

### 315. *The Infra-red Spectra of Organo-phosphorus Compounds.* *Part II.\* Esters, Acids, and Amines.*

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Correlations suggested earlier for the  $\text{P}=\text{O}$ ,  $\text{P}-\text{O}-\text{C}(\text{aromatic})$ , and  $\text{P}-\text{O}-\text{C}(\text{aliphatic})$  bands have received additional confirmation from studies on a further series of compounds. It has been shown that hydrogen bonding in amino- and organic derivatives of phosphorus acids causes a considerable shift of the  $\text{P}=\text{O}$  absorption towards lower frequency, together with an increase in overall intensity. Additional correlations involving the  $\text{P}-\text{O}-\text{Et}$ ,  $\text{P}-\text{OH}$  (stretching and deformation modes),  $\text{P}-\text{NH}_2$ , and ionic phosphate groupings have been examined and are discussed.

In Part I\* we described the infra-red spectra of a number of organo-phosphorus compounds and suggested correlations for a number of structural units. This work has now been extended by the examination of a further series of compounds, in which the correlations previously established have received confirmation and new correlations have been suggested. Particular attention has been paid to the acid and amino-derivatives in an attempt to resolve some anomalies found in respect of the  $\text{P}-\text{OH}$  and  $\text{P}=\text{O}$  bands in these compounds.

#### EXPERIMENTAL

The compounds examined are listed in the tables. The majority were prepared in these laboratories by standard methods but a substantial number were a gift from Dr. Clarke of Cambridge University. In all cases the physical constants conform with those given in the literature and the samples are believed to be of reasonably high purity.

All spectra were obtained by using the Perkin-Elmer 21B recording double-beam spectrometer with a rock-salt prism.

The general insolubility of the majority of the acids and amines in common solvents has precluded their examination in solution, and most of them were examined as solid pastes ground in paraffin oil. In all cases in which the material could be obtained in a convenient solvent, however, the solution spectra have also been measured.

#### RESULTS AND DISCUSSION

In discussing the results obtained it is convenient to consider separately the three main groups of esters, amino-derivatives, and acids, and to discuss under each group the correlations which can be made for the various types of linkage.

(a) *Esters*.—This group of materials serves mainly to provide additional confirmation for the correlations put forward in Part I (*loc. cit.*) for the  $\text{P}=\text{O}$ ,  $\text{P}-\text{O}-\text{C}(\text{aromatic})$ , and  $\text{P}-\text{O}-\text{C}(\text{aliphatic})$  linkages, but the additional number of compounds available has also made it possible to examine further correlations in this series. Table 1 summarises the findings confirming earlier correlations, and includes also the acids, anilides, and amines except as regards the  $\text{P}=\text{O}$  link which will be discussed separately in each case. It will be seen that in all cases bands are found in the expected positions as given in Part I (*loc. cit.*).

As regards further correlations, Daash and Smith (*Analyt. Chem.*, 1951, **23**, 853) have pointed out that the  $\text{P}-\text{O}-\text{Et}$  linkage gives rise to absorption almost exactly at  $1160\text{ cm}^{-1}$ . We have confirmed this but have noticed also that aromatic phosphates absorb at this point. Altogether 64 organo-phosphorus compounds have been examined, in addition to the salts of the acids, and it is significant that a band in the narrow range  $1156\text{--}1163\text{ cm}^{-1}$  is shown by all those in which the  $\text{P}-\text{O}-\text{Ph}$  or the  $\text{P}-\text{O}-\text{Et}$  group is present. The only exception is ethyl dichlorophosphinite in which the band is at  $1143\text{ cm}^{-1}$ . With heavy substituents present in the aromatic ring, the band appears to shift to lower frequencies. In none of the other substances does this particular band appear. Studies of solutions of

\* Part I, *J.*, 1952, 475.

comparable concentrations in the same cell also indicate very clearly that there is a correlation between the intensity of this band and the number of either of these groupings in the molecule. On passing through the series triphenyl phosphate, diphenyl chlorophosphonate, and phenyl dichlorophosphinate, for example, there is a progressive weakening in the

