53. *Vibrational Spectra of Alkyl Esters of Phosphorus Oxy-acids.*

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The infra-red and Raman spectra of some alkyl esters of phosphorus oxy-acids have been measured and correlated with the molecular structure. The dialkyl hydrogen phosphites show a band which indicates a P—H bond, and implies a structure $(RO)_2HPO$ for these compounds. Characteristic frequencies for the P=O and P—O links are also suggested, and other correlations are discussed. There is reason to suppose that the P—H bond can undergo hydrogen bridge formation with neighbouring oxygen atoms.

ALTHOUGH few previous studies of the vibrational spectra of the organic derivatives of phosphorus oxy-acids have been recorded, the subject is interesting in several connexions. First, it would be useful to know whether characteristic oscillation frequencies exist for the P=O and P—O linkages, and the measurement of band intensities in the infra-red and Raman spectra might provide information about the ionic character and polarisability of these bonds. Similar measurements have recently been made for silicon–oxygen bonds (Richards and Thompson, *J.*, 1949, 124) and for related structures such as the C=O linkage (Hartwell, Richards, and Thompson, *J.*, 1948, 1436). Secondly, the increasing application of infra-red measurements to biochemical problems, both for analysis and for structural diagnosis, makes it desirable to have spectra of relevant compounds containing phosphorus for reference purposes in connexion with possible studies of phosphate metabolism and general work of this kind. Thirdly, some questions about the structure of the phosphorus oxy-acids themselves may be elucidated from the vibrational spectra.

A survey has therefore been begun of the Raman and infra-red spectra of a series of alkyl esters of phosphorus oxy-acids, and the present paper summarizes the results for several classes of compound. It will be found that useful conclusions can already be drawn with regard to some of the points indicated above.

EXPERIMENTAL METHOD.

The compounds whose spectra have been measured were synthetic products supplied by the Chemical Defence Experimental Establishment, Porton :

	n_D^{20}.	B. p.
Dimethyl hydrogen phosphite	1·4030	38°/2·5 mm.
Diethyl hydrogen phosphite	1·4080	77/17 mm.
Di*iso*propyl hydrogen phosphite	1·4080	41·5/0·5 mm.
Trimethyl phosphite	1·4088	86—86·5/351 mm.
Triethyl phosphite	1·4130	74/21 mm.
Dimethyl methylphosphonate	1·4148	79·7/20 mm.
Diethyl methylphosphonate	1·4140	56·5/3·5 mm.
Di*iso*propyl methylphosphonate	1·4109	50·5—51·5/1 mm.
Diethyl ethylphosphonate	1·4161	66—66·5/3 mm.
Di*iso*propyl ethylphosphonate	1·4151	38/0·09 mm.

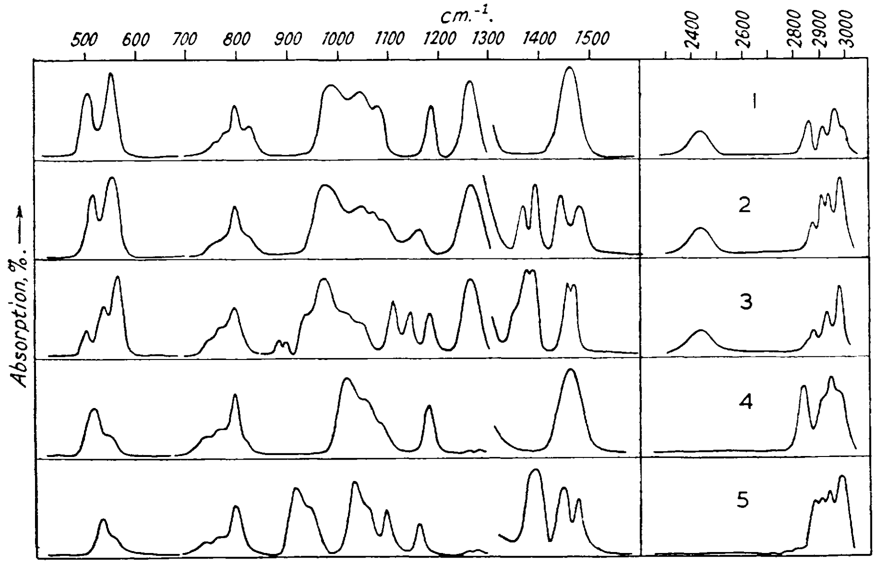
The infra-red spectra between 2 and 2·5μ. were measured with a Perkin Elmer 12 C recording spectrometer, with prisms of rock salt, potassium bromide, and lithium fluoride. Some spectra between 6 and 15μ. were also recorded on a single-beam spectrometer which has been described elsewhere (Whiffen and Thompson, *J.*, 1945, 268). Hitherto, thin films of the liquids have been used, pressed between a pair of rock salt or potassium bromide plates. Care was taken to minimise hydrolysis of the samples in damp air, and the measurements were made as rapidly as possible. As explained below, some measurements were repeated after the sample had been left in contact with damp air, and these served to indicate some of the spectral changes likely to occur in such circumstances.

