988. *Hydrogen Bonding in Some Adducts of Oxygen Bases with Acids. Part I. Infrared Spectra and Structure of Crystalline Adducts of Some Phosphine, Arsine, and Amine Oxides, and Sulphoxides with Strong Acids.*

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Infrared spectra of adducts of triphenylphosphine oxide, dimethyl sulphoxide, diphenyl sulphoxide, triphenylarsine oxide, pyridine 1-oxide, and 2-picoline 1-oxide with nitric acid, trichloroacetic acid, hydrogen chloride, and hydrogen bromide have been investigated, as well as their deuterated analogues. The absorption of some samples was followed down to 150 cm.$^{-1}$ in order to find the low-frequency stretching vibrations of the hydrogen bridge. The spectra of the sulphur, phosphorus, and arsine oxides do not indicate a proton transfer to the basic oxygen, with the possible exception of triphenylphosphine oxide hydrobromide. Such a transfer seems to occur with the *N*-oxide hydrohalides. In this group, α-picoline oxide takes a special place: it forms a 2 : 1 adduct with hydrogen bromide, having a spectrum very different from that of the 1 : 1 adducts, that is interpreted in terms of a symmetrical hydrogen bond with the proton bridging the two oxygen atoms. With pyridine 1-oxide hydrochloride and hydrobromide, and with 2-picoline 1-oxide hydrochloride, low-frequency absorption in the range 180—240 cm.$^{-1}$ was observed, believed to be due to the stretching vibrations of the heavy parts of the hydrogen bond.

INFRARED spectroscopy has been used [1,2] in conjunction with proton magnetic resonance to characterise substances which contain very short hydrogen bonds, and to differentiate hydrogen bonds with a double potential minimum and a low barrier from such bonds with a vanishing barrier. The materials were mainly crystalline, the protons connecting symmetrical or nearly symmetrical molecules or ions, and correlations between spectral features and the type of potential have been advanced.[3] This paper concerns work on substances in which hydrogen bonds between dissimilar partners would be expected. It raises the problem of the site of protonation, *i.e.*, whether to consider these substances as

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[1] Blinc and Hadži, *Spectrochim. Acta*, 1960, **16**, 852.

[2] Blinc, Hadži, and Novak, *Z. Elektrochem.*, 1960, **64**, 567.

[3] Hadži and Novak, " Infrared Spectra of, and Hydrogen Bonding in, Some Acid Salts of Carboxylic Acids," University of Ljubljana, 1960.

salts or hydrogen-bonded adducts. Definite conclusions about this have been reached in most of the examples studied, which comprise some new adducts as well as others long known. It is believed that the results have additional interest since the bases involved, such as sulphoxides, phosphine oxides, and arsine oxides, are important in co-ordination chemistry. The behaviour of the X–O bands of the bases on hydrogen bonding should also be of interest.

Most of the substances display very unusual spectral features due to strong hydrogen bonding. Particularly interesting are picoline 1-oxide hemihydrobromide and the trichloroacetates of triphenylarsine oxide and of pyridine 1-oxide. Their spectra resemble those obtained previously[3] for substances containing symmetrical hydrogen bonds. It is possible that the bonds are indeed symmetrical in the first case, but this appears less likely with the other two for structural reasons.

The spectrum of triphenylphosphine oxide trichloroacetate links the present group of solids with the liquid adducts of carboxylic acids and bases which will be the subject of a later paper. The two types exhibit similar features, and this will be helpful in interpreting the spectra of the liquids because in the solid the complicating possibility of equilibria between different protonated species is eliminated.

Infrared spectra of most of the substances have been investigated down to 200 cm.$^{-1}$, but only the *N*-oxide hydrohalides had bands that could be attributed to the stretching vibration of the hydrogen bond, *i.e.*, the vibration of the heavy parts against each other. In view of the scarcity of this kind of data, the force constants calculated here are important.

EXPERIMENTAL

Commercial products were used. The composition of the adducts was checked by titration (Table 1). Saytseff's preparation[4] of Me_2SO,HNO_3 has been simplified to slow addition of the base to an excess of nitric acid with cooling; the excess of acid was removed under a vacuum until crystallisation set in on cooling. Nitric acid adducts of diphenyl sulphoxide and triphenylphosphine oxide were prepared by adding, slowly and with cooling, the concentrated acid to a concentrated solution of the base in ethanol. The products were recrystallised from ethanol. The adducts of bases with the hydrohalides were obtained by saturating ethanol solutions of the bases with hydrohalide gas. The *N*-oxide adducts were recrystallised from ethanol. The hydrohalides of triphenylphosphine oxide cannot be recrystallised from ethanol because hemihydrohalides result. This was deduced from the results of the potentiometric titrations which showed equivalent weights close to the 2 : 1 base–acid ratio. The 1 : 1 adducts of triphenylphosphine oxide with hydrohalides are not stable under ordinary conditions; slow loss of hydrogen chloride or bromide occurs and the final result is the hemihydrohalide. The 2 : 1 hydrogen chloride adduct seems to be stable for at least several months. The corresponding hydrogen bromide adduct has not been kept for any long period. Pickard and Kenyon[5] give the m. p. of Ph_3PO,HCl as 183—185°. This seems to be in error. We obtained ~120° for the 1 : 1 adduct and ~70° for the 2 : 1 adduct. Slow decomposition occurs before melting and these values can be obtained only by spreading the substance on an appropriately

TABLE 1.

