127. *The Characteristic Infra-red Absorption of Some Organic Derivatives of Phosphoric Acid.*

By M. Halmann and S. Pinchas.

The infra-red spectra of a number of mixed organic phosphates, dialkyl chlorophosphonates, and dialkyl alkylaminophosphonates were measured in the 1060—900 cm.$^{-1}$ region. They all show the characteristic absorption bands of the simple trialkyl phosphates, usually accompanied by some other bands.

In a previous communication (Bergmann, Littauer, and Pinchas, *J.*, 1952, 847), it was shown that various trialkyl phosphates show two strong bands in the 1060—900 cm.$^{-1}$ region, at about 1040—1030 and 970—1000 cm.$^{-1}$. These were assigned to the P–OR stretching modes of vibration and it was assumed that the 1030-cm.$^{-1}$ band is due to the out-of-phase stretching of the three alkoxy-groups, while that of 970 cm.$^{-1}$ belongs to the more symmetrical in-phase stretching. It was therefore interesting to see whether the less symmetrical mixed trialkyl phosphates also show these characteristic bands at the same places, and equally whether the dialkyl chlorophosphonates which contain only two alkoxy-groups bound to the phosphorus atom, and contain in addition the heavy and negative chlorine atom, have their P–OR stretching bands at the same frequencies.

In spite of the seemingly large differences between the dialkyl chlorophosphonates and the trialkyl phosphates, such an analogy could be expected in the light of the fact that many

similar compounds of the general structure $R{\cdot}PO(OR')_2$, where R and R' are alkyl groups, show strong bands at about the same frequencies (Meyrick and Thompson, *J.*, 1950, 225; Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 853), and that even in the case of the negatively substituted diethyl fluorophosphonate two strong bands appear at about 1040 and 980 cm.$^{-1}$ (Daasch and Smith, *loc. cit.*). Of the dialkyl chlorophosphonates, however, only the diethyl chlorophosphonate seems to have been measured (Gore, *Discuss. Faraday Soc.*, 1950, **9**, 138) and indeed it showed bands at about 1030, 990, and 970 cm.$^{-1}$ (read from the curve). Some diethyl phenyl phosphates have been investigated, all of them showing strong bands at about 1060—1040 and 970 cm.$^{-1}$ in addition to some other bands (*loc. cit.*), but no simple mixed phosphates seem to have been measured. Table 1 summarises some of our measurements for a number of mixed alkyl phosphates and chlorophosphonates.

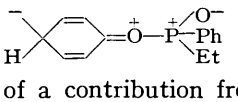
TABLE 1. *Infra-red absorption of mixed organic phosphates and dialkyl chlorophosphonates in the* 1060—900 *cm.*$^{-1}$ *region.*

(Solvent: 1 c.c. of carbon tetrachloride.)

No.	Substance	G.	Cell thickness, mm.	Absorption bands (cm.$^{-1}$)
1	$PO(OEt)(OMe)_2$	0·042	0·1	1036 (broad; strongest), 968
2	$PO(OEt)(OPr^i)_2$	0·016	0·1	1059, 1005 (strongest), 899 [a] (very weak)
3	$PO(OEt)(OPh)_2$	0·030	0·1	1043, 1025, 1006, 952 (strongest)
4	$Cl{\cdot}PO(OMe)_2$	(0·25 c.c.)	0·03	1037 (strongest), 969
5	$Cl{\cdot}PO(OEt)_2$	0·019	0·1	1043 (strongest), 1010, 979
6	$Cl{\cdot}PO(OPr^i)_2$	(0·25 c.c.)	0·03	997 (strongest), 930 (shoulder) [a]
7	$Cl{\cdot}PO(OPh)_2$	0·051	0·1	1025 (s), 1010, 999, 962 (strongest), 930 (shoulder)

[a] Probably an *iso*propyl-group absorption.

