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Bond ionization energies: thiophosphoryl compounds

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Chimica. — *Bond ionization energies: thiophosphoryl compounds* (*). Nota di MARCO V. ANDREOCCI, CARLA CAULETTI (**) e CLAUDIO FURLANI, presentata (***) dal Socio G. SARTORI.

RIASSUNTO. — Negli spettri fotoelettronici (p.e.) indotti da radiazione ultra-violetta di serie omologhe di composti, si trovano bande in ben definite regioni di energia, che possono essere assegnate empiricamente a ionizzazione di legami specifici o di coppie solitarie di elettroni.

L'effetto dell'intorno chimico sulle energie di ionizzazione si esplica in piccoli spostamenti, che hanno una dipendenza approssimativamente lineare dall'ettronegatività di atomi o gruppi vicini.

La discussione riguarda alcuni legami tipici e gruppi atomici appartenenti a composti di fosforo, la maggior parte dei quali contiene il gruppo funzionale — P = S.

I dati spettroscopici p.e. delle molecole $[(CH_3)_2 PS]_2$ e $(CH_3)_2$ — P (S) Br e la loro analisi sono originali.

Photoelectron (p.e.) spectra of molecular systems taken under far ultraviolet irradiation (UPS) afford a simple and remarkably extensive experimental picture of the energy levels of molecular orbitals, often extended to the whole valence shell, and subject, as the only restriction of validity, to the assumption of identity between experimental values of ionization energies and the absolute values of calculated m.o.-s.c.f. eigenvalues (Koopmans' theorem [1]). A considerable amount of data, not otherwise accessible, becomes thus available for correlations with structural properties of molecules both by comparison with calculated m.o.-.s.c.f. eigenvalues, and through the evidence of empirical regularities in the p.e. spectra of structurally related molecules. While the former interpretation of structural effects is far more common, the latter and more empirical type of correlations, arising from the evident fact that p.e. bands appear and are located in restricted energy regions whenever a given atomic group is present in a series of molecules, with slight energy shifts depending on the chemical constitution of the intramolecular environment, is less commonly considered, but undoubtedly represents a useful approach and deserves more careful consideration.

It is from this angle of empirical structural correlation that we want to discuss a representative case of a group of substances whose p.e. spectra show evident regularities, that of thiophosphoryl compounds, for which many

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p.e. data are available from previous reports in the literature [2, 3] and from recent published and unpublished investigations in our laboratory [4, 5, 6]. All these substances contain the $>P^{+}-S^{-}$ group, and some p.e. data can be related in a particularly evident manner to the electronic structure of the thiophosphoryl group and to the effect of its substituents; we shall extend the results obtained from this particular group of substances in order to attempt a possible generalization, i.e. the definition of " bond ionization energies " or " group ionization energies ", and a discussion of its applicability. Clearly, the latter concepts would be untenable from a rigorous theoretical point of view, since p.e. ionization peaks come from molecular orbitals, whose energies vary, along series of analogous or related compounds, both by effect of the potential generated by neighbouring atoms, and by changes in eigenvector composition; therefore, the two effects cannot be sorted out from one experimentally observed shift. However, empirical correlations do not consider such limitations explicitly.

TABLE I

Bond ionization energies of the sulfur lone pairs (n_S) and of the σ_{SP} bonding electron pair in thiophosphoryl derivatives (experimental vertical i.e. in eV)

$R_1R_2R_3PS$	n_S	σ_{SP}	Ref.	$\Sigma[x(R_i)-x(P)]$ (Pauling)	$\Sigma[x(R_i)-x(P)]$ (Pauling mod) (*)
$[(CH_3)_2PS]_2$	8.66 (a)	11.31 (b)	(c) ,6	0.90	0.90
$(CH_3)_3PS$	8.53	11.35	2	1.35	1.35
$(CH_3)_2P(S)Br$	9.10	12.00	(c)	1.70	1.70
Br_3PS	9.89 (d)	11.83 (e)	3	2.40	2.40
Cl_3PS	10.11 (d)	12.40 (e)	3	3.00	3.00
$(CH_3O)Cl_2PS$	9.85	12.09	4	3.35	2.65
$F_2P(S)SH$	10.47	11.52 13.50	7	3.95	3.95
F_3PS	11.10	14.47	5	5.25	5.25

(*) Electronegativity values x (Pauling's scale) modified by assuming $x\,(\underline{O}CH)_3 = 2.80$ (see text).