Equivalent weights of the adducts (potentiometric titrations).

(PyrO = pyridine 1-oxide. PicO = 2-picoline 1-oxide.)

	Calc.	Found		Calc.	Found		Calc.	Found
Ph_3PO,HNO_3	341·3	343·1	$PyrO,CCl_3{\cdot}CO_2H$	259·3	261·2	Ph_3PO,HCl...	314·7	318·1
Ph_2SO,HNO_3	265·3	263·2	PyrO,HCl	132·4	132·8	$(Ph_3PO)_2,HCl$	593·0	589·5
Me_2SO,HNO_3	141·1	139·5	PyrO,HBr	176·8	177·2	Ph_3PO,HBr	359·2	357·7
$Ph_3PO,CCl_3{\cdot}CO_2H$	441·7	438·9	PicO,HCl	149·6	149·4	$(Ph_3PO)_2,HBr$	637·5	641·4
$Ph_3AsO,CCl_3{\cdot}CO_2H$	485·6	482·8	$(PicO)_2,HBr$	299·2	303·7			

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[4] Saytseff, *Annalen*, 1866, **139**, 354.

[5] Pickard and Kenyon, *J.*, 1906, **89**, 262.

preheated stage. With normal heating, only 156° is obtained which is the m. p. of the oxide itself.

The adducts with trichloroacetic acid were prepared by mixing warm saturated solutions of the acid and of the base. The m. p. of $Ph_3PO,CCl_3{\cdot}CO_2H$ was ~80° (decomp.). As described below, there are apparently two crystal modifications of this adduct. One, designated form I, is obtained by crystallising the solution in ethanol. The other, II, develops when a concentrated solution in ethanol is rapidly evaporated on a preheated rock-salt plate. The second form spontaneously reverts to the first rather rapidly and therefore no characterisation other than the infrared spectrum was possible. In contrast to $Ph_3PO,CCl_3{\cdot}CO_2H$ which is stable at room temperature, the adducts of trichloroacetic acid with triphenylarsine oxide and pyridine 1-oxide decompose within a few days, apparently with decarboxylation.

Most of the deuterated analogues were prepared by recrystallisation from D_2O or deuteroethanol. Complexes Ph_3PO,DCl and Ph_3PO,DBr were obtained directly by introducing deuterium chloride or bromide into solutions of the oxide in deuteroethanol.

The spectra were recorded on a Beckman IR-4 spectrophotometer equipped with sodium chloride and cæsium bromide prisms. For the region below 300 cm.$^{-1}$ a grating instrument was used and the samples were supported on Polyethylene plates. The substances were mulled with Nujol and Fluorocarbon, respectively.

SPECTRA

Adducts with Nitric and Trichloroacetic Acid.—The bands due to the acid portion of the adducts are most relevant to proton transfer and are collected in Tables 2 and 3, with the frequencies of the X=O groups. The spectra are reproduced in Figs. 1—3. The assignments of the bands of the acid portion of the nitric acid adducts have been made by analogy with those of Cohn, Ingold, and Poole[6] and are supported by the deuteration shifts. However, the NO_2 symmetrical stretching band shifts to higher frequencies on deuteration of the adduct, which is opposite to the direction observed with HNO_3 and DNO_3 in the vapour phase. Apparently there is a strong coupling between this mode and the NOH bending mode for the adduct, which may be due to some changes in the bonding of the atoms in the acid molecule in consequence to the strong hydrogen bonds. Most of the bands show greater hydrogen-bonding shifts with respect to the frequencies of

TABLE 2.

Some infrared bands of adducts with HNO_3.

Ph_3PO,HNO_3	Ph_3PO,DNO_3	Ph_2SO,HNO_3	Me_2SO,HNO_3	Assignment
1640	1590	1660	1660	NO_2 asym. stretching
1420	1023 (or 1047)	1420	1400	NOH(—D) bending
1260	1300	1300	1300	NO_2 sym. stretching
955	960	940	920 (or 950)	N–OH stretching
788	788	?	800	ONO_2 out-of-plane deformation
652	645	*	*	
350	?	*	*	NOH deformation (?)
1060	1050	1040	1100	P=O or S=O stretching

* Region not investigated.