TABLE 1. *Confirmation of previous correlations.\**

Compound	P=O	P-O-C (Arom- atic)	P-O-C (Ali- phatic)	P-O-Et or P-O-Ar	P-H
Dibenzyl phosphite .....	1256	—	1020	—	2410
Di-(1 : 2 : 2-trimethylpropyl) phosphite .....	1258	—	1020	—	2410
<i>Dineopentyl</i> phosphite .....	1250	—	1026	—	2381
<i>Diisobutyl p</i> -(2-ethylhexyl)phenyl phosphate .....	1279	1215	1020	1174	—
Diethyl .....	1272	1218	1031	1174—1163	—
Ethyl dichlorophosphinite .....	—	—	1020	1143	—
Tri-(2-ethylhexyl) phosphate .....	1282, 1266	—	1031	—	—
Ethyl di-(2-ethylhexyl) phosphate .....	1250	—	1026	1156	—
Diethyl 2-ethylhexyl phosphate .....	1250	—	1026	1156	—
Tri- <i>p</i> -nitrobenzyl phosphate .....	1287, 1269	—	1047, 1034	—	—
Tetrabenzyl pyrophosphate .....	1290	—	1026	—	—
Diphenyl anilinophosphonate .....	See	1172	—	1163, 1153	—
Phenyl dianilinophosphinate .....	Table	1190	—	1163	—
Dibenzyl anilinophosphonate .....	2	—	1026	—	—
Dibenzyl benzylaminophosphonate .....	—	—	1015	—	—
Dibenzyl <i>N</i> -methylanilinophosphonate .....	1274	—	1026	—	—
Dibenzyl 2-phenylethylaminophosphonate ...	See Table 2	—	1042	—	—
Dibenzyl morpholinophosphonate .....	1250	—	1037	—	—
Diphenyl aminophosphonate .....	See	1190	—	1163	—
Dibenzyl aminophosphonate .....	Table	—	1036, 1020	—	—
Phenyl diaminophosphinate .....	2	1220	—	1159	—
Diphenyl hydrogen phosphate .....	—	1215	—	1156	—
Phenyl dihydrogen phosphate .....	—	1183	—	1159	—
Dibenzyl hydrogen phosphate .....	—	—	1036	—	—
Di-2 : 4 : 6-trichlorophenyl hydrogen phos- phate .....	See Table	1235	—	1130	—
Phenyl hydrogen anilinophosphonate .....	3	1183	—	1156	—
Di- <i>p</i> -nitrophenyl hydrogen phosphate .....	—	1190	—	1147	—
Di- <i>o</i> -methoxyphenyl hydrogen phosphate ...	—	1190	—	1163	—
Benzyl hydrogen aminophosphonate .....	—	—	1026	—	—

\* This table omits additional bands in the appropriate regions which we can attribute with reasonable certainty to other causes. Thus a number of the benzylanilino-derivatives absorb at 1220  $\text{cm}^{-1}$  in the P-O-C(Aromatic) region but this is omitted as we shall show later that this is due to the bonded P=O group.

intensity of this band, and the same effect can be observed in the corresponding ethyl esters. This band is relatively more intense with P-O-C(aromatic) substitution than with P-O-Et, giving a strong band in the first case and a medium to weak one in the second. Most of the benzyl and anilino-derivatives give a very weak inflection near 1160  $\text{cm}^{-1}$ , which is probably due to the benzene ring itself, but this is so weak that it is not likely to be confused with the P-O-Et or P-O-C(aromatic) band. Presumably this vibration is connected with some mode of the P-O-Et link in the one case, and with an aromatic ring vibration enhanced in intensity by association with the phosphate ester in the other case.

(b) *Amino-derivatives of Phosphorus Acids.*—(1) *N-H Stretching vibration.* It will be seen from Table 2 that the primary and secondary amino-compounds examined exhibit considerable hydrogen bonding in the solid state, as shown by the occurrence of the N-H stretching vibration between 3125 and 3333  $\text{cm}^{-1}$ . In several cases two, and even three, bands appear in this region and we would attribute this to different types of hydrogen bonding. Thus the secondary amino-compounds show two peaks in this region when more than one amino-group is present, and this probably arises from the fact that in one group hydrogen is more strongly bonded than in the other. In solution the bonding is broken or much reduced in all these cases and a new band appears in the 3390- $\text{cm}^{-1}$  region.

With the primary amino-compounds three peaks are shown in some cases which

presumably arise from free NH, inter-molecularly bonded NH, and intra-molecularly bonded NH. Some support for this is provided by the persistence of a band (of diphenyl aminophosphonate) in the bonded NH region in solution.

TABLE 2. Primary, secondary, and tertiary amino-derivatives of phosphorus.

