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Chemical Effects on the X-ray *K* Emission Spectra of Phosphorus in Organic Compounds

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Spectral changes in the P $K\alpha$ and P $K\beta$ X-ray emission lines of solid organic phosphorus compounds were measured with a two-crystal X-ray spectrometer. The P $K\alpha$ line shifted to higher energies with an increasing number of oxygen atoms attached directly to a phosphorus atom. Similar shifts were found in the P $K\alpha$ satellites, which were always 1.5—2.0 times larger than those of the parent $K\alpha$ line. There was no simple correlation for relating the P $K\beta_1$ shift to the phosphorus form. The P $K\beta$ profiles of organic phosphorus seemed to be characterized by the surrounding atoms or groups. The appearance of the $K\beta'$ band offered possible evidence for the existence of phosphorus–oxygen bonding in the samples.

It has been found that the chemical bonding forms of phosphorus affect the wavelenghts, spectral profiles and intensities of the phosphorus X-ray emission lines to a measurable degree.[1-5] These phenomena have received considerable attention from analytical chemists, since they can offer much direct information about phosphorus forms in unknown samples.[6,7] Most of the published work on the spectral changes in the P $K\alpha$ and P $K\beta$ lines has been concentrated on inorganic phosphorus compounds such as phosphides, phosphates and glasses.[8-11] However, so far as organic phosphorus is concerned, there is a lack of the experimental evidence for the chemical shifts and profile changes in the P K emission lines. Only a few measurements on the P $K\beta$ profile changes have been directed to the theoretical interpretation of the phosphorus–ligand bonding in certain organic coordination compounds.[12,13]

In a preceding paper,[14] more reliable data related to the chemical shifts of the sulfur $K\alpha$ and $K\beta$ lines from many organic compounds were shown together with certain regularities in their profile changes. The present paper deals in an analogous way with several solid organic phosphorus compounds. The observed spectral changes are discussed qualitatively with regard to phosphorus bonding forms.

Experimental

The P $K\alpha$ and P $K\beta$ spectra were automatically measured by a step-scanning method at regular intervals of 0.005° or 0.01° 2θ using a Rigaku SX X-ray fluorescence spectrometer equipped with a two-crystal spectrometer. Ge(111) ($2d$= 6.5327 Å) analyzer crystals and a flow proportional counter were used. The primary radiation used for exciting the spectrum was provided by a chromium X-ray tube operated at 50 KV, 35 mA. The 2θ positions of the P $K\alpha$, its satellite and P $K\beta$ lines were determined by averaging the goniometer settings at which the same intensity was measured on either side of the peak at the approximately 90% of the maximum intensity. The values of the chemical shifts of the P $K\alpha$ and P $K\alpha_4$ satellite were determined as an energy difference between a compound and red phosphorus and those of the P $K\beta_1$ were determined in relation to that of Li_3PO_4. At least three independent measurements were made for each compound. The experimental errors were estimated to be nearly 0.01 eV for the P $K\alpha$ shifts and 0.04 eV for the other shifts. Background corrections were made regarding the intensity measurements.

Organic phosphorus compounds used in this study were of the highest commercial grade available. Each sample was prepared by pressing a fine powder into an aluminium ring using a sample preparation kit. All compounds were confirmed by X-ray diffraction or IR analysis.

Results and Discussion

P K$\alpha_{1,2}$ *Spectrum.* The P $K\alpha_1$ and P $K\alpha_2$ emission lines appeared as an unresolved $K\alpha_{1,2}$ doublet under the present experimental conditions. By convention, this doublet is designated as P $K\alpha$ throughout this paper. The P $K\alpha$ width, at half-maximum intensity, was constant at about 1.78 eV in all compounds and red phosphorus. This suggests that the compounds used were not contaminated by significant amounts of phosphorus in a different bonding form. Table 1 lists the data of the P $K\alpha$ chemical shifts of organic phosphorus compounds and some inorganic phosphorus compounds chosen as a difference, together with their P $K\alpha_4$ and P $K\beta_1$ shifts to be discussed below.