TABLE 3.

Some infrared bands of adducts with $CCl_3{\cdot}CO_2H$.*

Ph_3PO (I)	Ph_3PO (II)	Pyridine oxide	Ph_3AsO	Assignment
1760	1680	1740	1740	C=O stretching
(1745) *	(1670)	(1715)	(1720)	
1270	1270	1260	1240	C–O stretching
(1312)	(1310)	(1330)	(1330)	
1136	1160	1230(?)	900(?)	P=O, N–O, or As=O stretching

* Values in parentheses are for the deuterated analogues.

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[6] Cohn, Ingold, and Poole, *J.*, 1952, 2552.

the free acid than are observed on going from the vapour to the liquid or even to the solid phase.[7] Unfortunately the OH stretching region, which should include the most interesting bands concerned with hydrogen bonding, shows a rather diffuse absorption with several superimposed minor peaks. The assignment of the band at 350 cm.$^{-1}$ to the NOH out-of-plane deformation is not very satisfactory, this frequency being too low when compared with the value in the free acid.[6] However, no other appropriate band sensitive to deuteration could be found.

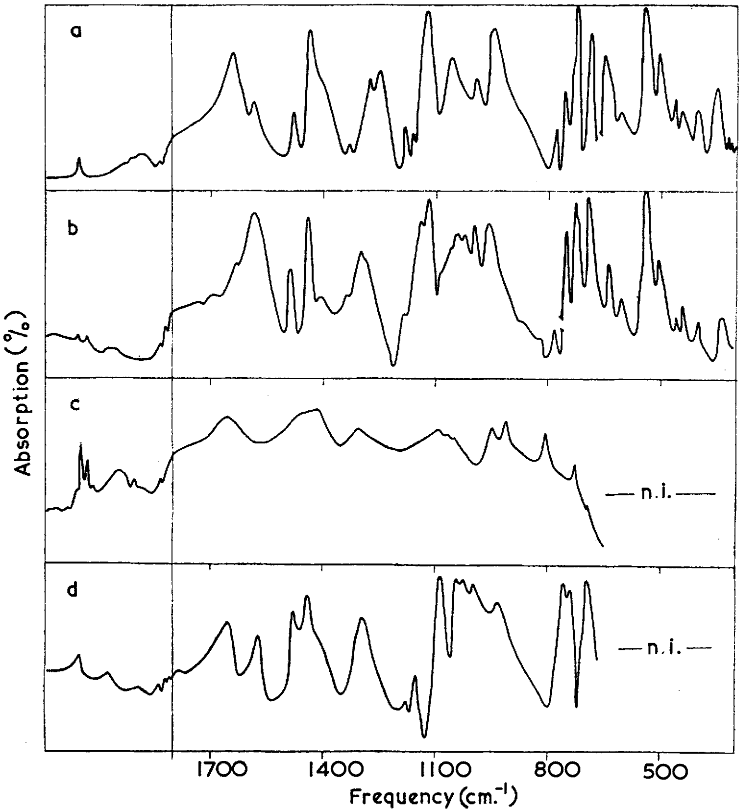

FIG. 1. Infrared spectra of adducts of nitric acid with: (a) triphenyl phosphine oxide; (b) same, but deuterated; (c) dimethyl sulphoxide; (d) diphenyl sulphoxide. n.i. = not investigated.

The P=O stretching band in the adduct has a frequency 135 cm.$^{-1}$ lower than that in triphenylphosphine oxide (1195 cm.$^{-1}$).[8] This exceeds the lowering observed in co-ordination complexes.[9] Surprisingly, the S=O band of Ph_2SO,HNO_3 has approximately the same frequency as in the sulphoxide. With the dimethyl sulphoxide adduct it is even slightly higher.

The fact that the spectra of the adducts with nitric acid contain bands which can be assigned to this molecule is a proof that no proton transfer to the base occurs. If this were the case the bands of the NO_3^- ion at 1381, 815, and 738 cm.$^{-1}$ would appear instead.[10]

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[7] Bethel and Sheppard, *J. Chim. phys.*, 1953, **50**, C72.

[8] Pinchas and Hellman, *J.*, 1958, 3264.

[9] Cotton, Barnes, and Bannister, *J.*, 1960, 2189.

[10] Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1947, p. 178.

