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X-ray Photoelectron Studies of some Phosphates

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The X-ray photoelectron spectra of sodium, potassium, magnesium and calcium salts of ortho-, pyro- and triphosphate were measured. The O (1s) electron spectra of the different salts showed the presence of only one kind of oxygen except in the case of acid phosphates where two types of oxygen were distinguished to account for the presence of protonated and non-protonated oxygen sites. The values of the binding energies measured were correlated with the calculated charges by applying an iterative Pauling's method. The chemical shift in P (2p) electron binding energies have been empirically correlated with the common logarithm of stability constants.

Introduction

Knowledge of the interactions between mono- and divalent metal ions and either simple ortho-, pyro-, and triphosphate anions or their derivatives with nucleotide bases is pertinent to the study of many natural systems. Of obvious interest is the interaction of these ligands with alkali and alkaline earth metal ions.

X-Ray photoelectron spectroscopy (XPS), which is sensitive to the charge distribution [1, 2] is a suitable technique for the examination of the mode of ligand coordination in complex compounds. This is in principle, based on the fact that attachment of a metal ion to a coordinating site leads primerly to a decrease in electron density and hence gives rise to an increase in the binding energies of the core electrons of the concerned atoms.

Earlier ESCA studies on phosphorus containing compounds are limited [3–8], none of which is concerned with the present systems.

Experimental

The X-ray photoelectron spectra were recorded on a vacuum Generators ESCA-3 spectrometer. Al k_α (1486.6 eV) and Mg k_α (1253.6 eV) X-ray radiations were used to produce photoionisation. Samples were ground to powder and then dusted onto a double-backed adhesive tape. In all measurements, gold was evaporated on the surface of the sample and the values of the binding energies were referred to the gold $4f_{7/2}$ (84.0 eV) peak.

Sodium and potassium salts were purchased as analytical grade reagents except sodium triphosphate which was purchased as a commercial grade reagent. The latter was recrystallised twice and analysed for its sodium, phosphorus and hydrogen contents to be $Na_5P_3O_{10}\cdot 6H_2O$. Calcium and magnesium salts were prepared in the laboratory and analysed for the metal ion and phosphorus contents.

Results and Discussion

A) – Oxygen (1s) and Phosphorus (2p) Spectra

The oxygen (1s) spectra of the different phosphates show the presence of only one peak, the full-width half height (FWHH) of which is a function of the degree of protonation of the salt. Figure 1 represents a sample of the spectra obtained in the case of tri-, di- and monobasic orthophosphates. A sharp narrow peak (FWHH = 1.85 eV) was obtained in the case of the tribasic salts (*cf.* Fig. 1A). This suggests the presence of a nearly equivalent four oxygen

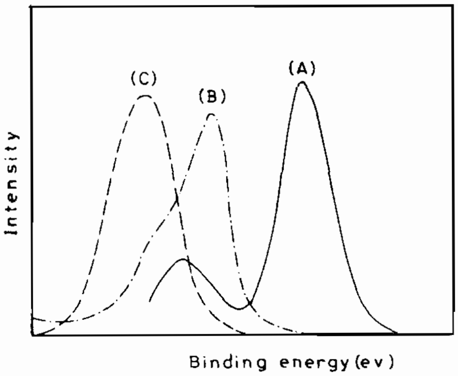

Fig. 1. Oxygen (1s) spectra. (A) Na_3PO_4. (B) Na_2HPO_4. (C) NaH_2PO_4.

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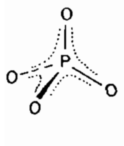
atoms (structure I). In the case of monobasic salts, only one peak was observed with FWHH approx. 1.5 times that obtained in the case of tribasic phosphates. The symmetry of the peak observed in addition to its large FWHH (see Fig. 1C) suggests the presence of equal amounts of two non-equivalent oxygens (structure II). The heigher binding energy component of the deconvoluted peak, accounts probably for the two protonated oxygens while the negative charge is delocalised between the other two and gives rise to the low binding energy component. This is consistent with the spectra observed in the case of dibasic salts (Fig. 1B). Deconvolution of the assymmetric peak obtained suggests that oxygen atoms are present in two environments in a ratio of 3:1 (structure III).



