

Intensity of Infrared Absorption Bands of Phosphoryl Groups in Organic Phosphorus Compounds

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Integrated absorption intensities of the ground stretching vibration bands of the P=O groups in 13 different organic phosphorus compounds dissolved in carbon disulphide are calculated by different methods. The relative and absolute errors of the measurements and calculations are discussed. No simple correlation between the frequency of the infrared absorption band of the P=O group and its intensity is found. The inductive effect of the substituents linked to the phosphorus atom appears to influence the intensity of the P=O band to a greater extent than does the conjugative effect.

Meyrick and Thompson¹ reported characteristic infrared bands in the region 1250–1260 cm⁻¹ in organic phosphonates and dialkyl phosphites. Since the observed bands were absent in trialkyl phosphites they assumed that the bands were due to the absorption of the phosphoryl group. Gore² has compared corresponding phosphorus compounds containing phosphoryl and thio-phosphoryl groups and found that the P=O groups of the compounds studied absorbed in the region 1250–1300 cm⁻¹. Since that time several workers³⁻⁵ have confirmed these findings. From infrared data of phosphoryl compounds which hitherto have been studied it is found that the ground stretching vibration frequency of the phosphoryl group lies in the region 1175–1414 cm⁻¹ depending upon the substituents linked to phosphorus.

In two previous papers^{6,7} the ability of the phosphoryl group in different organic phosphorus compounds to participate in hydrogen bond formation with phenol was studied. Since the position of the infrared phosphoryl band as well as its ability to form hydrogen bonds are strongly dependent on the substituents linked to phosphorus we were interested to know whether the intensity of P=O band was similarly influenced by the substituents, and whether there might exist a correlation between position and intensity of infrared P=O bands.

CALCULATIONS OF INTENSITIES OF PHOSPHORYL BANDS

Definition. The extinction coefficient (K_ν) at wave number ν is defined by

$$K_\nu = \frac{1}{cl} \cdot \ln\left(\frac{I_0}{I}\right)_\nu \quad (1)$$

where $c = \text{gmole/l}$ and $l = \text{cm}$;

$$\ln\left(\frac{I_0}{I}\right)_\nu = -\ln D = E_\nu \quad (2)$$

where $D = \text{transmittance}$ and $E_\nu = \text{optical density}$. The true integrated absorption intensity (A) is given by

$$A = \frac{1}{cl} \int \ln\left(\frac{I_0}{I}\right)_\nu d\nu \quad (3)$$

The apparent integrated intensity (B) is defined by

$$B = \frac{1}{cl} \int \ln\left(\frac{T_0}{T}\right)_\nu d\nu \quad (4)$$

where $T_{0\nu}$ and T_ν are the intensities of the incident and transmitted radiation when the spectrophotometer is set at wave number ν and the radiation is not assumed to be monochromatic.

The wave number, optical density and molar maximal extinction coefficient at the peak wave number of the band are designated ν_0 , E_{ν_0} , and K_{ν_0} respectively. The half band width is designated $\Delta\nu_{\frac{1}{2}}$.

True and apparent values are marked (t) and (a); thus, the measured optical density are designated $E_{\nu}^{(a)}$ whereas the true optical density after correction of $E_{\nu}^{(a)}$ for the finite slit width of the instrument is designated $E_{\nu}^{(t)}$.

Methods of calculation. The methods used are taken from the work of Ramsay². "Method I" is based upon a direct integration of a Lorentz shaped absorption band:

$$A = \frac{1}{cl} \int_{-\infty}^{+\infty} \frac{a d\nu}{(\nu - \nu_0)^2 + b^2} = \frac{1}{cl} \pi \frac{a}{b} \quad (5)$$

Since $a/b^2 = E_{\nu_0}$ and $2b = \Delta\nu_{\frac{1}{2}}$ we get for the true intensity

$$A = \frac{1}{cl} \cdot \frac{\pi}{2} E_{\nu_0}^{(t)} \cdot \Delta\nu_{\frac{1}{2}}^{(t)} \quad (6)$$