The difference in behaviour between the P=O and the S=O band on adduct formation might be taken as evidence that the sulphur atom is the site of bridging. However, this is not sufficient in view of the fact that the N–O stretching frequency of trimethylamine *N*-oxide does not change with the formation of the hydrochloride.[11]

In all adducts with trichloroacetic acid the C=O stretching band is observed, but it is weaker than in the spectra of the dimeric acid. In the spectrum of the triphenylphosphine oxide adduct the C–O stretching band may be readily identified by the shift to higher frequencies on deuteration which is analogous to that for carboxylic dimers.[12] Although less obvious, this band may be detected also in the spectra of the adducts with pyridine oxide and triphenylarsine oxide. The high-frequency region of the spectra of both modifications of $Ph_3PO,CCl_3{\cdot}CO_2H$ contains bands at 1850 and 2250 cm.$^{-1}$, whereas the adducts of pyridine oxide and triphenylarsine oxide show no bands in this region which could be attributed to the O–H stretching vibration. The spectra of these two adducts are characterised by strong absorption which sets in at about 1400 cm.$^{-1}$ and extends to below 600 cm.$^{-1}$. Sharp transmission windows appear near 1200 cm.$^{-1}$ in the spectrum of the pyridine oxide adduct, and near 900 cm.$^{-1}$ with the triphenylarsine oxide adduct, *i.e.*, near the frequencies at which the N–O and As–O stretching bands should appear.

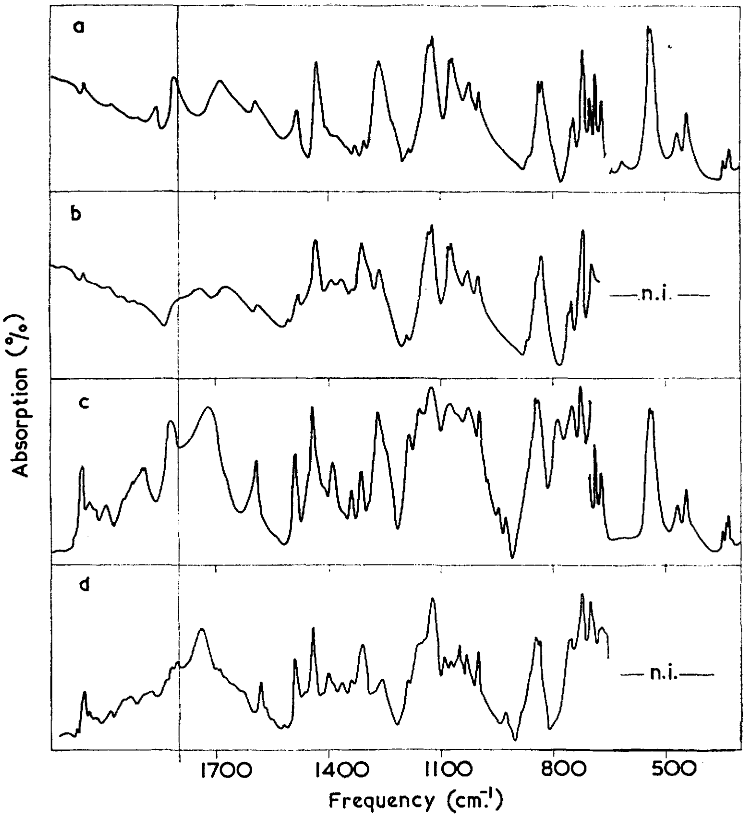

FIG. 2. Infrared spectra of adducts of triphenylphosphine oxide with trichloroacetic acid: (a) Modification I; (b) same, but deuterated; (c) modification II; (d) same, but deuterated.

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[11] Giguère and Chin, *Canad. J. Chem.*, 1961, **39**, 1165.

[12] Hadzi and Sheppard, *Proc. Roy. Soc.*, 1953, *A*, **216**, 247.

Although this broad absorption is modified on deuteration the maximum cannot be located.

The presence of the C=O and C–O stretching bands demonstrates that no proton transfer occurs in these adducts. The bands in the O–H stretching region of the triphenylphosphine oxide adduct are very similar to those observed for liquid mixtures of carboxylic acids and pyridine and for solid pyridinecarboxylic acids.[13,14] Many more examples have been found in other liquid mixtures of carboxylic acids and weak bases and will be described later. This pattern of bands has been attributed to the effects of a double minimum potential for the proton in the respective hydrogen bonds.[13,14] In the spectra of the triphenylphosphine oxide adduct, as well as in other similar spectra mentioned, the OH deformation bands could not be found although a thorough search has been made.