TABLE 1. THE CHEMICAL SHIFTS OF THE PHOSPHORUS $K\alpha$ AND $K\beta$ LINES

Compound	Chemical shift/eV		
	$K\alpha$	$K\alpha_4$	$K\beta_1$
P	0	0	+2.36
Ph_3P	+0.02	+0.20	+0.91
Ph_3PO	+0.37	+0.76	+0.43
Ph(H)PO(OH)	+0.47	+0.83	−0.43
$PhPO(OH)_2$	+0.62	+1.03	+0.53
$PhPO(ONa)_2 \cdot xH_2O$	+0.66	+1.06	+0.05
$(PhO)_3PO$	+0.74	+1.16	−0.10
$PhOPO(OH)_2$	+0.78	+1.16	+0.55
$PhOPO(ONa)_2 \cdot xH_2O$	+0.78	+1.19	+0.55
$NO_2PhOPO(ONa)_2 \cdot 6H_2O$	+0.78	+1.19	+0.58
$C_{12}H_{25}OPO(ONa)_2$	+0.78	+1.19	+0.58
$NH_2CONH_2 \cdot H_3PO_4$	+0.78	+1.19	+0.58
$NaPH_2O_2 \cdot H_2O$	+0.46	+0.90	−0.43
$NaPHO_3$	+0.62	+1.03	−0.05
Na_2HPO_4	+0.81	+1.19	+0.24
Li_3PO_4	+0.81	+1.26	0

The P $K\alpha$ line of all compounds investigated here shifted to higher energies than that of red phosphorus. A relatively small shift of +0.02 eV was obtained for triphenylphosphine, Ph_3P. For triphenylphosphine oxide, Ph_3PO (in which one oxygen is attached directly to phosphorus) the P $K\alpha$ line moved +0.37 eV. A further positive shift was observed for phenylphosphinic acid, Ph(H)PO(OH), in which two oxygen atoms are bonded directly to phosphorus. The observed P $K\alpha$ shift of +0.47 eV for this acid agreed closely to that of sodium phosphinate. Phenyl phosphonic acid, $PhPO(OH)_2$, and its disodium salt (with three adjacent oxygen atoms) exhibited P $K\alpha$ shifts of +0.62 and +0.66 eV, respectively. These are almost comparable to that of sodium hydrogenphosphate. Except for triphenyl phosphate, $(PhO)_3PO$, with a P $K\alpha$ shift of +0.74 eV, the remaining organic phosphates gave a constant P $K\alpha$ shift of +0.78 eV. The data were slightly less than those for inorganic phosphates. More recently, Maekawa *et al.*[16] reported a significant difference in the P $K\alpha$ shifts among inorganic phosphates. However, such differences were not found in most organic phosphates of interest here.

From the above results, it is concluded that the P $K\alpha$ line of organic phosphorus compounds is successively shifted to higher energies with an increase in the number of oxygen atoms bonded directly to a phosphorus atom. Therefore, the data on the P $K\alpha$ shifts (listed in Table 1) can be expected to be utilized to analyze phosphorus forms in unknown organic samples.

P K$\alpha_{3,4}$ *Satellite Spectrum.* The P $K\alpha_{3,4}$ group of satellites was observed on the high-energy tails of the parent $K\alpha$ line. Figure 1 shows the spectral profiles of the P $K\alpha_{3,4}$ satellites for several compounds. In every case, three components $K\alpha_4$, $K\alpha_3$, and $K\alpha'$ could be resolved from the high-energy side, but the remaining components, $K\alpha_3'$ and $K\alpha''$, reported in the literature[17,18] were obscure. The intensity of the $K\alpha_4$ or $K\alpha_3$ satellite was approximately 4% of that of the parent $K\alpha$, whereas the $K\alpha'$ satellite was quite low in intensity, and sometimes even ambiguous. Spectral changes related to phosphorus bonding forms were observed in the relative intensities and energy positions of the resolved satellites. The intensity ratio, $K\alpha_4/K\alpha_3$, at each peak position increased slightly with an increasing number of oxygen atoms attached directly to the phosphorus. The ratio changed from nearly 0.57 in Ph_3P to 0.85 in Ph_3PO and to 0.90 in phosphates. A similar trend has been found in the sulfur $K\alpha_{3,4}$ satellites of organic sulfur compounds.[14]