The Raman spectra were measured photographically using a Hilger E518 instrument with glass prism, Ilford H.P. 3 plates being used. The exciting source was a 500-watt Hanovia cylindrical mercury arc, placed alongside a cylindrical glass tube containing a copper–ammonium salt solution. The latter acted both as a filter for the 4358A. line and as a condensing lens. The slight continuum was reduced by the introduction of further filters, a dilute solution of a rhodamine dye being sometimes used. Lines from a copper arc and neon discharge tube were used as reference standards.

RESULTS.

The infra-red absorption spectra are shown in Figs. 1 and 2. The intensities for different compounds are not strictly comparable owing to the small differences in the thickness of the liquid used; and also different spectral regions for a given compound were measured with different thicknesses of material in order to bring up weak bands. This does not, however, affect the main conclusions of the present work. For later quantitative measurements on the intensities of the bands, it will be necessary to use known concentrations in a solvent, or alternatively known pressures of the vapours. It may be noted that the bands between 1300 and 1550 cm.$^{-1}$ are usually much weaker than many others in the spectra.

FIG. 1.

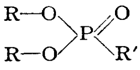


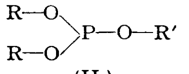
(1) *Dimethyl hydrogen phosphite.* (2) *Diethyl hydrogen phosphite.* (3) *Diisopropyl hydrogen phosphite.* (4) *Trimethyl phosphite.* (5) *Triethyl phosphite.*

The Raman data and the position of the infra-red absorption bands are summarised in Table I and II.

DISCUSSION.

A number of interesting deductions can be made from these results. For example, in both the infra-red and the Raman spectra, the dialkyl hydrogen phosphites show a band near 2435 cm.$^{-1}$ which is absent from the spectra of all other compounds. There can be no doubt that this is due to a stretching vibration of the P—H link, corresponding to that of Si—H bonds near 2200 cm.$^{-1}$. In phosphine there is a P—H stretching vibration frequency at 2327 cm.$^{-1}$. Now the phosphonates have formula (I), and the trialkyl phosphites (II). For the dialkyl hydrogen phosphites two possibilities arise, namely (III) and (IV), and the spectra therefore indicate (IV), at any rate for the compounds measured. It is possible, however, that when the radicals R are changed this conclusion may not apply.


(I.)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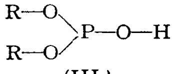
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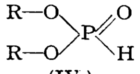
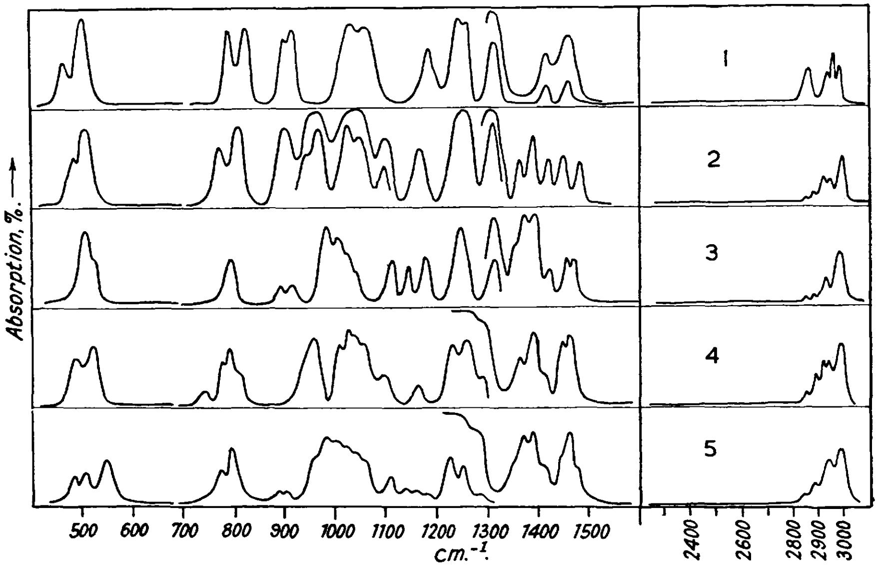

(IV.)

