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VIBRATIONAL SPECTRA OF ORGANOPHOSPHORUS COMPOUNDS

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I. INTRODUCTION

At the present time organophosphorus compounds are being intensively studied. This fact is related to their great theoretical importance and to their various applications in industry and agriculture. They have been used for some time as flotation agents, plasticisers, additives for lubricating oil, etc. Since many organophosphorus compounds exhibit a specific physiological activity, their use as medical preparations is becoming more and more widespread. In recent years they have been widely used for chemical crop protection. Various phosphorothioates have proved particularly valuable, being considerably more effective than many previously known insecticides. The prospects in the development of the chemistry of organic phosphorus compounds, including polymers, are very good. The possibilities of practical utilisation of these compounds are far from exhausted and in some fields their application is only beginning.

In the synthesis of new organophosphorus compounds many problems arise in establishing their structure and studying their reactions. In particular, the study of tautomerism, isomerism, and molecular rearrangements in a series of organophosphorus compounds is of great theoretical and practical interest to organic chemistry. A wide range of physical and chemical methods is necessary to solve these and other problems. Among the physical methods, vibrational spectra are very important.

Many investigations have been reported of the vibrational spectra of organophosphorus compounds, mainly in recent years. In some of these, mostly qualitative in character, the spectra of compounds of known structure are analysed and the observed frequencies are assigned to the vibrations of individual bonds or groups of bonds. Many of these assignments have been made by comparison of the spectra of a large number of compounds and are well established; others are insufficiently well founded and cannot always be recommended for use in structure determination. In a number of publications on the vibrational spectra of organophosphorus compounds attempts are made to explain shifts in the so-called characteristic frequencies, when comparing the spectra of certain compounds with those of others. As a rule, the frequency shifts are ascribed to the influence of some particular factor, *e.g.* polarity of bonds, mass of atoms, etc.

Experimentally and theoretically it is well known that the characteristic vibration frequencies of bonds can change considerably when the intramolecular environment of the bonds to which these frequencies are assigned is changed. The reasons for changes in characteristic frequencies, even if one considers only isolated molecules, can be very varied.

If the frequency is not entirely characteristic of one co-ordinate, *i.e.* the vibration is not localised within a given bond or angle, it is highly probable that the frequency will be sensitive to changes in the force and kinematic parameters of all the co-ordinates of the vibration. The frequencies of such vibrations change markedly, for example, when the distribution of bonds in a group is altered. This property is of particular value in investigations of rotational isomerism of molecules based on vibrational spectra. When a vibration is localised preferentially within one bond (or angle), a considerable change of frequency with change in environment is brought about by a change in the force field of the bond itself. Changes in frequency, caused not by the direct participation of neighbouring bonds and groups in the vibration but by their influence on the electronic configuration of the bond, are of considerable interest in studies of the nature of bonds and the interaction of atoms.

It is very difficult to draw a definite conclusion, exclusively from experimental spectroscopic data, concerning the reasons for the shift of a frequency characteristic of some bond or group of bonds. In fact, even when only one atom in a molecule is exchanged for another, changes in many kinematic and force parameters occur (mass, interatomic distance, angles, force constants). One cannot therefore (with rare exceptions) compare the spectra of substances differing only in one parameter and thus trace its effect on frequency. To reach a firm conclusion, theoretical analysis of the molecular vibrations is essential as well as consideration of the experimental data.

This review discusses the interpretation of the vibrational spectra of organophosphorus compounds, the theoretical analysis of the vibrations of phosphorus-containing molecules, and the application of vibrational spectra to the solution of certain problems in the chemistry of organophosphorus compounds.

The Appendix lists the organophosphorus compounds whose vibrational spectra have been published.

II. ANALYSIS OF THE VIBRATIONAL SPECTRA OF ORGANOPHOSPHORUS COMPOUNDS. IDENTIFICATION OF VARIOUS GROUPS

1. The P=O Group

For structural and analytical studies of the chemistry of phosphorus compounds, the spectral characteristics of P=O and P=S groups are of great interest. For this reason most of the work on the vibrational spectra of organophosphorus compounds has been devoted to elucidation and analysis of the characteristic frequencies of these groups.

Arbuzov *et al.*[1], in a Raman spectral study of the structure of dialkyl phosphites, first suggested that the lines of medium intensity in the 1250–1260 cm^{-1} region for dialkyl phosphites and in the 1280–1300 cm^{-1} region for trialkyl phosphites were due to stretching vibrations of the P=O link. Later, this assignment was confirmed by the work of Meyrick and Thompson[2] on the infra-red and Raman spectra of dialkyl phosphites and esters of alkylphosphinic acids. The infra-red spectra of these compounds showed intense bands in the 1250–1260 cm^{-1} region which were absent in the spectra of trialkyl phosphites.

These investigations were continued by Gore[3] and by Daasch and Smith[4], who studied a large number of infra-red spectra of organophosphorus compounds of various types. Gore compared the spectra of trialkyl phosphates with those of trialkyl phosphorothioates. The chief difference between the spectra of these compounds was observed in the 1250–1300 cm^{-1} region, where the spectra of trialkyl phosphates contain intense absorption bands, ascribed to stretching vibrations of the P=O link.

Daasch and Smith[4] showed that the so-called P=O frequency can vary over a wide range according to the nature of the substituent on the phosphorus atom. Thus, in the spectrum of $(CH_3O)_3PO$ the P=O frequency is 1176 cm^{-1}; 1305 cm^{-1} in that of $(CH_3O)_2POF$; and, according to Gutowsky and Liehr[5], 1415 cm^{-1} in POF_3. Daasch and Smith concluded that the value of the P=O frequency is determined by the electronegativity of the substituent. Bell *et al.*[6] found a linear relation between the frequency of the stretching vibrations of P=O in infra-red and Raman spectra and the sum of the Pauling electronegativities of the halogens in the compounds POX_3. The authors ascribed this relation to the strong polarisation of the P=O bond due to its position between two atoms of such widely different electronegativities. As a result, the phosphorus atom acquires a positive charge and the oxygen atom a negative one. Therefore the P=O bond becomes very sensitive to the polar influences of substituents. This is reflected in the force constant of the bond and hence in the frequency of stretching vibration. To derive the relationship between the P=O frequency and the electronegativity sum, the authors used the infra-red spectra of three compounds: POF_3, $POCl_3$, and $POBr_3$. From the linear relationship obtained and the known frequencies of the stretching vibrations of the P=O bond in various organophosphorus compounds, the authors determined "shift constants" for various substituents. They identified these "shift constants" with the Pauling electronegativities of the substituents and, from their values for many radicals, far-reaching conclusions were drawn about the order of the P=O bond and its character in various phosphorus compounds.

It should be noted that there is no foundation for reducing the many factors responsible for the value of the frequencies of molecular vibrations to one, in this case to the polar factor. The change in frequency between one type of compound and another cannot be ascribed to a polar effect without first calculating the molecular vibrations and determining the amplitude of the vibrations and the sensitivity of the frequencies to a change in the force and kinematic parameters of the molecule. The change in the P=O frequency when substituents are replaced by others can be due not only to a change in the force constant of the bond, but to the fact that the vibration is not fully characteristic of this bond. It is extremely probable that this vibration is not characteristic of the isolated P=O bond but of a tetrahedron with a phosphorus atom at its centre and including this bond and other bonds and angles. Cotton *et al.*[7] consider that in such a case it would be more correct to use not the frequency of vibration but the force constants of the P=O bond in molecules with different substituents at the phosphorus atom. The many experimental data in the paper by Bell *et al.* confirm a more complex relationship between the P=O frequency and the nature of the substituents at the phosphorus atom. The spectra of

compounds having identical "shift constants" should have had closely similar values of P=O stretching vibration frequencies. This however was not so. For example, compounds with a sum of electronegativities (ΣX) = 9 have P=O frequencies in the 1250–1315 cm^{-1} region, those with (ΣX) = 8 in the 1220–1260 cm^{-1} region, those with (ΣX) = = 9.3 in the 1270–1320 cm^{-1} region, and so on. Furthermore, the infra-red spectra of the overwhelming majority of organophosphorus compounds containing the P=O bond have an intense absorption band in the 1200–1320 cm^{-1} region. Therefore one cannot forecast P=O frequencies on the basis of "shift constants".

Objections can also be raised on other assumptions made by these authors. For calculating the so-called "shift constants" the infra-red spectra of substances in different states are used. In some cases P=O frequencies are taken from spectra of solid substances, in others from spectra of liquids and solutions. It is well known[8,9] that the state of a compound can have an appreciable influence on the position of the P=O band. Further, the absorption band assigned to the P=O stretching vibration is often a doublet. In order to obtain the best fit to a linear relationship, the authors arbitrarily use a single frequency. For the same reason they conveniently displace the straight line, initially drawn through three points, and change its slope. Finally, it should be noted that interpretation of the "shift constants" in terms of Pauling electronegativities of the substituents has no physical meaning.

As a result of this experimental work and that of Bellamy and Beecher[10-12], who studied the infra-red spectra of about 100 organic derivatives of phosphoric and phosphinic acids, the work of Holmstedt and Larsson[13], Bergmann *et al.*[14], Harvey and Mayhood[15], Baudler[16], and others[17-21], it is conclusively established that, when a molecule contains a P=O bond, the infra-red and Raman spectra contain a frequency in the 1180–1400 cm^{-1} region, while for the majority of compounds this interval is considerably narrower (1200–1320 cm^{-1}).

A theoretical analysis of the experimental data is essential as a basis for experimental assignments and for the correct interpretation of the changes in spectra when comparing one molecule with another. Mayants *et al.*[21-23] calculated the characteristic vibrations of a number of phosphorus-containing molecules and made a numerical analysis of the relation between these frequencies and the force and kinetic parameters of the molecule; these calculations were based on a theory of characteristic frequencies, developed by Mayants[24].

A calculation of the frequencies and modes of vibration of molecules of the type POX_3, namely $POCl_3$ and $POBr_3$, shows that the vibrations corresponding to the so-called P=O frequencies are not fully characteristic of the P=O bond. Other bonds and angles vary appreciably during this vibration. However, the observed dependence of the frequency of this vibration on various parameters shows that plausible changes in all the force constants (excluding the P=O bond force constant) cannot significantly change the P=O frequency. Numerical analysis of the dependence of the frequency on kinematic parameters[25] showed it to be extremely insensitive to changes in the mass of the atom X, the length of the P–X bond, and the bond angles.

To clarify the part played in this vibration by more distant angles and bonds, the same authors calculated[23] the fully symmetrical vibrations of some of the possible conformations of the molecule $(CH_3O)_3PO$. The calculation showed that vibration involves primarily the P=O bond; some part in the vibration is played by P–O bonds nearest to the P=O bond and by the angles , , and ; the remaining co-ordinates are hardly involved in this vibration and do not affect its frequency. Thus, taking into account the results of the calculations for $POCl_3$, $POBr_3$, and $(CH_3O)_3PO$, it can be stated that this vibration is highly characteristic of the P=O bond and the bonds and angles directly adjacent to it, *i.e.* it is localised within a tetrahedron. This is consistent with the experimental data on the vibration spectra of organophosphorus compounds. Table 1, taken from the paper cited above[23], lists the values of the P=O frequencies for certain types of phosphorus compound. The variation of the P=O frequencies in the spectra of compounds having phosphorus atoms with identical immediate environment, does not exceed 10 cm^{-1}. It must be remembered, however, that this conclusion is drawn from calculation of a mechanical model of an isolated molecule. It is not valid for compounds whose molecules are strongly associated or in which intramolecular hydrogen bonding exists. For example, the frequencies of the P=O stretching vibration in the spectra of dialkyl and trialkyl phosphates differ markedly, in spite of the identical immediate environment of the phosphoryl groups. A decrease of 40–50 cm^{-1} in the P=O frequency in dialkyl phosphates occurs as a result of an intermolecular hydrogen bond (see below).

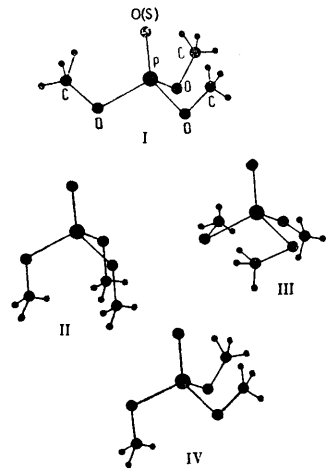
TABLE 1. P=O frequencies in spectra of phosphorus compounds..

Compound	$\nu_{P=O}$, cm^{-1}	Lit. ref.	Compound	$\nu_{P=O}$, cm^{-1}	Lit. ref.
$POCl_3$	1290	3	CH_3POCl_2	1285	26
$(CH_3O)_2POCl$	1286	16	$C_2H_5POCl_2$	1285	26
$(C_2H_5O)_2POCl$	1289	16	$(C_2H_5O)C_2H_5P(O)SCH_3$	1215	20
$(C_3H_7O)_2POCl$	1291	16	$(C_2H_5O)C_2H_5P(O)SC_2H_5$	1215	20
$(CH_3O)_3PHO$	1258	16	$(C_4H_9O)C_2H_5P(O)SC_4H_9$	1215	20
$(C_2H_5O)_2PHO$	1257	16	$(C_2H_5O)_2P(O)SCH_3$	1258	19
$(C_3H_7O)_2PHO$	1254	16	$(C_2H_5O)_2P(O)SC_2H_5$	1257	18
$(C_4H_9O)_2PHO$	1258	16	$(C_2H_5O)_2P(O)SCH_2OCH_3$	1255	19
$(CH_3O)_2CH_3PO$	1243	2	$(C_2H_5O)_2P(O)SCH_2C_6H_5$	1254	19
$(C_2H_5O)_2CH_3PO$	1250	2	$(C_2H_5O)_2P(O)SCOOCH_3$	1263	19
$(iso\text{-}C_3H_7O)_2CH_3PO$	1249	2	$(C_2H_5O)_2P(O)SCH_2CH_2SC_2H_5$	1255	27
$(C_4H_9O)_2CH_3PO$	1250	18	$(CH_3O)_2POF$	1305	4
$(C_4H_9O)_2C_2H_5PO$	1250	18	$(C_2H_5O)_2POF$	1309	4
$(C_4H_9O)_2C_4H_9PO$	1250	4			
$(C_2H_5O)_2C_4H_9PO$	1243	10			

The fact that the spectra of many organophosphorus compounds show a doublet P=O band is of some interest. Gore[3] observed a doublet band in the spectra of phosphates containing the OC_2H_5 group and explained this by the proximity of the P=O and OC_2H_5 vibration frequencies. Later, Bellamy and Beecher[10] noted that doublets also occur in the spectra of certain triaryl phosphates, while Holmstedt and Larsson[13] observed them in organophosphorus compounds containing amino groups. This is evidence that both frequencies are connected with the P=O group. Mortimer[17] investigated the infra-red spectra of trimethyl, triethyl, and triphenyl phosphates in the crystalline and liquid states at various temperatures and in solution in iso-octane, carbon tetrachloride, carbon disulphide, acetone, and chloroform. The bands at 1290 cm^{-1} and 750 cm^{-1}, observed in the spectrum of crystalline trimethyl phosphate and assigned to P=O and P–O, split

into the doublets 1290, 1275 cm^{-1}, and 755, 740 cm^{-1} respectively in the spectra of the liquid material and its solutions. The relative intensities at the maxima (J) of corresponding absorption bands vary appreciably with temperature and with the solvent. Thus J 1290/1275 and J 740/755 vary from 0.93 to 4.5 and from 0.26 to 0.67, respectively. When trimethyl phosphate is heated to 125° an increase in the intensities of the 1275 and 755 cm^{-1} bands is observed. Similar changes occur in the spectra of triethyl and triphenyl phosphate. The authors concluded that, in the liquid state and in solution, several rotational isomers of these phosphates existed, differing in the angle between the O=P–O and P–O–C planes. The frequencies 1290 and 740 cm^{-1} in the spectrum of trimethyl phosphate were ascribed to the conformation that is most stable at low temperatures and the frequencies 1275 and 755 cm^{-1} to a conformation whose concentration increases with rise in temperature.