For an apparent absorption band we may write:

$$A = \frac{1}{cl} K E_{\nu_0}^{(a)} \cdot \Delta\nu_{\frac{1}{2}}^{(a)} \quad (7)$$

$$\text{where } K = \frac{\pi}{2} \frac{E_{\nu_0}^{(t)} \cdot \Delta\nu_{\frac{1}{2}}^{(t)}}{E_{\nu_0}^{(a)} \cdot \Delta\nu_{\frac{1}{2}}^{(a)}} \quad (8)$$

"Method II" (designated "Method III" in the paper of Ramsay⁸) was first used by Bourgin⁹ and later discussed by Wilson and Wells¹⁰. The area (A') under the absorption curve expressed as fractional absorption, $1 - (I/I_0)_\nu$ versus wave number is given by

$$A' = \int [1 - (I/I_0)_\nu] d\nu \quad (9)$$

Since the area A' under the fractional absorption curve is independent of the resolution we may also write:

$$A' = \int [1 - (T/T_0)_\nu] d\nu \quad (10)$$

Substituting Beer's equation ($I = I_0 \exp(-K_\nu c l)$) into (9) and expanding the exponential term gives:

$$A' = cl \int \left[K_\nu - \frac{K^2_\nu \cdot c \cdot l}{2!} + \frac{K^3_\nu (cl)^2}{3!} + \dots \right] d\nu \quad (11)$$

If the shape of the absorption band is given by a Lorentz curve (eqn. 5) then by substitution of this into (11) the following expression is obtained:

$$\frac{A'}{cl} = A \left[1 - \frac{1}{2!} \cdot \frac{1}{2} \cdot E\nu_0^{(t)} + \frac{1}{3!} \frac{3 \cdot 1}{4 \cdot 2} (E\nu_0^{(t)})^2 - \frac{1}{4!} \frac{5 \cdot 3 \cdot 1}{6 \cdot 4 \cdot 2} (E\nu_0^{(t)})^3 \dots \right] \quad (12)$$

When A has to be calculated, eqn. (12) is written as

$$A = \varphi \cdot \frac{A'}{cl} \quad (13)$$

$$\text{where } 1/\varphi = 1 - \frac{1}{2!} \cdot \frac{1}{2} E\nu_0^{(t)} + \frac{1}{3!} \frac{3}{4} \cdot \frac{1}{2} (E\nu_0^{(t)})^2 \dots \quad (14)$$

Ramsay⁸ has quoted values of φ for various values of $E\nu_0^{(t)}$.

Since both of the methods above is dependent on a Lorentz shaped absorption curve they are less suitable to use for unsymmetrical absorption bands. In a few cases where the phosphoryl bands were unsymmetrical an extrapolating method independent of the Lorentz function was used. "Method III" is based upon eqn. (11) wherefrom is seen that A can be found by plotting A'/cl against cl and extrapolating $cl \rightarrow 0$:

$$\lim_{cl \rightarrow 0} A'/cl = \int K_\nu d\nu = A \quad (15)$$

The values of the true integrated absorption intensity (A) obtained after correction for the finite resolution of the instrument together with "wing" correction are calculated according to descriptions given by Ramsay⁸.

EXPERIMENTAL

The infrared absorption bands of the phosphoryl groups were recorded on a Unicam infrared spectrophotometer (Model SP 100.MK 2) containing NaCl-prism as well as gratings. The spectra were recorded in the region $\pm 70 \text{ cm}^{-1}$ from the band maximum using