Compound	N-H (stretching)	NH-C(Ar) (stretch- ing)	P-NH <sub>2</sub> (deform- ation)	P=O
Diphenyl anilinophosphonate, solid .....	3125	1290	Nil	1220
" " " 5% soln. in CHBr <sub>3</sub> ..	3333, 3125, 3520	1290	"	1290,* 1227
Phenyl dianilinophosphinate, solid .....	3125, 3333	1277	"	1220
" " " 5% soln. in CHBr <sub>3</sub> ..	3378	1290	"	1290 *
Trianilinophosphine oxide, solid .....	3125—3333	1279	"	1214
" " " 1% soln. in CHBr <sub>3</sub> .....	3367	1274	"	1290
Dianilinochlorophosphine oxide, solid .....	3125	1290	"	1198
Dibenzyl anilinophosphonate, solid .....	3125	1282	"	1212
" " " 4% soln. in CHBr <sub>3</sub> ..	3125—3378	1290	"	1290,* 1250
Dibenzyl benzylaminophosphonate, solid .....	3175	Nil	"	1220—1235
" " " 4% soln. in CHBr <sub>3</sub> .....	3378	"	"	1290
Dibenzyl <i>N</i> -methylanilinophosphonate .....	Nil	"	"	1274
Dibenzyl 2-phenylethylaminophosphonate, solid ..	1325	"	"	1212
" " " 4% soln. in CHBr <sub>3</sub> .....	3390	"	"	1290
Dibenzyl morpholinophosphonate .....	Nil	"	"	1250
Trianilinophosphine sulphide .....	3125—3333	1274	"	Nil
Diphenyl aminophosphonate, solid .....	3226, 3436	Nil	1543	1250
" " " 2% soln. in CH <sub>3</sub> CN ..	3300 (solvent)	"	1580	1274
Dibenzyl aminophosphonate .....	3125, 3257, 3333	"	1565	1220
Phenyl diaminophosphinate .....	3096, 3195, 3333	"	1558	1176
Phenyl hydrogen anilinophosphonate .....	3205	1295	Nil	1205
Silver phenyl anilinophosphonate .....	3175	1290	"	Nil
Dianilinophosphinic acid .....	3289	1282	"	1220
Silver dianilinophosphinate .....	3125, 3367	1282	"	Nil
Benzyl hydrogen aminophosphonate .....	Nil	Nil	"	1190

\* Intensity increase over -NH-C(Ar) stretching intensity. As explained in the text it is not possible to differentiate NH-C(Ar) stretchings and P=O variations near 1300 cm.<sup>-1</sup>, as bromoform has some absorption in this region. A very marked diminution of the band near 1220 cm.<sup>-1</sup> and an increase at 1290 cm.<sup>-1</sup> are taken as evidence for breaking of hydrogen bonds on solution. However, this is supported by similar shifts in other compounds in which the anilino-group is absent.

(2) R·NH<sub>2</sub> Bending. The three primary amino-compounds examined show a band in the range 1543—1565 cm.<sup>-1</sup> which is slightly above the normal C-NH<sub>2</sub> bending region. This is probably also associated with hydrogen-bonding effects, for in solution there is a shift to 1580 cm.<sup>-1</sup> with diphenyl aminophosphonate. Benzyl hydrogen aminophosphonate exhibits no band in this region but there is strong evidence that this exists in the zwitterion form <sup>-</sup>O·P·NH<sub>3</sub><sup>+</sup> (Clarke and Todd, *J.*, 1950, 2030).

(3) P=O. Examination of the spectra of the series of amino-derivatives given in Table 2 shows that none of the primary amines absorbs strongly in the normal 1250—1300-cm.<sup>-1</sup> region which we have earlier associated with the P=O link. On the other hand, a strong band appears in the 1175—1250-cm.<sup>-1</sup> region which is additional to any band arising from the P-O-C(aromatic) linkage. Two of the secondary amines behave similarly, and the remainder show absorption both near 1280 cm.<sup>-1</sup> and at 1175—1250 cm.<sup>-1</sup>. The tertiary amines appear to be normal in having a P=O absorption between 1250 and 1280 cm.<sup>-1</sup>. Colthup (*J. Opt. Soc. Amer.*, 1950, 40, 397) has shown that secondary aromatic amines give a band of medium to strong intensity about 1280 cm.<sup>-1</sup>, and we have confirmed this in a number of diphenylamines and related compounds. It is therefore probable that in the secondary amino-compounds the 1250—1280-cm.<sup>-1</sup> vibration is related to the Ph-NH link, and that in all these compounds, except the tertiary bases, the P=O vibration occurs between 1175 and 1250 cm.<sup>-1</sup>. Confirmation of this has been obtained from studies of solution and salts. It will be seen from Table 2 that on dissolution in bromoform the primary and secondary amines show marked changes in the 1175—1300-cm.<sup>-1</sup> region. In general, the band between 1175 and 1250 cm.<sup>-1</sup> which we ascribe to bonded P=O is markedly less intense, whilst the 1300-cm.<sup>-1</sup> band is stronger. At the same time, any other

