Perkin-Elmer PS 18 instrument with He(I) radiation on vapours from a probe for liquid samples. Calibration was with Ar 3*p* and Xe 5*p* lines. Common impurities in the investigated samples were HX and MeX, which could be easily removed by repeated evacuation of the frozen samples. Spectral intensities were corrected for the dependence of ΔE on $E_{kin.}$ in the electrostatic-deflection analyzers. The effective spectral resolution was *ca.* 40 meV at an ionization potential (i.p.) of 15.76 eV. Spectra of the corresponding (thio)phosphoryl halides were run for comparison, and were in complete agreement with previous data.[6-8]

RESULTS

The He(I) p.e. spectra of the investigated compounds are reported in the Figure, together with the spectra of the corresponding (thio)phosphoryl halides. The spectra of the methyl phosphates bear a clear resemblance to those of the corresponding phosphoryl halides, so that it appears reasonable to attempt a correlation and to base assignments on the already known assignments of the p.e. bands of the (thio)phosphoryl halides.[6-8] In general, the p.e. spectra of the methyl dihalogenophosphates differed from those of the corresponding (thio)phosphoryl trihalides in: (*i*) a general shift of the peaks to lower i.p., corresponding to lower electronegativity of OMe with respect to X (this effect is larger for F); (*ii*) more diffuse and less resolved band contours, probably related to the lower symmetry of the phosphates which causes splitting of degenerate orbitals (the possible effect of configurational changes is discussed below); and (*iii*) the appearance of a few new bands, corresponding to the bond structure of the OMe group.

Analysis of the P.e. Spectra.—$PF_2O(OMe)$. Like the other methyl dihalogenophosphates, this 38-electron molecule should give rise to 19 distinct ionization levels from its closed-shell structure; five such levels, derived predominantly from 2*s* atomic orbitals of C, O, and F, are expected to be too low in energy to be ionized by the He(I) photons of 21.21 eV. Of the remaining 14 levels, 12 could be identified in the observed He(I) p.e. spectrum; reasonable considerations of correlation suggest that the orbital energies of the two missing orbitals lie just below the 21.21 eV limit.

An assignment of the observed peaks to the molecular orbitals (m.o.s) of the molecule can be attempted on the basis of correlation with the known, and assigned, spectrum

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† Throughout this paper: 1 Torr = (101 325/760) Pa; 1 eV ≈ 1.60 × 10^{-19} J.

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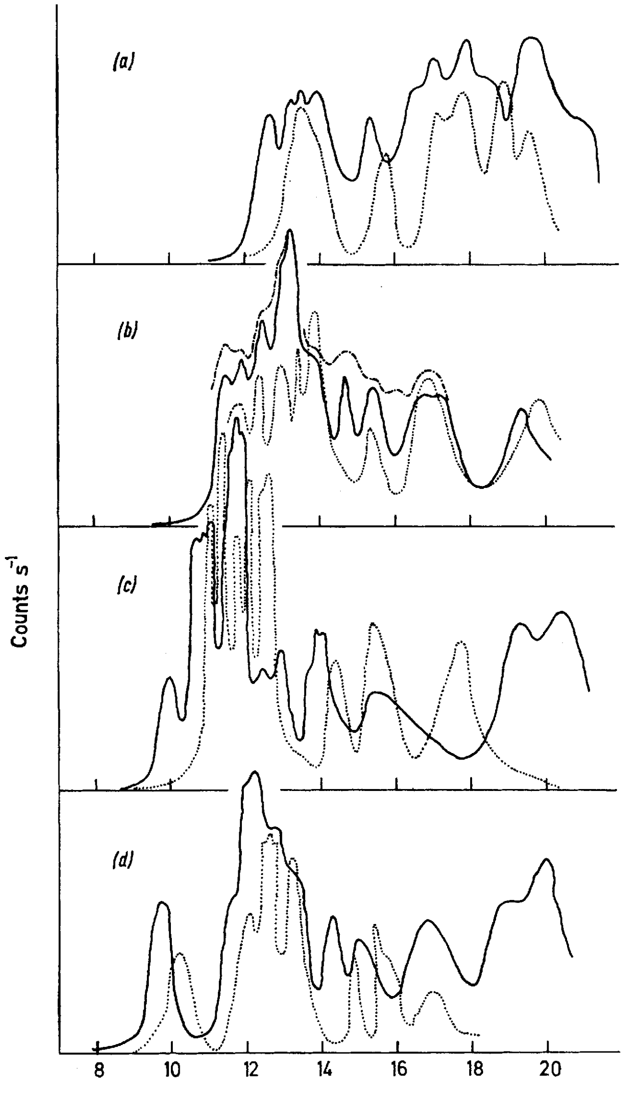
of POF_3, and of CNDO/2 calculations on both POF_3 and $PF_2O(OMe)$ (see Table). Comparison with the p.e. spectrum of POF_3 suggests a division into three regions. (*a*) The energy levels above the fluorine π orbitals contain the ionization of the σ and π electrons of the P=O group. In $PF_2O(OMe)$, these three levels are shifted by 1—2 eV to lower energies with respect to POF_3 ($\pi_{P=O}$ at 12.64 and 13.31 eV, $\sigma_{P=O}$ at 13.48 eV), and the CNDO/2 calculations suggest a more delocalized m.o. composition. In addition, two new bands appeared in this region at 13.90 and 15.34 eV, from levels characterized by contributions from the π lone pair of methoxo-oxygen (*cf. ca.* 11.2 eV in MeOH or *ca.* 12.6 in water) and of σ_{CH} (*cf. ca.* 15.4 eV in MeOH). (*b*) Orbitals composed predominantly of F lone pairs have energies between 17.09 and 19.61 eV in POF_3, and are nearly constant for other P–F compounds. In $PF_2O(OMe)$, four orbitals, mostly composed of π_F but with a mixture of other bond orbitals, were found between 16.56 and 18.67 eV. (*c*) The region of the lowest orbital energies contains levels predominantly derived from σ-bond orbitals [three in POF_3, five in $PF_2O(OMe)$].