The presence of two P=O frequencies instead of one in the spectrum of liquid trimethyl phosphate could be explained both by a change in kinematics and by a change in the force field of the molecule on changing from one conformation to the other. A calculation[23] which assumes the equality of the force fields of four of the possible conformations (see diagram)† shows that P=O practically coincides for them while the difference in frequency of the stretching vibrations of the single P–O bonds in conformations I and III is close to the experimental value. Taking account of the possible errors in selecting values of the force constants and kinetic parameters cannot bring $\Delta\nu$ P=O for the various conformations close to the experimental value. To explain the observed difference $\Delta\nu$ P=O, it was assumed that the force fields of different conformations are somewhat different, in particular because of differences in the force constants of the P=O bond (~2%). This can arise from a very weak intramolecular interaction between the oxygen atom of the P=O group and hydrogen of the methyl group in one isomer, which is absent in another isomer. The conditions for creating this interaction are most favourable in isomers I and IV and are absent in isomers II and III. Realisation of isomer II is improbable because of steric hindrance. The probable errors in selecting force constants likewise cannot appreciably affect the difference $\Delta\nu$ P–O for the various conformations. Since the difference $\Delta\nu$ P–O for conformations I and III is close to the observed value, it was suggested that the observed frequency 740 cm^{-1} relates to a conformation of type III. The frequency 755 cm^{-1} probably corresponds to a conformation of type I, so that the frequency 1290 cm^{-1} relates to conformation III and 1275 cm^{-1} to conformation I. This choice of a realisable type of conformation agrees with the assumption that their P=O force constants differ; thus conformation I must correspond to a lower value of the constant and hence to a lower value of the P=O frequency.



It might appear that the 1290, 1275 cm^{-1} doublet in the spectrum of trimethyl phosphate could arise from association of $(CH_3O)_3PO$ molecules and not because of the existence of different conformations, since the relative intensity of the bands at 1290 and 1275 cm^{-1} in the infra-red spectrum of a solution of trimethyl phosphate depends on its concentration. However, the hypothesis of $(CH_3O)_3PO$ association does not agree with a number of known facts.

1. The molecular weights of trialkyl phosphates, determined cryoscopically in benzene, are close to the theoretical values[30,31]: if there is an interaction between molecules of trimethyl phosphate, it must be a weak one.
2. If the doublet were caused by a weak intermolecular interaction, the doublet frequencies would not remain constant when passing from the pure liquid to solutions in different solvents and at different temperatures. The frequencies 1290 and 1275 cm^{-1} retain their value and do not depend greatly on the solvent and the temperature[17].
3. If there were association between trimethyl phosphate molecules the nature of the P=O absorption band would differ from that observed. In the case of weak association between the oxygen atom of the P=O group in one molecule and the hydrogen atoms of the methyl group in another, the P=O band of lowest frequency should be more diffuse than the P=O band in a non-associated molecule. This is not observed.
4. Finally, if one assumes a dipole–dipole interaction of the type $O^- \cdots P^+$ $\|$ $\|$ $P^+ \cdots O^-$ the spectrum should show, not two P=O frequencies, but three, of which two should again be diffuse.

The concentration dependence of the relatively intense bands at 1290 and 1275 cm^{-1} does not contradict the hypothesis of the existence of different conformations of the trimethyl phosphate molecule. This dependence may be ascribed to the differing capacities of different rotational isomers for solvation by solvent molecules, as a result of which the equilibrium constant between different conformations, defined by the ratio of the activities, also depends on the concentration of the solution.

† Model I was first proposed by Gibling[28] for molecules of alkyl esters of phosphoric acid, on the basis of the good agreement between calculated and experimental values of the parachors, and was later supported by studies of the parachors by Arbuzov and Vinogradova[29].

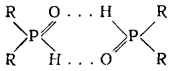
A further property of the P=O frequency is its sensitivity to any form of association of organophosphorus molecules either with themselves or with solvent molecules. Daasch and Smith[4] first noted that the maximum of the P=O band shifts by 50–80 cm^{-1} in the direction of lower frequencies compared with spectra of the corresponding esters of alkyl- and aryl-phosphonic acids, and the absorption band is more diffuse. This is accompanied by a large shift of the OH stretching vibrations band (see below). This was ascribed to the formation of an intermolecular hydrogen bond P=O···H–O. Bellamy and Beecher[11,12] confirmed the existence of association in a large number of spectra of compounds containing $P\langle^{O}_{OH}$ groups and also concluded that P=O forms a hydrogen bond with the NH group. They observed that formation of a hydrogen bond was accompanied by an increase in intensity of the P=O band but no quantitative measurements were made. The infra-red spectra[25] of solutions of $(C_2H_5O)_2P(O)OH$, $(C_2H_5O)_3PO$, and $(C_2H_5O)_2C_2H_5PO$ show a noticeable solvent effect on the P=O frequency. Solvents containing hydroxyl and amino groups have a particularly marked effect. Thus in the spectra of substances in formamide solution the P=O frequencies are lower than those of the pure liquids and solutions in carbon tetrachloride, *e.g.* with $(C_2H_5O)_2P(O)OH$ the frequency drops from 1230 cm^{-1} to 1205 cm^{-1}, with $(C_2H_5O)_3PO$ from 1270 cm^{-1} to 1240 cm^{-1} and with $(C_2H_5O)_2.C_2H_5PO$ from 1265 cm^{-1} to 1220 cm^{-1}. Large shifts are also observed in the spectra of aqueous and alcoholic solutions. Bellamy *et al.*[9] studied the influence of many solvents, not containing hydroxyl or amino groups, on the P=O frequency in $POCl_3$ and $(CH_3O)_2PHO$. The greatest shift occurred with solutions in methylene iodide.

Cryoscopic determinations of the molecular weights of certain organophosphorus compounds in benzene and naphthalene[30,31] have shown that, in compounds of the type $(RO)_2PO(OH)$, the molecules are dimerised while, in compounds of the type $(RO)PO(OH)_2$, polymers of higher complexity are formed. In acetic acid the compounds are monomeric. With trialkyl phosphates, the molecules of which cannot form intermolecular hydrogen bonds, the experimental molecular weights agreed with the theoretical values. As was shown[25] with $(C_2H_5O)_2P(O)OH$, the degree of association of dialkyl phosphates depends very much on concentration. Increasing concentration increases association and the molecules are converted into di- and then poly-associated complexes.

Miller *et al.*[8] studied the infra-red spectra of dialkyl-α-hydroxyalkylphosphine oxides and dialkyl-α-hydroxyalkylphosphonates in the crystalline state and in CS_2 solution. The P=O and O–H frequencies in the spectra of the crystalline phosphine oxides occur in the regions 1100–1140 cm^{-1} and 3050–3100 cm^{-1} respectively; in the spectra of the alkyl phosphonates they occur in the regions 1230–1232 cm^{-1} and 3180–3250 cm^{-1}. The low values of these frequencies and their negligible enhancement in the spectra of the solutions were ascribed by the authors to intramolecular hydrogen bonding of the type:



The authors consider that the enhancement of the P=O frequency from 1150 to 1190 cm^{-1} in the spectra of the CS_2 solutions is caused by dipole–dipole association of the molecules, *e.g.* $P^+–O^-\cdots P^+–O^-$. Association of dialkylphosphinous acids by means of intermolecular hydrogen bonding of the type



they considered improbable, because an analogous change of P=O frequencies also occurs in the spectra of trialkylphosphine oxides. It was noted that the P–H frequency (see below) was lower in the spectra of solutions than in those of the crystalline compounds. With intermolecular hydrogen bonding the opposite should have been observed. The existence of association in compounds of this type is confirmed by the results of Kosolapoff and McCullough[32] on heats of mixing.

Vibrational spectra have been used to study the ability of phosphorus compounds to complex with metal cations[7,33–35]. Cotton *et al.*[7] examined the infra-red spectra of mixtures of trimethyl- and triphenyl-phosphine oxides with halides of Cd, Zn, Co, Cu, Mn, Ni, and Fe. Complex formation caused a diminution of the P=O stretching frequency by 40–70 cm^{-1}, and the absorption band broadened or split into two components. This is explained by the formation of a bond between the oxygen of the phosphoryl group and the metal ion and this, in turn, causes a reduction of the force constant of the P=O bond. Sheldon and Tyree[33] had earlier observed a similar phenomenon in the spectra of the crystalline addition products of $POCl_3$, $POBr_3$, and $(C_6H_5)_3PO$ with $TiCl_4$, $SnCl_4$, and $FeBr_2$.

Kinell *et al.*[35] investigated the Raman spectra of mixtures of $POCl_3$ and $PO(CH_3)_3$ with $SbCl_5$ in 1,2-dichloroethane solution. The spectra show that, in the ternary solution, all the $SbCl_5$ molecules react with $PO(CH_3)_3$, not with $POCl_3$, to form the complex $SbCl_5.PO(CH_3)_3$. This indicates that the donor properties of the phosphine oxide are greater than those of phosphorus oxychloride.

2. The P=S Group

The spectral characteristics of the P=S group are of considerable interest in the chemistry of organothiophosphorus compounds.

There are many studies of the vibrational spectra of compounds of this class. Thus, Gore[3] investigated more than thirty infra-red spectra of organothiophosphorus and organophosphorus compounds. The spectrum of $PSCl_3$ has an intense band at 748 cm^{-1} which is absent in the spectrum of $POCl_3$. The spectra of diethyl phosphorochloridothionate and diethyl phosphorochloridate differ markedly in the 660 and 1290 cm^{-1} regions. The presence, in the first compound, of a band at 660 cm^{-1} and, in the second, at 1290 cm^{-1} is explained by the presence of P=S and P=O bonds, respectively. In most cases, however, the absorption bands in the infra-red spectra could not be related to the thiono group in thiophosphorus compounds. Gore concluded that the P=S group did not have characteristic frequencies. The same conclusion was reached by Daasch and Smith[4], and Bellamy and Beecher[10]. In a number of other publications[19,27,36] the absorption due primarily to the P=S bond was not identified. Bellamy[37] concluded that the P=S absorption occurred in the 600–750 cm^{-1} region and varied considerably in intensity. The absence of a marked absorption in this region cannot therefore be taken as an indication of the absence of the P=S group in a molecule.

McIvor *et al.*[18] studied the infra-red spectra of 50 organothiophosphorus compounds: the thiono group was characterised by frequencies in the 740–830 cm^{-1} region. However, this conclusion is not supported by a comparison of the spectra of the thiono compounds with the spectra of the thiolo and oxygenated organophosphorus compounds quoted. For example, in the spectrum of CH_3PSCl_2 a band at 780 cm^{-1} was assigned by the authors to the P=S bond, but the spectrum of CH_3POCl_2 has a band at 770 cm^{-1}, of similar intensity. The spectra of diethyl phosphorochloridothionate and diethyl phosphorochloridate have absorption bands of comparable intensity in the 800 cm^{-1} region, but the band at 817 cm^{-1} in the spectrum of diethyl phosphorochloridothionate was assigned to the thiono group. The infra-red spectra of $(CH_3O)_2P(S)H$ and $(CH_3O)_2P(O)H$ contain bands of equal intensity at a frequency of 795 cm^{-1}, but the authors assigned this band in dimethyl phosphonothionate to the thiono group. Similarly, other assignments made by McIvor *et al.* are doubtful. Later[38], the authors themselves expressed doubts about their assignments; however, in a summarising table they still indicate the 740–830 cm^{-1} region as the region of P=S stretching vibrations.

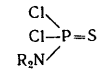
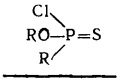
Only a few studies of Raman spectra of thiophosphorus compounds have so far been made. From the work of Simon and Schulze[39], Delwaulle and François[40-42], and others[36,43], it is known that the P=S bond in phosphorochloridothioic acids produces intense lines in the Raman spectra, the frequencies of which coincide with those of the infra-red absorption bands. Simon and Schulze[39,44], and Michalski *et al.*[45] report the spectra of several trialkyl phosphorothionates but do not analyse them.

To determine the characteristic frequencies of the P=S group, Popov *et al.*[26] examined the infra-red and Raman spectra of a large number of organic phosphorothionates, together with the corresponding phosphorothiolates and phosphates. It was observed that, in the infra-red spectra of molecules of different types, the P=S absorption bands differ widely in intensity. In investigations of the structure of many organothiophosphorus compounds the use of infra-red spectra alone cannot therefore be recommended. In addition, one must take into account the possibility of P–S–R (R = alkyl) groups giving rise to intense bands in the P=S region. In the Raman spectra of all the organothiophosphorus compounds examined, the P=S bands are considerably more intense than the P=O bands. This is possibly due to the small polarity of this bond and its readier polarisability. The P=S bands in infra-red spectra of organothiophosphorus compounds often consist of two or three frequencies. By comparing the P=S and P=O absorption band, it was concluded that the complexity of the P=S bands was due, as in phosphoryl compounds, to rotational isomerism. In the spectra of analogous thiono and phosphoryl molecules, the P=O and P=S bands are identical in character. For example, in the spectra of $RPSCl_2$ and $RPOCl_2$ the P=S and P=O bands are single when R = CH_3 and complex when R = C_2H_5 and C_3H_7.

Analysis of the spectra of the compounds and published data show that the frequencies associated with the P=S group are in the 550–750 cm^{-1} region and only have a constant value when the environment of the phosphorus atom is identical. Table 2 gives the mean values of the characteristic P=S frequencies for different types of organothiophosphorus compounds.

Simultaneously with the work of Popov *et al.*[26], Hooge and Christen[46] determined the stretching vibration frequencies of the P=S group in the infra-red spectra of the compounds $X_3P=S$ (X = CH_3, C_2H_5, CH_3O, C_2H_5O, C_2H_5, C_2H_5S), and gave a theoretical analysis of this vibration. The assignment of frequencies in the spectra of compounds examined in both studies agree with each other. Hooge and Christen also assume that the doublet character of the P=S and P=O bands, observed in the spectra of many organophosphorus compounds, is due to rotational isomerism.

TABLE 2.* P=S frequencies (cm^{-1}).

	750 cm^{-1}		580 cm^{-1}
			580 cm^{-1}
	700 cm^{-1}		670 cm^{-1}
	660 cm^{-1}		640 cm^{-1}
	610 cm^{-1}		655 cm^{-1}
	665 cm^{-1}		655 cm^{-1}
	550 cm^{-1}		685 cm^{-1}
	625 cm^{-1}		635 cm^{-1}

* R = alkyl radical.

This work shows that the frequencies assigned to the P=S group remain constant only if the immediate environment of the phosphorus atom does not change. This conclusion was confirmed by Mayants *et al.*[22,23] by a calculation of the normal vibrations and a numerical analysis of the dependence of frequency on force and kinetic parameters of the molecules $PSCl_3$, $PSBr_3$, and four of the possible conformations of $(CH_3O)_3PS$.

Table 3 lists the P=S frequencies for different types of thiophosphorus compound. The P=S frequencies, like the P=O frequencies, remain constant within the limits of experimental error so long as the environment of the thiono group is unchanged. This rule has the same limitations as the analogous rule for the P=O frequencies (see p. 364).