a recording rate of 18 cm⁻¹/min. The theoretical spectral slit width was about 4 cm⁻¹ in the region 1200–1300, cm⁻¹. The phosphoryl compounds were dissolved in carbon disulphide. The self absorption of CS₂ was compensated against CS₂ in the reference cell. The cells were fitted with sodium chloride windows and had path lengths of 0.1 mm. The spectra of the phosphoryl compounds were recorded at 3–4 different concentrations in the transmittance region between 15–65 %. Three separate recordings were made for each concentration and the average values of the 3 separate $E_{\nu_0^{(a)}}$ and $\Delta\nu_{\frac{1}{2}^{(a)}}$ were used in all cases. The area under the experimental absorption bands (A') were calculated in the region of approximately ± 50 cm⁻¹ from the absorption peak. This was done by cutting out the band and weighing the paper. The average value of the area of two separate bands were used. Phosphoryl bands which were not quite resolved from neighbouring infrared bands in the spectrum were extrapolated to give a Lorentz shaped band. This was done for compounds Nos. 2, 4, 6, and 11 in Table 1.

DISCUSSION OF THE ERRORS IN THE CALCULATED INTENSITIES

Relative errors. In Table 1 are recorded the calculated values of the integrated intensities of the absorption bands of phosphoryl compounds. The intensities designated (A) are true intensities. The intensities (B) are directly calculated from the observed experimental values without correction for finite slit width. In the following the errors in the experimental and calculated values will be discussed. The error in the wave number has been estimated as less than ± 3 cm⁻¹ so that the error in the peak frequency of the phosphoryl bands is less than 0.25 %. Before we can calculate the error in the integrated intensities we need to know the errors in the observed maximal optical density $E_{\nu_0^{(a)}}$ and the half band width $\Delta\nu_{\frac{1}{2}^{(a)}}$. Each separate measurement of $E_{\nu_0^{(a)}}$ is dependent on three recordings: (1) the transmitted energy at ν_0 , (2) the 100 % transmittance line and (3) the 0 % transmittance line. Fig. 1 shows the connection between the relative maximal error (in %) in $E_{\nu_0^{(a)}}$ for an error of $\frac{1}{2}$ % in transmittance (D), 100 % line and 0 % line, respectively. It is seen that the relative error in $E_{\nu_0^{(a)}}$ is less than 3.5 % in the region 15–65 % transmittance in which the measurements have been performed. Since the average of three separate measurements is used the maximal error in $E_{\nu_0^{(a)}}$ must be assumed to be less than 3.5 %. The error of $\Delta\nu_{\frac{1}{2}^{(a)}}$ is estimated to be approximately ± 0.5 cm⁻¹. Since the half band width of all of the phosphoryl bands measured are greater than 12 cm⁻¹ we find that the relative maximal error in $\Delta\nu_{\frac{1}{2}^{(a)}} < 0.04$.

The relative probable error in A according to "Method I" is found upon logarithmic derivation of eqn. (7):

$$\frac{dA}{A} = \left[\left(\frac{dE_{\nu_0^{(a)}}}{E_{\nu_0^{(a)}}} \right)^2 + \left(\frac{d(\Delta\nu_{\frac{1}{2}^{(a)}})}{\Delta\nu_{\frac{1}{2}^{(a)}}} \right)^2 + \left(\frac{dc}{c} \right)^2 + \left(\frac{dl}{l} \right)^2 \right]^{\frac{1}{2}}$$

when K is assumed to be constant. This last assumption is found experimentally to be approximately fulfilled (cf. Table 3 in the paper of Ramsay⁸). The relative error of the path length of the cell is neglected since the same cell was used throughout the experimental series. If the error in the concentration of the sample is supposed to be kept below 1 % we can calculate the relative probable error in A :

$$\frac{dA}{A} = (0.035^2 + 0.04^2 + 0.01^2)^{\frac{1}{2}} = 0.054$$

Table 1. Calculated intensities of the phosphoryl band in organic phosphorus compounds.
Intensity unit = mole⁻¹ liter cm⁻² × 10⁴