He(I) p.e. spectra of (*a*) $PFO_2(OMe)$, (*b*) $PCl_2O(OMe)$, (*c*) $PBr_2O(OMe)$, and (*d*) $PCl_2(OMe)S$. The broken curves represent (*a*) POF_3,[8] (*b*) $POCl_3$,[6] (*c*) $POBr_3$,[6] and (*d*) $PSCl_3$,[6] (— · —) in (*b*), $PCl_2O(OEt)$

CNDO/2 calculations suggest that this group of orbitals can be further subdivided into two sub-groups, three upper levels (a double band at 19.73 and the peak at 21.02 eV) mainly related to the σ orbital formed by phosphorus (including admixtures with π_F), and a lower doublet mainly corresponding to σ_{CH} and σ_{CO}; the latter doublet was not seen in the He(I) spectrum of $PF_2O(OMe)$, but could be identified, at least partially, in the chloro- and bromo-analogues.

$PCl_2O(OMe)$. An approximate classification of the m.o.s corresponding to the observed photoionization levels can be achieved by comparison with $POCl_3$ and with $PF_2O(OMe)$, the main difference from the fluoro-compound being obviously the shift to considerably lower i.p.s of the orbitals mainly based on π(halogen); this results in complete overlap of the first and second spectral regions identified for $PF_2O(OMe)$, and in more extensive intermixing of bond orbitals in the actual m.o.s. Nevertheless, specific assignments can still be made if we believe CNDO/2 predictions of the m.o. eigenvectors, and can be supported by comparison of the trends in the observed spectral shapes. Thus, the first two levels at 11.50 and 12.02 eV are the only ones to contain a large contribution from $\pi_{P=O}$, even if π_{Cl} contributions are predominant and resemble fully the doublet at 11.89 eV of $POCl_3$. The peak at 12.51 eV has the highest predicted π_{Cl} contribution, and correlates with the purely π_{Cl} a_2 orbital of $POCl_3$ at 12.38 eV. The peak at 13.05 eV is largely $\sigma_{P=O}$, and corresponds to the band at 13.47 eV of $POCl_3$ and at 13.48 eV of $PF_2O(OMe)$. Three other bands with predominant π_{Cl} character were seen at 13.22, 13.78, and 15.44 eV, while the second component of the double band at 13.22 eV is predicted to contain a high percentage of π_{OC}, like the band at 13.20 eV for the fluoro-analogue, and the band at 14.76 eV has substantial σ_{CH} character (15.34 eV for the fluoro-compound).

