154. *The Infra-red Absorption of Pyrophosphates.*

By Ernst D. Bergmann, U. Z. Littauer, and S. Pinchas.

The infra-red spectra of inorganic and organic phosphates and pyrophosphates have been investigated. The origin of the observed absorption bands is discussed. The band at 930—950 cm.$^{-1}$ found in the spectra of the organic pyrophosphates is characteristic of the P–O–P bond.

During a study of organic pyrophosphates, it became desirable to investigate whether their infra-red spectra and those of inorganic salts of that acid exhibit a band characteristic of the P–O–P linkage. Whilst the infra-red absorption of the esters of several phosphorus oxyacids has been studied, *e.g.*, by Meyrick and Thompson (*J.*, 1950, 225) who assigned the main band in their spectrum to the P=O stretching frequency (1250—1260 cm.$^{-1}$) (cf. Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397; Gore, *Discuss. Faraday Soc.*, 1950, No. 9, 138), alkyl pyrophosphates do not seem to have been investigated.* Inorganic pyrophosphates have been studied by Laforgue-Kantzer (*Ann. Chim.*, 1950, **5**, 819); for the tetrasodium and disodium salts, *e.g.*, the following bands have been observed (cm.$^{-1}$) :

$Na_4P_2O_7$	1666	1539	1449	1429	1250	1088	995	926	893	800
$Na_2H_2P_2O_7$ ...	—	1539	1449	1389	—	1076(s)	1030	943	893(s)	802(s)

In the present study, suspensions of silver orthophosphate, silver acetyl phosphate, and silver pyrophosphate in medicinal liquid paraffin were investigated and the following intense bands observed, respectively, in the 980—900-cm.$^{-1}$ region (see below) : 947, 914, 903 cm.$^{-1}$. The last one very probably corresponds to the 893-cm.$^{-1}$ band reported for the sodium salts.

A number of alkyl phosphates and pyrophosphates was then compared in the 910—1060-cm.$^{-1}$ region of the typical covalent phosphate bands (Colthup, *loc. cit.*) (Table below).

Infra-red spectra of alkyl phosphates and pyrophosphates in the 910—1060-*cm.*$^{-1}$ *region.*
(*Solvent, carbon tetrachloride, cell thickness,* 0·1 *mm.*)

	Concn. (g./c.c. of solvent)	Bands in cm.$^{-1}$ (optical density)				
Phosphate.						
Methyl	0·022	—	1043 (1·60)	—	—	—
Ethyl	0·043	—	1036 (1·37)	—	974 (0·83)	—
n-Propyl	0·040	1051 (0·38) [a]	1039 (0·40)	998 (0·87)	—	—
*iso*Propyl ...	0·020	—	—	995 (2·0) [b]	—	931 (0·08) [c]
n-Butyl	0·017	—	1026 (0·81)	991 (0·39)	—	—
Pyrophosphate.						
Methyl	0·020	1046 (0·80)	—	970 (0·39)	—	—
Ethyl	0·048	1036 (1·55)	—	980 (1·15)	939 (1·20)	—
n-Propyl	—	—	—	—	—	—
*iso*Propyl ...	0·017	—	1006 (0·71) [b]	—	950 (0·45)	934 (0·27) [c]
n-Butyl	—	[1035(s)]	—	980	950 [d]	—

[a] Probably the propyl absorption. [b] Probably a superposition of the two bands expected. [c] Probably the *iso*propyl absorption. [d] Data of Daasch and Smith (*loc. cit.*).

In addition to the strong bands in that region, the substances show, of course, the intense above-mentioned P=O stretching frequency (*e.g.* : triethyl phosphate 1257 cm.$^{-1}$; tetraethyl pyrophosphate 1284 cm.$^{-1}$).

Colthup (*loc. cit.*) records for phosphate ions a band at 1100—1040 cm.$^{-1}$ only, but none corresponding to the intense 947-cm.$^{-1}$ peak, observed here for silver orthophosphate (Duval and Lecomte, *Bull. Soc. chim.*, 1947, 101, record a band at 970 cm.$^{-1}$; at least part of this discrepancy is probably due to the great breadth of the band and to the fact that the measurements have been made in a suspension, not in solution). The existence, in the spectra of phosphates, of two bands would seem probable from a comparison with the Raman frequences of the phosphate ion, which lie at 980 and 1082 cm.$^{-1}$ (Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," New York, 1945, p. 167). The 980-cm.$^{-1}$ frequency, however, is usually infra-red inactive, owing to symmetry conditions (being the ν_1 fundamental which is infra-red-inactive for a XY_4 molecule; Herzberg, *op. cit.*, p. 259). From the presence of the peak at 947 cm.$^{-1}$, one will conclude that this symmetry is destroyed in the silver salt. Pauling ("The Nature of the Chemical Bond," New York, 1940, p. 243) has also commented on the partly covalent character of the Ag–O bond and the distorted configuration of the phosphate ion in silver orthophosphate, as inferred from the bond-length measurements. The absence, in the inorganic phosphate, of the P=O stretching frequency (1240—1300 cm.$^{-1}$) of the covalent phosphates can be ascribed to hybridisation between the P=O and the P–O bonds.