band in the 1190—1220-cm.<sup>-1</sup> region due to the presence of the P—O—C(Ph) group remains unaffected. The increase in intensity of the 1300-cm.<sup>-1</sup> band is partly obscured by a small absorption due to bromoform in this region, but the enhancement is nevertheless well marked, especially in those compounds in which there is no Ph—NH absorption in this region. These changes are coupled with a corresponding shift of the NH stretching bands in the 3330-cm.<sup>-1</sup> region which revert to the 3380-cm.<sup>-1</sup> position corresponding to unbonded NH. In the case of diphenyl aminophosphonate there is evidence of some continued bonding in solution, since the band at 1250 cm.<sup>-1</sup> does not disappear entirely, and some NH bonding also continues to appear in the 3330-cm.<sup>-1</sup> region. Nevertheless, the strength of the 1274-cm.<sup>-1</sup> band in solution indicates that the extent of this association is probably quite small.

Further evidence for the assignment of the bonded P=O absorption to the 1175—1250-cm.<sup>-1</sup> region is obtained from the comparison of the spectra of the silver salts of dianilino-phosphinic acid and *P*-anilino-*P*-phenylphosphinic acid with those of the acids themselves. In the former case the P=O absorption would be expected to vanish and be replaced by the bands of ionic phosphate  $\overset{+}{P} \begin{smallmatrix} \text{O}^- \\ \diagdown \\ \text{O}^- \end{smallmatrix}$ , and it will be seen that in both cases the 1205—1220-cm.<sup>-1</sup> band present in the acids is absent from the salts, whereas the 1300-cm.<sup>-1</sup> Ar—NH band remains substantially unaffected.

This assignment is also supported by the absence of any strong band in the 1175—1250-cm.<sup>-1</sup> region in aliphatic-type tertiary amines in which hydrogen bonding to the NH is precluded. In these compounds the P=O absorption occurs in the expected region, 1250—1300 cm.<sup>-1</sup>.

*Organic Acids and Esters of Phosphorus.*—A number of acids of various types have been examined. In most cases their insolubility in organic solvents has necessitated their examination in the solid state, but a few were also examined in solution. The spectra of the silver salts of the majority of these acids have also been obtained for comparative purposes.

(1) *The P—OH stretching vibration.* Daash and Smith (*loc. cit.*) have examined several acids of this type and report that in no case could any free hydroxyl be detected in the 3620-cm.<sup>-1</sup> region. Instead, a broad band appears at about 2680 cm.<sup>-1</sup> which they attributed to the bonded hydroxyl absorption. It will be seen from Table 3 that our findings confirm this observation and that, in the series of acids we have examined, a shallow, broad band appears near 2560—2700 cm.<sup>-1</sup> in all cases. In solution in non-polar solvents this band persists and there is no evidence of any free hydroxyl-group absorption. This assignment is considerably beyond the region in which bonded hydroxyl groups normally appear, but exceptional cases of very strong bonding are known in which the OH absorption appears in this region. Thus, Rasmussen, Tunnicliffe, and Brattain (*J. Amer. Chem. Soc.*, 1949, **71**, 1070) find bonded-hydroxyl absorption in the 2700-cm.<sup>-1</sup> region in  $\beta$ -diketones showing conjugate chelation, and Reid and Ruby (*ibid.*, 1951, **73**, 1054) find that in five substituted tetrionic acids the O—H stretching band appears near 2500 cm.<sup>-1</sup>. Further support for this assignment is provided by the disappearance of this band from the spectrum of the silver salts of the corresponding acids.

(2) *The P—OH deformation vibration.* The O—H deformation vibration is normally subject to considerable influences from the surrounding structure and is therefore liable to show marked shifts in position with alteration in the nature of adjacent groups. However, on general grounds, it would be expected to appear in the 1050-cm.<sup>-1</sup> region of the spectrum. In the case of acids containing P—O—C(aliphatic) linkages, this region of the spectrum is obscured by the strong phosphorus-ether-link absorption, but with all the other acids it will be seen that there is a strong band in the 1000—1040-cm.<sup>-1</sup> region. Furthermore, this band vanishes on conversion of the acid into the silver salt, a new band appearing near 1075 cm.<sup>-1</sup> which, as will be seen later, we attribute to an ionic-phosphate vibration.