It is to be noted that in the present series of compounds the composition of the levels characterized as $4a_1$ and $5a_1$ in POX_3 alternates; these orbitals contain, as bonding components, $\sigma_{P=O}$ and one of the π_X combinations. In POF_3 and $PF_2O(OMe)$ the upper level is predominantly $\sigma_{P=O}$ and the lower $4a_1$ is predominantly π_F, while in the chloro-compounds admixture is stronger and makes assignment in terms of P=O bonds less clear; eventually, the degree of intermixing could be reversed in the bromo-derivatives, where the upper orbitals are probably mainly π_{Br} (and $\pi_{P=O}$) in character while $\sigma_{P=O}$ character should be predominant in the lower a_1 orbital at 14.64 eV in $POBr_3$ and in the corresponding orbital at 13.90 eV in $PBr_2O(OMe)$. The region of lower orbital energies (σ_{PX}, σ_{CH}, and σ_{PO} in the fluoro-compound) contains a double band at 17.04 and a peak at 19.44 eV; calculated eigenvectors suggest less defined σ_{PO} character; in particular the band at 19.44 eV appears to be related more to σ_{OC} than to σ_{P-Cl} or $\sigma_{P=O}$.

$PCl_2O(OEt)$. This compound has a spectrum very similar, as expected, to the methyl derivative; minor shifts, of *ca.* 0.2—0.3 eV, are the usual effect of larger alkyl groups resulting in lower i.p. The splitting between the first two bands, with substantial π_{PO} character, is distinctly smaller in the ethyl (0.31 eV) than in the methyl compound (0.52 eV); this may be an effect of the different configurations, as discussed later. Additional ionizations, as expected on

Experimental vertical ionization potentials (in eV) [a]

	POF$_3$		PFO$_2$(OMe)			POCl$_3$		PCl$_2$O-(OEt)	PCl$_2$O(OMe)		PSCl$_3$		PCl$_2$(OMe)S		POBr$_3$		PBr$_2$O(OMe)	
		Squared eigen-vectors [b]		Squared eigen-vectors [b]			Squared eigen-vectors [b]			Squared eigen-vectors [b]		Squared eigen-vectors [b]		Squared eigen-vectors [b]		Assign-ment		Assign-ment
πP=O, πP=S	13.52 (17.68)	70 A, 21 C	12.64 (15.64)	52 A, 31 D		11.89 (14.58)	30, A, 68 C	11.42	11.50 (14.24)	30 A, 64 C	10.11 (12.79)	49 A, 44 C	9.85 (12.44)	49 A, 42 C(E)	11.02		9.97	πP=O
	13.52 (17.68)	70 A, 21 C	13.31 (16.07)	60 A, 12 C, 10 F		11.89 (14.58)	30 A, 68 C	11.73	12.02 (14.68)	39 A(B), 60 C	10.11 (12.79)	49 A, 44 C	9.85 (12.77)	60 A, 26 C	11.02		10.65	
σP=O	15.68 (17.74)	81 B	13.48 (16.39)	77 B(A) 12 C	πX	12.38 (14.85)	100 C	12.38	12.51 (14.80)	80 C, 14 D	12.00 (14.33)	100 C	11.78 (14.26)	86 C, 11 D	11.38		10.82	πX
πOMe			13.90 (17.56)	43 D, 28 F		13.47 (15.81)	54 B, 44 C(E)	12.65	13.05 (15.78)	64 B(A) 20 C	12.40 (14.38)	54 B, 37 C	12.09 (14.31)	69 B, 20 C			11.07	+
σCH			15.34 (18.37)	39 F, 19 D, 29 B	πX	12.98 (16.26)	73 C(E)	13.01	13.22 (16.17)	81 C(E) 12 D	12.54 (15.59)	94 C			11.74	πX	11.70	πP=O
	17.09 (21.10)	100 C				13.09 (16.26)	10 A				12.66 (15.59)	94 C			11.74	+	11.87	
	17.68 (22.10)	88 C	16.56 (20.15	62 C, 27 G			73 C(E), 10 A	13.01	13.22 (14.69)	39 D, 28 C, 19 F			12.33 (15.56)	77 C, 11 D	12.43	πP=O	12.63	πOMe
πX	17.68 (22.10)	88 C	17.00 (20.87)	68 C, 11 (A, B)	πX	13.85 (18.58)	78 C(E), 17 A	13.93	13.72 (17.46)	44 C, 27 A, 14 F	13.39 (17.89)	91 C(E)	12.75 (16.09)	37 A, 34 C, 19 F	12.66			
	18.83 (24.00)	75 C(E),	17.74 (21.53)	66 C(E), 23G		13.85 (18.58)	78 C(E) 17 A				13.39 (17.89)	91 C(E)	12.33 (16.64)	68 C, 13 A, 13 F,	12.66			
	18.83 (24.00)	75C (E) 10 A	18.67 (22.94)	72 C(E) 10 A				14.48	14.76 (17.67)	41 F, 23 D, 33 C			14.31 (17.18)	21 A, 35 F, 28 C			13.05	σCH
								14.48										
	19.61 (24.51)	81 C(E), 11 B																
			19.73 (23.28)	77 E(C) 10 B		15.35 (18.93)	59 C, 34 B	15.48	15.44 (18.62)	66 C(E) 18 D	14.76 (18.15)	66 C(E) 26 B	14.95 (18.15)	54 (C,E) 21 (A,B)	14.64	σP=O	13.90	σP=O
σPX	20.82 (24.87)	84 E(C)						16.24										
	20.82 (24.87)	84 E(C)	19.73 (23.80)	89 (E,C)		16.53 (19.60)	64 E(C), 30 A	17.28	17.04 (19.19)	48 A, 42 E(C)	15.84 (19.09)	65 E, 18 C, 12 A	16.80 (18.62)	64 E(C), 16 A	15.39	σPX	14.17	σPX
(πX, σPOC)	23.40 (25.34)	92 E	21.02 (23.97)	57 E, 35 G		16.53 (19.60)	64 E(C), 30 A	17.28	17.04 (20.04)	66 (E,C) 18 B	15.84 (19.09)	65 E, 18 C, 12 A	16.80 (19.06)	48 E(C), 29 B(A)	15.39		15.37	+
						19.55 (21.67)	87 E(C), 12 B	19.17	19.44 (22.20)	70 G, 17 (A,B)	18.70 (20.85)	77 E, 18 B	18.79 (22.0)	78 G, 14 B			19.34	σPOC
σCH			(25.67)	45 F, 33 G				20.84	(24.93)	53 F, 34 D			20.27 (24.59)	52 F, 32 D			20.57	σCH
σOC			(26.23)	41 F, 36 G					(25.36)	48 F, 28 G(D)			(24.99)	43 F, 30 (D,G				σOC
a	(3.55)		(2.92)			(3.10)			(3.01)		(2.30)		(2.02)					
b	(1.01)		(1.03)			(1.01)			(0.99)		(1.02)		(1.06)					

