

442. *The Effect of Complex-formation by Phosphine Oxides on their P-O Stretching Frequencies.*

By F. A. COTTON, R. D. BARNES, and E. BANNISTER.

The infrared spectra of trimethyl- and triphenyl-phosphine oxide and a number of their complexes with various transition-metal cations have been examined. Complex-formation causes the P-O stretching frequencies to shift $\sim 50 \text{ cm.}^{-1}$ to lower values. Since a simple kinematic effect would raise the frequency, an explanation in terms of a lowering of the P-O bond order is proposed.

In connection with a broad study of metal complexes of trialkyl- and triaryl-phosphine oxides and dialkyl and diaryl sulphoxides, we required knowledge of the effect of co-ordination *via* oxygen upon P-O and S-O stretching frequencies. Since in phosphine oxides co-ordination can take place only through oxygen we have examined the infrared spectra of representative complexes of trimethyl- and triphenyl-phosphine oxide, and the results are reported and discussed here.

The Table lists the complexes studied by us, giving the frequencies of their "P-O" stretching modes. The only previous observations of this kind of which we are aware are a few reported by Sheldon and Tyree.¹ They found "P-O" stretching bands at 1125 cm.^{-1} for $(\text{Ph}_3\text{PO})_2\text{SnCl}_4$, $(\text{Ph}_3\text{PO})_2\text{SnBr}_4$, and $(\text{Ph}_3\text{PO})_2\text{FeBr}_2$, and at 1130 cm.^{-1} for $(\text{Ph}_3\text{PO})_2\text{TiCl}_4$. However, they report a frequency of 1180 cm.^{-1} for Ph_3PO in Nujol which does not agree with our observation of 1195 cm.^{-1} under the same conditions. Halman and Pinkas² have reported that the P-O stretching frequency occurs at 1190 cm.^{-1} in the solid. Thus Sheldon and Tyree's value appears to be slightly low for some unknown reason.

Of the compounds listed in the Table, nos. 7—12 are new, having been prepared in this laboratory.³ Compounds 2—4 and 14 have been reported by Pickard and Kenyon.⁴ The analogous compounds, 5, 6, and 15, are new, but were easily prepared by the general procedure of Pickard and Kenyon.

"P-O" stretching frequencies in Ph_3PO and Me_3PO and their complexes.

Compound	"P-O" stretching frequency (cm.^{-1})	Shift	Medium
1. Ph_3PO	1195	—	Nujol
2. $(\text{Ph}_3\text{PO})_2\text{CdI}_2$	1153	-42	"
3. $(\text{Ph}_3\text{PO})_2\text{ZnI}_2$	1151	-44	"
4. $(\text{Ph}_3\text{PO})_2\text{CoCl}_2$	1155	-40	"
5. $(\text{Ph}_3\text{PO})_2\text{CoBr}_2$	1153	-42	KBr
6. $(\text{Ph}_3\text{PO})_2\text{CoI}_2$	1153	-42	"
7. $(\text{Ph}_3\text{PO})_4\text{Zn}(\text{ClO}_4)_2$	1156	-39	Nujol
8. $(\text{Ph}_3\text{PO})_4\text{Cu}(\text{ClO}_4)_2$	1134	-61	"
9. $(\text{Ph}_3\text{PO})_4\text{Ni}(\text{ClO}_4)_2$	1145, 1170	-38 (av.)	"
10. $(\text{Ph}_3\text{PO})_4\text{Co}(\text{ClO}_4)_2$	1146	-49	"
11. $(\text{Ph}_3\text{PO})_4\text{Mn}(\text{ClO}_4)_2$	1157	-38	"
12. $(\text{Ph}_3\text{PO})_4\text{Fe}(\text{ClO}_4)_3$	1125	-70	"
13. Me_3PO	1174	—	KBr
14. $(\text{Me}_3\text{PO})_2\text{ZnI}_2$	1120, 1135	-47 (av.)	"
15. $(\text{Me}_3\text{PO})_2\text{CoCl}_2$	1100, 1125	-62 (av.)	"
16. $(\text{Me}_3\text{PO})_4\text{Co}(\text{ClO}_4)_2$	1150	-24	"

The spectra of the two oxides have been assigned by Daasch and Smith.^{5,6} While all their assignments may not be correct, there can be no doubt, from the excellent work of

¹ Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4775.

