668. *The ^{18}O Effect on the Infrared Absorption of Triphenylphosphine Oxide, and the Structure of Triphenylphosphine Oxide Hydrate.*

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The stretching vibration of the phosphoryl group in triphenylphosphine [^{18}O]oxide was compared with that of normal triphenylphosphine oxide. The frequency and intensity of the P–^{18}O band are appreciably lower than those of the P–^{16}O band. The results were used for determination of ^{18}O content in triphenylphosphine oxide. The absence of oxygen exchange between triphenylphosphine oxide and water indicates that triphenylphosphine oxide hydrate does not have the dihydroxy-structure.

IN a study of the effect of ^{18}O on the infrared absorption of various compounds, the spectrum of triphenylphosphine [^{18}O]oxide was compared with that of the normal phosphine oxide.

The infrared spectra of a mineral oil mull and of a carbon disulphide solution of normal triphenylphosphine oxide have been reported.[1] For the mull there is a strong phosphoryl absorption band at 1190 cm.$^{-1}$, as well as a strong band at about 1125 cm.$^{-1}$ which was not assigned. For a carbon disulphide solution these bands appear at 1203 and 1121 cm.$^{-1}$, respectively. In the present work the absorption of the two triphenylphosphine oxides, containing 86 and 0·2 atom % of ^{18}O respectively, was measured for carbon tetrachloride solutions. The results are in agreement with those previously observed (Table 1). The spectrum is almost the same in the two cases. The strong band of the normal compound at 1202 ± 1 cm.$^{-1}$ is however much weaker in the spectrum of the phosphine oxide containing 86 atoms % ^{18}O. In the spectrum of the labelled compound an intense band appears at 1172 cm.$^{-1}$, where the normal oxide does not absorb significantly. It is thus evident that the band at 1202 cm.$^{-1}$ belongs to the $P^+–^{16}O^-$ stretching vibration.

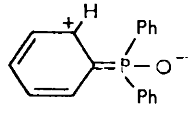
TABLE 1. *Major absorption bands of triphenylphosphine [^{16}O]- and [^{18}O]-oxide.*

Normal Ph_3PO [a]	3070	1438	1313	1202(s)	—	1123(s)	1070	752	746	694	690	683 cm.$^{-1}$
Labelled oxide [b]	3065	1438	1314	1205	1172(s)	1123(s)	1072	751	746	694	689	682 cm.$^{-1}$

The bands down to 1070 cm.$^{-1}$ were measured with a 0·1 mm. cell filled with a 0·05 g./ml. solution in carbon tetrachloride; the lower bands with a Nujol mull. [b] The bands down to 1072 cm.$^{-1}$ refer to a 0·2 mm. cell and a 0·04 g./ml. carbon tetrachloride solution; the lower ones with a mull. s = A strong band.

The small decrease in the frequency (1190 cm.$^{-1}$) observed for the $P^+–^{16}O^-$ vibration in a mull of the oxide[1] must be attributed to the effect of intermolecular forces in the solid state. A mull of the labelled compound shows its $P^+–^{18}O^-$ absorption band at about 1152 cm.$^{-1}$.

The neighbouring absorption band at 1123 cm.$^{-1}$ occurs at the same frequency and with the same intensity in both the normal and the labelled triphenylphosphine oxide. There is thus no possibility that this band also belongs to a P–O stretching vibration of a rotational isomer.[2] It seems to be due to an in-plane (phenyl ring) C–H deformation vibration, by analogy with the 1157 cm.$^{-1}$ band of chlorobenzene.[3] The somewhat lower frequency in this case, which is also outside the region 1175—1125 cm.$^{-1}$ usually assigned to monosubstituted benzenes,[4] might be the result of weak interaction of the ring π-electrons with the positively charged phosphorus atom. This interaction would give rise to resonating contributing structures such as (I) which have a positive charge on *ortho*- or *para*-positions, thereby weakening their C–H bonds. The intensity of this band in this case, compared with the usual weakness of this band



(I)

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[1] Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 857; Geddes, *J. Phys. Chem.*, 1954, **58**, 1062.

[2] Mortimer, *Spectrochim. Acta*, 1957, **9**, 270.

[3] Hellwaege, " Landolt-Boernstein, Zahlenwerte und Funktionen," Springer Verlag, Berlin, VIth edn., Vol. I, Part 2, p. 304.