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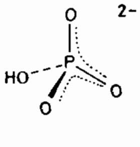

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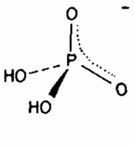

III

Table I summarises all the values of the binding energies of O(1s) electrons. The values reported here are those representing the intense components. Shoulders representing the binding energies of the protonated oxygens are approximately 1.0 eV higher than these values. Satellite signals on the higher energy side were observed only in the case of tribasic spectra.

Pyro- and tripolyphosphates showed the presence of only one type of oxygen apart from that represented by the water contents. It is difficult to differentiate from the spectra observed between bridging and non-bridging oxygens. This may be attributed to the small differences in the partial charges and/or the relatively small contents of the bridging oxygens.

TABLE I. Phosphorus (2p) and Oxygen (1s) Binding Energy (B.E.) Values.

Serial Number	Compound	B.E. of phosphorus (2p) electron[a] eV.	B.E. of oxygen (1s) electron[a] eV.
1	Na_3PO_4	132.9	531.2
2	K_3PO_4	132.8	530.7
3	$Ca_3(PO_4)_2$	133.5	531.9
4	$Mg_3(PO_4)_2$	134.2	532.0
5	Na_2HPO_4	133.0	531.6
6	K_2HPO_4	133.1	530.8
7	$CaHPO_4$	133.5	531.5
8	NaH_2PO_4	134.7	532.2
9	KH_2PO_4	134.6	531.4
10	$Na_4P_2O_7$	133.6	531.4
11	$Mg_2P_2O_7$	134.4	532.3
12	$Ca_2P_2O_7$	134.1	531.8
13	$Na_5P_3O_{10}$	133.7	531.9
14	$Ca_5(P_3O_{10})_2$	134.4	531.9

[a] All the measured values were estimated with a maximum error ± 0.1 eV.

Similar spectral patterns were also observed in the case of calcium and magnesium species.

Symmetrical narrow peaks have been observed for the phosphorus (2p) spectra in all compounds except that obtained in the case of tripolyphosphate which has a FWHH of 2.10 eV. The relative broadness of these peaks compared to the orthophosphate analogue (1.75 eV), is presumably due to a small difference in the charge density between terminal and bridging phosphorus atoms in the triphosphate samples (*cf.* Fig. 2).

B) – Binding Energy Correlations with the Calculated Charges

Siegbahn *et al.* [1, 2] were able to show that, for a point charge model, the core electron binding energies can be expressed as follows:

$$E_B = k_A q_A + V + E_R + l_A \qquad (1)$$

where, q_A is the net charge on the atom, A, E_R is the relaxation energy attributable to photoionisation, k_A and l_A are constants for the same system, V denotes the electrostatic potential at the nucleus caused by the surrounding atoms (B) and is expressed by the summation, $\sum_{A \neq B} q_B/R_{A-B}$ where R_{A-B} is the interatomic distance between atoms A and B.

The values of the relaxation energy, E_R, is expected to be insignificantly small, since in all measurements, the binding energies are referred to the Au $4f_{7/2}$ peak under similar experimental conditions. Several studies [1, 2, 9, 10] have revealed a linear correlation between chemical shifts and the fractional atomic charges, q_A. This suggests that the contribution of V to the chemical shift is also negligible. However, this is not always the case, Nordberg *et al.* [11], showed that the N (1s) binding energies measured

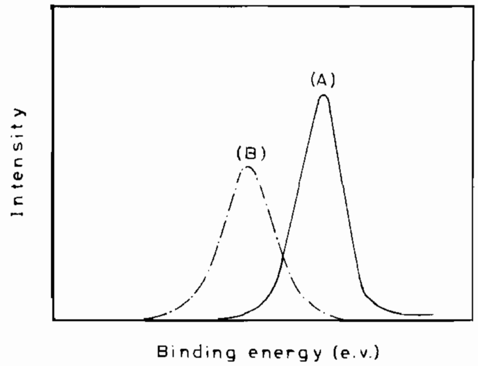

Fig. 2. Phosphorus (2p) spectra. (A) Na_3PO_4. (B) $Na_5P_3O_{10}$.

for a series of nitrogen containing compounds varies non-linearly with the charge calculated.

Table I lists the compounds investigated and the corresponding binding energies measured for the phosphorus (2p) and oxygen (1s) electrons. The maximum chemical shift in binding energies was found to be 1.9 and 1.6 eV in both cases respectively. The method used for charge calculation has been described before [12] which is based upon an iterative way of Pauling's method. Table II summarises the values calculated for q_P and q_O. The corresponding maximum shifts amounts to 0.17 and 0.15 unit charge respectively.