(a) ... average of a 1 : 2 : 1 multiplet of n_S signals [6] at 8.06,8.65 and 9.27 eV.

(b) ... highest and only distinct component of a group of levels sharing partial σ_{PS} character (see Table II).

(c) ... this work.

(d) ... highest e level, containing n_S mixed with n (halogen).

(e) ... a_1 level (mixed with n (halogen)) within the multiplet of n (halogen) levels.

Table I lists data on the p.e. bands of several thiophosphoryl derivatives, which we assign to the $>P^{+}-S^{-}$ group itself, and specifically to the n_S lone pair (π-type), and to the σ_{SP} bond. Little or no theoretical aid is needed for the gross assignments to n_S and σ_{SP} contained in Table I; if we choose not to resort to theoretical calculations, a preliminary but often sufficient criterion can be based on the rough, provocative assumption that chemical bonds are just a small perturbation superimposed on atomic electronic states, so that molecular energies are in any case expected close to the energies of the main parent atomic orbitals, with minor shifts according to the molecular function taken by the involved electron pairs, leading to the energy order antibonding > nonbonding or lone pair > π-bonding > σ-bonding. This simple criterion tells us that sulfur has the lowest atomic ionization energies of valence orbitals of all elements involved in the compounds of Table I (except phosphorus, whose valence shell is however wholly engaged in σ bonds), so that the two p.e. peaks of lowest i.e. should be assigned to the couple of lone pairs of sulfur (degenerate, or nearly so), respectively to the σ_{PS} bonding pair. This assignment is further supported by the intensity ratio of both bands tending constantly to 2 : 1. Examples of this situation are presented by the

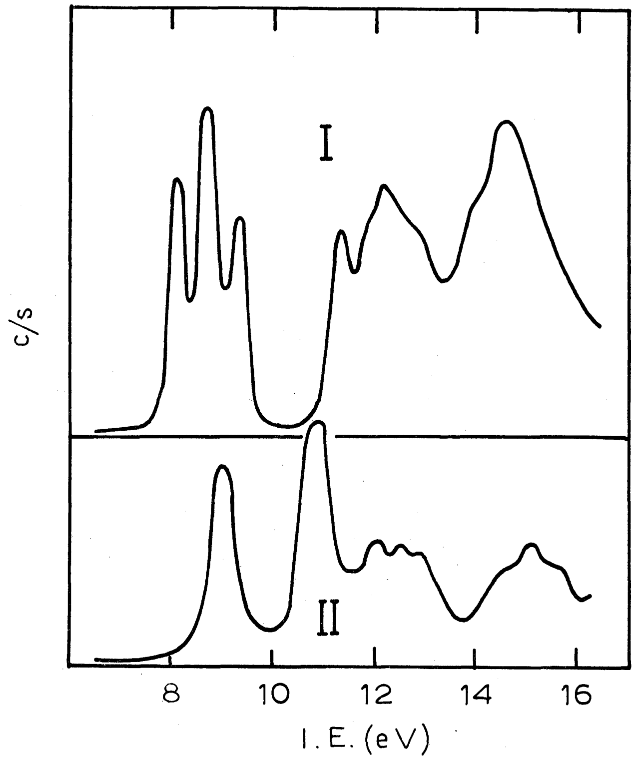

Fig. 1. – He (I) photoelectron spectra of two thiophosphoryl derivatives.

TABLE II

P.e. spectra of two thiophosphoryl derivatives: trans-$[(CH_3)_2PS]_2$ *and* $(CH_3)_2P(S)Br$. *Experimental data (vertical ionization energies) and comparison with CNDO/2 calculated m.o. energies (in* eV) $^{(*)}$

trans-$[(CH_3)_2PS]_2$		$(CH_3)_3PS$		$(CH_3)_2P(S)Br$	$(CH_3)_2P(S)Cl$	calcd. main eigenvalues
Exp. $^{(a)}$	Calcd.	Exp. $^{(b)}$	Calcd.	Exp. $^{(c)}$	Calcd.	
8.06 $^{(d)}$	9.62 $^{(d)}$					
8.65 $^{(e)}$	10.51 $^{(e)}$ 10.60 $^{(e)}$	8.53	12.41	9.10	12.58 12.68	n_S (π_S)
9.27 $^{(f)}$	11.15 $^{(f)}$					
				10.82		n_{Br} $^{(g)}$
11.31 $^{(h)}$	13.15 $^{(h)}$					
(11.80)	14.79 $^{(h)}$	11.35	13.78	12.00	13.85	σ_{PS}
(12.08)	15.15 $^{(h)}$					
					14.72	n_{Cl}
12.08	15.30	12.40	15.55	12.35	15.80 $^{(i)}$	σ_{PC} ("e")
(13.0)	16.57			(13.25)	16.57 $^{(i)}$	
13.90sh	19.05	$\gtrsim 14$	18.26	14.4	20.10	σ_{CH}
14.7	20.13		.....	15.0	20.26	
.....	......			15.7	.....	