FIG. 2.



(1) *Dimethyl methylphosphonate.* (2) *Diethyl methylphosphonate.* (3) *Di*iso*propyl methylphosphonate.* (4) *Diethyl ethylphosphonate.* (5) *Di*iso*propyl ethylphosphonate.*

TABLE I.

Phosphites.

(Position of bands in cm.$^{-1}$; s = strong, m = medium, w = weak, b = broad.)

Dimethyl hydrogen phosphite.		Diethyl hydrogen phosphite.		Di*iso*propyl hydrogen phosphite.	
Infra-red.	Raman.	Infra-red.	Raman.	Infra-red.	Raman.
505 s		517 s		504	
554 s		555 s		538 m	
759	762 s		737 s	560 s	
777		760 ?			720 s
795 s		780 ?		760	765 w
825 m		795 s	802 ?	775	
985 s	990 m	822 ?		795 s	
1045 s		980 s		885	888 s
1080 m			1000 w	894	
1190 m	1199 w	1046 m		937	
1266 s	1258 m	1074		975 s	
1460	1458 s	1100	1100 m	1020	
2434 m.b.	2432 s.b.	1165		1053	
2856 m	2860 s	1261 s	1250 m	1110 m	1113 w
2922		1370		1146 m	1144
2962 s	2960 s	1392		1180 m	
2998	3010 m	1445	1445 s	1262 s	1258 m
		1480		1350 ?	1352 m
		2434 m.b.	2432 s.b.	1375	
		2851 ?		1390	
		2874		1458	1450 s
		2910 m		1468	
		2936 m	2940 s	2434 m.b.	2435 s.b.
		2981 s	2975 s	2852 ?	
				2880	2882 m
				2937 m	
				2981 s	2982 s

TABLE I (*continued*).

Trimethyl phosphite.				Triethyl phosphite.			
Infra-red.	Raman.	Infra-red.	Raman.	Infra-red.	Raman.	Infra-red.	Raman.
516 m	509 s	1462	1458 s	536 m		1265	1272 ?
552			2785	555		1275	
738	744 s.b.	2838 s	2840 s	737	740 s	1390	
775		2902 m		772		1445	1445 s
795 s		2946 s	2942 s	795 s		1478	
1014 s	1015 s	2990 m	2985 m	918 s		2764	
1060 m	1058 m			942 m		2821	
1088				1035 s	1030 m	2888 m	2874 s
1121				1061		2903 m	
1183 s				1097	1095 m	2933 s	2928 s
1265				1163		2981 s	2975 s

TABLE II.

Phosphonates.

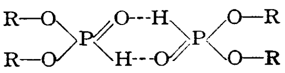
(Position of bands in cm.$^{-1}$; s = strong, m = medium, w = weak, b = broad.)

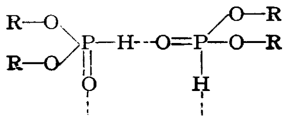
Dimethyl methylphosphonate.		Diethyl methylphosphonate.		Di*iso*propyl methylphosphonate.	
Infra-red.	Raman.	Infra-red.	Raman.	Infra-red.	Raman.
	300 ?	485	470 w	504 s	495 m
463		502 s			710 s
500 s	495 m		715 s	794 m	793
	706 s	771 m		898	880 m
789 s	788 m	806 s		918	915 w
822 s	816 m	898 s		983 s	
897 m		939		1008 s	
913 s		965 s		1034	
1032 s	1072 w	1023 s		1059	
1060 s	1057 w	1049 s		1112 m	1102 m
1185 m		1099 s	1100 m	1146 m	1140 w
1241 s	1240 m	1164 m		1180 m	
1256 ?		1250 s	1239 m	1248 s	1240 m
1315 m		1314 s		1315 m	
1419	1421 m	1365		1375	1350 m
1463	1465 m	1390		1390	
2864 s	2851 m	1420		1420	
2938 m	2929 s	1448	1445 m	1458	1445 s
2966 s	2961 w	1480		1468	
2989 s	2990 s	2863			2778 m
		2885	2880 w	2851	2835 w
		2923 m		2879	2870 m
		2943 m	2935 s	2934 m	2930 s
		2995 s	2990 s	2983 s	2985 s