² Halman and Pinkas, *J.*, 1958, 3264.

³ Cf. Cotton, Bannister, Barnes, and Holm, *Proc. Chem. Soc.*, 1959, 158.

⁴ Pickard and Kenyon, *J.*, 1906, **89**, 262.

⁵ Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 853.

⁶ Daasch and Smith, *J. Chem. Phys.*, 1951, **19**, 22.

Halman and Pinkas,² that the "P-O" stretching frequency in the phenyl, and presumably also that in the methyl compound, have been correctly assigned. The spectra of all of the complexes of metal halides are virtually identical in the rock-salt region with the spectra of the free phosphine oxides except for the shift of the "P-O" band, and, in two cases, also a definite splitting of this band. In a few cases the shifted band does appear to be somewhat broadened. Broadening or outright splitting of the "P-O" band in the complexes could be caused by several things, the most likely of which are: (1) coupling between the two P-O vibrations *via* the metal atom to which both are co-ordinated, tending to

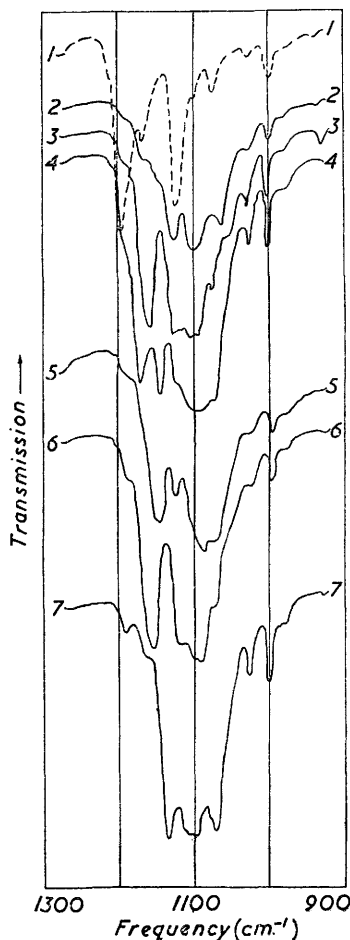


FIG. 1. *Infrared spectra of $(\text{Ph}_3\text{PO})_4\text{M}(\text{ClO}_4)_n$ complexes, taken as Nujol mulls.*

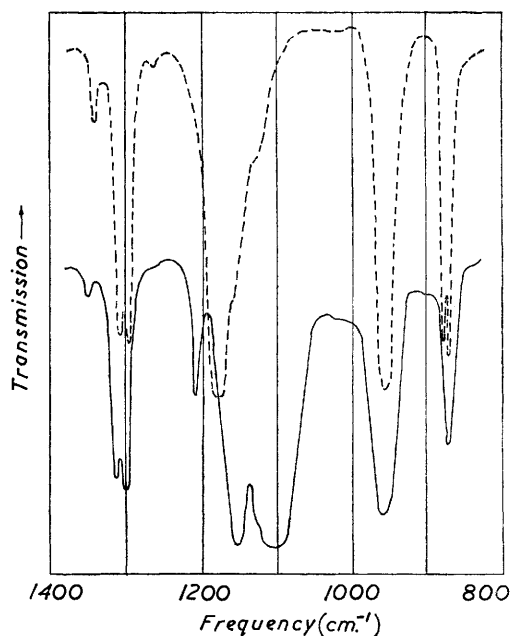
- 1, Ph_3PO .
- 2, $(\text{Ph}_3\text{PO})_4\text{Fe}(\text{ClO}_4)_3$.
- 3, $(\text{Ph}_3\text{PO})_4\text{Mn}(\text{ClO}_4)_2$.
- 4, $(\text{Ph}_3\text{PO})_4\text{Ni}(\text{ClO}_4)_2$.
- 5, $(\text{Ph}_3\text{PO})_4\text{Co}(\text{ClO}_4)_2$.
- 6, $(\text{Ph}_3\text{PO})_4\text{Zn}(\text{ClO}_4)_2$.
- 7, $(\text{Ph}_3\text{PO})_4\text{Cu}(\text{ClO}_4)_2$.