[4] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen & Co., London, 1956, p. 55.

in other cases,[4] can also be explained by this interaction. This interaction cannot be assumed to be appreciable, however.[5],

The difference of 30 cm.$^{-1}$ between the stretching vibrations of P–^{16}O and P–^{18}O is similar to that observed [6] with the carbonyl vibrations of normal and labelled benzophenone (29 cm.$^{-1}$) and can be compared with the value of 45 cm.$^{-1}$ calculated for it according to Hooke's law when account is taken only of the phosphoryl group.

It has been observed [6] that when ^{18}O is introduced into benzophenone instead of ^{16}O the (apparent) molecular extinction coefficient of the RO band (R = P or C) drops from 360 to 300 l. mole^{-1} cm.$^{-1}$. When the corresponding molecular extinction coefficients of the triphenylphosphine oxides were calculated from the optical densities of their solutions in carbon disulphide at the R–O frequencies a similar drop from 425 to 360 l. mole^{-1} cm.$^{-1}$ was again observed. The half-intensity band width in both cases is equal and amounts to 13 cm.$^{-1}$, so that if a similar shape is assumed for the two bands the calculated absolute integrated intensities of these bands are in the same ratio as the corresponding molecular extinction coefficients. When the $P^+–O^-$ molecular extinction coefficients were measured in carbon tetrachloride solutions the values obtained were 410 and 310 l. mole^{-1} cm.$^{-1}$ and the half-widths 17 and 19 cm.$^{-1}$, respectively. If one takes the product of the extinction coefficient and the half-width as a measure of the corresponding integrated intensity of absorption,[7] one gets the results summarised in Table 2.

TABLE 2. *The relative absorption intensity* [a] (*l. mole*$^{-1}$ *cm.*$^{-1}$) *of the phosphoryl stretching vibration.*

Vibration	In CCl_4	In CS_2
$P^+–{}^{16}O^-$	7000	5500
$P^+–{}^{18}O^-$	5900	4700

[a] Expressed as the product of the apparent molecular extinction coefficient and the half-intensity band width.

Table 2 shows that the absorption intensity of the $P^+–{}^{18}O^-$ band is always lower by about 15% than that of the corresponding $P^+–{}^{16}O^-$ band. This lower intensity of the absorption of the heavier isotopic group is larger than that calculated according to Crawford's rule.[8] As shown above the only frequency really affected by the ^{18}O replacement of ^{16}O in this case is the P–O frequency. One can therefore assume the intensities of all the other bands to be the same in the isotopic pair, as was found experimentally for the 1123 cm.$^{-1}$ band (see p. 3266). Crawford's rule therefore reduces here to the form: [9] $I_{16}/\nu_{16}^2 = I_{18}/\nu_{18}^2$ where I is the integrated intensity of the P–O band and ν is the P–O frequency. Hence, according to Crawford's rule the ratio I_{18}/I_{16} should be here $\nu_{18}^2/\nu_{16}^2 = 1172^2/1202^2 = 0{\cdot}95$, instead of the observed value of $0{\cdot}85 \pm 0{\cdot}05$.

The absolute absorption intensity of a vibration band is a function of the change of dipole moment of the vibrating molecule with the change in its normal co-ordinates during this vibration.[10] It seems therefore that the degree of polarisation of the P=O bond to $P^+–O^-$ is not the same in the two isotopic groups resulting in a bigger free charge e on the ^{16}O atom. This will give a larger bond moment $M = er$ (where r is approximately equal to the P–O bond length), and a higher molecular dipole moment. The change of the unequal molecular dipole moments of the normal and the labelled triphenylphosphine oxide with the change of the normal co-ordinates during a $P^+–O^-$ stretching vibration would probably also be unequal, resulting in different values for the relative absorption intensity of the P–O band.

A similar effect was observed by Nolin and Jones,[11] who found that the absorption

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[5] Yaffe and Freeman, *J. Amer. Chem. Soc.*, 1952, **74**, 1069; *J. Chem. Phys.*, 1954, **22**, 1430.

[6] Halmann and Pinchas, *J.*, 1958, 1703.

[7] Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.

[8] Crawford, *J. Chem. Phys.*, 1952, **20**, 977.

[9] See, *e.g.*, Eggers, Hisatsune, and Van Alten, *J. Phys. Chem.*, 1955, **52**, 1124.

[10] Herzberg, "Infrared and Raman Spectra," Van Nostrand Co., New York, 1945, pp. 260—261.