(*) Since our CNDO/2 method is not adequately parametrized for Br, comparison with the experimental data for $(CH_3)_2P(S)Br$ is made with calculations carried out for the analogous molecules $(CH_3)_2P(S)Cl$ and $(CH_3)_3PS$.

(*a*) ... this work and Ref. [6].

(*b*) ... from Ref. [2].

(*c*) ... this work.

(*d*) ... antibonding combination of sulfur lone pairs in the SPPS plane, with small admixture of σ_{PP} bonding.

(*e*) ... sulfur lone pairs $\perp$ to the SPPS plane.

(*f*) ... bonding combination of sulfur lone pairs in the SPPS plane, with small admixture of σ_{PP} antibonding.

(*g*) ... empirical assignment (cf. 11.68–12.01 eV in HBr [8] or 10.54–10.85 eV in CH_3Br[9]).

(*h*) ... a series of three levels mainly containing σ_{PS}, with admixture of σ_{PP}; experimentally, only the peak at 11.31 eV is evident as a separate component.

(*i*) ... mixed composition $\sigma_{PC} + \sigma_{PCl}$.

p.e. spectra of SPF_3 [5], $[(CH_3)_2PS]_2$ and $(CH_3)_2P(S)Br$, measured in our laboratory and not reported previously in detail (1) (fig. 1 and Table II); CNDO/2 calculations [13] lend additional support to the assignment and are therefore reported in Table II, although their use does not actually belong to the approach developed here.

From the data collected in Table I, the group ionization energy of the sulfur lone pairs in thiophosphoryl compounds ranges between 8.53 eV in $(CH_3)_3PS$ [2] and 11.10 eV in SPF_3 [5], while the σ_{PS} bonds in the same compounds are comprised between 11.34 and 14.47 eV. Shifts between these interval limits depend on the nature of the environment, so e.g. the plot of fig. 2 suggests a nearly linear and additive dependence on the electronegativities of the other three groups bonded to P. The effect of substituents is slightly

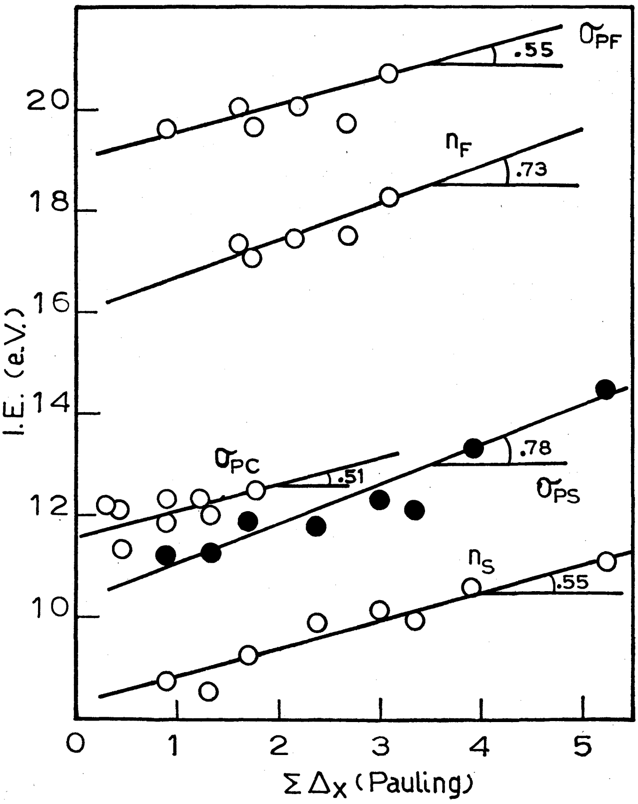

Fig. 2. – Bond ionization energies of the S and F lone pairs, and of the σ_{PF}, σ_{PS} and σ_{PC} bonds in phosphorus compounds containing $\rangle P = S$, $\rangle PF_2$ or $\rangle P(CH_3)_2$ groups, as a function of the electronegativity of substituents (Pauling's scale) (see Tables I, III and IV).