Compound	ν_o (cm ⁻¹)	Method I			Method II			Method III
		A	A _{mean}	B _{mean}	A	A _{mean}	B _{mean}	A
1. Cl ₃ P=O	1306	1.91 1.89 2.00	1.9	2.0	2.14 1.90 1.9 2.47	1.9	2.1	—
2. $\begin{array}{c} \text{Cl} \\ \\ \text{H}_5\text{C}_2\text{O}-\text{P}=\text{O} \\ \\ \text{Cl} \end{array}$	1299	1.70 1.65 1.66 1.71	1.7	1.7	1.70 1.63 1.57 1.53	1.6	1.6	—
3. $\begin{array}{c} (\text{H}_5\text{C}_2\text{O})_2\text{P}=\text{O} \\ \\ \text{CHCl}_2 \end{array}$	1281	3.28 3.34 3.26 3.26	3.3	3.4	3.19 3.21 3.30 3.29	3.3	3.3	3.24
4. $\begin{array}{c} \text{Cl} \\ \\ (\text{CH}_3)_2\text{N}-\text{P}=\text{O} \\ \\ \text{Cl} \end{array}$	1274	1.42 1.49 1.45 1.44	1.5	1.5	1.26 1.27 1.45 1.29	1.3	1.3	—
5. $\begin{array}{c} (\text{H}_5\text{C}_2\text{O})_2\text{P}=\text{O} \\ \\ \text{CH}_2\text{Cl} \end{array}$	1271	2.60 2.66 2.63 2.75	2.7	2.7	2.80 2.85 3.03 3.14	3.0	3.0	—
6. (H ₅ C ₂ O) ₃ P=O	1265	2.02 2.07 1.98	2.0	2.1	2.04 2.16 1.84	2.0	2.0	—
	1281	3.76 3.79 3.77	3.8	3.8	3.48 3.65 3.44	3.5	3.5	—
7. $\begin{array}{c} (\text{H}_5\text{CO})_2\text{P}=\text{O} \\ \\ \text{H} \end{array}$	1267	4.09 4.22 3.53 3.87	3.9	3.9	3.39 3.44 3.30 3.33	3.4	3.4	3.23
8. $\begin{array}{c} (\text{H}_5\text{C}_2\text{O})_2\text{P}=\text{O} \\ \\ \text{H} \end{array}$	1262	3.76 3.79 3.67 3.44	3.7	3.7	3.59 3.86 3.68 3.89	3.8	3.8	—
9. $\begin{array}{c} (\text{H}_5\text{C}_4\text{O})_2\text{P}=\text{O} \\ \\ \text{H} \end{array}$	1262	4.29 4.31 4.30 4.49	4.4	4.4	3.71 3.81 3.81 3.99	3.8	3.9	3.88
10. $\begin{array}{c} (\text{H}_5\text{C}_2\text{O})_2\text{P}=\text{O} \\ \\ \text{N}(\text{CH}_3)_2 \end{array}$	1257	2.80 2.90 2.98 2.91	2.9	2.9	2.74 2.83 2.99 2.59	2.8	2.8	—
11. $\begin{array}{c} [(\text{CH}_3)_2\text{N}]_2\text{P}=\text{O} \\ \\ \text{Cl} \end{array}$	1246	1.79 1.77 1.77 1.78	1.8	1.8	2.00 1.91 1.97 1.85	1.9	2.0	—
12. $\begin{array}{c} \text{H}_5\text{C}_2\text{O}-\text{P}=\text{O} \\ \\ \text{N}(\text{CH}_3)_2 \end{array}$	1228	3.76 3.74 3.77 3.85	3.8	3.8	3.71 3.68 3.56 3.59	3.6	3.7	—
13. (C ₆ H ₅) ₃ P=O	1205	2.86 2.93 2.97	2.9	3.0	3.02 3.09 3.28	3.1	3.1	—