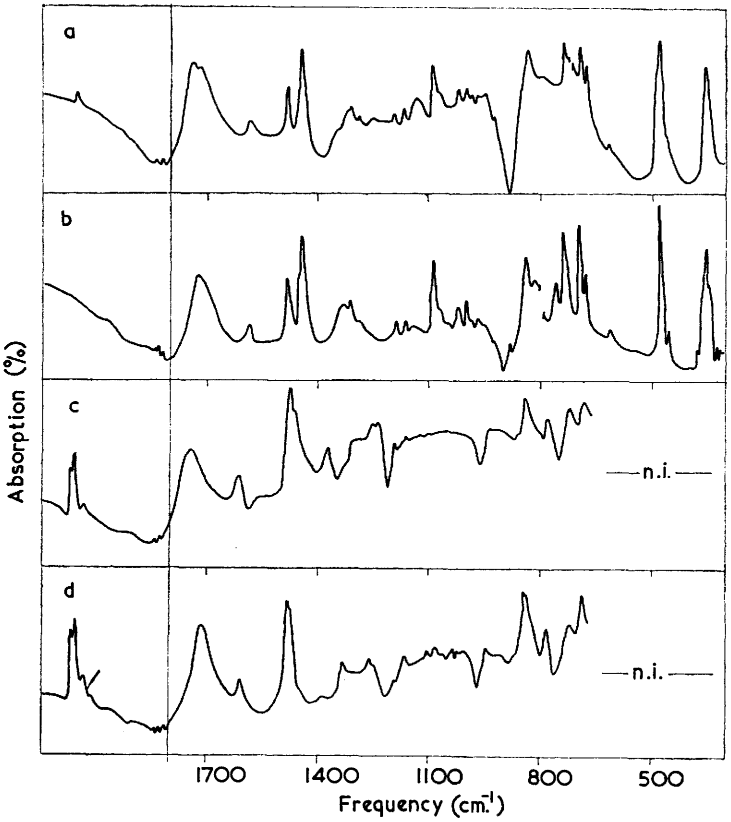

FIG. 3. Infrared spectra of adduct of triphenylarsine oxide with: (a) trichloroacetic acid; (b) same, but deuterated; (c) adduct of pyridine 1-oxide with trichloroacetic acid; (d) same, but deuterated.

The lack of O–H stretching bands in the region above 1700 cm.$^{-1}$ and the broad absorption in the lower frequency region of the spectra of triphenylarsine and pyridine oxide adducts are similar to characteristics observed in the spectra of some acid salts of carboxylic acids which have been shown to contain symmetrical hydrogen bonds.[3] However, in the latter group of compounds the hydrogen bond is formed between identical

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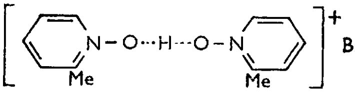
[13] Hadži, *Z. Elektrochem.*, 1958, **62**, 1157.

[14] Hadži, *Vestnik. Slovensk. kem. Društva*, 1958, **5**, 21.

partners, whereas this is not the case with these trichloroacetic acid adducts. It is nevertheless possible that the force field for the proton approaches symmetry in these adducts in spite of the formal differences between the atoms supporting it.

Adducts with Hydrogen Bromide and Chloride.—The spectra of the 1 : 1 adducts of the pyridine oxides [Fig. 4 shows the spectrum of PicO,HCl (PicO = 2-picoline 1-oxide); the other spectra were recently published [15]] have strong bands in the O–H stretching region [PyrO,HCl 2180; PyrO,HBr 2400; PicO,HCl 2100 cm.$^{-1}$ (PyrO = pyridine 1-oxide)], whereas no such band appears in the spectrum of $(PicO)_2$,HBr. There is, however, a broad, strong absorption culminating at about 1350 cm.$^{-1}$ which is strongly reduced upon deuteration. From 1200 cm.$^{-1}$ downward a very broad absorption band sets in which can be followed down to about 290 cm.$^{-1}$. It is interrupted by narrow transmission windows. The strong N–O stretching bands of the pyridine oxides at 1293 (PyrO) and 1260 cm.$^{-1}$ (PicO) do not appear in the spectra of the adducts. A very weak band remains near these frequencies and there are new bands in the region 1180—1200 cm.$^{-1}$. It is reasonable to expect the N–O band in the adducts to have a lower frequency than in the base itself, and therefore the 1180—1200 frequencies are assigned to the N–O stretching mode in the adducts. In the case of $(PicO)_2$,HBr this band can be detected at 1240 cm.$^{-1}$ only after deuteration.

Besides the bands in the O–H stretching region, several in the lower-frequency regions of the spectra of PyrO,HCl, PyrO,HBr, and PicO,HCl move on deuteration. These shifts are small and suggest that the vibrations of the exchanged hydrogen atom couple with the motions of the pyridine ring and its hydrogen atoms. This is to be expected in the case of proton transfer to the base. Other evidence for this is the higher O–H stretching frequency for PyrO,HBr than for PyrO,HCl. If there were a hydrogen bond NO • • • HX, the bromide should have the lower frequency because of the larger mass of the bromine.