The similarly situated two frequencies of the trialkyl phosphates recorded in the Table (at about 1030 and 980 cm.$^{-1}$, respectively) have very probably to be assigned to the $P(OR)_3$ grouping (Colthup, *loc. cit.*, records only one band in this region)—one to the

---

* After completion of this investigation, Daasch and Smith (*Analyt. Chem.*, 1951, **23**, 853) reported the spectra of methyl, ethyl, and *n*-butyl pyrophosphate. Their results agree fairly well with those recorded in the present paper.

stretching of all three alkoxy-groups in phase, the other to the stretching of two of them against the third. The same assignment appears likely for the analogous frequencies in the spectra of the alkyl pyrophosphates.

The validity of this assignment is supported by the following considerations: these two intense bands occur also with similar intensities—though occasionally shifted somewhat—in the spectra of the dialkyl phosphites and phosphonates (Meyrick and Thompson, *loc. cit.*) and in the substances studied by Gore (*loc. cit.*) which contain at least two alkoxy-groups linked to phosphorus. They are absent in substances such as $C_6H_5{\cdot}PSCl_2$. Furthermore, no other vibration is likely to cause an absorption of such high extinction coefficient [*e.g.*, for triethyl phosphate, $\varepsilon_{1036} = 6 \times 10^2$, $\varepsilon_{974} = 4 \times 10^2$ (for 1 mole/l. and a cell of 1 cm. thickness)]. Thirdly, it is reasonable to expect that the stretching of the three P–OR bonds in phase will have a frequency similar to that of the symmetrical stretching in the phosphate ion which lies at 980 cm.$^{-1}$ (Herzberg, *op. cit.*, p. 167). This, incidentally, leads to the conclusion that the frequency of about 1030 cm.$^{-1}$ belongs to the unsymmetrical out-of-phase mode vibration of the three P–OR bonds (symmetrical vibration, lower in energy content). The assumption of Daasch and Smith (*loc. cit.*), that it corresponds to the PO–C bond, thus does not seem justified.

The Table shows that the pyrophosphate always contains one band more (970, 939, 950 cm.$^{-1}$) than the corresponding phosphate. This frequency must be characteristic of the P–O–P grouping and very probably represents its antisymmetrical stretching vibration (the symmetrical one would probably be very weak or even infra-red-inactive). It is not present as a distinct band in silver pyrophosphate (for the Raman spectrum of inorganic pyrophosphates, see Hanwick and Hoffmann, *J. Chem. Physics*, 1951, **19**, 708), but seems to manifest iself in the shift of the second phosphate band from 947 cm.$^{-1}$ (silver phosphate) to 903 cm.$^{-1}$ (silver pyrophosphate), possibly because of the hybridisation of the P–O–P bonds under the influence of the ionic charges (cf. Kalckar, *Chem. Reviews*, 1941, **28**, 71; Hill and Morales, *J. Amer. Chem. Soc.*, 1951, **73**, 1656).

The introduction of a branched alkyl (*iso*propyl) group causes a shift to longer wavelengths in the frequency of the 1030-cm.$^{-1}$ band and brings about its merging with the band at about 980 cm.$^{-1}$. An analogous effect can be deduced for the 1030-cm.$^{-1}$ band from the data reported by Meyrick and Thompson (*loc. cit.*) for the alkyl phosphites and phosphonates.

Attention is drawn to the unexpected disappearance of one band in the spectra of the *methyl* esters of both phosphoric and pyrophosphoric acid. One frequently finds, however, that the lowest member of a homologous series differs somewhat from the higher ones. Also in the recorded Raman spectrum of trimethyl phosphate (Simon and Schulze, *Naturwiss.*, 1937, **25**, 669), the 980-cm.$^{-1}$ band is missing.

Materials and Apparatus.—Silver orthophosphate was prepared according to Lipmann and Tuttle (*J. Biol. Chem.*, 1944, **153**, 571); silver pyrophosphate by precipitation of an ice-cold aqueous solution of pyrophosphoric acid with a 25% silver nitrate solution, washing with ice-water, and drying *in vacuo* over phosphoric oxide. For the preparation of silver acetylphosphate, the instructions of Lipmann and Tuttle (*loc. cit.*) were followed. The esters had the following properties: Triethyl phosphate (Limpricht, *Annalen*, 1865, **134**, 347), b. p. 78—80°/4·5 mm., n_D^{20} 1·4056. Trimethyl phosphate (Evans, Davies, and Jones, *J.*, 1930, 1310), b. p. 93°/29 mm., n_D^{20} 1·3961. Tri-*n*-propyl phosphate (*idem, ibid.*), b. p. 95°/0·5 mm., n_D^{25} 1·4139. Tri*iso*propyl phosphate (*idem, ibid.*), b. p. 76°/3 mm., n_D^{20} 1·4057. Tri-*n*-butyl phosphate (*idem, ibid.*), b. p. 136°/5 mm., n_D^{25} 1·4220. Tetramethyl pyrophosphate (Toy, *J. Amer. Chem. Soc.*, 1949, **71**, 2268), b. p. 118°/0·5 mm., n_D^{25} 1·4120. Tetraethyl pyrophosphate (Toy, *ibid.*, 1948, **70**, 3882), b. p. 132—134°/0·8 mm., n_D^{20} 1·4189. Tetra*iso*propyl pyrophosphate (*idem, ibid.*), b. p. 120°/0·1 mm., n_D^{25} 1·4150.

The apparatus used was a Perkin–Elmer Model 12 C Infra-red Spectrometer, mounted with a rock-salt prism. The slit width used was approx. 0·3 mm., varying somewhat from measurement to measurement.

DANIEL SIEFF RESEARCH INSTITUTE, WEIZMANN INSTITUTE OF SCIENCE,
REHOVOTH, ISRAEL.

[*Received, October 8th,* 1951.]