produce or actually producing separate symmetric and asymmetric stretching modes; (2) the existence, in many possible ways, of non-equivalent ligands in the crystal which would differ more or less in their vibrational frequencies.

For the perchlorate complexes, the spectra are again practically identical with those of the free ligand except for (a) a shift of the "P-O" band, and (b) the appearance of the T_{2u} Cl-O stretching vibration and the T_{2u} deformation vibration of ClO_4^- at ~ 1100 and ~ 620 cm^{-1} , respectively. The former causes some possible uncertainty in the interpretation of the results for the perchlorate complexes. The reason for this will be apparent on inspection of Figs. 1 and 2. Fig. 1 shows the spectra of triphenylphosphine oxide and

those of its metal perchlorate complexes in the region of interest. The spectra of ammonium, sodium, potassium, and magnesium perchlorate, reported by Miller and Wilkins,⁷ show that crystalline-field effects tend to make the $\sim 1100\text{ cm}^{-1}$ band of the perchlorate ion rather broad in the first three, and actually afford a doublet for the magnesium salt, probably due to the effect of non-cubic site symmetry in splitting the degeneracy. Thus we must consider the possibility of a similar effect in the compounds studied here. This could mean that some of the assignments given in the Table, for instance, those for $(\text{Ph}_3\text{PO})_4\text{Cu}(\text{ClO}_4)_4$ and $(\text{Ph}_3\text{PO})_4\text{Fe}(\text{ClO}_4)_3$ are too high, the band assigned to P-O being actually due to Cl-O while the former is unresolved in the heavy absorption around 1100 cm^{-1} . If this is the case, then the effect of complex-formation is even greater than we assume and this further strengthens the following proposals as to the cause and significance of the frequency shifts. In the case of $(\text{Me}_3\text{PO})_4\text{Co}(\text{ClO}_4)_2$ (Fig. 2), we have assumed that

FIG. 2. Infrared spectra of Me_3PO (broken curve) and blue $(\text{Me}_3\text{PO})_4\text{Co}(\text{ClO}_4)_2$ (solid curve) both pressed in KBr.



the very strong band at 1150 cm^{-1} is due to complexed P-O; we cannot offer any assignment for the weak band at 1208 cm^{-1} , which does not appear in the spectrum of the free ligand.

In discussing the interpretation of these frequency shifts, we must first recognize that, in principle, the coupling of the two oscillators, P-O and O-M, will tend to raise the "P-O" frequency. By using appropriate kinematic equations for the stretching modes of an A-B-C system, and taking $k_{\text{PO}} = 8.73\text{ md}/\text{\AA}$ and $k_{\text{MO}} = 0.5\text{--}2.5\text{ md}/\text{\AA}$, it can be shown that a purely kinematic effect would tend to raise the "P-O" frequencies by $50\text{--}150\text{ cm}^{-1}$ for k_{MO} values in the above range. Thus the observed decreases in "P-O" frequencies represent only a part of the total effect of a lowering of k_{PO} which presumably reflects a decrease in the P-O bond order.