TABLE II. Calculated Charges and log β_{1x1}^T Values for some Phosphates.

Compound No.	Average calculated -ve charge on the oxygen atom[a]	Calculated charge on the phosphorus atom	log β_{1x1}^T
1	0.757	0.948	
2	0.785	0.937	
3	0.710	0.962	6.46
4	0.668	0.975	5.14
5	0.718	0.978	1.24
6	0.743	0.971	1.13
7	0.677	0.989	2.79
8	0.644	1.008	–
9	0.663	1.006	–
10	0.718	0.982	2.29
11	0.640	1.004	7.20
12	0.678	0.999	6.80
13	0.699	0.995	2.70
14	0.660	1.004	8.10

[a] For the acid phosphates, the charges on the hydrogenated oxygens were not included in the listed average. [b] log β_{1x1}^T are corrected to a zero ionic strength in water.

A plot of the measured binding energy of the phosphorus (2p) electrons *vs.* q_P showed a smooth curved relationship fitting all points except calcium and magnesium orthophosphates. The non-linear correlation may be qualitatively explained [11] in terms of a gradual contraction of the valence shell around the phosphorus atom as more charge is removed from it. This may lead to a corresponding change in the crystal potential, V, and hence to the chemical shift.

The discrepancy in the P (2p) binding energy of calcium and magnesium orthophosphates could be ascribed to one or more of the following factors. Recently [13], it has been reported that tribasic orthophosphates are inclined to absorb atmospheric carbon dioxide to form the dibasic salts and bicarbonates. This is very unlikely in the present systems since one would expect a greater deviation in the values obtained for P (2p) B.E. of the highly alkaline sodium phosphate. Furthermore, a splitting or broadening in the oxygen peaks should also be noticeable to account for the bicarbonate oxygens. This deviation might also be interpreted in terms of a change in the orbital electronegativity and the type of hybridisation as a result of a change in the degree of d-character in going from sodium to magnesium to calcium salts [6]. However, if this argument holds, a corresponding change would be expected within pyro- and triphosphates which is not found. Recently, Drissens and Verbeeck [14] pointed out that calcium phosphate species with Ca/P ratio of 1.5 could have a surface composition of what has been called defective hydroxyapatite which has the formula, $Ca_9(HPO_4)_n(PO_4)_{6-n}(OH)_n$ where the value of n is a function of the amount of water contents. A comparison of the binding energies of P (2p) electrons in compounds 3 and 7 suggests that both samples have similar surface compositions which is in reasonable agreement with Driessens and Verbeeck assumption.

Similar arguments could be challenged to account for the discrepancy observed in case of magnesium orthophosphate.

For the oxygen (1s), the correlations of q_O with the binding energy is invariably linear though it is more scattered (Fig. 3B). This is due to the difficulties encountered in determining accurately the binding energies of the non-protonated oxygens in acid phosphates. It is worth mentioning here to note also

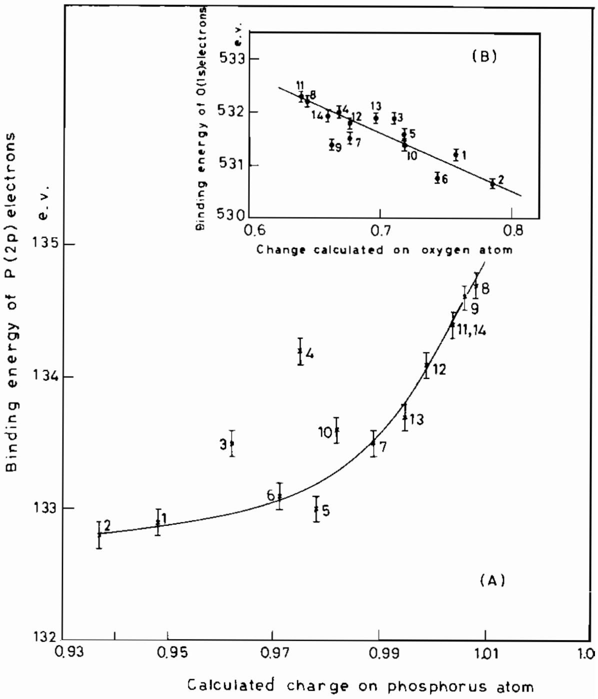

Fig. 3 (A) Binding energy–charge correlation for the phosphorus atom. (B) Binding energy–charge correlation for the oxygen atom.

that the average values of q_O quoted in Table II in the case of acid phosphates does not include the charge on the protonated oxygens.