The P $K\alpha_{3,4}$ satellites moved as a group with an almost constant offset of about 2.56 eV between $K\alpha_4$ and $K\alpha_3$ and of about 5.10 eV between $K\alpha_3$ and $K\alpha'$. Therefore, only the P $K\alpha_4$ shift of each compound relative to red phosphorus is shown in Table 1. The direction of the P $K\alpha_4$ shift was quite similar to that of the parent P $K\alpha$ line, while the data of the $K\alpha_4$ shifts were always 1.5—2.0 times larger than those of the P $K\alpha$ line. This result supports the general prediction[17] that the chemical shift of the $K\alpha$ satellites should be much more sensitive to the chemical-bonding forms of elements than is the parent $K\alpha$ line. However, more valuable information about the phosphorus forms than those from P $K\alpha$ shifts could not be obtained from the spectral changes in the P $K\alpha$ satellites.

P Kβ *Spectrum.* The high-resolution P $K\beta$ spectra of organic phosphorus compounds revealed very complex band structures, composed of several strongly overlapping lines caused by transitions involving valence-band electrons.[9] In this study, some attempts were made to reveal possible regularities in the chemical shift of the $K\beta_1$ and in the P $K\beta$ profile changes. The most intense peak in each spectrum was noted to be $K\beta_1$ and additional low-energy bands were noted to be $K\beta_x$ and $K\beta'$. As shown in the last column of Table 1, the observed P $K\beta_1$ chemical shifts of organic phosphorus compounds relative to that of Li_3PO_4

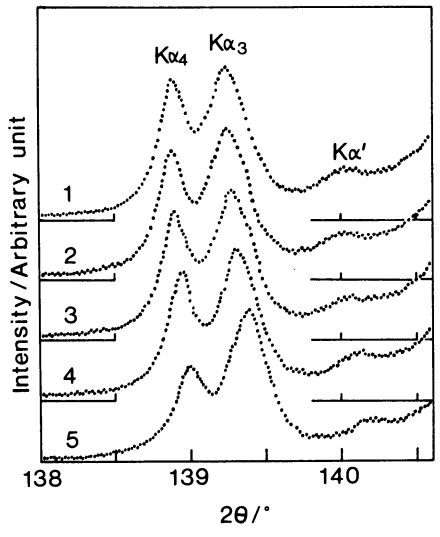

Fig. 1. Phosphorus $K\alpha_{3,4}$ satellite spectra.
1: $PhOPO(OH)_2$, 2: $PhPO(OH)_2$, 3: Ph(H)PO(OH), 4: Ph_3PO, 5: Ph_3P.

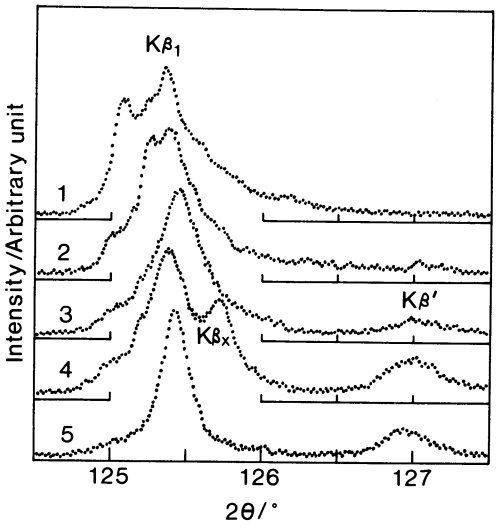

Fig. 2. Phosphorus $K\beta$ spectra.
1: Ph_3P, 2: Ph_3PO, 3: Ph(H)PO(OH), 4: $PhPO(OH)_2$, 5: $PhPO(ONa)_2 \cdot xH_2O$.