In order to decide how and why the force constant of the P-O bond decreases on complex-formation, we must first consider the nature of the P-O bond in a phosphine oxide. The literature apparently contains no conclusive information on this point, but

⁷ Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

we can perhaps reason by analogy with the S-O bonds in sulphoxides which have been the subject of informative study. In both phosphine oxides and sulphoxides we may assume that the bonding involves first a co-ordinate $\overset{+}{\text{P}}\rightarrow\bar{\text{O}}$ or $\overset{+}{\text{S}}\rightarrow\bar{\text{O}}$ bond, in addition to which there will be some degree of back-bonding, $\bar{\text{P}}\leftarrow\overset{+}{\text{O}}$ and $\bar{\text{S}}\leftarrow\overset{+}{\text{O}}$ by overlap of filled $p\pi$ -orbitals of oxygen with the appropriate empty $d\pi$ -orbitals of phosphorus or sulphur. For the sulphoxides, a careful and well reasoned analyses of dipole-moment data, taking account of the effects of lone-pair moments, led Cumper and Walker⁸ to conclude that this $p\pi\rightarrow d\pi$ -back-bonding was sufficient to make the S-O bond approximately a double bond. Unfortunately, the data necessary for a similar analysis of the P-O bond are lacking,* but it is reasonable to assume that an appreciable amount of $p\pi\rightarrow d\pi$ -back-bonding exists also in P-O bonds. Some support for this is afforded by the work of Bell *et al.*⁹ who found that in X_3PO compounds the P-O stretching frequency increases with increasing electronegativity of the atoms X. While it would, of course, be more desirable to have a comparison of P-O stretching force constants since mass effects are unlikely to be completely negligible as Bell *et al.* assume, the results do suggest that back-bonding must be of importance. If the bond were purely $\overset{+}{\text{P}}\rightarrow\bar{\text{O}}$, we should expect that an increase of electronegativity of the groups attached to phosphorus could only decrease the strength of the P-O bond, whereas, if we assume the existence of varying amounts of back-bonding, the increase in electronegativity, while lowering the strength of the $\overset{+}{\text{P}}\rightarrow\bar{\text{O}}$ bond, can at the same time enhance the strength of the $p\pi\rightarrow d\pi$, $\bar{\text{P}}\leftarrow\overset{+}{\text{O}}$ bond, thus giving a net increase in bond strength. Certainly we should expect trimethylphosphine oxide to have the least amount of back-bonding, but we can see no basis for the suggestion of Bell *et al.* that there is *no* back-bonding in this compound if we consider the closely related sulphoxides. A second line of evidence suggesting that the P-O and S-O bonds have comparable degrees of double-bond character comes from consideration of bond lengths. While we have found no data on P-O bond lengths for alkyl- or aryl-phosphine oxides, the following comparisons are significant. The S-O distance in Me_2SO ¹⁰ is 1.43 Å, in Me_2SO_2 ,¹¹ 1.44 Å, and in Ph_2SO ,¹² 1.47 Å, while it is 1.45 Å in Cl_2SO ¹³ and 1.41 Å in F_2SO .¹⁴ Thus it appears that the typical bond lengths in alkyl and aryl sulphoxides and sulphones are only ~ 0.03 Å greater than those in the thionyl halides. Now the P-O distances in Cl_3PO and F_3PO are both 1.45 Å according to microwave studies.¹⁵ Hence it is very reasonable to suppose that the P-O distances in phosphine oxides will be of the order of 1.45–1.50 Å. This is considerably less than the expected single-bond distance (~ 1.7 Å) and suggests that there is considerable back-bonding.

If then we accept the view that the P-O bond has at least partial multiple character, we can consider the following three effects of complex-formation upon the P-O bond order and hence on the bond-stretching force constant: (1) When the oxygen atom is placed close to the positively charged metal ion, to which it may also, to some extent, form an actual covalent bond, an enhancement of the $\overset{+}{\text{P}}\rightarrow\bar{\text{O}}$ σ -bond will be expected. This effect tends to raise k_{PO} . (2) At the same time the $p\pi\rightarrow d\pi$ -back-bonding, $\bar{\text{O}}\rightarrow\overset{+}{\text{P}}$ will tend to be decreased, thus lowering k_{PO} . (3) Conceivably, for transition-metal ions where there are low-energy filled d -orbitals, there may be a drift of metal $d\pi$ -electrons toward oxygen

* Such a study is in progress in this laboratory.