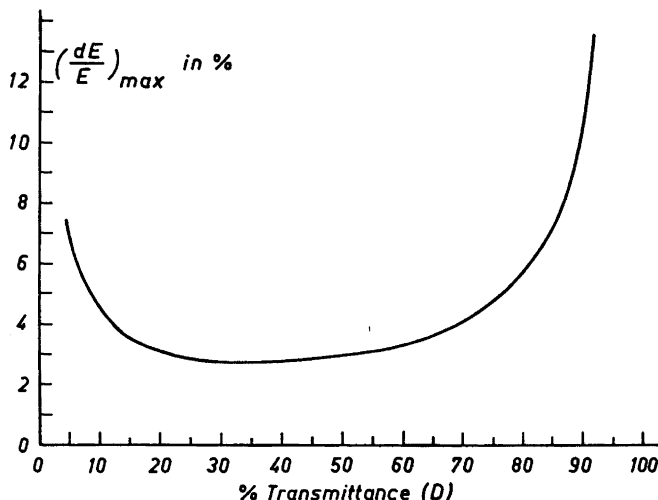


Fig. 1. Relative error in optical density as function of transmittance.

The relative probable error in A for each separate measurement should thus be less than 5.4 % as long as the measurements are performed between 15 and 65 % D . From Table 1 is seen that the individual variation of the A -values in "Method I" from the mean value of A is less than 4.3 %. The only exception is shown by the phosphites which have very unsymmetrical bands.

The relative error of the individual values of A according to "Method II" is in the same way estimated to be approximately 10 % which is in agreement with the calculated values of A (Table 1).

Absolute errors. "Method I and II" are both dependent on the assumption that the true band shape is given by a Lorentz curve. This assumption is most critical for "Method I" since the calculation of the intensity is dependent on only three points on the curve whereas "Method II" depends on measurements of the whole experimental curve. Small deviation from symmetrical Lorentz shape of the absorption bands may therefore give great error in "Method I" whereas in "Method II" small humps are liable to be averaged out in the calculation so that the absolute error in the intensity must be assumed to be much less for the latter method. On comparing the results of the two methods the differences in the intensities are normally less than 12 %; however, "Method II" must be assumed to give the most correct values. This is clearly recognized in the intensities of the P=O bands of dimethyl and di-butyl phosphites which have band shoulders on the high frequency side of the bands. We find for these two bands that the extrapolating method ("Method III", eqn. 15) which is independent of the Lorentz function gives A -values in good agreement with the values obtained by "Method II" whereas the A -values according to "Method I" are much too high.

It is important to recognize that the differences between true and apparent intensity values (A and B in Table 1) are very small as compared to the individual errors of the calculated A -values.

DISCUSSION OF THE INTENSITY DATA

The data on the intensities of the stretching vibration bands of phosphoryl groups in different organic phosphorus compounds show that the dependence between the intensity of the P=O band and the substituents linked to the phosphorus atom is very complex. From the data in Table 1 is seen that there is no obvious connection between the frequency of the phosphoryl band and its intensity. There is, however, a tendency for strongly inductive substituents ($-I$) linked directly to phosphorus to reduce the intensity of the phosphoryl band. A greater positive charge on phosphorus will increase the π "back bonding" from oxygen to phosphorus and accordingly reduce the variation of the dipole moment ($d\mu/dQ$) of the P=O bond during its stretching vibration. Since the intensity is proportional to $(d\mu/dQ)^2$ the $-I$ substituents should decrease the intensity. In Table 1 the influence of the $-I$ effect on the intensity of the P=O band is most pronounced for the chloro substituted compounds. However, the effect seems not to be strictly additive since the P=O band of phosphorus oxychloride (compound No. 1) has higher intensity than the P=O bands of compounds Nos. 2 and 4 with only two chloro substituents.

The intensity of carbonyl bands increases strongly when conjugative substituents are linked to the carbonyl carbon atom¹². It appears that conjugative substituents linked to phosphorus have much smaller effect on the intensities of the P=O bands (Table 1). We may, therefore, conclude that the intensity of the stretching vibration bands of the phosphoryl groups in organic phosphorus compounds is strongly affected by the inductive effects of the substituents linked to phosphorus but less so by their conjugative effects.

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