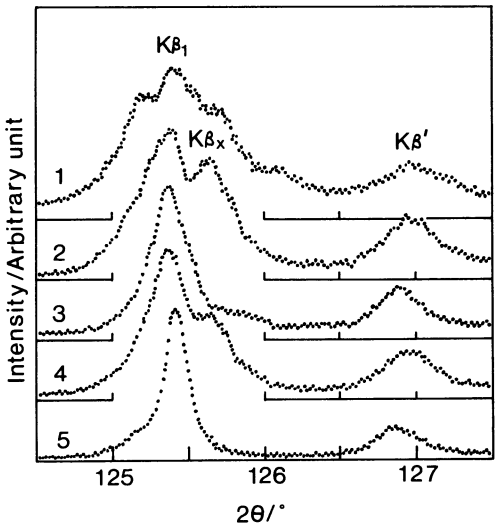

Fig. 3. Phosphorus $K\beta$ spectra.
1: $(PhO)_3PO$, 2: $PhOPO(OH)_2$, 3: $PhOPO(ONa)_2 \cdot xH_2O$, 4: $NH_2CONH_2 \cdot H_3PO_4$, 5: Li_3PO_4.

varied from −0.43 eV for Ph(H)PO(H) to +0.91 eV for Ph_3P. However, a simple correlation between the P $K\beta_1$ shifts and the chemical-bonding forms of phosphorus could not be found.

The P $K\beta$ profiles of organic phosphorus varied from compound to compound. Some of them are shown in Figs. 2 and 3. Each spectrum was normalized relative to the maximum intensity of $K\beta_1$. The $K\beta$ profiles of red phosphorus and inorganic phosphorus compounds tested here are almost identical to those reported by Fichter[9]; therefore, they are not shown. The first characteristic feature of the P $K\beta$ profile change was the occurrence of a low-energy band $K\beta'$ in the $K\beta$ spectra involving compounds with phosphorus–oxygen bonding. This band was observed at about 13.5—14.0 eV below $K\beta_1$ and its intensity increased slightly with an increasing number of oxygen atoms attached directly to the phosphorus. Consequently, it seems reasonable to assume that the appearance of the $K\beta'$ band can offer evidence for phosphorus–oxygen bonding. This feature was the only possible regularity obtained in the present study on the P $K\beta$ profile changes of organic phosphorus compounds. Such a feature is also supported by the fact that the $K\beta'$ band disappeared in the $K\beta$ spectra involving red phosphorus and Ph_3P. However, in the $K\beta$ spectrum of Ph_3PO with a phosphorus–oxygen bonding, the $K\beta'$ band became obscure and its $K\beta$ profile was rather closer to that of Ph_3P which exhibited a clearly resolved high-energy band at about 2.6 eV above $K\beta_1$.

The next interesting feature of the P $K\beta$ profile change was the behaviour of the low-energy band $K\beta_x$ adjacent to $K\beta_1$. For phenyl dihydrogenphosphate, $PhOPO(OH)_2$, and $PhPO(OH)_2$, the $K\beta_x$ band was clearly resolved at about 2.7 eV below $K\beta_1$. However, this band was no longer detectable in the $K\beta$ spectra from their disodium salts in which two hydrogen atoms in hydroxyl groups are substituted by two sodium atoms. These salts exhibited a relatively sharp $K\beta_1$ with a nearly symmetrical structure. Similar $K\beta$ profiles were obtained for the other disodium salts such as $NO_2PhOPO(ONa)_2 \cdot 6H_2O$ and $C_{12}H_{25}OPO(ONa)_2$. Such a behaviour of the $K\beta_x$ band suggests that this band may be associated with bonding between phosphorus and a hydroxyl group. This feature was supported by the appearance of a $K\beta_x$ band from urea phosphate, which involves three hydroxyl groups. However, in the $K\beta$ spectrum from Ph(H)PO(OH), which has one hydroxyl group attached to phosphorus, the $K\beta_x$ band was unclear or extremely weak. The high-energy subband $K\beta''$ has been frequently resolved from the $K\beta$ spectra of third-period elements[15] in certain compounds such as sulfites, sulfoxides and chlorates. However, the corresponding $K\beta''$ band was not discernible in the P $K\beta$ spectra of any of the compounds studied here.

The present study does not cover more extensive organic phosphorus compounds and, hence, there is a lack of data for certain forms of organic phosphorus. Consequently, a clear rule for relating the P $K\beta$ profile changes to various phosphorus forms could not be established. However, it seems possible to predict phosphorus forms of unknown samples by a comparison with the P $K\beta$ profiles shown in Figs. 2 and 3.

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