(A)

The sequence of frequencies I < Br < Cl has been observed also with the pyridine hydrohalides.[16] Consequently, these adducts should be written $PyrOH^+Cl^-$, etc. The adduct $(PicO)_2$,HBr evidently has a different structure. Its spectral features, mentioned above, are similar to those exhibited by substances with symmetrical hydrogen bonds.[2,3] In particular, di(acetamide) monohydrochloride has a related type of spectrum,[17] and it has been shown to contain a symmetrical hydrogen bond between the two amide-oxygen atoms.[18] In view of all this the structure (A) is proposed for $(PicO)_2$,HBr. It is interesting that the spectrum of a chloroform solution of this adduct is essentially different. The broad absorptions do not appear there, but a strong band near 2400 cm.$^{-1}$ is present. Such a difference between the solid and the solution has been noticed in another case of symmetrical hydrogen bonding.[19]

The spectra of most of the adducts of triphenylphosphine oxide with hydrogen chloride and bromide show diffuse absorption in the high-frequency region, with some ill-defined maxima (Figs. 5 and 6, and Table 4). The spectrum of the adduct Ph_3PO,HBr contains, however, a very strong, broad band near 1780 cm.$^{-1}$ which shifts on deuteration to lower frequencies. This adduct gives also a similar band near 1480 cm.$^{-1}$, shifting to 1060 cm.$^{-1}$ on deuteration. No analogous band appears with the other adducts. The original P=O stretching band of this oxide is replaced in the spectra of the adducts by a lower-frequency band which is in some cases represented only as a shoulder on the strong aromatic band

[15] Tsoucaris, *J. Chim. phys.*, 1961, **58**, 619.
[16] Hadži, unpublished work.
[17] Albert and Badger, *J. Chem. Phys.*, 1958, **29**, 1193.
[18] Takei, Ph.D. Thesis, California Inst. Technology, 1957.
[19] Hadži and Novak, *Proc. Chem. Soc.*, 1960 240.

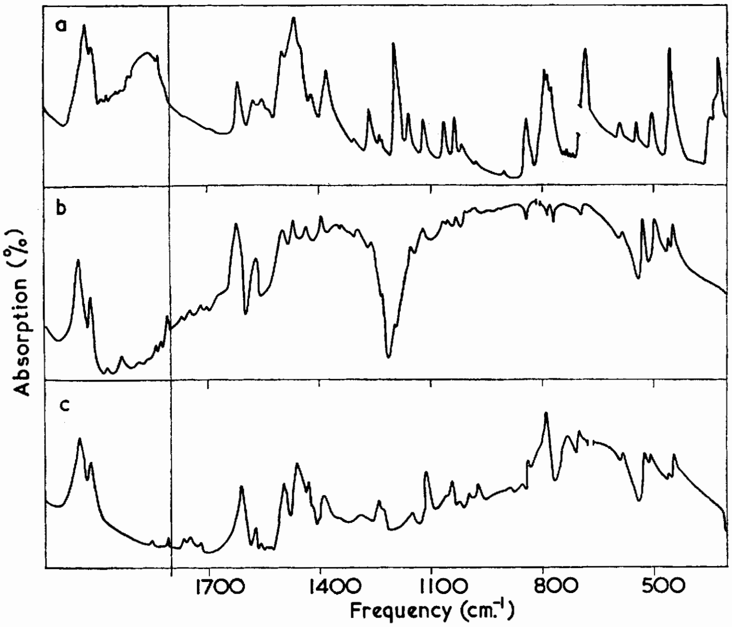


FIG. 4. Infrared spectra of adducts of 2-picoline 1-oxide with: (a) hydrogen chloride; (b) hydrogen bromide; (c) deuterium bromide.