[a] Calculated (CNDO/2) eigenvalues (ϵ in eV) are given in parentheses; *a* and *b* are least-square coefficients of the linear regression i.p. = $a + b\epsilon$. [b] Approximate bonding-orbital composition of the calculated (CNDO/2) m.o.s, expressed through the squared eigenvectors (main contributions). A = $\pi_{P=O}$ or $\pi_{P=S}$; B = $\sigma_{P=O}$ or $\sigma_{P=S}$; C = π_X (X = F, Cl, or Br); D = π_{OMe}; E = σ_{PX}; F = σ_{CH}; G = σ_{POC}.

replacement of Me by Et, are evident in the doubling of intensity of the band at 14.48 eV, thus confirming the predominant σ_{CH} character of the corresponding peak at 14.76 eV of the methyl derivative, and in a new band at 16.24 eV.

$PCl_2(OMe)S$. The main feature of the spectrum is the marked shift to lower i.p.s of the orbitals based on the S atom. Thus we have $\pi_{P=S}$ at 9.85 and σ_{PS} at 12.09 eV, only slightly lower than for $PSCl_3$. The π_{Cl} orbitals gave peaks at 11.78, 12.33, 13.33, and 14.95 eV, with intermediate peaks at 12.75 eV as mainly π_{O-CH_3} and at 14.31 eV as σ_{CH} [*cf.* 13.22 and 14.76 eV for $PCl_2O(OMe)$]. The double band at 16.80 eV probably corresponds to other σ_P bonds, while the bands at 18.79 and 20.27 eV account for two of the residual three σ bonds.

$PBr_2O(OMe)$. The p.e. spectrum is different from the previous ones in having a particular large shift to low i.p.s of the first π_{PO} band (9.97 eV), followed by a narrow group of five orbitals which, on the grounds of their energy and shape (which indicates spin–orbit splitting), are assigned as mainly formed from Br. The six bands between 9.97 and 11.87 eV therefore account for all the π orbitals of Br and of P=O, and the bands at 12.63 and 13.05 eV, clearly related to π_{OCH_3} and σ_{CH} respectively through the shapes and correlations with analogous bands of the previous compounds, are at higher i.p.s than the halogen orbitals, instead of being mixed with them as in the chloro-compound or lower in i.p. as in the fluoro-compound. Furthermore the band at 13.90 eV, which correlates with $4a_1$ of POX_3, appears to be mainly $\sigma_{P=O}$, and is thus closer to the other σ_P ionizations at 14.17 and 15.37 eV. The two bands at 19.34 and 20.57 eV probably contain ionizations from the fourth σ_P bond (not reported [6] for $POBr_3$), and from one of the σ_{OMe} bonding pairs.