If the results for the mixed phosphates are compared with those obtained for the corresponding normal phosphates, *viz.*, trimethyl phosphate 1043 (s), tri*iso*propyl phosphate 995 (s), 931 (very weak) (Bergmann, Littauer, and Pinchas, *loc. cit.*), triphenyl phosphate 1060, 1030, 1010 (s), 960 (very strong) (Daasch and Smith, *loc. cit.*), it can be seen that the characteristic phosphate bands are remarkably steady and are only very little affected by the destruction of the high symmetry of the homogeneous phosphates. (The small dissymmetry which may be introduced by free rotation along the C–O bonds probably cannot bring about marked differences in the P–OC frequencies of the ensuing rotational isomers and *this* dissymmetry can therefore be overlooked as far as the P–OC frequencies are concerned.) This loss of symmetry, as could be expected, brings about, however, an additional band in this region (968 cm.$^{-1}$ in No. 1, 1059 cm.$^{-1}$ in No. 2; in No. 3 it may be concealed by the numerous bands already existing). It can further be seen that the merging together of the two phosphate bands which occurs in tri*iso*propyl phosphate takes place also in ethyl di*iso*propyl phosphate; it seems, further, that the additional 1059 cm.$^{-1}$ band is due to that mode of vibration in which the stretching of the P–OEt bond is not in phase with that of the two *iso*propoxy-groups (as the value of ε_{1059} is as high as 400, it is improbable that it is an ordinary ethyl absorption). The in-phase stretching, as well as that in which one *iso*propoxy-group is out of phase, appears to remain more or less as in tri*iso*propyl phosphate. In ethyl dimethyl phosphate the presence of the 968 cm.$^{-1}$ band is noteworthy, since in the more symmetrical methyl phosphate and methyl pyrophosphate it is absent (Bergmann, Littauer, and Pinchas, *loc. cit.*). Another band is possibly concealed in the high-frequency side of the broad 1038 cm.$^{-1}$ band. Of the four bands of ethyl diphenyl phosphate, some seem to be due to the monosubstituted benzene (cf. Colthup's table, *J. Opt. Soc. Amer.*, 1950, **40**, 397) and the additional P–OEt stretching. The two characteristic phosphate bands appear to be shifted from the usual 1030—1040 cm.$^{-1}$ and 970—1000 cm.$^{-1}$ frequencies to 1006 and 952 cm.$^{-1}$, respectively, with the relative intensity also changed in favour of the latter. Such is also the case in triphenyl phosphate (Daasch and Smith, *loc. cit.*), in diphenyl chlorophosphonate (Table 1, No. 7), and in diphenyl di-*n*-butylaminophosphonate (Table 2, No. 5). It seems that this lowering of the P–OR frequencies reflects a weakening of the P–$OC_{ar.}$ bond as compared with a P–$OC_{aliph.}$ bond, possibly because of a contribution from resonating structures such as (I) to the actual state of phenyl phosphates (mutual electrostatic repulsion between P–O tending to rupture the bond).


(I)

Examination of the results for the dialkyl chlorophosphonates reveals that here also the characteristic phosphate bands appear always at about the same frequencies as in the corresponding trialkyl phosphates, thus proving anew the validity of their assignments. The interesting conclusion which emerges, *viz.*, that the additional alkoxy-group in trialkyl phosphates does not change appreciably the characteristic absorption of the system $\cdot PO(O\cdot C_nH_m)_2$ existing in the chlorophosphonates (and, of course, in the various phosphonates studied by Meyrick and Thompson, *loc. cit.*) has its immediate analogy in the acetals and ortho-esters (Bergmann, Bograchov, and Pinchas, *J. Amer. Chem. Soc.*, 1951, **73**, 2352). In this connection it is noteworthy that even a system (which contains one P–OC bond only) like that of $PO(SEt)_2(OEt)$, also has two strong bands at about 1030 cm.$^{-1}$ and 950 cm.$^{-1}$ (Gore, *loc. cit.*).

The presence of the 969-cm.$^{-1}$ band in dimethyl chlorophosphonate is again (cf. No. 1, 968 cm.$^{-1}$) noteworthy, the more so because dimethyl fluorophosphonate (Daasch and Smith, *loc. cit.*) lacks this band for some unknown reason. The absorption bands of diethyl chlorophosphonate are in perfect agreement with those of ethyl phosphate (Bergmann, Littauer, and Pinchas, *loc. cit.*), *viz.*, 1036 and 974 cm.$^{-1}$, the additional band at 1010 cm.$^{-1}$ being probably due to some other mode of vibration; their values as measured by us are, however, somewhat different from those read from Gore's curve (*loc. cit.*). In di*iso*propyl chlorophosphonate we find once more the two characteristic bands merged together under the influence of the branched alkyl groups. Diphenyl chlorophosphonate, finally, shows great similarity to the absorption of the triphenyl phosphate as quoted above.

In view of the great likeness, as far as the molecular spectra are concerned, between an oxygen and a nitrogen atom, especially when bound to a hydrogen atom (*e.g.*, dibutyl ether and dibutylamine have similar infra-red spectra—see curves Nos. 126 and 238, Barnes, Gore, Liddel, and Williams, " Infra-red Spectroscopy," New York, 1944), it was interesting to see whether the dialkyl alkylaminophosphonates would show the characteristic absorption of the tri-esters. As Table 2 shows, this is the case.