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(1) While our present work was being completed, two papers by S. Elbel and H. Tom Dieck appeared in « J. Chem. Soc. » (Daldon) 1757 and 1762 (1976), reporting p.e. data on SPF_3 and $(CH_3)_2P(S)Br$, in substantial agreement with our present data.

TABLE III

Bond ionization energies of the σ_{PC} bonding electron pairs in dimethylphosphorus derivatives (experimental vertical ionization energies, in eV)

$(CH_3)_2PR_1R_2$	σ_{PC} [(a)]	Ref.	$\Sigma(x(R_i)-x(P)]$ (Pauling)	$\Sigma[x(R_i)-x(P)]$ (Pauling,mod.)[(b)]
$(CH_3)_3P\cdot BH_3$	12.15	2	0.30	1.10
$(CH_3)_3P$	11.30	10	0.45	0.45
$[(CH_3)_2PS]_2$	12.08	(d)	0.45	0.45
$(CH_3)_3P = CH_2$	11.9	2	0.90	0.90
$(CH_3)_3PS$	12.40	2	0.90	0.90
$(CH_3)_2P(S)Br$	12.35	(d)	1.25	1.25
$(CH_3)_3P = NH$	12.0 [(c)]	2	1.35	1.35
$(CH_3)_3PO$	12.5 [(c)]	2	1.80	1.80

(*a*) ... σ_{PC} bonds formed mainly by phosphorus 3*p* (not *s*) orbitals; for trimethylphosporus derivatives, this corresponds to the "*e*" component of σ_{PC}.

(*b*) ... electronegativity values (Pauling's scale) modified by assuming $X(-\underline{B}H_3) = 2.80$ (see text).

(*c*) ... mixed composition $\sigma_{PC} + \sigma_{PN}$ (or σ_{PO}).

(*d*) ... this work.

TABLE IV

Bond ionization energies of fluorine-based molecular orbitals in difluorophosphine derivatives (experimental vertical ionization energies, in eV)

$F_2PR_1R_2$	n_F [(a)]	σ_{PF} [(b)]	Ref.	$\Sigma[x(R_i)-x(P)]$ (Pauling)	$\Sigma[x(R_i)-x(P)]$ (Pauling mod.)
$F_2P(S)SH$	17.8	19.6	7	0.90	0.90
$F_3P\cdot BH_3$	17.33	20.0	11	1.60	2.40
F_3P	17.00	19.6	12	1.75	1.75
F_3PS	17.46	20.05	5	2.20	2.20
$F_2P(OCH_3)O$	17.49	19.73	4	2.70	2.00
F_3PO	18.29	20.82	12	3.10	3.10

(*a*) ... average of the 4 (or 6) highest levels in the fluorine p.e. spectral region, containing mainly n_F.

(*b*) ... σ_{PF} bonds formed mainly by phosphorus 3*p* (not *s*) orbitals; for trifluorophosphoshine derivatives, this corresponds to the "*e*" component of the σ_{PF} set.

(*c*) ... electronegativity values x (Pauling's scale) modified by assuming $x(\underline{O}CH_3) = 2.80$ and $x(-BH_3) = 2.80$ (see text).

greater on the ionization energies of σ_{PS}, and smaller on the sulfur lone pairs, a fact clearly related to the closer spatial proximity of the σ_{PS} electron distribution to the perturbing groups. This case exemplifies the fact that a change in the chemical composition of the environment exerts the same types of shift, but with some quantitative difference, on the ionization energies of different bonds or groups. Thus, Tables III and IV and the corresponding plots in fig. 2 show that an analogous near-constancy of ionization energies with minor constitutive shifts can be recognized also for other groups or bonds, such as n_F and σ_{PF} in phosphorus-fluorine compounds and σ_{PC} in compounds containing the — P $(CH_3)_2$ moiety, with an overall variation range, hence an intrinsic sensitivity of the involved groups or bonds to substituent effects, corresponding to slopes of the order of 0.5 to 0.9 eV per unit of electronegativity difference. Such slope values are consistent with a perturbative first-order effect exerted by the first bond-neighbours; it is to be recalled that direct, or zero order effects arising from substitution of the atom(s) directly involved in the ionization process along series of homologous compounds, should tend to a slope of 3.15 eV per electronegativity unit, i.e. one order of