The results of these calculations and experimental assignments of frequencies[22,23,26] contradict the conclusions of McIvor *et al.*[18,38], which were criticised above.

Hooge and Christen[46] calculated the P=S vibration frequencies for $(CH_3)_3P=S$, $Cl_3P=S$, $Br_3P=S$, $-O_3P=S$, and $S_3P=S$. Using the same P=S bond force constant for all the models, it was concluded that the P=S stretching vibration frequency for molecules of the type $X_3P=S$ depends only on the mass of the atoms X and the force constants of the P–X bonds. The conclusion concerning the

TABLE 3. P=S frequencies in spectra of thiophosphorus compounds.

Compound	$\nu_{P=S}$, cm^{-1}	Lit. ref.	Compound	$\nu_{P=S}$, cm^{-1}	Lit. ref.
$PSCl_3$	748	3	$(C_3H_7O)_2P(S)NHCH_3$	645	26
CH_3PSCl_2	664	26	$(C_4H_9O)_2P(S)NHCH_3$	645	26
$C_2H_5PSCl_2$	665	26	$(iso\text{-}C_3H_7O)_2P(S)NHCH_3$	637	26
$C_3H_7PSCl_2$	660	26	$(CH_3O)CH_3PSCl$	620	26
$(CH_3O)_3PS$	646	46	$(C_2H_5O)CH_3PSCl$	625	26
$(C_2H_5O)_3PS$	608	26	$(iso\text{-}C_3H_7O)CH_3PSCl$	629	18
$(C_2H_5O)_2P(S)OH$	618	46	$(CH_3O)P(S)SH$	654	18
$(C_2H_5O)_2P(S)OCH_2CH_2SC_2H_5$	607	27	$(C_2H_5O)_2P(S)SH$	654	26
$(C_2H_5O)_2P(S)OPO(OC_2H_5)_2$	609	26	$(CH_3O)_2P(S)SCH_3$	655	26
$(CH_3O)_2PHS$	636	4	$(C_2H_5O)_2P(S)SC_2H_5$	655	26
$(C_2H_5O)_2PHS$	633	26	$(C_2H_5O)_2P(S)SCH_2SC_3H_7$	655	26
$(CH_3O)_2PSCl$	660	26	$(C_2H_5O)_2P(S)SCH_2CH_2SC_3H_7$	656	26
$(C_2H_5O)_2PSCl$	660	26	$(CH_3S)_3PS$	685	46
$(C_3H_7O)_2PSCl$	665	26	$(CH_3S)_2(iso\text{-}C_3H_7S)PS$	685	46
$(C_4H_9O)_2PSCl$	667	26	$(C_2H_5S)_2CH_3SPS$	685	46
$(iso\text{-}C_3H_7O)_2PSCl$	656	26	$(C_2H_5S)_3PS$	685	46
$(CH_3O)_2P(S)NHCH_3$	635	26	$(C_3H_7S)_3PS$	685	46
$(C_2H_5O)_2P(S)NHCH_3$	638	26	$(C_4H_9S)_3PS$	685	46

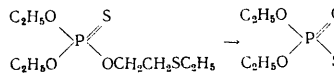
effect of the mass of the atoms X contradicts some of the data cited by the authors themselves; neither does it agree with the results of the calculation and analysis of the vibration frequencies of the molecules $PSCl_3$, $PSBr_3$, and $(CH_3O)_3PS$ made by Mayants *et al.*[22,23,25] Thus, according to the constant used by Hooge and Christen in their calculation, the force fields of $PSCl_3$ and $PSBr_3$ are effectively the same. The calculated P=S frequencies, in spite of the difference in mass of the chlorine and bromine atoms, are closely similar (750 and 736 cm^{-1} respectively) notwithstanding the conclusions of the authors. Where it has some effect, increase in mass must necessarily lower the frequency; however, the calculated P=S frequency in $(CH_3)_3P=S$ (555 cm^{-1}) is considerably lower than the frequency in $PSBr_3$ (736 cm^{-1}). The same is observed in the experimental vibrational spectra of these compounds (558 cm^{-1} and 718 cm^{-1} respectively).

The results of a more detailed and rigorous calculation[22,23,25] show that the so-called stretching vibration of the P=S bond is not confined only to this bond but is a more complex molecular vibration. In addition to P=S, the bonds and angles directly adjacent to the group play an appreciable part in this vibration. Therefore the force constants of PX, like other force constants of a tetrahedron with a phosphorus atom at the centre, have a definite influence on the P=S frequency. A quantitative estimate was also made[22,23,25] of the extent to which this vibration is characteristic, and the sensitivity of the frequency to variation of the force and kinematic parameters of the molecule was determined. According to these data, this frequency is most sensitive to variation of the force constant of the P=S bond. Likely changes in the values of other force constants cannot substantially affect the P=S frequency. Numerical analysis of the dependence of frequency on kinematic parameters proved that the effects of mass of the atoms X, of the length of the P–X bonds, and of the X–P–X and X–P=S angles, must be extremely small.

It can be seen from the above work on thiophosphorus compounds that vibrational spectra can, comparatively quickly and in most cases unambiguously, decide between a thiono or a thiolo structure in organothiophosphorus compounds. Vibrational spectra are therefore a useful means of investigation of thiono–thiolo isomerism, discovered by Pishchemuka[47] and Emmett and Jones[48] in trialkyl phosphorothioates.

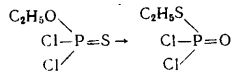
On heating, trialkyl phosphorothionates isomerise to trialkyl phosphorothiolates: $(RO)_3P=S \rightarrow (RO)_2(RS)P=O$. The difference in structure of the isomeric molecules has a substantial effect on their infra-red spectra. The marked difference in the spectra enables them to be used for qualitative and quantitative analysis both in the laboratory and in industry.

Henglein *et al.*[27] studied the isomerisation of the well-known insecticide *OO*-diethyl-*O*-ethylthioethyl phosphorothionate:



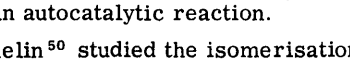
The quantity of thiolo isomer produced was determined chemically by oxidation with nitric acid and by means of infra-red spectroscopy; the results agreed well. The spectrum of *OO*-diethyl-*S*-ethylthioethyl phosphorothiolate, obtained by isomerisation, has an intense absorption band with a maximum at 1255 cm^{-1} associated with the P=O stretching vibration. The spectrum of the thiono isomer has no appreciable absorption in this region. The spectra of both compounds have a band at 1165 cm^{-1}, associated with vibrations of the $P-O-C_2H_5$ group. On isomerisation the position and intensity of this band remain unchanged. It can thus be used as an internal standard in quantitative analysis. The determination of isomer concentration by this method is very simple and exceptionally rapid.

Popov and Medenikova[49] used infra-red spectra to investigate the thermal isomerisation of ethyl phosphorodichloridothioate, an intermediate in the synthesis of a series of important organothiophosphorus insecticides.



In the spectra of ethyl phosphorodichloridothionate maintained at 120° for 1, 3, 4, 5, and 6 hours, it can be clearly seen that the bands characteristic of the groups $P-O-C_2H_5$ and P=S diminish in intensity with increase in the duration of heating, while the intensity of the P=O band of the thiolo isomer increases. After heating 6 h at 120° ethyl phosphorodichloridothionate has an infra-red spectrum similar to that of ethyl phosphorodichloridothiolate. For quantitative analysis the bands at 795 and 1270 cm^{-1} were chosen; these were convenient because they do not overlap any other bands and each is fairly intense only in the spectrum of one compound. The results of spectral analysis and refractometric measurements show that heating ethyl phosphorodichloridothionate for 6 h at 80° does not bring about any isomerisation; at 100° only a negligible amount of isomerisation occurs, while at 120° isomerisation is complete. The kinetics of the isomerisation are satisfactorily described by the equation for an autocatalytic reaction.

Tammelin[50] studied the isomerisation of *OO*-diethyl-*O*-ω-dimethylaminoethyl phosphorothionate by infra-red spectroscopy and paper chromatography. He showed that on heating for several hours at 100° the thiono isomer changes to *OO*-diethyl-*S*-ω-dimethylaminoethyl phosphorothiolate:



3. The P=N Group

Of the compounds in which phosphorus forms multiple bonds, those containing a P=N group have been least studied.

Daasch[51] analysed the Raman and infra-red spectra of the trimer and tetramer of phosphonitrilic chloride. Intense bands at 1218 cm^{-1} for the trimer and 1315 cm^{-1} for the tetramer were assigned to vibrations of the respective rings. Analogous bands were observed in the same region in the spectra of other trimers: $P_3N_3Cl_5Br$ 1205 cm^{-1}, $P_3N_3Cl_4Br_2$ 1202 cm^{-1}, $P_3N_3Cl_2Br_4$ 1180 cm^{-1},[52] $P_3N_3(N_2H_3)_6$ and its benzaldehyde and salicylaldehyde derivatives 1218 cm^{-1}.[53] The spectra of aliphatic esters of trimeric nitrilophosphoric acid do not have intense bands in this region[4]. Shaw[54] investigated the spectra of a large number of trimeric and tetrameric phosphonitrilic derivatives: the frequencies assigned to vibrations of six-and eight-membered rings were in the 1180–1270 cm^{-1} region for the trimers and 1270–1330 cm^{-1} for the tetramers.

Kabachnik *et al.*[55] investigated the infra-red spectra of phosphorimidates $(RO)_3P=NC_6H_5$ and phosphonimidates $(RO)_2R'P=NC_6H_5$ (R and R' = alkyl) containing a P=N group outside a ring. Intense bands in the 1350–1385 cm^{-1} region in the spectra of these compounds were assigned to P=N stretching vibrations. In the spectra of the isomeric anilidophosphates and anilidophosphonates there is no absorption in this region but an intense absorption occurs in the 1210–1270 cm^{-1} region, characteristic for compounds with a P=O group. To clarify the influence of substituents at the nitrogen atom on the absorption associated with the P=N vibration, the infra-red spectra of $(C_2H_5O)_3P=NC(O)CH_3$ and $(RO)_3P=NCH_3$ were obtained[55]. Absorption bands in the 1325–1385 cm^{-1} region were assigned to stretching vibrations of the P=N group. Horner and Oldiger[55a] studied the infra-red spectra of the compounds p-$R-C_6H_4-N=P(C_6H_5)_3$ (R = H, CH_3, CH_3O, Cl, $COOC_2H_5$, NO_2, and CN) and assigned to the P=N stretching vibration some absorption bands, very variable in intensity, in the 1160–1180 cm^{-1} region. The only basis for this was the assignment by Daasch[51] of a band at 1218 cm^{-1} to analogous vibrations of the molecule $(PNCl_2)_3$. It would possibly be correct to associate the P=N vibration in these compounds with the intense bands in the 1330–1370 cm^{-1} region, which is in good agreement with the data on phosphorimidates and phosphonimidates[55]. The correctness of the assignment by Horner and Oldiger of the bands in the 1330–1370 cm^{-1} region to N–C vibrations is doubtful.

Further accumulation of experimental data and theoretical consideration of the vibrations of phosphoronitrogen molecules is required before a final conclusion can be made concerning the characteristic nature of vibrations of the P=N group.

Associated with the question of identification of the P=N group is the question of structure and tautomerism of the N-substituted dialkyl phosphoramidates and phosphonamidates.

The tautomerism of the acid amides of pentavalent phosphorus are of some interest



This tautomerism is analogous to the lactam–lactim tautomerism.

The work of Bellamy and Beecher[11] and Holmstedt and Larsson[13] on the infra-red spectra of dialkyl N-alkylphosphoramidates shows that the tautomeric equilibrium in these substances is displaced towards the amide form (I).

In order to confirm the possibility of a tautomerism of this type (I ⇌ II) in a series of phosphoronitrogen compounds, Kabachnik *et al.*[56] displaced the equilibrium by introducing substituents of different electrophilic character at the nitrogen atom. The following N-substituted phosphoramidates and phosphonamidates were investigated and their infra-red spectra studied:

$(C_2H_5O)_2P(O)NHCOCH_3$,
$(C_2H_5O)CH_3P(O)NHCOCH_3$,
$(C_2H_5O)C_2H_5P(O)NHCOCH_3$,
$(C_2H_5O)_2P(O)NHP(O)(OC_2H_5)_2$,
$(C_2H_5O)_2P(O)NHSO_2CH_3$.

The spectroscopic data show that the amide form (I) predominates in the N-acetyl-substituted phosphoramidate and phosphonamidates. Thus intense absorption bands are observed in the 1200–1250 cm^{-1} and 3100 cm^{-1} regions, which are assigned to P=O and N–H vibrations, respectively.

The spectra of diethyl-N-diethylphosphoryl-phosphoramidate and diethyl-N-methanesulphonyl-phosphoramidate are different in appearance. In the spectrum of the first, absorption bands at ~1250 cm^{-1} and ~1390 cm^{-1} are assigned to stretching vibrations of P=O and P=N respectively. In that of the second, the band at 1390 cm^{-1}, characteristic of P=N, remains. Bands at 1235 cm^{-1} and 1315 cm^{-1} are ascribed to symmetric and asymmetric vibrations of the sulphonyl group. In addition, the spectra of both compounds have very diffuse bands in the 3000 cm^{-1} region, which are assigned to vibrations of hydrogen-bonded hydroxyl groups. When these compounds are deuterated their spectra change only in the hydroxyl group region: the intensity of the bands at 2700 cm^{-1} and 3000 cm^{-1} diminishes and new bands appear in the 2170–2320 cm^{-1} region. The presence of OH and P=N bands and the absence of clearly defined NH and P=O bands shows that the tautomeric equilibrium in these two compounds is displaced towards the imidol form (II).

Thus the introduction of the more electrophilic substituents, the phosphoryl and methanesulphonyl radicals, at the nitrogen atom in phosphoramidates displaces the tautomeric equilibrium towards the imidol form and proves the tautomerism of this type of compound.

4. The P–O–R Group

The experimental study of the vibrational spectra of organophosphorus compounds enabled a number of other assignments of bands to individual bonds and groups of bonds to be made.

In an investigation of the infra-red spectra of aliphatic esters of phosphoric and alkylphosphonic acids, Daasch and Smith[4] established the connection between the P–O–C group and a strong absorption band in the 1030–1050 cm^{-1} region. The extensive studies of Bellamy and Beecher[10-12] confirmed this assignment. At present, the spectra of a large number of alkyl phosphates and other compounds containing the P–O–C group are known (see Appendix); in all cases there is a very intense absorption band in the 995–1050 cm^{-1} region, the overwhelming majority of compounds absorbing at 1030 cm^{-1}.

In the same way that frequencies ascribed to C–O–C (alkyl) and C–O–C (aryl) bonds in ethers differ appreciably from each other, there is a marked difference between the frequencies for analogous P–O–C bonds. This difference was demonstrated by Bellamy and Beecher[10] with the spectra of triphenyl, diphenylethyl, phenyldiethyl, and triethyl phosphate. At the same concentration and in the same cell, a progressive weakening and then the complete disappearance of the 1200 cm^{-1} band was observed; at the same time the 1030 cm^{-1} band, absent in triphenyl phosphate, increased in intensity. Later it was established[11,12] that frequencies assigned to the P–O–C (aryl) group occurred in the range 1190–1240 cm^{-1} in the spectra of aromatic phosphates, phosphines, and phosphites.