The phosphate bands appear in all the substances but are usually shifted towards the longer wave-lengths (especially the second band) and are often accompanied by more bands because of their lower symmetry. This shift seems to suggest that the P–NC bond is weaker than the P–OC bond, which is to be expected. [Although no data seem to be available for the relative strengths of these two bonds we can assume them to be parallel to those of the di-atoms PO and PN, respectively, for which Linnett (*Trans. Faraday Soc.*, 1942, **38**, 1) calculated the heats of dissociation to be 14·75 and 7·81 *A.* erg/molecule, respectively.] All the di*iso*propyl esters in Table 2 seem to regain the normal double (or multiple) character of the phosphate bands under the influence of the substituted amino-group; the dimethyl derivative (No. 2), however, retains its singularity of not showing the

TABLE 2. *Infra-red absorption of dialkyl aminophosphonates in the* 1060—900 *cm.*$^{-1}$ *region.*

(Solvent: 1 c.c. of carbon tetrachloride; 0·1 mm. cell thickness.)

No.	Substance	G.	Absorption bands (cm.$^{-1}$)
1	$NHBu\cdot PO(OPr^i)_2$	0·015	1011, 984 (strongest), 894 [a]
2	$NBu_2\cdot PO(OMe)_2$	0·019	1032 (strongest), 926 (weak)
3	$NBu_2\cdot PO(OEt)_2$	0·016	1031 (strongest), 956, 938
4	$NBu_2\cdot PO(OPr^i)_2$	0·016	1006, 979 (strongest), 929 [a]
5	$NBu_2\cdot PO(OPh)_2$	0·022	1059, 1022, 920 (strongest)
6	$NHPh\cdot PO(OPr^i)_2$	0·040	1031 (shoulder), 1011, 990 (strongest), 958, 932 [a]
7 [b]	$PO(OEt)_3$	0·043	1036 (strongest), 974

[a] Probably an *iso*propyl-group absorption. [b] For comparison (see Bergmann *et al.*, *loc. cit.*).

second band (970—1000 cm.$^{-1}$; the 926-cm.$^{-1}$ band seems to be additional) in spite of the destruction of the high symmetry of the tri-ester. Noteworthy is the large shift in the frequency of the second band of the diphenyl derivative (No. 5) as a result of the superposition of the two effects mentioned, *viz.*, that of the phenyl group and that of the P–NC bond.

Experimental

The instrument used for the infra-red measurements has already been described (Bergmann *et al., loc. cit.*) The dialkyl chlorophosphonates were obtained by chlorination of the corresponding dialkyl hydrogen phosphites (McCombie, Saunders, and Stacey, *J.*, 1945, 380), purified by vacuum distillation, and identified by chlorine determination. Diphenyl chlorophosphonate, prepared from phosphorus oxychloride and phenol (Brigl and Mueller, *Ber.*, 1939, **72**, 2121), had b. p. 150—153°/1 mm.

The following phosphate esters $PO(OR)_2(OEt)$ and aminophosphonate esters $NR'R''\cdot PO(OR)_2$ were synthesised from the corresponding chlorophosphonate $Cl\cdot PO(OR)_2$ by reaction with ethanol and the appropriate amine, respectively (details will be published separately): Ethyl dimethyl phosphate, b. p. 112—113°/41 mm., n_D^{22} 1·3984 (prepared by Drushel, *Amer. J. Sci.*, 1918, **43**, 57); ethyl di*iso*propyl phosphate, b. p. 110—112°/23 mm., n_D^{25} 1·4044, d_{25}^{25} 1·0066; ethyl diphenyl phosphate, b. p. 181—185°/2 mm., n_D^{30} 1·5250, d_{25}^{25} 1·185 (see Morel, *Compt. rend.*, 1898, **127**, 1024; 1899, **128**, 508; *Bull. Soc. chim.*, 1899, **21**, 492); dimethyl di-*n*-butylaminophosphonate, b. p. 81—82°/0·5 mm., n_D^{25} 1·4327; diethyl di-*n*-butylaminophosphonate, b. p. 93—100°/0·5 mm., n_D^{25} 1·4299; di*iso*propyl di-*n*-butylaminophosphonate, b. p. 110—112°/2 mm., n_D^{25} 1·4272; di*iso*propyl *n*-butylaminophosphonate, b. p. 99—101°/0·5 mm., n_D^{25} 1·4239; di*iso*propyl anilinophosphonate, m. p. 120° (McCombie *et al., loc. cit.*); diphenyl di-*n*-butylaminophosphonate, b. p. 190—200°/2 mm., b. p. 170—173°/0·5 mm., n_D^{25} 1·5173.

Weizmann Institute of Science,
Rehovoth, Israel.

[*Received, February 4th*, 1952.]