⁸ Cumper and Walker, *Trans. Faraday Soc.*, 1956, **52**, 193.

⁹ Bell, Heisler, Tannenbaum, and Goldenson, *J. Amer. Chem. Soc.*, 1954, **76**, 5185.

¹⁰ Rundle, quoted by Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

¹¹ Lister and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 497.

¹² Abrahams, *Acta Cryst.*, 1957, **10**, 417.

¹³ Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360.

¹⁴ Ferguson, *J. Amer. Chem. Soc.*, 1954, **76**, 850.

¹⁵ Williams, Sheridan, and Gordy, *J. Chem. Phys.*, 1952, **20**, 164.

$p\pi$ -orbitals, displacing the oxygen $p\pi$ -electrons toward empty $d\pi$ -orbitals of phosphorus. This would probably also tend to increase k_{PO} .

Evidently, the second effect must be dominant, since k_{PO} does drop on complex-formation. It is possible to estimate the decrease in k_{PO} . If we insert a value of ν_{PO} of 1120 cm^{-1} into the appropriate dynamical equations and assume $m_{\text{X}} = 100$ and $k_{\text{OX}} = 2.0$ millidynes \AA^{-1} , we calculate that k_{PO} equals 6.84 millidynes \AA^{-1} . Thus, very roughly, the stretching constant has dropped by $\sim 20\%$. It is not possible to deduce from this the change in bond order in any very precise way, but as a rough indication we note that for carbon-carbon bonds the average force constants are, for $\text{C}\equiv\text{C}$, ~ 15 , for $\text{C}=\text{C}$, ~ 10 , and for $\text{C}-\text{C}$, ~ 5 . Thus a decrease of $\sim 20\%$ in the force constant indicates a decrease of perhaps $20-30\%$ in the P-O bond order.

In conclusion, the effect which an interaction between metal-oxygen and phosphorus-oxygen bond stretching will have on the "P-O" stretching frequency may be considered. In approximate calculations we obtain 7.55 millidynes \AA^{-1} for k_{PO} when $\nu = 1120 \text{ cm}^{-1}$. This still represents a substantial lowering of k_{PO} by complex-formation. Incidentally our calculations involve a positive interaction constant of significant magnitude, which is in itself a consequence of the effect of complex-formation in lowering k_{PO} .

EXPERIMENTAL

The phosphine oxides were prepared by the careful addition of an ethereal solution of trichlorophosphine oxide to a stoichiometric amount of the appropriate Grignard reagent.^{4,16,17} Triphenylphosphine oxide was purified by dissolving it in hot benzene and adding light petroleum to first appearance of turbidity, then slowly cooling the whole, finally in ice. Trimethylphosphine oxide was recrystallized from chloroform. Both oxides were stored in a vacuum over phosphoric oxide.

The metal halide complexes were prepared by mixing alcohol solutions of the halide and the phosphine oxide as described by Pickard and Kenyon.⁴ For the compounds previously reported by Pickard and Kenyon we obtained good carbon and hydrogen analyses and m. p.s in agreement with those previously given. For the new compounds the following analyses and melting points were obtained:

$(\text{Ph}_3\text{PO})_2\text{CoBr}_2$: Found: C, 55.8; H, 3.9. Required C, 55.8; H, 3.9%. M. p. 223° .

$(\text{Ph}_3\text{PO})_2\text{CoI}_2$: Found: C, 48.5; H, 3.4. Required C, 49.7; H, 3.5%. M. p. 232° .

All of the perchlorate complexes are to be described fully in the near future.

The spectra were obtained on a Perkin-Elmer model 21 double-beam spectrometer with a sodium chloride prism.

We thank the United States Atomic Energy Commission for financial support under Contract AT(30-1)-1965.

DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE 39, MASS., U.S.A.

[Received, July 8th, 1959.]

¹⁶ Burg and McKee, *J. Amer. Chem. Soc.*, 1951, **73**, 4590.

¹⁷ Grignard and Savard, *Compt. rend.*, 1931, **192**, 592.