Up to the present time, the spectra of only a few compounds containing the P–O–C (acyl) group have been studied[19,20]. It is very probable that the intense absorption band in the 1180–1200 cm^{-1} region in the spectra of these compounds is associated with this group. Thus, the experimental data show that the P–O–C frequencies are extremely sensitive to the type of substituent at the carbon atom. However, they remain practically unchanged in the spectra of organic phosphates, phosphorothionates, and phosphorimidates, and compounds of trivalent phosphorus.

Several publications discuss the more detailed assignment of frequencies in the 1000–1050 cm^{-1} region in spectra of alkyl phosphates. Thus Bergmann *et al.*[14] suggested that the absorption in this region was due to asymmetric vibration of the three P–O–C groups. The band at 980 cm^{-1} is assigned to the symmetrical vibrations of these groups. However, if this were the case, one would have expected a shift of the absorption band in spectra of compounds with two or one P–O–C groups: this is not observed.

Bellamy and Beecher[10-12] assigned the band in the 1000–1050 cm^{-1} region to the (P)O–C vibration and that at 980 cm^{-1} to the P–O(C) vibration. Baudler[16], Meyrick and Thompson[2], and others[17] assign a band in the 730–800 cm^{-1} region to the P–O(C) vibration.

Ketelaar and Gersmann[57] considered the vibration of a P–O–C group isolated from the rest of the molecule and concluded that, in molecules of phosphoric acid esters, the vibrations corresponding to P–O and C–O bonds in the P–O–C group are to a considerable extent isolated, the greater frequency being associated with the C–O vibration. Considering the unjustified assumptions made in the calculation, the authors' conclusions cannot be regarded as substantiated. A full calculation and analysis[23] of the vibration frequencies of the molecules $(CH_3O)_3PO$ and $(CH_3O)_3PS$ show that in these molecules local (P)O–C, P–O(C), and even P–O–C vibrations are absent. Frequencies in the 1000–1050 cm^{-1} and 730–800 cm^{-1} regions can only very provisionally be identified with O–C and P–O vibrations because, although the C–O bond (1000–1050 cm^{-1}) and the P–O bond (730–800 cm^{-1}) play the major part in these vibrations, the bonds and angles of the organic part of the molecule also vary appreciably. At the same time, the phosphoryl group in $(CH_3O)_3PO$ and the thiono group in $(CH_3O)_3PS$ take practically no part in these vibrations.

Analysis of the frequencies shows, on the one hand, their great sensitivity to changes in the force constants of the organic part of the molecule and, on the other hand, their small sensitivity to changes in the phosphorus part. This is in agreement with experiment. The so-called (P)O–C frequencies differ substantially in spectra of compounds containing alkyl, aryl, and acyl substituents at the phosphorus atom but coincide in spectra of compounds with P=O, P=S, or P=N groups and also in spectra of compounds of 5- or 3-valent phosphorus. The P–O(C) frequencies in spectra of trialkyl phosphates and trialkyl phosphorothionates change when one alkyl radical is exchanged for another. Calculation and experiment[17,23] show that the P–O frequencies differ by 15 cm^{-1} in rotational isomers of the molecule $(CH_3O)_3PO$, indicating that the vibration is sensitive to change in the angle of rotation of the methoxyl groups about the P–O bond.

The data of Daasch and Smith[4] show that in the spectra of compounds containing $(P)O-C_2H_5$ groups there is, in addition to the intense band at 1030 cm^{-1}, another sharp band of medium intensity at 1160 cm^{-1}. Bellamy and Beecher[10-12] confirmed this and noted that a similar band, but of greater intensity, appears in spectra of compounds containing the (P)O–C(aryl) group. In 70 compounds studied by them, containing a group of this kind, the band appears in the 1156–1163 cm^{-1} region. The presence in a spectrum of a band in this region and an intense band in the 1200 cm^{-1} or 1030 cm^{-1} region identifies one of these groups. For the $(P)O-CH_3$ group, there is also a characteristic band at 1190 cm^{-1} which, according to much of the data[4], is very constant and can be used as confirmation of the presence of methoxyl groups in phosphorus compounds.

Baudler[16] studied the Raman spectra of 22 compounds of the following types: $(RO_3)P$, $(RO)_2PX$, $ROPX_2$, $(RO)_3PO$, $(RO)_2POX$, and $(RO)_2POH$, where R = alkyl, X = Cl or Br. Lines of low intensity in the 950–1070 cm^{-1} region were assigned to the (P)O–C(alkyl) group; lines of frequency 1190 and 1160 cm^{-1} in cases where R = CH_3 and C_2H_5, were not observed in the Raman spectra.

5. The O–H and S–H Groups

It was noted above that the stretching vibration frequency of OH is shifted considerably to lower values as a result of intermolecular hydrogen bonding in compounds containing  groups. The corresponding absorption band in the infra-red spectra of dialkyl phosphates is very diffuse and occurs[4,10,12] in the 2560–2700 cm^{-1} region. This band persists in solutions in non-polar solvents. In the Raman spectrum of Cl_2POOH a diffuse band at 2819 cm^{-1} is assigned[58] to OH stretching vibrations. The spectrum of Cl_2POOD does not have a band at 2819 cm^{-1} but has a low-intensity OD stretching vibration band at 2093 cm^{-1}.

In spectra of compounds containing the  group[18,19] the absorption band that can be assigned to the OH stretching vibration is found in the 3100–3150 cm^{-1} region. There is no doubt that such low values for the OH frequencies are connected with association, while the diffuse nature of the absorption bands is evidence of intermolecular interaction between molecules of the organophosphorus acids. The association of alkyl alkylphosphonothioic acids is confirmed by cryoscopic data[20,25]. The molecular weight of acids of the (RO)P(S)OH type in benzene considerably exceeds the theoretical value, while corresponding exactly to it in phenol. The infra-red spectrum of alkyl alkylphosphonothioic acids heated to 90° show a shift of the absorption maximum by 60 cm^{-1} to higher frequency. Molecules of dialkyl phosphoric and phosphorothioic acids are also

associated[25,30,31]. A study of the concentration dependence of the association of these compounds[25] shows that the degree of association of dialkyl phosphates greatly exceeds that of dialkyl phosphorothioates. The more stable intermolecular hydrogen bond in diethyl phosphate also brings about a greater shift of the absorption maximum of the OH stretching vibration (2640 cm^{-1}) compared with diethyl phosphorothioate (3120 cm^{-1}).

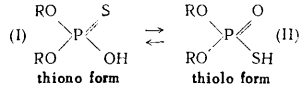
Molecules of dialkyl phosphorothioates, like molecules of the half esters of alkylphosphonothioic acid, can form a hydrogen bond by interaction between a proton and either the thiono group (O–H· · · S=P) or the oxygen atoms of the ester groups (O–H· · · O<P/R). To clarify this question, a study of the spectra of alkyl alkylphosphonothioic acids and cryoscopic measurements would be useful. The absence of ester groups in these acids would enable conclusions to be made concerning the interaction of a proton with the thiono group. Existing data allows one only to state that association of the type OH· · · S=P is either absent or very weak and that the intermolecular hydrogen bonding is mainly with oxygen atoms. This proposition is based on the position of the P=S frequencies in the spectra of phosphorus thio-acids. In the case of association with the thiono group, the P=S frequency should be markedly lower than in the corresponding ester; this occurs with dialkyl or trialkyl phosphates, for example, or with the esters and half esters of alkylphosphonic acids. In fact, the observed P=S frequencies[46] for diethyl phosphorothioate (618 cm^{-1}) and the ethyl ester of ethylphosphonothioic acid (586 cm^{-1}) practically coincide with the P=S frequencies for, respectively, trialkylphosphorothionates and dialkyl esters of alkylphosphonothioic acids; this is expected for molecules with identical immediate environments of the phosphorus atom and in the absence of strong intermolecular hydrogen bonding with the thiono group.

A few spectra of compounds containing the P–S–H group are known. Thus the infra-red spectra of phenyl phenylphosphonodithioic and ethyl ethylphosphonodithioic acids have been studied[59]. The spectra of the solid and fused compounds and also of their concentrated solutions have bands at 2420 and 2560 cm^{-1} which, by analogy with the spectra of mercaptans, were assigned to stretching vibrations of the thiol group. On dilution of the solutions and raising the temperature, the intensity of the diffuse 2420 cm^{-1} band diminishes appreciably. The authors explain the existence of two bands and the diffuse nature of the 2420 cm^{-1} band by the formation of polymeric complexes $(R_2PSSH)_n$ associated by SH· · · S hydrogen bonds. The doublet character of the 2420 cm^{-1} band in the spectra of ethereal solutions of phenyl phenylphosphonodithioic acid is related to the existence of two forms of association, SH· · · S and SH· · · O(ether). The infra-red spectra of pure dialkyl phosphorotetrathioic acids[60] have a diffuse SH stretching band at 2435 cm^{-1}. The 2435 cm^{-1} band disappears in spectra of solutions of the acids in carbon tetrachloride and a sharp band is found at 2545 cm^{-1}. This is considered to be caused by intermolecular hydrogen bonding SH· · · S=P which breaks down on dilution[60].

According to cryoscopic data[25], the molecular weight of diethyl phosphorodithioate in benzene, in the range permitted by the method, does not depend on concentration and agrees with the theoretical value. This shows that even if the molecules of acid are associated at higher concentrations, this is due only to a weak interaction, which is easily destroyed by the molecules of inert solvent. The infra-red spectrum of diethyl phosphorodithioate[18,25] and also the spectra of other dialkyl phosphorodithioates[18] has a diffuse doublet with maxima at 2540 and 2475 cm^{-1}. The spectrum of the acid in acetone has bands with maxima at 2500 and 2425 cm^{-1}. The spectrum of diethyl phosphorodithioate in carbon tetrachloride under the same conditions has sharp bands at 2590 and 2565 cm^{-1}. The doublet character of the bands cannot be due to intermolecular association in this case, since the acid is monomeric[25]. It is possible that the appearance of two S–H frequencies is due to the formation of two rotational isomers, in one of which hydrogen bonding occurs with an oxygen atom of the ester groups. This is confirmed by the fact that the spectra of thiophosphorus compounds whose molecules have no oxygen atoms show only one S–H frequency in inert solvents.

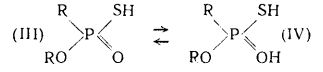
The question of structure and tautomerism of dialkyl phosphorothioates and half esters of alkyl phosphonothioic acids is closely related to the identification of P=O, P=S, O–H, and S–H groups.

The dialkyl phosphorothioates can be represented by two tautomeric forms, differing in the position of a hydrogen atom



Because of the rapid interconversion in this thiono–thiolo tautomeric system, the equilibrium cannot be studied by purely chemical means.

The tautomerism of the half esters of alkyl phosphonothioic acids is of the same type:



Kabachnik *et al.* studied the infra-red spectra of diethyl phosphorothioate[25] and a series of half esters of alkyl phosphonothioic acids[61]. In the spectra of these compounds there are no P=O and S–H bands of the thiolo isomer; instead there are intense diffuse bands with maxima in the 3100–3140 cm^{-1} region which can certainly be assigned to associated hydroxyl groups. The spectrum of diethyl phosphorothioate[46] also has a band at 618 cm^{-1} and that of ethyl hydrogen ethylphosphonothioic acid has a band at 586 cm^{-1} assigned to P=S stretching vibrations. Thus the spectra show that the favoured tautomeric forms are thiono forms (I) and (III). This aspect of thiono–thiolo tautomerism has been studied in greater detail by other methods[62-64].

Owing to the dual reactivity of salts of dialkyl hydrogen phosphorothioic and alkyl alkylphosphonothioic acids, it is not possible to draw any conclusions about the structure of the salts from the structure of the reaction products. Gore[3] studied the infra-red spectrum of crystalline potassium diethyl phosphorothioate and, on the grounds that there was no absorption in the 1200–1320 cm^{-1} region, concluded that it had a thiono structure. Kabachnik *et al.*[19,26] studied the infra-red spectra of crystalline sodium diethyl phosphorothioate and its solutions in absolute alcohol and chloroform. The spectra were similar to those of the potassium salt.

The spectra of the salts have a band in the 600–610 cm^{-1} region which is connected with the presence of a P=S group. Thus the alkali metal salts of dialkyl phosphorothioates have a similar, evidently thiono, structure.

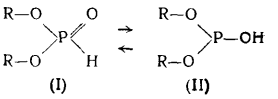
The infra-red spectra of the solid sodium salts of half esters of alkylphosphonothioic acids[21] and their solutions in absolute alcohol also show appreciable absorption in the 1200–1300 cm^{-1} region, which may be taken as evidence of the absence of the P=O bond. Further, a band at 580 cm^{-1} confirms their thiono structure. The structure of the salts of monothio acids of phosphorus has not yet been adequately studied.

Kabachnik and Mastryukova[65] showed that alkylation of the sodium and potassium salts of dialkyl phosphorothionic acids with ethyl bromide yielded thiolo derivatives. Hoegberg and Cassaday[66] came to the same conclusion from a study of the infra-red spectra of alkylation products. The alkylation products of the sodium salts of the half esters of alkylphosphonothioic acids also have a thiolo structure[20,21]. The spectra of these compounds have intense absorption bands in the 1215–1225 cm^{-1} region which are undoubtedly associated with P=O stretching vibrations. The products of acylation of sodium diethyl phosphate with acetyl chloride and propionyl chloride[19] do not absorb in the 1200–1300 cm^{-1} region. This establishes that they are thiono derivatives, *i.e.* acylation, in contrast to alkylation, proceeds without transfer of the reaction centre.

6. The P–H Group

The frequency of the P–H stretching vibration in liquid phosphine is[67] 2306 cm^{-1}. The Raman spectra of six dialkyl hydrogen phosphites, studied by Arbuzov *et al.*[1] have, in this region, an extremely intense broad band, the centre of which is at practically the same frequency near 2435 cm^{-1}. The authors assigned this band at 2435 cm^{-1} to the P–H stretching vibration and ascribed its somewhat diffuse nature to strong intermolecular interaction of the type P–H$\cdots$O. Meyrick and Thompson[2] showed that the P–H stretching vibration in infra-red spectra is associated with a band of medium intensity at 2435 cm^{-1}. Daasch and Smith[4] studied the infra-red spectra of $C_6H_5(OH)P(O)H$, $CH_3C_6H_4(OH)P(O)H$, $C_2H_5C_6H_4(OH)P(O)H$, $C_{10}H_7(OH)P(O)H$, $C_6H_5(C_2H_5O)P(O)H$, $(C_2H_5O)_2P(O)H$, $(C_4H_9O)_2P(O)H$, and found the P–H frequencies to be in the 2350–2440 cm^{-1} region. This assignment is confirmed by the fact that when hydrogen in the P–H group is replaced by deuterium, the band at 2381 cm^{-1} in the spectrum of phenylphosphonous‡ acid disappears and a new one appears at 1750 cm^{-1}, which can without doubt be assigned to P–D stretching vibrations. According to Simon and Feher[68] the Raman spectra of the alkali salts of phosphorous acid have the P–H stretching vibration at 2396 cm^{-1}. In a study of isotopic substitution in phosphorous acid in acid solution, Simon and Schulze[69] observed in the Raman spectra a diminution of intensity of the P–H band at 2485 cm^{-1} and an increase in intensity of the P–D band at 1744 cm^{-1}. In two months the intensity of both bands became equal. In the Raman spectrum[26] of $(C_2H_5O)_2P(S)H$ the P–H stretching vibration frequency is 2407 cm^{-1}; in the infra-red spectrum[70] of $(C_6H_5O)_2P(O)H$ it is 2420 cm^{-1}. Miller *et al.*[8], in an analysis of the infra-red spectra of a number of dialkylphosphinic acids, noted that the P–H stretching vibration frequency was sensitive to the nature of the substituent at the phosphorus atom and to the electronic state of the phosphoryl group. The authors made an unsuccessful attempt to relate P–H frequencies to the so-called "shift constants" obtained by Bell *et al.*[6] Houalla and Wolf[71] quote data on the integral intensities of the P–H stretching absorption bands for a number of dialkyl hydrogen phosphites. Because the intensities were close in value, in the range $0.6-0.7\times10^4$ $mole^{-1}$ cm^{-2}, they concluded that the P–H bonds in the compounds studied were identical in nature. On considerable dilution, the P–H frequencies are enhanced by only 10–15 cm^{-1} compared to the pure liquids. This indicates the low capacity of the hydrogen atom in a P–H bond for hydrogen bonding.