DISCUSSION

The utility of u.v. p.e. spectroscopy in the elucidation of molecular electronic structures lies mainly in the quantitative determinations of m.o. energies (within the limitations of Koopman's theorem, and provided reliable assignments can be achieved for all the observed levels), and in the possibility of analyzing m.o. energies in terms of bond orbitals and of explaining trends due to structural effects, *e.g.* the presence of substituent groups or symmetry changes. As to the first point, the present compounds probably represent a limiting case, since the low symmetry and the presence of several neighbouring and overlapping p.e. bands makes a one-to-one assignment difficult and uncertain. The spectrum of an individual compound of the investigated group, taken in isolation, would offer only limited possibilities for detailed assignments; however, a plausible and fairly detailed assignment scheme can be deduced from a comparison of the p.e. spectra of all the compounds in the series and of other related substances, aided by suggestions and checks from approximate CNDO/2 calculations. It is also evident from empirical assignment criteria, and again supported by CNDO/2 predictions, that most m.o.s in our compounds have a complicated, thoroughly intermixed, composition, so that no simple analysis in terms of bond orbitals is possible, and bands clearly correlated in the spectra of analogous compounds often correspond to large changes in the eigenvector composition of the levels involved. Nevertheless, some structural trends are evident in our spectra such as: (*a*) the decreasing i.p.s of the halogen π pairs with increasing atomic number; (*b*) the inductive effect of halogens on the i.p.s of bond orbitals of the other atoms; (*c*) the marked decrease in i.p. of orbitals containing sulphur contributions as opposed to oxygen; (*d*) the identification of orbital levels containing relevant contributions of π_O of the alkoxo-groups from 12.6 to 13.9 eV, and of δ_{CH} from 13.0 to 15.3 eV, subject to the inductive effect of the halogens.

An interesting point is the actual amount of the splitting of '*e*' orbitals of POX_3 on passing to the lower symmetry of methyl dihalogenophosphates, particularly for the π pairs of P=O (P=S) which have the lowest i.p.s. Experimentally, this splitting ranges from negligible in $PCl_2(OMe)S$ where the first p.e. band is unsplit and practically as wide as in $PSCl_3$, to a few tenths of an electron volt in $PCl_2O(OMe)$ and $PF_2O(OMe)$, to presumably larger values in $PBr_2O(OMe)$, where the shapes of the bands clearly suggest that the first component of $\pi_{P=O}$ is at 9.97 eV while the second one is dispersed among the group of orbitals between 10.65 and 11.87 eV predominantly based on bromine. The larger splitting in the bromo-compound is also responsible for the particularly large decrease in the first i.p. with respect to the corresponding POX_3 molecules, and of the fact that while an oxygen-based orbital is higher than bromine-based orbitals in $PBr_2O(OMe)$, these orbitals are mixed and cannot be distinguished in $POBr_3$.[6] Such different splitting can probably be related to the different configurations of the OMe group with respect to the rest of the molecule. Experimental data on such configurations are difficult to obtain and only scarcely reported in the literature. N.m.r. spectra of $PF_2O(OMe)$ were reported by Roesky and Loker [10] and by Reddy and Schmutzler,[14] and conformers of $PX_2O(OMe)$ with C in the OPO or in an XPO plane were suggested by Christol and Christol [12] from i.r. data. Our CNDO/2 calculations suggest slightly different values of the orbital energies for the different configurations; although the accuracy of the method is too low to enable reliable quantitative predictions to be made, it appears that the splitting should be at a minimum for a *trans* configuration (180° between the POC and OPO planes), still small (up to 0.5 eV) for intermediate angles, and larger (up to 1 eV) for a *cis* configuration; the latter possibility is also a position of less negative total energy, but could be enforced by steric constraints such as are likely with the bulky Br atom or by the electrostatic interactions with oxygen.[12] Thus, since conformational changes are slow on the p.e. time scale, the observed bandwidths of the p.e. peaks could be due also to superimposition of easily interchanged configurations of $PX_2O(OR)$ molecules in the gas phase.

[6/1472 *Received, 27th July,* 1976]

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