C) – Binding Energy Correlations with the Stability Constants

It is still somewhat of an open question as to whether the electron binding energies of the molecules in the solid state could reflect other charge related properties in solution or liquid state. Part of the difficulties encountered in relating both behaviours is the different factors that contribute to this charge property in both states such as lattice effects and solvation phenomenon. However, several thermodynamic approaches to the theoretical elucidation of core electron shifts have drawn the attention to a possible connection between the shifts and chemical equilibria [10], proton affinity [15–18] and Hammett substitution constants [19].

According to Martin and Shirley [16], the variation in proton affinity (ΔPA) of a series of alcohols, amines,... *etc.* should be nearly equal to the variation in the (1s) electron binding energy of the protonated site, X,

$$i.e.\quad \Delta(\mathrm{PA}) \cong -\Delta E_{B(X,1s)} \qquad (2)$$

Neglecting entropy effects and substituting for the proton affinity by ΔH, it was possible to show that,

$$K \cong e^{\Delta E_B/kT} \qquad (3)$$

or

$$\Delta E_B = kT \ln K \qquad (4)$$

where K is the equilibrium constant for the studied reaction.

Equation (4) is also consistent with Lindberg *et al.* [19] conclusions. Based on the thermodynamic model for ESCA shifts [20], the authors were able to demonstrate the existence of a linear relationship between ΔE_B and Hammett substitution constant (σ),

$$\begin{aligned} E_B &= k'\sigma \\ &= k' \ln K/K^o \qquad (5) \end{aligned}$$

where, k′ is a constant related to the type of reaction studied. Equations 4 and 5 are virtually the same. Yoshida and Swada [10] illustrated similar trends between $\log \beta_{101}$ and the chemical shifts of the N (1s) electron B.E. for a series of bivalent metal–EDTA complexes.

In the present study, the alkali and alkaline earth phosphato complexes have an indentical chelating unit, *i.e.* PO_4^{z-} group. In turn, one would expect a similar relationship between $\log \beta_{1x1}$ and the binding energies of the core electrons of oxygen or phosphorus atom. Because of the uncertainties in the exact BE of the O (1s) electrons, the values of $\log \beta_{1x1}$ are presented here only as a function of P (2p) electron BE (see Fig. 4). The values of $\log \beta_{1x1}$ (x = 0 or 1) reported in the literature [21] and quoted in Table II are corrected for the differences in ionic strength, I, using the relationship,

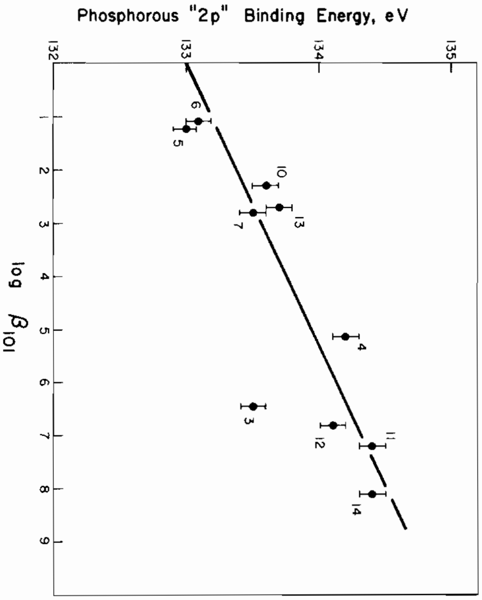

Fig. 4. The binding energy *vs.* the common logarithm of the 1st stability constant.

$$\log \beta^{I}_{1x1} = \log \beta^{O}_{1x1} + 2\alpha Z_1 Z_2 \sqrt{I}/(1+\sqrt{I}) \qquad (6)$$

where Z_1 and Z_2 are the charges of the cation and anion respectively, and α is a constant (= 0.502).

Excluding $Ca_3(PO_4)_2$, for the reasons discussed in the previous section, eqn. 4 (5) holds fairly well (corr. coeff. 0.95).

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