[11] Nolin and Jones, *J. Amer. Chem. Soc.*, 1953, **75**, 5626.

of the CD_3 and CD_2 groups in deuterated ketones is much weaker than that of the corresponding CH_3 and CH_2 groups.

The higher values for the absorption intensity obtained for the solutions in carbon tetrachloride than for carbon disulphide solutions are worthy of note. It was found that when no solvent–solute interaction takes place the integrated absorption of a band measured in carbon disulphide solution is about 1·1 times that measured in carbon tetrachloride. This is due to the difference in the electric polarisability of the solvents.[12] It may therefore be concluded that the triphenylphosphine oxide forms association complexes with the carbon tetrachloride molecules, in which the polarisation of the $P^+–O^-$ bond is increased by some kind of interaction. This conclusion would also explain why the $P^+–O^-$ band is broader in carbon tetrachloride solutions than in solutions in carbon disulphide, since the intermolecular forces inside the complex present in carbon tetrachloride solution can be expected to modify the " pure " $P^+–O^-$ frequency somewhat differently for different configurations of this complex. A host of $P^+–O^-$ bands will thus be formed, all merging together to one broad band. This effect will then be somewhat similar to that of hydrogen bonding which also both increases the integrated absorption intensity of bands and broadens them.[13]

The benzophenone C=O band, measured for a carbon disulphide solution, has a half-intensity width not much different from that for a carbon tetrachloride solution (18 and 19 cm.$^{-1}$ respectively). The difference in the relative absorption intensity of the C=O band in these solvents is also smaller in this case, being only about 14% higher in carbon tetrachloride than in carbon disulphide, compared with 27% for the normal triphenylphosphine oxide. The width of the C=O band in solutions of normal and labelled benzophenone in carbon tetrachloride is practically the same. It can thus be assumed that the carbon tetrachloride–[^{16}O or ^{18}O]benzophenone interaction is only weak.

The relative absorption intensity of the 1123 cm.$^{-1}$ band was found to be constant within the experimental error when ^{16}O was replaced by ^{18}O in triphenylphosphine oxide, its value being always 4000 ± 200 l. mole^{-1} cm.$^{-2}$.

It seems that this effect of the ^{18}O isotope on the intensity of the R=O band should be taken into account when the additivity of the bond moments in carbon dioxide is investigated by measuring the intensity of the $^{16}O=C=^{18}O$ absorption.[14]

The characteristic $P–^{18}O$ infrared absorption of triphenylphosphine oxide was used in a tracer study for the elucidation of the structure of triphenylphosphine oxide hydrate which has been in some doubt. It is prepared by hydrolysis of triphenylphosphine dihalides [15] or by recrystallising the phosphine oxide from water.[16] Our analytical results fit best a hemihydrate formula $(Ph_3PO)_2,H_2O$, whereas previous authors [15,16] suggested a monohydrate formula Ph_3PO,H_2O. Jensen concluded from the considerable dipole moment of triphenylphosphine oxide that the phosphoryl bond is semipolar.[16] The dipole moment of triphenylphosphine oxide hydrate is even larger and therefore the water molecule could be expected to be bound by a hydrogen bridge to the oxygen atom of the phosphoryl group. The increased dipole moment in the hydrate was also explained by formation of a phosphonium hydroxide: [16] $Ph_3P^+–O^- \cdots H–OH \rightleftharpoons Ph_3P^+OH\ OH^-$. An altogether different structure might, however, be proposed on the basis of the short length of the P–O bond in the oxide,[17] which was assumed therefore to be a double bond. The hydrate could then be formed by addition of water to the double bond: $Ph_3PO + H_2O \rightleftharpoons Ph_3P(OH)_2$. In this dihydroxy-structure the two oxygen atoms become equivalent. To decide this, triphenylphosphine oxide was refluxed with an excess of water containing 87 atoms % of ^{18}O for 16 hr.; the phosphine oxide was then recovered

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[12] Yaffe and Kimel, *J. Chem. Phys.*, 1956, **25**, 374.

[13] See, *e.g.*, Wenograd and Spurr, *J. Amer. Chem. Soc.*, 1957, **79**, 5844.

[14] Eggers and Arends, *J. Chem. Phys.*, 1957, **27**, 1405.

[15] Michaelis and Gleichman, *Ber.*, 1882, **15**, 801; Michaelis and Soden, *Annalen*, 1885, **229**, 306.