The question of structure and tautomerism of organic derivatives of phosphorous acid is closely linked to the identification of the P–H group. Dialkyl hydrogen phosphites may be depicted in two tautomeric forms, in one of which phosphorus is pentavalent (I) and in the other, trivalent (II)



(I) (II)

In the work of Arbuzov *et al.*[1], mentioned earlier, Raman spectra were used to establish the structures of dialkyl hydrogen phosphites. The P–H and P=O stretching vibration frequencies found by the authors in spectra of the liquid compounds confirmed that these compounds had a structure based on pentavalent phosphorus. In addition, narrow weak bands at 3150 cm^{-1} were found in the spectra of dipropyl and dibutyl hydrogen phosphites, which were assigned to stretching vibrations of associated OH groups in molecules containing a trivalent phosphorus atom. The authors thus concluded that dialkyl hydrogen phosphites existed in two tautomeric forms, the equilibrium being displaced towards form I.

Later Meyrick and Thompson[2] studied the Raman and infra-red spectra of dimethyl, diethyl, and di-isopropyl hydrogen phosphites. The spectra contained only bands specific for form I and the compounds studied were assigned structures based on pentavalent phosphorus.

Daasch[72] studied the infra-red spectra of liquid and crystalline dialkyl hydrogen phosphites and their solutions in dioxan and triethylamine. When the temperature, state of aggregation, and medium were changed, no absorption bands were observed in the spectra of diethyl, dibutyl, and di-iso-octyl hydrogen phosphites that could be associated with the formation of OH groups, which would have indicated the marked displacement of the tautomeric equilibrium towards form II. Baudler[73] came to the same conclusion in a study of the Raman spectra of dialkyl hydrogen phosphites (R = CH_3, C_2H_5, C_3H_7, and C_4H_9).

Thus, from the results of spectroscopic studies it may be considered as established that the position of tautomeric equilibrium of dialkyl hydrogen phosphites is strongly displaced towards the form containing a pentavalent phosphorus atom. Only in the work of Arbuzov *et al.*[1] were bands found in the spectra of dialkyl hydrogen phosphites that could be ascribed to vibrations of molecules of form II. However, these results have not been confirmed by later investigations.

Some interesting results, confirming the presence of a tautomeric equilibrium of the type I $\rightleftharpoons$ II in phosphonites, have recently been published by Griffiths and Burg[74]. The infra-red spectrum of ditrifluoromethylphosphonous acid

‡ The term alkyl phosphonous acid has been used in the translation since it is closest to the original Russian nomenclature, although these compounds are probably better described as alkyl phosphinic acids (Ed. of Translation).

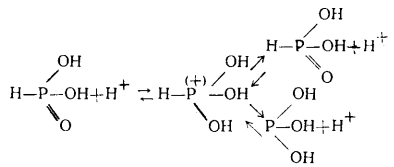
had no P=O and P–H absorption band corresponding to a molecule based on pentavalent phosphorus, but did have an intense band at 3620 cm^{-1}, assigned to the free stretching vibrations of the hydroxyl groups of the form $(CF_3)_2P-OH$. This shows that, when a strong electron-acceptor substituent is introduced into the molecule, the tautomeric equilibrium shifts towards the form containing trivalent phosphorus (II).

Numerous chemical investigations show that dialkyl hydrogen phosphites do not, in most cases, display properties characteristic of trivalent phosphorus compounds. The chemical properties of diphenyl hydrogen phosphite, studied by Kabachnik and Polikarpov[70], on the other hand, definitely testify to the presence of an appreciable quantity of form II in equilibrium with form I. However, the infra-red spectra of diphenyl hydrogen phosphite, studied by the same authors, favour the structure with the pentavalent phosphorus atom. It should be borne in mind that the absence of a band characteristic of molecules of the other form does not mean the complete absence of a tautomeric equilibrium but only that the concentration of that form is less than a few parts per cent.

The structure of salts of dialkyl hydrogen phosphites is of some interest. Daasch[72] studied the infra-red spectra of the following dialkyl phosphite salts: $(C_2H_5O)_2PONa$, $(C_2H_5O)_2POAg$, $(C_4H_9O)_2PONa$, $(C_4H_9O)_2POAg$, and $(C_4H_9O)_2POK$ in the crystalline state and in cyclohexane solution. The spectra of the salts of different metals are very similar and differ considerably from the spectra of the corresponding dialkyl hydrogen phosphites. They have no P=O stretching vibration bands. This establishes that they are derivatives of trivalent phosphorus: $\begin{matrix} R-O \\ R-O \end{matrix}\!\!>\!P-OM$.

The covalent structure of the salts studied by Daasch is supported by their solubility in non-polar solvents (limited, it is true, but quite sufficient for obtaining infra-red spectra). Daasch's conclusion concerning the structure of dialkyl phosphite salts cannot, however, be extended to salts of other acids derived from tervalent phosphorus. Thus, the infra-red spectrum of the sodium salt of trifluoromethylphosphonous acid, obtained by Bennett, Emeléus, and Haszeldine[75] corresponds completely to the formula $CF_3P(O)H(ONa)$ [*i.e.* sodium trifluoromethylphosphinate (Ed. of Translation)] and is inconsistent with $CF_3P(OH)(ONa)$. The spectrum contains bands at 2381 cm^{-1} and 1242 cm^{-1}, associated with P–H and P=O stretching vibrations. Salts of phosphorous acid itself apparently also have a structure based on pentavalent phosphorus. Simon and Schulze[69] made a detailed study of the structure of the barium salt of phosphorous acid. After prolonged exposure, the Raman spectrum of solid $BaHPO_3$ contained a P–H stretching vibration band. Earlier, Simon and Feher[68] obtained Raman spectra of the alkali salts of phosphorous acid. They also found P–H frequencies in the spectra of KH_2PO_3 (2396 cm^{-1}) and K_2HPO_3 (2314 cm^{-1}). From a study of the spectra of the alkali salts of phosphorous acid in crystalline form and in aqueous solutions, Tsuboi[76] also concluded that P–H bonds were present in the salt molecules. The author assigned frequencies to vibrations of PO_3 groups and the P–H anion, having C_{3v} symmetry.

Simon and Schulze[69] studied the tautomerism of phosphorous acid. Raman spectra of H_3PO_3 in alkaline and in acid solutions were identical. The spectrum of an alkaline solution of H_3PO_3 in heavy water, recorded two months after the solution was prepared, had no P–D stretching vibration bands. In acid solution, the P–D band appears within 24 h from the preparation of the solution, and after two months the P–D and P–H bands are of equal intensity. The isotopic exchange takes place only in an acid medium; it is catalysed by H^+ and apparently proceeds according to the following scheme:



The authors suggest that both tautomeric forms of H_3PO_3 exist but that the concentration of the form $P(OH)_3$ is negligible.

7. The P–O–P, P–X and Other Groups

In the literature on the vibrational spectra of phosphorus compounds many other experimental assignments are discussed and attempts are often made to find a characteristic frequency for each bond in the molecule. Since this is not possible in principle, the assignments by many authors are extremely nominal and have a limited applicability.

Bergmann *et al.*[14] studied the infra-red spectra of tetramethyl, tetraethyl, and tetraisopropyl pyrophosphate and compared them with the spectra of the appropriate phosphates. Merely on the grounds that the spectra of the pyrophosphates contained bands at 970, 939, and 950 cm^{-1} respectively, which were not found in the spectra of the phosphates, the authors assigned these bands to asymmetric vibrations of the P–O–P group, in spite of the fact that phosphates also have intense absorption bands in this region. For example, the spectrum of tri-isopropyl phosphate has bands at 995 and 931 cm^{-1} and that of triethyl phosphate has one at 974 cm^{-1}. Holmstedt and Larsson[13], having evidently found no substantial difference in the infra-red spectra of phosphates and pyrophosphates in the 930–970 cm^{-1} region, proposed that the vibration of the pyrophosphate P–O group appears in the 700 cm^{-1} region. Their assignments too are insufficiently well founded, since they were obtained from the spectra of only two compounds. Other conclusions[10,15,18] concerning the characteristic nature of vibrations of the pyrophosphate group are also open to doubt.

Authentic characteristic frequencies of the P–C bond in the spectra of aliphatic compounds have not been established. Daasch and Smith[4] associate the vibration of the group with absorption in the 650–760 cm^{-1} region. However, many organophosphorus compounds that have no P–C group absorb in this region. Daasch and Smith[4] also obtained the spectra of a large number of phosphorus-containing aromatic compounds with the P–C (aryl) group. In all cases sharp bands of medium intensity were found in the 1435–1450 and 995–1005 cm^{-1} regions. These bands were assigned to vibrations of the $P-C_6H_5$ bond, but the authors point out that they could with equal justification be ascribed to vibrations of the benzene ring.

Phosphorus trichloride[77] has two absorption bands, 488 and 511 cm^{-1}, which correspond to P–Cl stretching vibrations. The spectrum of $POCl_3$ [3,4,37] similarly has two bands at 486 and 582 cm^{-1}; that of $PSCl_3$ [3,26,87] has two at 430 and 540 cm^{-1}, corresponding to the symmetrical and doubly degenerate P–Cl vibrations. Daasch and Smith[4]

studied the infra-red spectra of seven other organophosphorus compounds containing the P–Cl group. The spectra of molecules containing two atoms of chlorine had bands in the 433–500 and 500–572 cm^{-1} regions. The spectrum of diphenylchlorophosphine oxide, as would be expected, has only one band in this region at 521 cm^{-1}. Bands corresponding to P–Cl stretching vibrations are usually very intense in both infra-red and Raman spectra. Daasch and Smith also studied the infra-red spectra of six fluorine-containing phosphorus compounds and made a tentative assignment of the P–F stretching vibrations in pentavalent phosphorus compounds to the 850–900 cm^{-1} region and in tervalent phosphorus compounds to the 750–900 cm^{-1} region. Other authors[5,79] give an analysis of the infra-red spectra of PF_3 (bands at 892 cm^{-1} and 860 cm^{-1} are assigned to symmetrical and asymmetrical P–F vibrations), PF_5, and POF_3.

The spectra of compounds with P–Br and P–I bonds have not received much study. The P–Br stretching vibration frequencies[77] in PBr_3 are 380 and 400 cm^{-1}, in $POBr_3$ 340 and 488 cm^{-1}, and in $PSBr_3$[40,24] 299 and 438 cm^{-1}. Baudler[16] obtained the Raman spectra of $(C_6H_5O)PBr_2$ and $(C_6H_5O)_2PBr$. Very intense bands in the 370 and 410 cm^{-1} region were assigned to the P–Br stretching vibration.

Calculation of the normal vibrations of the molecules $POCl_3$, $POBr_3$, $PSCl_3$, and $PSBr_3$[22,24] confirms the experimental assignments of frequencies to P–X (X = = halogen) bonds. The values of these frequencies are determined mainly by the P–X force constants. Determination of the sensitivity of frequency to isotopic variations in the mass of the chlorine atoms[24] shows that, in the molecules $POCl_3$ and $PSCl_3$, the frequencies of symmetrical vibration with ^{37}Cl atoms should be ~10 cm^{-1} less and those of asymmetric vibration ~5 cm^{-1} greater than with ^{35}Cl atoms.

The assignment of frequencies to other bonds and groups is also discussed in the literature. Thus, attempts have been made to find characteristic frequencies for the stretching vibrations of P–S,[18] P–S–P,[18] P–N,[11,13] the deformation vibrations of H–P=O, O–P–O, etc.[16,73] The data concerning these groups are not very reliable and cannot as yet be applied.

Thus, a large quantity of experimental data has been accumulated on the vibrational spectra of organophosphorus compounds, and has formed the basis of many assignments of frequencies to various groups. In some cases, the experimental data have been examined theoretically; this has made possible the interpretation of the changes occurring in the spectra between one molecule and another.

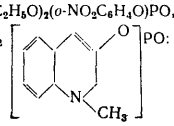
APPENDIX

In this section of the review are listed the phosphorus compounds whose vibrational spectra has been published up to the middle of 1960.

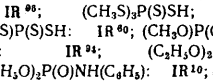
The substances are divided into four groups, *viz.* organic phosphates, compounds containing a carbon-phosphorus bond, phosphites, and certain inorganic phosphorus compounds whose spectra could be of some interest in a study of organic phosphorus compounds. After the formula of the compound the literature reference is given and an indication of the type of spectrum studied (infra-red spectrum IR, Raman spectrum R). [*i*- stands for iso-, as in the original Russian text (Ed. of Translation)].

Phosphates

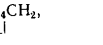
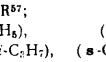
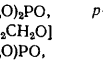
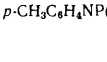
$(CH_3O)_3PO$: IR[4,14,17], R[1,16]; $(C_2H_5O)_3PO$: IR[3,10,14,17], R[1,16,26,45]; $(C_3H_7O)_3PO$: IR[14], R[1]; $(i\text{-}C_3H_7O)_3PO$: IR[14], R[80]; $(C_4H_9O)_3PO$: IR[10,14,81,82], R[1,16]; $i\text{-}C_4H_9O)_3PO$: R[1]; $(C_4H_9CH(C_2H_5)CH_2O)_3PO$: IR[11,12]; $(cyclo\text{-}C_6H_{11}O)_3PO$, $(p\text{-}NO_2C_6H_4CH_2O)_3PO$, $(C_4H_9CH(C_2H_5)CH_2O)(C_2H_5O)_2PO$, $(C_4H_9CH(C_2H_5)CH_2O)_2(C_2H_5O)PO$: IR[11]; $(C_{18}H_{37}O)_3PO$: IR[12]; $(CH_3O)_2P(O)OCH{=}CCl_2$: IR[83], $(CH_2Cl{-}CH_2O)_3PO$: IR[10]; $(C_2H_5O)_2P(O)OCH{=}CCl_2$: IR[84]; $(C_2H_5O)_2P(O)OCCl{=}CCl_2$: IR[85]; $(C_6H_5O)(C_2H_5O)_2PO$: IR[3,10]; $(p\text{-}CH_3C_6H_4O)(C_2H_5O)_2PO$: IR[3]; $(p\text{-}NO_2C_6H_4O)_2(C_2H_5O)PO$: IR[3,10,86], R[86]; $[(p\text{-}COONa)C_6H_4O](C_6H_5O)_2PO$, $[(m\text{-}COONa)C_6H_4O](C_2H_5O)_2PO$, $(CH_3O)_2$ $m\text{-}[N(CH_3)_3^+]C_6H_4OPO$, $(C_2H_5O)_2[m\text{-}C(O)OC_6H_4CH_2]C_6H_4OPO$: IR[57]; $(C_2H_5O)_2p\text{-}(C_2H_5C_6H_{12}C_6H_4OPO$: IR[11]; $(C_2H_5O)_2(o\text{-}NO_2C_6H_4O)PO$, IR[3]; $(C_2H_5O)_2(p\text{-}ClC_6H_4O)PO$,