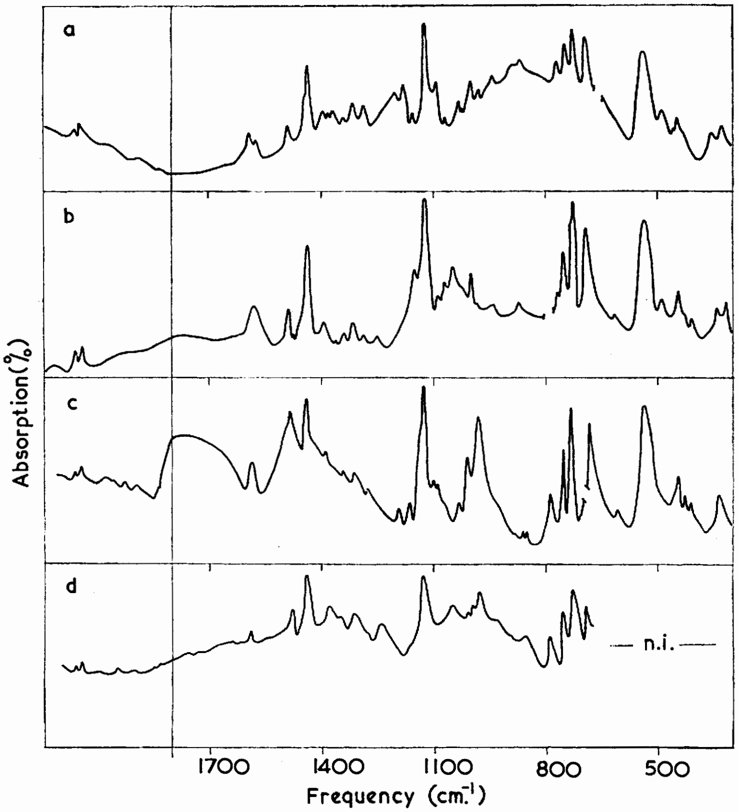


FIG. 5. Infrared spectra of 1 : 1 adducts of triphenylphosphine oxide with: (a) hydrogen chloride; (b) deuterium chloride; (c) hydrogen bromide; (d) deuterium bromide.

near 1120 cm.$^{-1}$. New or enhanced bands appear on adduct formation also between 1050 and 1100 cm.$^{-1}$, but their origin is not clear. The spectrum of the compound Ph_3PO,HBr differs from the others in showing a strong band at 982 cm.$^{-1}$ which is assigned to a strongly modified P=O group. All the adducts have a band between 300 and 350 cm.$^{-1}$ which replaces that at 290 cm.$^{-1}$ in the spectrum of the oxide.

The deuteration-sensitive band near 1480 cm.$^{-1}$ in the spectrum of Ph_3O,HBr is very likely due to an OH deformation mode and its existence suggests proton transfer. This is in agreement with the very low P–O stretching frequency. The band at 1780 cm.$^{-1}$ is consequently attributed to a PO–H stretching vibration, and the extremely low frequency to strong hydrogen bonding. In view of the differences between the spectrum of this adduct and the other hydrohalide adducts of triphenylphosphine oxide it is believed that in the latter no proton transfer occurs. However, the type of hydrogen bonding cannot yet be discussed further because of the complicated situation in the high-frequency

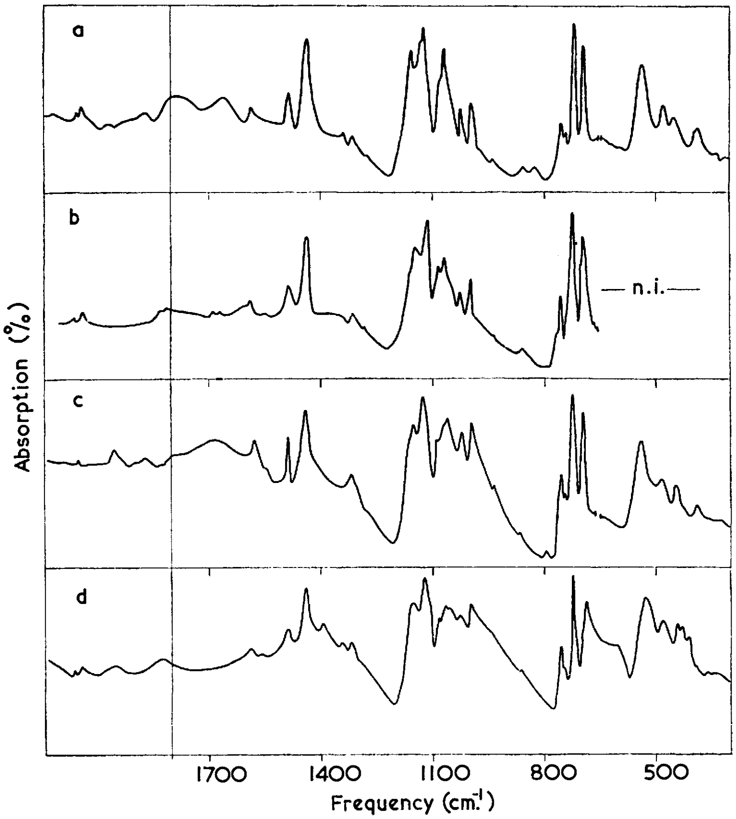


FIG. 6. Infrared spectra of 2 : 1 adducts of triphenylphosphine oxide with: (a) hydrogen chloride; (b) deuterium chloride; (c) hydrogen bromide; (d) deuterium bromide.

TABLE 4.

Infrared bands associated with the N–O (or P=O) stretching of the adducts with hydrohalides.

PyrO,HCl	PyrO,HBr	PicO,HCl	$(PicO)_2$,DBr	Ph_3PO,HCl	$(Ph_3PO)_2$,HCl	Ph_3PO,HBr	$(Ph_3PO)_2$,HBr
1200	1180	1198	1240	1180, 1200	1160, 1073	982	1158, 1060

region of the spectrum and the lack of correlation between the bands of the proton- and deuterium-containing adducts. The possibility should be stressed that the P=O group adds an HX molecule. In that case we should expect a phosphorus–halogen stretching band somewhere below 500 cm.$^{-1}$. There is no appropriate band in the spectra of the adducts except that mentioned between 300 and 350 cm.$^{-1}$. However, this band appears also in the spectrum of Ph_3PO,H_2O which was recorded for comparison and, moreover, its frequency does not depend upon the mass of the halogen. Therefore it cannot represent the phosphorus–halogen stretching and assignment to a C–P–O angle deformation is proposed.