[16] Jensen, *Z. anorg. Chem.*, 1943, **250**, 270.

[17] Phillips, Hunter, and Sutton, *J.*, 1945, 146.

by drying the reaction mixture in a high vacuum. It did not become enriched in ^{18}O, within experimental error. Also, triphenylphosphine [^{18}O]oxide was boiled and recrystallised from normal water: its ^{18}O content did not decrease appreciably. The absence of oxygen exchange between triphenylphosphine oxide and water indicates that in the hydrate the oxygen atoms are not identical; the dihydroxy-structure can therefore be excluded.

The infrared spectrum of the normal hydrate also shows that it does not have the dihydroxy-structure. Its solution (0·05 g./l.) in carbon tetrachloride in a 0·02 mm. cell showed bands at 3410 (bonded OH stretching), 3070, 1483, 1438, 1311, 1201 (vs), 1119 (s), 1072, 1029, 1000. Comparison with Table 1 shows that the bands of the oxide are almost unaffected by the added water molecule, the presence of the latter in the solution being clearly demonstrated by the band at 3410 cm.$^{-1}$. It must be concluded that the hydrate is a molecular complex between the phosphine oxide and the water molecule. This complex would seem to be held together more by interactions between the aromatic rings and the water molecule than by hydrogen bonding to the phosphoryl group. This seems to be indicated by the lack of decrease in the P^+–O^- frequency in the hydrate and, on the other hand, the decrease of 4 cm.$^{-1}$ in the C–H bending frequency.

EXPERIMENTAL

A solution of bromine (0·2 ml.; vacuum-distilled from P_2O_5) in dry carbon tetrachloride (5 ml.) was slowly added to a stirred solution of triphenylphosphine (0·80 g.; Eastman Organic Chemicals) with exclusion of moisture ($CaCl_2$). Triphenylphosphine dibromide was precipitated and the solution became brown owing to excess of bromine. After 10 minutes' stirring, water containing 87 atoms % of ^{18}O (0·5 ml., from the fractionating plant of this Institute) was added at once by means of a syringe, and the mixture was refluxed for ½ hr. with stirring. The carbon tetrachloride and most of the excess of water were then distilled off. The residual viscous mass crystallised from a large volume of normal distilled water; crystals of triphenylphosphine [^{18}O]oxide were obtained (0·27 g.) which, dried in a vacuum, had m. p. 158·5—159·5° (lit.,[17] m. p. 159°).

Triphenylphosphine oxide hydrate, prepared according to Michaelis's procedure,[15] was recrystallised from water; it had m. p. 154—157° (Michaelis [15] reports 148°) [Found: C, 75·25; H, 5·6; H_2O, 3·6 (Karl Fischer). Calc. for the hemihydrate $C_{36}H_{32}O_3P_2$: C, 75·3; H, 5·6; H_2O, 3·1%). The average of Jensen's cryoscopic molecular-weight determinations [16] in benzene is 287 (calc. for hemihydrate: 287; for monohydrate, 296; on the assumption that in the benzene solution the water molecule remains attached to one triphenylphosphine oxide molecule).

The infrared light absorption was measured with a Perkin–Elmer infrared spectrophotometer Model 12C equipped with a sodium chloride prism. The molecular extinction coefficients of the isotopic pairs were determined in the same cell and usually on more than one solution. The thickness of the cells is, however, known only to the first decimal figure, hence the relative values for the molecular extinction coefficient are estimated to be correct to within 10 l. mole^{-1} cm.$^{-1}$, but the " absolute " (apparent) values are much less exact. The relative intensity values are estimated to be correct to about 200 units. The slit width used at 1100—1300 cm.$^{-1}$ was about 0·15 mm.

Determination of the ^{18}O content in triphenylphosphine oxide was at first attempted by the method of Rittenberg and Ponticorvo.[18] It was found, however, that a mixture of mercuric chloride and the phosphine oxide at 425° did not liberate carbon dioxide. Triphenylphosphine oxide was decomposed by heating it (about 15 mg.) with mercuric chloride (about 15 mg.) and mercuric cyanide [19] (about 25 mg.) in an evacuated break-seal tube. The remaining procedure was as described in the literature.[18]

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[18] Rittenberg and Ponticorvo, *J. Appl. Rad. Isot.*, 1956, **1**, 208.

[19] We are indebted to Dr. M. Anbar for suggesting the use of mercuric cyanide.