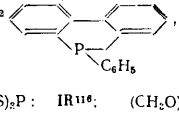
$(i\text{-}C_4H_9O)_2(p\text{-}C_4H_9CH(C_2H_5)CH_2{-}C_6H_4O)PO$: IR[11]; $(CH_3O)(p\text{-}NO_2C_6H_4O)_2PO$, IR[57]; $(C_2H_5O)(C_6H_5O)_2PO$: IR[10]; $(C_2H_5O)(p\text{-}NO_2C_6H_4O)_2PO$: IR[57]; $(C_6H_5O)_3PO$: IR[4,10,17,82,87] $(p\text{-}CH_3C_6H_4O)_3PO$, $(m\text{-}CH_3C_6H_4O)_3PO$: IR[10,87]; $(o\text{-}CH_3C_6H_4O)_3PO$: IR[10]; $(p\text{-}NO_2C_6H_4O)_3PO$: IR[57]; $(CH_3O)(C_2H_5O)POOH$: IR[4]; $(C_2H_5O)_2POOH$: IR[9,26,57] $(i\text{-}C_3H_7O)_2POOH$: IR[80], R[80]; $(C_4H_9O)_2POOH$, $(i\text{-}C_4H_9O)_2POOH$, $(C_5H_{11}O)_2POOH$, $(i\text{-}C_5H_{11}O)_2POOH$, $(C_6H_5CH_2)_2POOH$, $(C_4H_9CH(C_2H_5)CH_2O)_2POOH$: IR[12]; $[(CH_3)_3CCH(CH_3)C_2H_4O]_2POOH$: IR[11]; $(C_6H_5O)_2POOH$, $[p\text{-}CH_3C(CH_3)_2CH_2C(CH_3)_2{-}C_6H_4O]_2POOH$: IR[30,31]; $(p\text{-}C_8H_{17}{-}$ $-C_6H_4O)_2POOH$: IR[12]; $(NO_2C_4H_8O)_2POOH$: IR[30,31], $(CH_3O)_2PO_2Na$, $(CH_3O)_2PO_2K$, $(CH_3O)_2PO_2Ag$, $[(CH_3O)PO_2]_2Ba$, $(CH_3O)_2PO_2\overset{+}{N}H_3C_6H_{11}$, $(C_2H_5O)_2PO_2Na$, $(C_2H_5O)_2PO_2K$, $(C_2H_5O)_2PO_2Ag$, $[(C_2H_5O)_2PO_2]_2Ba$, $(C_2H_5O)_2PO_2\overset{+}{N}H_3C_6H_{11}$: IR[88]; $(i\text{-}C_3H_7O)_2PO_2Na$: IR[38,88]; $(i\text{-}C_3H_7O)PO_2K$, $(i\text{-}C_3H_7O)_2PO_2Ag$, $[(i\text{-}C_3H_7O)_2PO_2]Ba$, $(i\text{-}C_3H_7O)_2PO_2\overset{+}{N}H_3C_6H_{11}$: IR[88]; $(C_4H_9O)_2PO_2Li$, $(C_4H_9O)_2PO_2Na$: IR[89]; $(C_4H_9O)_2PO_2Ag$: IR[12,89]; $[(C_4H_9O)_2PO_2]_2Ba$, $[(C_4H_9O)_2PO_2]_2Mn$, $[(C_4H_9O)_2PO_2]_2Cu$, $(C_4H_9O)_2PO_2Ni$, $[(C_4H_9O)_2PO_2]_2Pb$, $[(C_4H_9O)_2PO_2]_2Hg$, $(C_4H_9O)_2PO_2Hg$, $[(C_4H_9O)_2PO_2]_3La$, $[(C_4H_9O)_2PO_2]_3Y$, $[(C_4H_9O)_2PO_2]_3Ce$, $[(C_4H_9O)_2PO_2]_4Ce$, $[(C_4H_9O)_2PO_2]_3Fe$, $[(C_4H_9O)_2PO_2]_3Bi$, $[(C_4H_9O)_2PO_2]_4Zr$, $[(C_4H_9O)_2PO_2]_6U$: IR[89]; $[(i\text{-}(C_4H_9O)_2PO_2]Pb$, $[(i\text{-}C_5H_{11}O)_2PO_2]_2Pb$; $[C_4H_9CH(C_2H_5)CH_2O]_2PO_2Ag$: IR[11]; $(C_6H_5CH_2O)PO_2Ag$: IR[11,12]; $[(C_6H_5CH_2O)_2PO_2]_2Pb$: IR[12]; $(C_6H_5O)_2PO_2Ag$, $(C_6H_5O)PO_3Ag_2$: IR[11]; $[(p\text{-}NO_2C_6H_4O)_2PO_2]_2Pb$, $(C_6H_5O)PO_3Pb$, $[(p\text{-}C_8H_{17}\cdot C_6H_4O)_2PO_2]_2Pb$: IR[12]; (2,4,6-$Cl_3C_6H_2O)_2PO_2Ag$: IR[12]; $CH_3C(O)OPO_3Li_2$: IR[57]; $(CH_3O)_2P(O)OP(O)(OCH_3)_2$: IR[4,14], R[90]; $(C_2H_5O)_2P(O)OP(O)(OC_2H_5)_2$: IR[4,13,14,18], R[90]; $(C_3H_7O)_2P(O)OP(O)(OC_2H_5)_2$ IR[14,18]; $(i\text{-}C_3H_7O)_2P(O)OP(O)(Oi\text{-}C_3H_7)_2$: IR[14]; $(C_4H_9O)_2P(O)OP(O)(OC_4H_9)_2$, IR[4,14]; $(C_6H_5CH_2O)_2P(O)OP(O)(OCH_2C_6H_5)_2$: IR[11]; $(CH_3O)_2POF$: IR[4]; $(CH_3O)_2POCl$: IR[18]; R[16]; $(C_2H_5O)_2POCl$: IR[3,4,10,13,18], R[16]; $(C_3H_7O)_2POCN$: IR[18]; $(C_3H_7O)_2POCl$: IR[18], R[16]; $(i\text{-}C_3H_7O)_2PO$: IR[38,90], R[38,90]; $(i\text{-}C_3H_7O)_2POCl$: IR[18,80], R[80]; $(CH_3O)_2P(O)P(O)(CH_3O)_2$: R[91]; $(C_6H_5O)_2P(O)P(O)(OC_6H_5)_2$: IR[92], R[93]; $(C_2H_5O)_2P(O)SCH_2$: IR[19]; $(C_2H_5O)_2P(O)SC_2H_5$: IR[3,16,87], R[26,45]; $(C_2H_5O)_2P(O)SC_5H_{11}$: IR[3]; $(C_2H_5O)_2P(O)SCH_2CH_2SC_2H_5$: IR[27], R[26]; $(C_2H_5O)_2P(O)SCH_2C_6H_5$: IR[19]; $(C_2H_5O)_2P(O)SC_6H_5$, IR[3]; $(C_2H_5O)_2P(O)SC(O)OCH_3$: IR[19]; $(C_4H_9O)_2P(O)Si(CH_3)_3$: IR[92]; $(C_6H_5O)_2POCl$: IR[10], R[16]; $(C_6H_5O)POCl_2$: IR[10], R[38]; $(C_2H_5S)POCl_2$: IR[26]; $(C_3H_7S)POCl_2$, $(C_4H_9S)POCl_2$: IR[38]; $(C_6H_5S)_2(O)OC_2H_5$: IR[3]; $(C_2H_5S)_2POCl$: R[26]; $(C_2H_5S)_3PO$: IR[18,87]; $(CH_3O)_3PS$: IR[4]; $(C_2H_5O)_2P(S)OCH_3$: IR[19] $(C_2H_5O)_3PS$: IR[3,18], R[26,45]; $(C_2H_5O)_2P(S)OC_6H_{13}$: IR[3]; $(C_2H_5O)_2P(S)OCH_2CH_2SC_2H_5$: IR[27], R[26]; $(C_2H_5O)_2P(S)OCH_2C_6H_5$: IR[19]; $(C_2H_5O)_2P(S)OC_6H_5(C_2H_5O)_2P(S)OC_6H_4{-}p\text{-}CH_3$: IR[3]; $(C_2H_5O)_2P(S)OC_6H_4{-}p\text{-}NO_2$: IR[3,10,86], R[86]; $(C_2H_5O)_2P(S)OC_6H_4{-}o\text{-}NO_2$: IR[3]; $(C_2H_5O)_2P(S)OC(O)CH_3$, $(C_2H_5O)_2P(S)OC(O)C_2H_5$: IR[19]; $(CH_3O)_2PSOH$: IR[39]; $(C_2H_5O)_2PSOH$: IR[18,57]; $(C_2H_5O)_2PSOK$: IR[8]; $(C_2H_5O)_2PSONa$: IR[19,26]; $(C_2H_5O)_2PSO\overset{+}{N}H(C_2H_5)_3$: IR[18,38]; $(C_3H_7O)_2PSO\overset{+}{N}H(C_2H_5)_3$, $(C_4H_9O)_2PSO\overset{+}{N}H(C_2H_5)_3$: IR[38]; $(p\text{-}NO_2C_6H_4O)_2P(S)OC_2H_5$: IR[10,57]; $(p\text{-}NO_2C_6H_4O)_3PS$: IR[57]; $(CH_3O)_2P(S)OP(O)(OCH_3)_2$, $(C_2H_5O)_2P(S)OP(O)(OCH_3)_2$, $(CH_3O)_2P(S)OP(O)(OCH_3)_2$: IR[18]; $(C_2H_5O)_2P(S)OP(O)(OC_2H_5)_2$: IR[18,26], R[45,90]; $(C_3H_7O)_2P(S)OP(O)(OC_3H_7)_2$: IR[18,38]; $(C_4H_9O)_2P(S)OP(O)(OC_4H_9)_2$, $(i\text{-}C_3H_7O)_2P(S)OP(O)(Oi\text{-}C_3H_7)_2$: IR[18]; $(C_2H_5O)_2P(S)OP(S)(OC_2H_5)_2$: IR[19,57]; $(CH_3O)_2P(S)NHCH_3$, $(C_2H_5O)_2P(S)NHCH_3$ $(C_3H_7O)_2P(S)NHCH_3$, $(i\text{-}C_3H_7O)_2P(S)NHCH_3$, $(C_4H_9O)_2P(S)NHCH_3$: IR[26]; $(C_6H_5O)_2P(S)N(CH_3)_2$: IR[38,94]; $(C_2H_5O)_2P(S)N(C_2H_5)_2$, $(C_2H_5O)_2P(S)N(C_3H_7)_2$, $(C_3H_7O)_2P(S)N(C_2H_5)_2$, $(C_4H_9O)_2P(S)N(C_2H_5)_2$, $(i\text{-}C_3H_7O)_2P(S)N(C_2H_5)_2$, $(i\text{-}C_3H_7O)_2P(S)N(C_3H_7)_2$, $(i\text{-}C_3H_7O)_3P(S)N(i\text{-}C_3H_7)_2$, $(C_4H_9O)_2P(S)N(C_2H_5)_2$, $(C_4H_9O)_2P(S)N(C_3H_7)_2$, $[(C_2H_5)_2NCH_2CH_2O](C_2H_5O)P(S)N(CH_3)_2$, $[(C_2H_5)_2NCH_2CH_2O](C_2H_5O)P(S)N(CH_3)_2$: IR[38]; $(CH_3O)_2PSCl$: IR[19,26]; $(C_2H_5O)_2PSCl$: IR[3,18,26], R[26]; $(C_3H_7O)_2PSCl$: IR[19,26]; $(i\text{-}C_3H_7O)_2PSCl$: IR[18,26,37]; $(C_4H_9O)_2PSCl$: IR[18,26]; $CH_3O)_2PSCl_2$: IR[18]; $(C_2H_5O)_2PSCl$: IR[18,26,39], R[26]; $(C_2H_5O)(CH_3)_2NPSCl$, $(C_4H_9O)(CH_3)_2NPSCl$: IR[33]; $(CH_3)_2NPSCl_2$: IR[26,38], R[26]; $(C_2H_5)_2NPSCl_2$: IR[38]; $(CH_3O)_2P(S)SCH_3$: IR[19]; $(C_2H_5O)_2P(S)SC_2H_5$: IR[19,28], R[26]; $(C_2H_5O)_2P(S)SC_6H_{11}$; IR[3]; $(C_2H_5O)_2P(S)SCH_2SC_2H_7$; IR[26]; $(C_2H_5O)_2P(S)SCH_2CH_2SC_2H_5$: IR[26], R[26]; $(C_4H_9O)_2P(S)SCH_2CH_2SC_2H_7$: IR[26]; $(C_2H_5O)_2P(S)SC_6H_5$, $(C_2H_5O)_2P(S)SC_6H_4{-}p\text{-}CH_3$: IR[3]; $(C_2H_5O)_2P(S)SC(O)OC_5H_{11}$: IR[3]; $(CH_3O)P(S)SH$: IR[18,39,95]; $(C_2H_5O)_2P(S)SH$: IR[3,18,26,38,95], R[26]; $(C_3H_7O)_2P(S)SH$, $(i\text{-}C_3H_7O)_2P(S)SH$, $(C_4H_9O)_2P(S)SH$: $(C_2H_5O)_2P(S)SNa$: IR[38]; $(C_2H_5O)_2P(S)SK$; $(C_2H_5O)_2P(S)SP(S)(OC_2H_5)_2$, $(i\text{-}C_3H_7O)_2P(S)SP(S)(Oi\text{-}C_3H_7)_2$, $[(C_2H_5)_2NCH_2CH_2S]C_2H_5OP(S)N(CH_3)_2$, $[(C_2H_5)_2NCH_2CH_2S]$- $-C_3H_7OP(S)N(CH_3)_2$, $(i\text{-}C_3H_7S)PSCl_2$; IR[38]: $(CH_3S)_2PS$, $(C_2H_5S)_2(CH_3S)PS$: IR[96];