There is also support for this assignment from the comparison of the spectra of the acids with three of the corresponding fully substituted esters. Triphenyl phosphate, for example, shows no absorption in the 1030-cm.<sup>-1</sup> region although this is present in both the mono- and the di-phenyl hydrogen phosphates. We would therefore assign the P—OH deformation mode to the 1030-cm.<sup>-1</sup> region at least insofar as the present range of materials is concerned.

(3)  $\text{P}=\text{O}$  in acids. In view of the results already obtained with amino-derivatives of phosphorus, and the fact that there is evidence of abnormally strong hydrogen bonding from the O-H stretching region, it is to be expected that the  $\text{P}=\text{O}$  absorption will be shifted into the 1175—1250- $\text{cm}^{-1}$  region. This has been found to be the case, and in only one of the acids examined has the frequency risen above 1250  $\text{cm}^{-1}$ . This is di-*o*-methoxyphenyl hydrogen phosphate ( $\text{P}=\text{O}$ , 1261  $\text{cm}^{-1}$ ), in which there is the possibility of a steric effect similar to the well-known *ortho*-effect in methoxyphenols which would reduce to some extent the tendency towards strong hydrogen-bond formation on the  $\text{P}=\text{O}$  group. The frequency shifts observed in the  $\text{P}=\text{O}$  absorption are in line with those reported by Daash and Smith (*loc. cit.*) for a number of other acids of phosphorus.

TABLE 3. *Acids and salts of phosphorus.*

Compound	P-OH (stretching) region	1600—2500- $\text{cm}^{-1}$	P=O	P-OH (deformation)	$\begin{matrix} \text{P} & \text{O} \\ \diagdown & / \\ & \text{O} \end{matrix}$	(ionic)	P-O- (970 $\text{cm}^{-1}$ )
Diphenyl hydrogen phosphate, anhydr., solid	2597 broad	1667 & 2000—2275	1250	1026	—	926 (w)	952
Diphenyl hydrogen phosphate, anhydr., soln. in $\text{CS}_2$ and $\text{CCl}_4$			as dry solid throughout				
Diphenyl hydrogen phosphate, anhydr., soln. in $\text{NEt}_3$	2597	1626 & 2470 both sharp	1242	Solvent	Solvent	885 & 909	Nil
Diphenyl hydrogen phosphate, anhydr., soln. in $\text{NEt}_2\text{Ph}$	2632	2381 (Solvent)	Solvent	Solvent	Solvent	885 & 909	Nil
Diphenyl hydrogen phosphate, anhydr., soln. in $\text{C}_5\text{H}_5\text{N}$	2564	1626, 2000, 2105, 2410	1250 (broad)	Solvent	Solvent	885 & 909	Nil
Diphenyl hydrogen phosphate dihydrate, solid	2667 broad	1709 & 2222	1212	—	1058	935 (s), 922 (s)	Nil
Silver diphenyl phosphate	Nil	Nil	Nil	Nil	1075	930	Nil
Phenyl dihydrogen phosphate, hydrate	2667 (shoulder)	2222 only	1220	1036	1087?	917	980 (w)
Phenyl dihydrogen phosphate, soln. in trioctyl phosphate	2597 (s)	2273 only			not measured		
Disilver phenyl phosphate	Nil	Nil	Nil	1034	1042?	1080, 917 (m)	985
Dibenzyl hydrogen phosphate	2564	1695, 2128, 2273	1250	P-O-C absorption	Nil	Nil	985'(s)
Silver dibenzyl phosphate	Nil	Nil	Nil	P-O-C absorption	1081	917 (m)	990 (m)
Di-2 : 4 : 6-trichlorophenyl hydrogen phosphate	2703	1709, 1942, 2174, 2353	1220	1015	Nil	Nil	957 (s)
Silver di-2 : 4 : 6-trichlorophenyl phosphate	Nil	Nil	Nil	Nil	1075, 1087	901 (s), 909	Nil
Phenyl hydrogen anilino-phosphonate	2564	1695, 2273	1205	1010 (v.s.)	Nil	Nil	975 (v.s.)
Silver phenyl anilino-phosphonate	Nil	Nil	Nil	Nil	1053	926 (v.s.)	Nil
Dianilinophosphinic acid	2667	1639, 2273, 2381	1220	1015	1031?	Nil	952
Silver dianilinophosphinate	Nil	Nil	Nil	Nil	1042 (s)	901 (w), 930	Nil
<i>cyclo</i> Hexylphosphonic acid	2667	2273 only	1220	1000?	Nil	Nil	952
Di- <i>p</i> -nitrophenyl hydrogen phosphate	2632	1667, 1923, 2353	1220	1010	Nil	935 (m)	980 (v.s.)
Di- <i>o</i> -methoxyphenyl hydrogen phosphate	2632	1639, 2000	1261	1026	Nil	909 (m)	975 (v.s.)
Benzyl hydrogen amino-phosphonate	w. shoulder only	1695, 1852, 2326	1190?	Nil (P-O-C)	1053	Nil	952