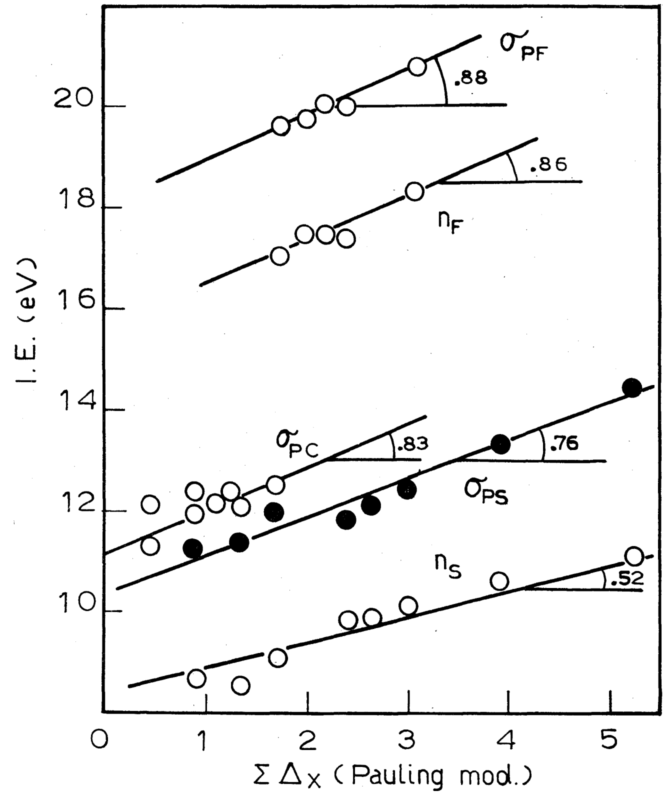

Fig. 3. – Bond ionization energies for the same groups and compounds as in fig. 2, but with modified Pauling electronegativity scale (see text and Tables I, III and IV).

magnitude larger than observed in our perturbative correlations (3.15 is the proportionality factor between eV and x units in the electronegativity scales where x is defined as linearly dependent on the energy, such as Mulliken's). Indeed, in those cases where p.e. data are available for the same orbital type in different atoms along homologous series (see Table V and fig. 4), the observed slopes, although not accurate because of the small amount of data, are of the order of 2–3 eV (2) i.e. of the order of the expected limiting zero-order Mulliken slope of 3 : 15 eV (that the actual slopes are smaller than the limiting value is obviously due to the fact that involved molecular orbitals are not completely localized on the atoms concerned).

TABLE V

Ionization energies of π-type lone pairs of different elements in homologous series (experimental vertical ionization energies, in eV)

Compound	Ionized element (π-type lone pairs)	X (Mulliken)	X(Allred–Rochow)	i.e.	Ref.
Br_3PO	Br	2.76	2.74	11.83 (a)	3
Cl_3PO	Cl	3.00	2.83	13.43 (b)	3
F_3PO	F	3.91	4.10	18.29 (c)	12
F_3PS	S	2.41	2.44	11.10	5
F_3PO	O	3.17	3.50	13.52	12
$(CH_3)_3P = CH_2$	C	2.63	2.50	6.83	2
$(CH_3)_3P = NH$	N	2.33	3.07	8.19	2
$(CH_3)_3PS$	S	2.41	2.44	8.53	2
$(CH_3)_3PO$	O	3.17	3.50	9.76	2

(*a*) ... average of the energies of the eight highest states. ($5\,a_1 + 1\,a_2 + 3\,e + 4e + 5e$), including $6\,n_{Br} + 2\,n_O$.

(*b*) ... weighted average of the energies of the states containing the six n_{Cl} pairs ($\frac{1}{2}(4\,a_1 + 5\,a_1) + 1\,a_2 + 3\,e + 4\,e$).

(*c*) ... average of the energies of the six states of predominant n_F character ($4\,a_1 + 1\,a_2 + 3\,e + 4\,e$).

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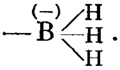
(2) The experimental slope for the OPX_3 series (4.4 with Allred–Rochow x values, or 5.5 with Mulliken's values) results from both zero- and first-order effects. The latter, arising from the mutual influence between X atoms, can be estimated as $2 \times 0.7\,[(x\,(X) - x\,(P)]$, i.e. a contribution of 1.6–1.8 to the total observed slope. This leaves a net zero-order slope of about 2.5 (Allred–Rochow) or 3.8 (Mulliken).