$(C_2H_5S)_3PS$: IR [8,95]; $(C_2H_7S)_3PS$, $(i\text{-}C_3H_7S)(C_2H_5S)(CH_3S)PS$, $(i\text{-}C_3H_7S)_2(CH_3S)PS$, $(i\text{-}C_3H_7S)_3PS$, $(C_4H_9S)_3PS$: IR [95]; $(CH_3S)_3P(S)SH$; $(CH_3S)(C_2H_5S)P(S)SH$, $(CH_3S)(C_2H_5S)P(S)SH$, $(CH_3S)(i\text{-}C_3H_7S)P(S)SH$: IR [60]; $(CH_3O)P(O)NH_2$, $(C_2H_5O)P(O)NH_3$: IR [13,36]; $(C_2H_5O)_2P(O)N(CH_3)_2$: IR [94]; $(C_2H_5O)_2P(O)N(CH_3)_2$: IR [15]; $(C_2H_5O)_2P(O)NHC(O)CH_3$: IR [97]; $(C_2H_5O)_2P(O)NH(C_6H_5)$: IR [10]; $(C_2H_5O)_2P(O)NCH_3(C_6H_5)$; $(C_2H_5O)_2P(O)NC_2H_5(C_6H_5)$: IR [95]; $(C_2H_5O)_2P(O)OP(O)[N(CH_3)_2]_2$: IR [15]; $(C_2H_5O)_2P(O)N(C_2H_5)P(O)[N(CH_3)_2]_2$, $(C_2H_5O)_2P(O)N(C_2H_5)P(O)(OC_2H_5)_2$, $(C_3H_7O)_2P(O)N(CH_3)_2$: IR [94]; $(i\text{-}C_3H_7O)_2P(O)NH_2$, $(i\text{-}C_3H_7O)_2P(O)NHCH_3$, $(i\text{-}C_3H_7O)_2P(O)N(CH_3)_2$: IR [80], R [80]; $(i\text{-}C_3H_7O)_2P(O)N(CH_3)_2$, $(i\text{-}C_3H_7O)_2P(O)N(C_2H_5)$, $(i\text{-}C_3H_7O)_2P(O)N(C_2H_5)P(O)(OC_2H_7)_2$: IR [94]; $(C_6H_5CH_2O)_2NH_2PO$, $(C_6H_5CH_2O)_2C_6H_3NHPO$, $(C_6H_5CH_2O)_2C_6H_5NCH_3PO$, $(o\text{-}C_2H_5NHC_6H_4O)(C_6H_5CH_2O)_2PO$,  $(C_3H_5CH_2O)PO$, $(C_6H_5O)_2NH_2PO$, $(C_6H_5O)_2C_6H_5NHPO$: IR [11]; $(p\text{-}Cl\cdot C_6H_4O)_2C_2H_5NHPO$: IR [57]; $(C_6H_5CH_2O)_2C_6H_5CH_2NHPO$: IR [11]; $(C_2H_5O)(CH_3)_2NP(O)OP(O)N(CH_3)_2(OC_2H_5)$: IR [18]; $(C_2H_5O)(CH_3)_2NPOOH$: IR [38]; $(CH_3)_2N]_2P(O)OP(O)[N(CH_3)_2](OC_2H_5)$: IR [15]; $(C_2H_5O)(CH_3)_2NPOCl$: IR [13,38]; $(C_2H_5O)(CH_3)_2NP(O)CN$: IR [13]; $[(CH_3)_2N]_2P(O)(OC_2H_5)$: IR [15]; $[(CH_3)_2N]_2P(O)(OC_4H_9)$: IR [94]; $(C_6H_5O)(NH_2)_2PO$: IR [11]; $(p\text{-}ClC_6H_4NH)NH_2P(O)OH$: IR [95]; $(C_6H_5O)(C_6H_5NH)_2PO$: IR [11]; $(p\text{-}ClC_6H_4O)(C_6H_5NH)_2PO$: IR [57]; $[(CH_3)_2N]_2P(O)OP(O)[N(CH_3)_2]_2$, $(C_6H_5NH)_2POOH$, $(C_6H_5NH)_2PO_2Ag$: IR [10]; $(CH_3)_2NPOCl_2$, $[(CH_3)_2N]_2POF$: IR [10]; $[(CH_3)_2N]_2PCCl$: IR [15]; $[(CH_3)_2N]_3PO$, $[(C_2H_5)_2N]_2PO$: IR [87]; $(C_2H_5O)_2PNC_6H_5$, $(C_2H_5O)_3PNC(O)CH_3$: IR [58]; $(C_2H_5O)_2O(OH)NP(O)(OC_2H_5)_2$, $(C_2H_5O)_2P(OD)NP(O)(OC_2H_5)_2$, $(C_2H_5O)_2P(OH)NSO_2CH_3$, $(C_2H_5O)_2P(OD)NSO_2CH_3$: IR [97]; $(C_3H_7O_3)PNC_6H_5$, $(i\text{-}C_3H_7O)_3PNC_6H_5$, $(C_4H_9O)_3PNC_6H_5$, $(C_2H_5O)_2C_6H_5NHPNC_6H_5$, $(C_3H_7O)_2C_6H_5NHPNC_6H_5$: IR [88]; $P_3N_3Cl_6$: IR [4,51,54], R [51]; $P_3N_3Cl_4[N(C_2H_5)_2]_2$, $P_3N_3Cl_4[N(CH_3)_2]_2$, $P_3N_3Cl_4[NHCH_3)_2$, $P_3N_3Cl_4(C_6H_5)_2$, $P_3H_3Cl_3[N(C_2H_5)_2]_3$, $P_3N_3Cl_2[N(CH_3)_2]_4$, $P_3N_3[N(CH_3)_2]_6$, $P_3N_3(N_2H_3)_6$, $P_3N_3Br_6$: IR [54]; $P_3N_3(OCH_3)_6$: IR [4,54]; $P_3N_3(OC_2H_5)_6$, $P_3N_3(OC_3H_7)_6$, $P_3N_3(Oi\text{-}C_3H_7)_6$, $P_3N_3(OC_6H_{17})_6$: IR [4]; $P_3N_3(CH_3)_6$: IR [90]; $P_4N_4Cl_8$: IR [4,51,54], R [51]; $P_4N_4Br_8$, $P_4N_4Cl_4(C_6H_5)_4$, $P_4N_4(OCH_3)_8$, $P_4H_4[N(CH_3)_2]_8$: IR [54]; $P_4N_4(CH_3)_8$: IR [99]; $(PNCl_2)_x$, $[PN(OC_6H_5)_2]_x$: IR [4]; $[(CH_3)_3SiO]_3PO$: R [100]$[(CH_3)_2NCH_2CH_2O](C_2H_5O)_2PO$, $[(CH_3)_2NCH_2CH_2S](C_2H_5O)_2PO$, $[(CH_3)_2NCH_2CH_2S](i\text{-}C_3H_7O)PO$, $[(CH_3)_2NCH_2CH_2O](C_2H_5O)_2PS$: IR [50]; $[HSi(C_2H_5)_2O]P(O)(OC_2H_5)_2$, $[HSi(C_2H_5)O_2]_2(C_2H_5O)PO$, $(C_2H_5)_3SiOSi(C_2H_5)_2O](C_2H_5O)_2PO$, $[(C_2H_5)_3SiOSi(C_2H_5)_2O]_2(C_2H_5O)PO$ $[(C_2H_5)_3SiO]C_2H_5SiO$ $P(O)(OC_2H_5)_2$, $[(C_2H_5)_2SiO]_3SiOP(O)(OC_2H_5)_2$, $(C_2H_5O)_2P(O)OSi[OSi(C_2H_5)_3]_2$: IR [101].

Compounds Containing a Carbon – Phosphorus Bond

$(CH_3O)_2P(O)CH_3$: IR [2]; $(CH_3O)_2P(O)C(O)CCl_3$: IR [85]; $(CH_3O)_2P(O)C(OH)HCCl_3$: IR [83]; $(CH_3O)_2P(O)CHCCl_2OP(O)(OCH_3)_2$: IR [85]; $(C_2H_5O)_2P(O)CH_3$: IR [2]; $(C_2H_5O)_2P(O)C_2H_5$: IR [2,10], R [26]; $(C_2H_5O)_2P(O)C_4H_9$: IR [10]; $[(C_2H_5O)_2P(O)CF_3$: IR [28]; $(C_2H_5O)_2P(O)CCl_3$, $(C_2H_5O)_2P(O)C_6H_5$; $(C_2H_5O)_2P(O)C_6H_4\text{—}p\text{-}Cl$: IR [4]; $(C_2H_5O)_2P(O)CH_2CH_3$: IR [57], R [16]; $(C_2H_5O)_2P(O)CH_2C(O)CH_3$: IR [102]; $(C_2H_5O)P(O)(CH)(CCH_3)_2$: IR [57]; $(C_2H_5O)_2P(O)C(O)(CH_2)_{12}CH_3$: IR [103]; $(C_2H_5O)_2P(O)C(O)C_6H_5$: IR [57]; $(C_2H_5O)_2P(O)CH_2C(O)C_2H_5$, $(C_2H_5O)_2P(O)CH(CH_3)C(O)CH_3$: IR [102]; $(C_2H_5O)_2P(O)C(OH)(CH_3)_2$, $(C_2H_5O)_2P(O)C(OH)(CH_2)_4CH_2$, $(C_2H_5O)_2P(O)CH(OH)C_6H_5$, $(C_2H_5O)_2P(O)CH(OH)C_6H_4\text{—}p\text{-}NO_2$, $(C_2H_5O)_2P(O)CH(OH)C_6H_4\text{—}3\text{-}NO_2$, $(C_2H_5O)_2P(O)CH(OH)C_6H_4\text{—}4\text{-}NO_2$, $(C_2H_5O)_2P(O)CH(OH)C_6H_4\text{—}2\text{-}Cl$: IR [8]; $(C_3H_7O)_2P(O)CH_3$: IR [2]; $(i\text{-}C_3H_7O)_2P(O)CH_3$: IR [80], R [80]; $(i\text{-}C_3H_7O)_2P(O)C_2H_5$: IR [2]; $(C_4H_9O)_2P(O)CH_3$, $(C_4H_9O)_2P(O)C_2H_5$: IR [18]; $(C_4H_9O)_2P(O)C_4H_9$: IR [4]; $(p\text{-}NO_2C_6H_4O)_2P(O)C_2H_5$: IR [57]; $(C_2H_5O)CH_3OP(O)P(O)CH_3(OC_2H_5)$, $(C_2H_5O)C_2H_5P(O)OP(O)C_2H_5(CC_2H_5)$, $(i\text{-}C_6H_{13}O)CH_3P(O)OP(O)CH_3(O\ i\text{-}C_5H_7)$, $(i\text{-}C_3H_7O)C_2H_5P(O)OP(O)C_2H_5(O\ i\text{-}C_5H_7)$, $(s\text{-}C_4H_9O)CH_3P(O)OP(O)CH_3(O\ s\text{-}C_4H_9)$, $(s\text{-}C_4H_9O)C_2H_5P(O)OP(O)C_2H_5(O\ s\text{-}C_4H_9)$: IR [15]; $CH_3OCH{=}C(POCl_2)CCl{=}CH_2$, $C_2H_5OCH{=}C(POCl_2)CCl{=}CH_2$, $C_2H_7CH{=}C(POCl_2)CCl{=}CH_2$, $C_4H_9OCH{=}C(POCl_2)CCl{=}CH_2$: IR [104]; $(CH_3O)_2P(O)C{\equiv}CH$, $(C_2H_5O)_2P(O)C{\equiv}CH$, $(i\text{-}C_2H_7O)_2P(O)C{\equiv}CH$: IR [132]; $(C_2H_5O)_2P(O)CCH_3(CC_6H_5)C(O)CH_3$, $(C_2H_5O)_2P(O)CC_2H_5(OC_2H_5)C(O)C_2H_5$, $(C_2H_5O)_2P(O)CC_3H_7(OC_2H_5)C(O)C_3H_7$, $(C_2H_5O)_2P(O)CC_4H_9(OC_2H_5)C(O)C_4H_9$: R [105], $(C_2H_5O)C_2H_5P(O)SCH_3$: IR [20]; $(C_2H_5O)CH_3P(O)SC_1H_5$: IR [20,21,26]; $(C_2H_5O)C_3H_7P(O)SC_2H_5$, $(C_2H_5O)C_4H_9P(O)SC_2H_5$, $(C_2H_5O)CH_3P(O)SCH_2OCH_3$: IR [21]; $(C_4H_9O)C_2H_5P(O)SC_4H_9$: IR [20]; $[(CH_3)_2SiO]_2P(O)C_4H_9$: IR [63]; CH_3POCl_2: IR [18,38]; $C_2H_5POCl_2$: IR [11,18,26], R [26]; cyclo-$C_6H_{11}FCCl_2$: IR [10]; $(C_4H_9O)C_4H_9P(O)NHC_6H_5$: IR [55]; $(C_2H_5O)PO(CH_3)_2$: IR [57];  CH_3POCl: IR [18]; $C_6H_5POCl_2$: IR [4]; $CH_3PO(OH)_2$: R [106]; $C_4H_9PO(OH)_2$: IR [4]; $C_6H_5PO(OH)_2$: IR [4,11]; $C_6H_5PO(OD)_2$, $p\text{-}ClC_6H_4PO(OH)_2$: IR [4]; $(C_6H_5CH_2)NH_2PO(OH)$: IR [11]; $CH_3PO_3Na_2$: R [106]; $(C_6H_5O)NH_2C_6H_4PO_2Ag$: IR [11];  CH_3PO_2Na: IR [18]; $CF_3PO(OH)(ONa)$, $CF_3PO_3Na_2$: IR [75]; $CH_3PO_3Na_2\cdot 6H_2O$: IR [107]; $CH_3FO_3K_2$: IR [106]; CH_3PO_3Ag, CH_3PO_3Mg, CH_3PO_3Ba, $CH_3PO_3Ca\cdot 2H_2O$, $CH_3FO_3Sr\cdot 2H_2O$, CH_3PO_3Pb: IR [107]; $C_4H_9PO_2(OH)\cdot NH_2C_6H_5$: IR [53]; $(CH_3)_2PO(OH)$: IR [57,106]; $(C_6H_5)_2PO(OH)$, $(C_6H_5CH_2)_2PO(OH)$, (2,4,6-$Cl_3C_6H_2)_2PO(OH)$, ($p\text{-}CH_3C_6H_4)C_2H_5PO(OH)$, $(p\text{-}NO_2\text{—}C_6H_4)_2PO(OH)$, ($o\text{-}CH_3O\text{—}C_6H_4)_2PO(OH)$: IR [10]; $(CH_3)_2PO_2Li$: IR [107]; $(CH_3)_2PO_2Na$: IR [106,107]; $(CH_3)_2PO_2K$: IR [106]; $(CH_3)_2PO_2K\cdot xH_2O$, $[(CH_3)_2PO_2]Ca\cdot xH_2O$, $[(CH_3)_2PO_2]Sr\cdot xH_2O$; $[(CH_3)_2PO_2]Ba\cdot xH_2O$: IR [107]; $(C_6H_5)_2POCl$: IR [4]; $(CH_3)_3PO$: IR [4,7,108], R [95]; $(CH_3)_3PO(+SbCl_5)$, $(CH_3)_3PO(+POCl_3+SbCl_5)$: R [35]; $(C_2H_5)_3PO$: IR [46]; ($m\text{-}CH_3\text{—}C_6H_4CH_2)_3PO$: IR [3]; ($o\text{-}CH_3\text{—}C_6H_4)_3PO$: IR [87]; $(C_6H_5CH_2)_2P(O)CH(OH)C_6H_4\text{—}2\text{-}Cl$, $(C_6H_5CH_2)_2P(O)C(OH)(CH_3)_2$, $(C_6H_5CH_2)_2P(O)CH(OH)CH(CH_3)_2$, $(C_6H_5CH_2)_2P(O)C(OH)(CH_3)C_2H_5$, $(C_6H_5CH_2)_2P(O)CH(OH)C_3H_7$, $(C_6H_{17})_2P(O)CH(OH).C_6H_4\text{—}2Cl$, $(C_6H_{17})_2P(O)CH(OH)C_6H_4\text{—}2\text{-}NO_2$, $(C_6H_{17})_2P(O)CH(OH)C_6H_5$, $(C_6H_{17})_2P(O)C(OH)(CH_2)_4CH_2$, $(C_6H_{17})_2P(O)C(OH)(CH_3)_2$: IR [6]; $(C_6H_5)_3PO$: IR [4,7,23,33,82,108]; $(C_6H_5)_3PO$[10]: IR [34]; $(C_6H_5)_3PO$ (+ **chloronil**): IR [110]; $[(C_6H_5)_3PO_2]SnCl_4$, $[(C_6H_5)_3PO]_2SnBr_4$, $[(C_6H_5)_3PO]_2TiCl_4$, $[(C_6H_5)_3PO]_2.FeBr_3$: IR [38]; $(p\text{-}CH_3\text{—}C_6H_5)_3PO$: IR [3]; $(o\text{-}NO_2\text{—}C_6H_4)_3PO$: IR [87]; $C_6H_5P(O)(NHNHC_6H_5)_2$: IR [4]; $(CH_3O)(C_2H_5O)P(S)C_2H_5$: IR [20]; $(C_2H_5O)_2P(S)CH_3$: IR [20,21,38]; $(C_2H_5O)_2P(S)C_2H_5$: IR [20,26,38], R [26]; $(i\text{-}C_3H_7O)_2P(S)CH_3$: IR [18,38]; $(C_4H_9O)_2P(S)C_2H_5$: IR [20]; $(C_2H_5O)[CH_3C(O)O]P(S)C_2H_5$: IR [21]; $(C_2H_5O)CH_3PS(OH)$, $(C_2H_5O)C_2H_5PS(OH)$, $(C_2H_5O)C_3H_7PS(OH)$, $(C_2H_5O)C_4H_9PS(CH)$: IR [20]; $(C_2H_5O)CH_3PS(ONa)$, $(C_2H_5O)C_2H_5PS(ONa)$: IR [21,26]; $(C_2H_5O)C_3H_7PS(ONa)$, $(C_2H_5O)C_4H_9PS(ONa)$: IR [31]; $(C_2H_5O)CH_3PSO^tNH(C_2H_5)_3$, $(C_2H_5O)CF_3PS(ONa)$: IR [38]; $(i\text{-}C_3H_7O)CH_3P(S)OP(O)CH_3(O\ i\text{-}C_3H_7)$: IR [19]; $(CH_3O)CH_3PSCl$, $(C_2H_5O)CH_3PSCl$: IR [26]; $(i\text{-}C_3H_7O)CH_3PSCl$: IR [18,38]; CH_3PSCl_2: IR [18,26,38], R [28]; $C_2H_5PSCl_2$: IR [38,46,26]; $C_3H_7PSCl_2$: IR [26,38]; $i\text{-}C_3H_7PSCl_2$, $C_4H_9PSCl_2$: IR [38]; $C_6H_5PSCl_2$: IR [3,4]; $C_6H_5PS[N(CH_3)_2]_2$, $C_2H_5PS[N(C_2H_5)_2]_2$, $C_6H_5PS[N(i\text{-}C_3H_7)_2]_2$, $C_6H_5PS[N(C_4H_9)_2]_2$, $C_6H_5PS[N(C_{10}H_{21})_2]_2$: IR [4]; $(C_2H_5)CH_3PS(OH)$, $(C_2H_5)CF_3PS(OH)$, $(CH_3CHFCH_2)CH_3PS(OH)$, $(FH_2C\text{—}C_2H_4)CH_3PS(OH)$, $(C_2H_5)CH_3PSCl$, (cyclo-$C_6H_{11})CH_3PSCl$, $(FH_2CCH_2)CH_3PSCl$, $(FH_2CC_2H_4)CH_3PSCl$: IR [38]; $(i\text{-}C_3H_7O)CH_3P(S)OCH_3P(S)OCH_3P(S)(O\ i\text{-}C_3H_7)$: IR [18]; $(C_3H_7O)CH_3P(S)OCH_3P(S)OCH_3P(O)(OC_3H_7)$: IR [33]; $[(CH_3)_2NCH_2CH_2O](C_2H_5O)CH_3PO$, $(CH_3)_3NCH_2CH_2S](C_2H_5O)CH_3PO$: IR [50]; $(C_2H_5)_2PS(SH)$, $(C_6H_5)_2PS(SH)$: IR [50]; $(CH_3)_4P_2S_2$: IR [87,111]; $(C_2H_5)_4P_2S_2$, $(C_3H_7)_4P_2S_2$, $(C_4H_9)_4P_2S_2$, $(i\text{-}C_4H_9)_4P_2S_2$: IR [111]; $(CH_3)_3PS$, $(C_2H_5)_3PS$: IR [46]; $(C_2H_5O)CH_3P(O)N(CH_3)_2$, $(C_2H_5O)CH_2P(O)N(C_2H_5)_2$: IR [15]; $(C_2H_5O)CH_2P(O)NHC(O)CH_3$, $(C_2H_5O)C_2H_5P(O)NHC(O)CH_3$: IR [97]; $(C_3H_7O)CH_3P(O)N(CH_3)_2$, $(i\text{-}C_3H_7O)CH_3P(O)N(CH_3)_2$, $(C_4H_9O)CH_3P(O)N(CH_3)_2$, $[(CH_3)_2N]_2CH_3PO$, $[(C_2H_5)_2N]_2CH_3PO$: IR [15]; $(C_6H_5NH)_2C_6H_5PO$: IR [4]; $(C_3H_7O)_2C_2H_5PNC_6H_5$, $(i\text{-}C_3H_7O)_2CH_3PNC_3H_5$, $(C_4H_9O)_2CH_3PNC_6H_5$, $(C_4H_9O)_2C_2H_5PNC_6H_5$, $(C_4H_9O)_2C_3H_7PNC_6H_5$, $(C_4H_3O)_2C_4H_9PNC_6H_5$, $(C_2H_5O)_2C_6H_5PNC_6H_5$, $(C_3H_7O)_2C_6H_5PNC_6H_5$: IR [55]; $p\text{-}CH_3OC_6H_4NP(C_6H_5)_3$, $p\text{-Cl—}C_3H_4NP(C_6H_5)_3$, $C_6H_5NP(C_3H_5)_3$, $p\text{-}CH_3C_6H_4NP(C_6H_5)_3$, $p\text{-}CO_2C_2H_5\text{—}C_6H_4NP(C_6H_5)_3$, $p\text{-}NO_2C_6H_4NP(C_6H_5)_3$, $p\text{-}CN\text{—}C_6H_4NP(C_6H_5)_3$, $(C_6H_5)_3P=$ , $(C_6H_5)_3P=$ , $(C_6H_5)_3PC(SO_2C_6H_5)_2$, $(C_6H_5)_3PC(CN)_2$, $(C_6H_5)_3PC(CN)CO_2CH_3$, $(C_6H_5)_3PC(CO_2C_2H_5)_2$: IR [55a].