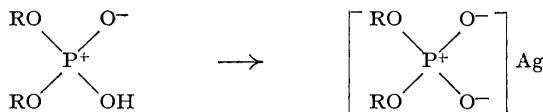
In the above analysis, a strong band occurring in the 1190—1220- $\text{cm}^{-1}$  region in the silver salts of aromatic acids has been ascribed to the P-O-C(Ar) link and in the absence of other bands the P=O has been marked absent.

In the case of the aromatic acids there is also a band in the 1190—1220-cm.<sup>-1</sup> region arising from the P—O—C(Ph) link and in some cases this coincides with the P=O absorption. The influence of the P=O absorption is, however, clearly shown on comparison with the spectra of the silver salts. In the latter case only the P—O—C(aromatic) band appears as a sharp peak clearly distinguishable from the broad band obtained when the P=O group is also present.

A number of the acids examined appear to exist as hydrates from which the water could only be removed with extreme difficulty. When this was done there appeared to be some resulting shift in the P=O absorption towards higher frequencies. Thus diphenyl hydrogen phosphate absorbs at 1250 cm.<sup>-1</sup> in the dry state and at 1212 cm.<sup>-1</sup> as the hydrate.

The frequency shift accompanying hydrogen bonding of the P=O group in both the acid and the amino-series appears to be associated with a very marked increase in the intensity. The shifts themselves are also very much greater than would be expected to result from normal hydrogen bonding. Thus normal hydrogen bonding of carbonyl linkages rarely results in shifts of more than 10—20 cm.<sup>-1</sup> (Rasmussen *et al.*, *loc. cit.*) and this order of shift is also shown by bonded sulphoxides (Barnard, Fabian, and Koch, *J.*, 1949, 2442). On the other hand, conjugated chelated  $\beta$ -diketones and some related unsaturated  $\beta$ -hydroxy-ketones show very considerable C=O shifts (Rasmussen *et al.*, *loc. cit.*) accompanied by considerable intensity increases. This effect is associated with the appearance of the O—H stretching absorption at 2700 cm.<sup>-1</sup>, at which point the O—H absorption is also found in our acid phosphates. Presumably, therefore, the organic derivatives of phosphoric acids and amides exist in a bonded form in which the strength of the bonds is comparable with those of these chelated products.

(4) *The ionic-phosphate vibration.* Salt formation with the organic acids of phosphorus would be expected to result in a considerable weakening of the P=O band, with consequent shift to lower frequencies. This would arise from the introduction of a second negatively charged oxygen atom so that the P=O group would become effectively the ionic phosphate group :



An analogous effect is well known with salts of carboxylic acids. This expectation is borne out in practice, and in all cases, the bands ascribed to the P=O vibration and to the P—OH deformation in the free acid disappear in the silver salts and are replaced by a single absorption band in the 1050—1110-cm.<sup>-1</sup> region. This is the region which Colthup (*loc. cit.*) has associated with the ionic-phosphate vibration and we would therefore assign it to that cause. It is noteworthy that certain of the hydrated compounds also show some evidence of a band in this region and it may be that they also tend to exist, in part, in the ionic form in the solid state. There is evidence of a second band near 900 cm.<sup>-1</sup> which may also be associated with the ionic phosphate group (see Table 3).

(5) *The 1660—2500-cm.<sup>-1</sup> band.* All the acids examined show broad shallow bands in this region which recall those arising from amino-acids and zwitterion substances. However, only the monobasic acids exhibit a broad band in the region of 1665 cm.<sup>-1</sup>, and possibly when a sufficient number of acids have been examined this may be of value in differentiating mono- and di-basic organic derivations of phosphoric acids.

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