First-order perturbative correlations, such as those of fig. 2, hold approximately in the same way for any scale of atomic electronegativities; rather, an improvement in linearity of correlation can be achieved by introducing modified electronegativity values assigned to substituent groups as a whole, instead of the elemental electronegativity of the atoms directly bonded. Fig. 3 shows how linearity of correlation improves over the analogous plots of fig. 2 if we adopt group electronegativity values (Pauling's scale) of 2.80 for $—OCH_3$ (instead of 3.50 for o), and of 2.80 for $—BH_3$ (instead of 2.0 for B); such variations can be easily rationalised, at least qualitatively, by the possible behaviour of methoxyl groups as $=\overset{+}{O}—CH_3$, and by the strict localization of one negative charge unit in the relatively rigid system of σ bonds of B in



$—\overset{(-)}{B}H_3$.

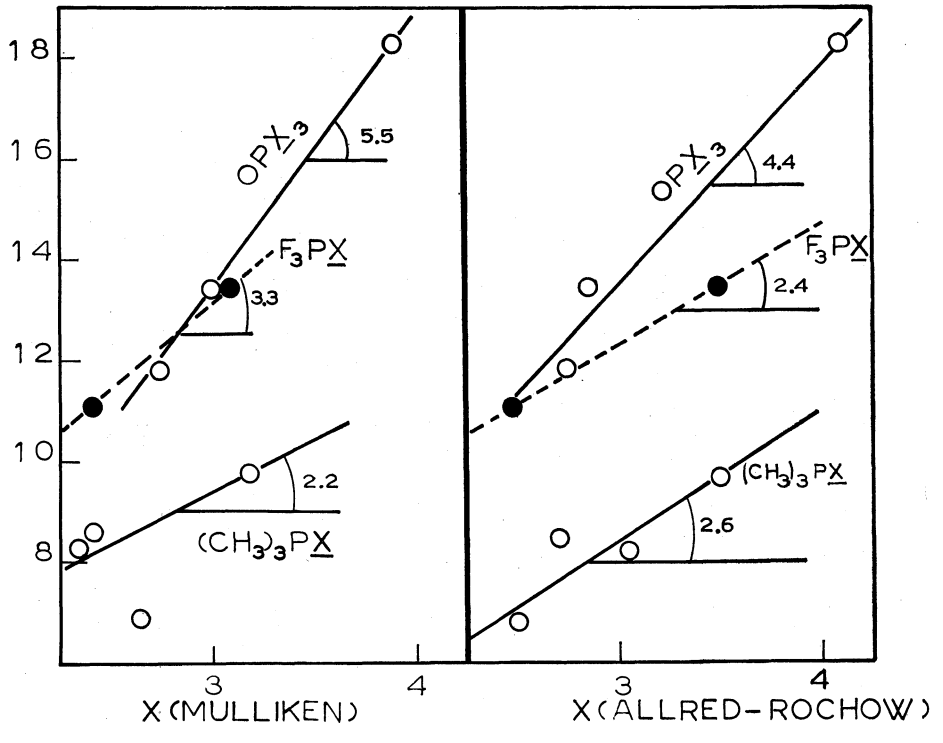


Fig. 4. – Ionization energies of π-type lone pairs in homologous series of phosphorus compounds (see Table V), as a function of the electronegativity x of the ionized atoms.

In conclusion, a survey of experimental p.e. data confirms that empirical regularities are well evident and generally occurring, so that, at least as far as can be judged from the examples discussed here, the definition of bond (or group) ionization energies can be regarded as well justified and practically meaningful. This suggests a future possibility of establishing a chart of bond and group ionization energies for all atomic grouping occurring in molecular structures, where two parameters can be defined for each atomic grouping: (i) a mean ionization energy (or ionization energy of a reference state), reflecting the more or less easy ionization, or more or less easy involvement in chemical changes, and (ii) a slope factor, reflecting the sensitivity or ease of perturbation of each atomic grouping by its chemical environment. The interpretation of both kinds of parameters in terms of theoretical calculations of molecular structures will probably be all but simple and will require much effort in clarifying, but the empirical validity of such parameters seems already established, and represents, even without the support of theoretical calculations, a valuable achievement in the field of electronic molecular structures, which is made possible by the use of UV photoelectron spectroscopy.

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