Phosphites

$(CH_3O)_3P$: IR [2], R [16]; $(C_2H_5O)_3P$: IR [2,3,4,10], R [16]; $(i\text{-}C_3H_7C)_3P$: IR [2,112]; $(C_4H_9O)_3P$: IR [4]; $(C_2H_5O)_2[C_4H_9\text{—}CH(C_2H_5)CH_2O]P$, $(C_2H_5O)[C_4H_9CH(C_2H_5)CH_2O]_2P$, $[C_4H_9CH(C_2H_5)CH_2O]_3P$, $[(CH_3)_3CCH_2CH(CH_3)CH_2O]_3P$: IR [10]; $(C_6H_5O)_3P$: IR [4,10,82]; $(C_2H_5O)_2C_2H_5P$: IR [4]; $(C_2H_5O)P\text{—}CCH_3C(O)CH_3$, $(C_2H_5O)P\text{—}CC_2H_5C(O)C_2H_5$, $(C_2H_5O)P\text{—}CC_3H_7C(O)C_3H_7$, $(C_2H_5O)P\text{—}CC_4H_9C(O)C_4H_9$: R [105]; $(CH_3O)_2PCl$, $(C_2H_5O)_2PCl$, $(C_3H_7O)_2PCl$, $(C_4H_9O)_2PBr$, CH_3OPCl_2: R [13]; $C_2H_5OPCl_2$: IR [10], R [16]; $C_6H_5OPCl_2$, $C_6H_5OPBr_2$: R [16]; $(CH_2S)_2P$: IR [86]; $C_2H_5PCl_2$: IR [4]; CH_3PH_2, SiH_3PH_2: IR [113]; $(CH_3)_2PH$: IR [114], R [114]; $(C_2H_5)_2PH$: R [115]; $(CF_2S)_2PH$: IR [116]; $(CH_3)_2P$: IR [117,118], R [118,119]; $(C_2H_5)_2P$: IR [46,120,121], R [115]; $(CH_2{=}CH)_2P$: IR [120,121]; $(C_2H_5)_2C_6H_5P$: IR [4]; $(C_6H_5)_2P$: IR [4,82,109,122] , IR [122]; $P(CN)_3$: IR [123,124]; $(CF_3)_2POP(CF_3)_2$: IR [74]; $(CF_2S)_2P$: IR [116]; $(CH_2O)_2PHO$: IR [2,9,18], R [1,2,16]; $(C_2H_5O)_2PHO$: IR [2,3,4,8,18,72], R [1,2,16]; $(C_3H_7O)_2PHO$; IR [18], R [1,16]; $(i\text{-}C_3H_7O)_2PHO$: IR [18,80], R [1,80]; $(C_4H_9O)PHO$: IR [4,18,72], R [1,16]; $(i\text{-}C_4H_9O)_2PHO$: R [1]; $(C_6H_5CH_2)_2PHO$: IR [10,11]; $[(CH_3)_3CCH(CH_3)O]_2PHO$: IR [11]; $[(CH_3)_3CCH_2CH(CH_3)O]_2PHO$: IR [10]; $(C_7H_{17})_2FHO$: IR [8]; $(CH_2O)C_6H_5PHO$: IR [92]; $(C_{10}H_7)(HO)FHO$: IR [4]; $(C_{11}H_{37})(HO)PHO$: IR [8]; $(C_4H_9)(DO)PDO$, $(C_6H_5)(HO)PHO$, $(C_2H_5O)C_6H_5PHO$, $(p\text{-}CH_3C_6H_4)(HO)PHO$, $(p\text{-}C_2H_5\text{—}C_6H_4)(HO)PHO$: IR [4]; $(CF_3)_2POH$: IR [74]; $(C_2H_5O)_2FCNa$, $(C_6H_5O)_2PCNa$, $(C_6H_5O)_2FOK$, $(C_2H_5O)_2POAg$, $(C_6H_5O)_2POAg$: IR [72]; $(CF_3)HP(O)ONa$: IR [75]; $(C_6H_5)_2PHFeCl_4$, $[(C_6H_5)_2P]_2HgCl_3$: IR [105]; $(CH_3O)_2PHS$: IR [18]; $(C_2H_5O)_2PHS$: IR [18], R [26]; $(C_2H_5)_2NPF_2$: IR [4]; $(CH_3)_2NPCl_2$: IR [15]; $(C_7H_{15}O)_2PN(CH_2)_2$: IR [54], $[(CH_3)_2SiO]_2P(O)H$, $[(C_2H_5)_2SiO]_2P(O)H$, $[CH_3(C_3H_7)_2SiO]_2P(O)H$: R [100].

Inorganic Phosphorus Compounds

PH_3: IR [125]; PF_3: IR [5,79]; PF_5: IR [5]; PCl_5: IR [126], R [126]; POF_3: IR [5]; $POCl_3$: IR [3,4,9,33,92], R [35,92]; $POCl_3(+SbCl_5)$: R [58]; $(POCl_3)_2TiCl_4$, $POCl_3.TiCl_4$, $(POCl_3)_2SnCl_4$: IR [33]; Cl_2FPO, Cl_2PCOH, Cl_2PCOD: R [58]; $POBr_3$: IR [4,33], R [40–42]; $PSCl_3$: IR [3,78], R [26]; FCl_2PS: IR [4]; $(POBr_3)_2TiBr_4$, $(POBr_3)FeBr_2$: IR [33]; $(NH_2)_3PO$, $(NH_2)_3PS$; $(NH_2)_2ClPO$: IR [11]; $(NH_4)_2HPO_4$: R [127]; $(NH_4)PO_2F_2$, $(NH_4)_2PO_3F.H_2O$, $Li_2FO_3F.3H_2O$, Na_2PO_3F, K_2PO_3F, $CaPO_3F.xH_2O$, $SrPO_3F.xH_2O$, $BaPO_3F$, $PbPO_2F$: IR [107]; $H_4P_2O_7$, $Na_4P_2O_7.10H_2O$, $Na_3HP_2O_7.H_2O$, $Na_2H_2P_2O_7$, $Na_4P_2O_7.10H_2O$, $Na_3HP_2O_7.9H_2O$, $Na_2HP_2O_7$, $Na_2H_2P_2O_7$, $NaH_3P_2O_7$: IR [128]; P_2H_4: R [129]; $P_2O_3Cl_4$: R [130]; $P_4O_4Cl_{10}$: IR [92], R [92]; H_3FO_3, KH_2PO_3, K_2HPO_3: R [100]; P_2O_5, (P_2O_{25}), P_2S_5: IR [3]; K_2HPO_4 $Zn_3(PO_4)_2$, Ag_3PO_4, Tl_3PO_4, Na_2PO_3F, K_2PO_3F, Ag_2PO_3F, $Na_2H_2P_2O_7$, $K_2H_2P_2O_7$, $K_2D_2P_2O_7$, $K_4P_2O_7.xH_2O$, $Ag_4P_2O_7$, $Tl_4P_2O_7$, $Zn_2NaP_3O_{10}$, $Ag_5P_3O_{10}$, $Ag_3P_3O_9$,

$Tl_3P_3O_9$, $Ag_4P_4O_{12}$, $Na_2PO_2NH_2$, $ZnPO_2NH_2$, $Ag_2PO_2NH_2$, $Tl_2PO_2NH_2$, $Zn[PO_2(NH_2)_2]_2$, $Na_4P_2O_6NH$, $K_2H_2P_2O_6NH$, $K_2D_2P_2O_6ND$, $K_4P_2O_6NH$, $Zn_2P_2O_6NH$, $Ag_4P_2O_6NH$, $Ag_4P_2O_6NAg$, $Tl_4P_2O_6NH$, $Na_5P_3O_8(NH)_2$, $Zn_2NaP_3O_8(NH)_2$, $Tl_5P_3O_8(NH)_2$, $K_3P_3O_7(NH)_2$, $Ag_3P_3O_7(NH)_2$, $Tl_3P_3O_7(NH)_2$, $Tl_3P_3O_7(NH)_2TlOH$, $H_3(PO_3NH)_3$, $NaH_2(PO_3NH)_3.2H_2O$, $Na_3(PO_2NH)_3.4H_2O$, $K_3(PO_2(NH)_3$, $K_3(PO_2ND)_3$, $A_3(PO_2NH)_3$, $Tl_3(PO_2NH)_3$, $Tl_3(PO_2NH)_3TlOH$, $(NH_4)_2H_2(PO_2NH)_4$, $(NH_4)(PO_2NH)_4.4H_2O$, $Na_2H_2(PO_2NH)_4$, $Na_4(PO_2NH)_4.3H_2O$, $K_4(PO_2NH)_4$, $Ag(PO_2NH)_4$, $Tl_4(PO_2NH)_4$, $P(O)(NH_2)_3$, $P(S)(NH_2)_3$: IR[121].

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EFFICIENCY CRITERIA IN GAS CHROMATOGRAPHY

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PART I

The study of the operating characteristics of chromatographic apparatus and of the efficiency of the resulting separations is of great relevance to the development of this important technique for physicochemical analysis. Contemporary gas chromatography includes a variety of different methods, each of which involves numerous parameters. Industrial concerns in many countries are marketing very diverse chromatographic assemblies, the types of which already exceed several dozen.

One is often faced with the problem of comparing different methods and their analytical results and thus defining the optimum experimental parameters. Unfortunately, the literature is strangely silent on the selection of the correct procedures for evaluating the effectiveness of the operation of chromatographic equipment, in spite of the large number of *ad hoc* criteria suggested by different authors. The necessary distinction between apparatus parameters and characteristics of the separation process is not always made. Many important questions (for instance, the effect of the ratio of the concentration of components) are not analysed in sufficient detail.