Diethyl ethylphosphonate.				Di*iso*propyl ethylphosphonate.			
Infra-red.	Raman.	Infra-red.	Raman.	Infra-red.	Raman.	Infra-red.	Raman.
483 s	500 w	1254 s		485		1165	
522 s		1292	1288 m	504	502 w	1180	
	699 s	1367		545 s		1224 s	
742		1392			700 s	1251 m	
777 m		1420 ?		778		1286	
794 s		1448		796 s		1375	
815	811 w	1460	1460 s	887	890 m	1388	
938		1480		897		1418	
958 s		2853		959		1450	1450 s
1010	996 ?	2893	2895 w	986 s		1460	
1026 s		2914 m		1008		1469	
1042	1040 w	2945 m	2940 s	1023		2855	
1060		2985 s	2990 s	1042		2889	2890 w
1098	1100 m			1059		2942 m	2940 s
1165				1107	1100 m	2983 s	2985 s
1230 s	1230 w			1142			

The very broad nature of the infra-red band at 2435 cm.$^{-1}$ and the equally broad and diffuse nature of the corresponding Raman line suggest that in the liquid state this P—H bond may be associated in a bridge through oxygen atoms similar to the familar hydrogen bridge in

- -O—H - - - O or -N—H - - - O- systems, in this case leading to structures such as (V). Measurements with dilute solutions are now being planned to examine this further.





(V.)

We may now consider other correlations involving the P—O—C skeleton. A previous suggestion for phosphites and phosphonates based upon a few isolated measurements (Thompson, *J.*, 1948, 328) must now be regarded as invalid, since it is not borne out by the present results and can now be interpreted in another way. All the compounds except the trialkyl phosphites have an intense band at 1250—1260 cm.$^{-1}$, although in the more complex derivatives a doubling occurs here. It seems very probable that this band is associated with the stretchings of the P=O linkage. In the case of phosphorus oxychloride, $POCl_3$, the Raman frequency of 1295 cm.$^{-1}$ has been assigned to this vibration (Yost and Anderson, *J. Chem. Physics*, 1934, **2**, 624), and there is usually a corresponding Raman frequency with the phosphites and phosphonates, as was also pointed out by Arbusov, Batuev, and Vinogradova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1946, **54**, 599).

All the compounds now measured have a band near 795 cm.$^{-1}$, with the exception of diethyl methylphosphonate where a splitting seems to occur. This frequency also occurs in some of the Raman spectra. It may be attributed to a vibration which is largely controlled by the stretching of the P—O bond in the skeleton P—O—C, and having regard to the change in reduced mass would fall roughly into line with the corresponding frequencies for C—O and Si—O bands found previously (Thompson and Torkington, *J.*, 1945, 640; Richards and Thompson, *J.*, 1949, 124). Although this correlation is still uncertain, a further argument in support of it is found in the result that when a dialkyl hydrogen phosphite hydrolyses in damp air, the band at 795 cm.$^{-1}$ disappears, as the skeleton undergoes the important change -P—O—C to -P—O—H.

The absorption bands in the region 2800—3000 cm.$^{-1}$, which are connected with stretching vibrations of C—H bonds, reveal a close parallelism between the different compounds examined. It is clear that there are frequencies typical of CH_3 and CH_2 groups which may also differ slightly according to whether they are attached to carbon or to phosphorus. The spectra of all the compounds containing two or three methoxy-groups have an infra-red band at 2840—2860 cm.$^{-1}$ lying lower than the remainder, and the location and relative intensities of the other bands between 2900 and 3000 cm.$^{-1}$ are closely parallel with the alkyl radicals concerned. It may also be noted that examination of the region 1350—1500 cm.$^{-1}$, where the deformation vibrations of alkyl groups occur, reveals similar regularities. The differences are so well marked as to be a possible means for the identification and estimation of the alkyl groups concerned.

In the other parts of the spectrum there are some regularities which suggest possible correlation rules, but with less convincing precision. The dialkyl hydrogen phosphites have a strong band near 550 cm.$^{-1}$, and in addition all the compounds have a band near 500 cm.$^{-1}$. Between 900 and 1200 cm.$^{-1}$ there will be skeleton vibrations controlled by -C—O and possibly -P—C bonds. Here too, some regularities occur according to the alkoxy-radicals concerned, but the situation is complex. In some respects the position is similar to that found in esters and alkoxysilanes. The derivatives containing *iso*propyl radicals show very similar spectra between 850 and 1050 cm.$^{-1}$.

It is evident that interesting comparisons may be made if the extinction coefficients of some of the key bands are determined. It may then be possible to correlate the ionic character of bonds such as P=O, S=O, and N=O, or P—O and C—O. These measurements are now to be carried out with vapours and solutions.

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