Far-infrared Bands.—In the spectra of $PyrOH^+Cl^-$, $PyrOH^+Br^-$, and $PicOH^+Cl^-$ strong and rather broad bands at 214, 180, and 241 cm.$^{-1}$, respectively, were detected. They do not appear for the bases, and shift only by a few wavenumbers on deuteration. In view of this and the fact that the frequency of the band in the bromide is lower than in the chloride of pyridine oxide, it is reasonable to assign them to the stretching vibration of the heavy partners in the hydrogen bond. We have calculated the force constants according to a simple linear model consisting of three masses only and by using the observed stretching frequencies.[20] For $PyrOH^+Cl^-$ the values $k_1 = 1{\cdot}3$ and $k_2 = 1{\cdot}5$, whereas for $PyrOH^+Br^-$ $k_1 = 1{\cdot}47$ and $k_2 = 2{\cdot}28$ were obtained. Here, k_1 is the force constant for the in-phase vibration and k_2 for the out-of-phase (=O–H stretching) vibration. The $PicOH^+Cl^-$ frequencies yielded complex values. The model used is a very rough approximation since the frequencies observed are not those of free molecules, but nevertheless the close approach of the k_1 and k_2 values appears significant in reflecting the strength of hydrogen bonding.

Conclusions.—The proton transfer should take place when the vacant proton level of the base is below the occupied level of the acid. A symmetrical hydrogen bond may be formed when the proton levels of both partners are equal. With small differences in the levels hydrogen bonds of asymmetrical double minimum type may be formed. Since absolute acidities and basicities are not known, we may use those against water as a rough scale. The dissociation constants of the acids in water are well known, but unfortunately this is not the case for our bases except for pyridine oxide, whose pK_a is 0·79.[21] However, relying on some incomplete data of Nylèn [22] we may expect that the basicities decrease in the order $Ph_3AsO > PyrO > Ph_3PO > Me_2SO > Ph_2SO$, the basicities of the last three being less than that of water. On the other hand, it is known that in the solid hydrates of nitric acid, hydrogen chloride, and hydrogen bromide the proton is transferred to the water molecule.[8,23] Therefore, it is not surprising to find the proton transferred from the hydrohalides to pyridine oxide, but not from nitric acid and the hydrohalogen acid to triphenylphosphine oxide and the sulphoxides. However, the level of hydrogen bromide, which is a stronger acid than the chloride or nitric acid,[24] may be slightly above the vacant level of triphenylphosphine oxide and hence the transfer may be possible here. The case of 2-picoline oxide and hydrogen bromide is especially interesting because there is apparently a proton transfer in solution (chloroform), but in the solid there is formed only an extremely strong and possibly symmetrical hydrogen bond. This demonstrates again [2] the importance of the crystalline forces in shaping the potential for the protons in the hydrogen bonds. Our stronger bases form with the weaker acid (trichloroacetic) extremely strong hydrogen bonds which appear to be close to the symmetrical one. Between the weaker base, triphenylphosphine oxide, and trichloroacetic acid, a weaker hydrogen bond is formed. It is probably of the double-minimum type, as will be discussed in more detail later.

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[20] Herzberg, ref. 10, p. 173.

[21] Jaffé and Doak, *J. Amer. Chem. Soc.*, 1955, **77**, 4441.

[22] Nylèn, *Z. anorg. Chem.*, 1941, **246**, 227.

[23] Ferriso and Hornig, *J. Chem. Phys.*, 1955, **23**, 1464.

[24] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

Finally, the behaviour of the X=O bands on adduct formation should be reviewed. We must restrict this to the P=O and S=O frequencies because the others are not readily identifiable. We should expect these frequencies to assume lower values on hydrogen bonding. In fact, in most of our examples the P=O band, which is at 1195 cm.$^{-1}$ in the spectrum of triphenylphosphine oxide, is replaced by lower-frequency bands. The extreme shift of more than 200 cm.$^{-1}$ appears with Ph_3PO,HBr. A notable exception is Ph_3PO,HCl where there is little or no shift although the hydrogen bond formed appears to be very strong. Also, no shift to lower frequencies is found with the solid sulphoxide adducts. With most of the triphenylphosphine oxide adducts we observe two new bands replacing the original P=O band: between 1100 and 1180, and between 1050 and 1080 cm.$^{-1}$. Without a more detailed knowledge of the structure of these adducts it is not possible to explain the appearance of two P=O bands.

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