THERMODYNAMIC PROPERTIES OF PHOSPHORUS - CONTAINING MOLECULES

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'To my Mother'

ABSTRACT

Syntheses, properties and reactions of some phosphorus compounds have been reviewed briefly.

The thermochemistry and infrared spectra of phosphoryl halide - boron halide complexes have been reported. The phosphoryl chloride - boron trichloride complex has been studied by a vapour tensimetric method and the derived thermodynamic data compared with that obtained directly by calorimetry.

The thermochemistry of phosphorus trihalide - boron trihalide complexes has been reported and the nature of donor acceptor bond is discussed.

The standard enthalpy of formation of diphosphorus tetraiodide has been determined followed by the estimation of P - P bond strength. A new value for the standard enthalpy of formation of phosphorous acid has been reported The phosphorus (V) chloride - boron trichloride complex has been studied both thermochemically and vapour tensimetrically.

The standard heats of hydrolysis of phenyl phosphorus dihalides and diphenyl phosphorus halides have been measured. The heat of solution of phenyl phosphonous acid has been determined. Infrared spectra of halo phosphines including the far infrared spectra of phenyl phosphorus dibromide and dipheynl phosphorus bromide have been recorded. The

existence of phenyl phosphorus mixed halide has been investigated by ^{31}P magnetic resonance.

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CONTENTS

Page

Chapter 1

Chapter 11

Chapter 111

Chapter IV

INTRODUCTION

A brief summary of some aspects of organophosphorus chemistry nomenclature used in this thesis is given below.

The current position regarding the nomenclature of such compounds is confusing. The compound $R_2PO(OH)$ is called dialkyl phosphinic acid in Chemical Abstracts, dialkyl phosphonic acid in Kosolapoff's book, and dialkyl phosphinous acid in Beilstein. The Chemical Society and American Chemical Society ultimately came to an agreement for naming these compounds and in this thesis their system will be used:-

(i) Phosphonic : $HPO(OH)_2$
(ii) Phosphinic : $H_2PO(OH)$
(iii) Phosphonous : $HP(OH)_2$
(iv) Phosphinous : H_2POH

The replacement of the hydrogen atom which is connected directly with the phosphorus atom by alkyl or aryl radical produces the corresponding organophosphorus acid.

Phosphorus is well known to react with halogens to form phosphorus halides. The best known of the phosphorus halides are the trihalides and the pentahalides. All of the halogens, except iodine form pentahalides. In addition, iodine, fluorine and possibly chlorine form compounds of the formula P_2X_4 (where X = halogen) and there are some polyhalides in which there aremore than five halogen atoms per phosphorus atom. Investigations of band spectra at high temperatures indicate that phosphorus forms diatomic molecules with the halogens. The molecules PCl, PBr, and PI have been reported. All of these are unstable under normal conditions.

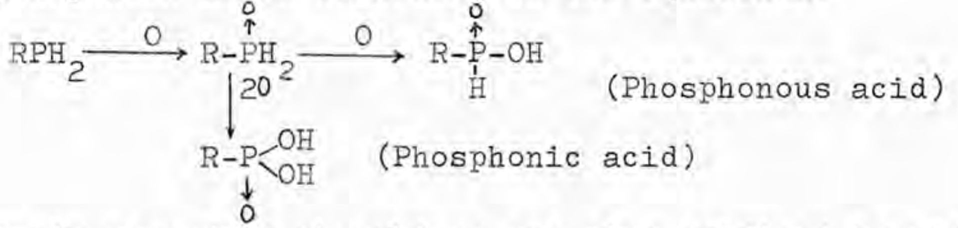
Trihalides[1-2] and diphosphorus tetrahalides[3] are usually made by the direct union of their elements. The pentahalides[4] are usually made by reacting trihalides with the appropriate halogen according to the equation : $PX_3 + X_2 \longrightarrow PX_5$. The phosphoryl halides[5] are made by the action of phosphorus pentahalide and phosphorus pentoxide according to the equation : $P_4O_{10} + 6PX_5 \longrightarrow 10POX_3$.

There are three simple organic derivatives of phosphorus trihalides : RPX_2, R_2PX and R_3P (R = alkyl or aryl radical). Phenyl phosphorus dichloride was first synthesised[6] by the action of benzene and phosphorus trichloride and also by the action of diphenyl mercury[7] and phosphorus trichloride. Phenyl phosphorus dibromide was synthesised by the bromination of ether phosphobenzene[8] or phenyl phosphine[9]. It was also synthesised by the reaction of bromobenzene[10] and yellow phosphorus in a sealed tube for 4 hours at 350°C. Recently it has also been made by the action of phenyl phosphorus dichloride and phosphorus tribromide followed by heating and distillation. The monochloro compound was synthesised by heating diphenyl[12] or dimethyl mercury with phenyl phosphorus dichloride. Diphenyl phosphorus bromide[11] was synthesised by heating diphenyl phosphorus chloride with phosphorus tribromide. Tervalent phosphorus is sensitive to oxygen and phosphorus -halogen bonds (except P-F) hydrolyse in water to give oxyacids of phosphorus.

On reduction with lithium aluminium hydride, RPX_2 and R_2PX produce primary and secondary phosphins respectively.

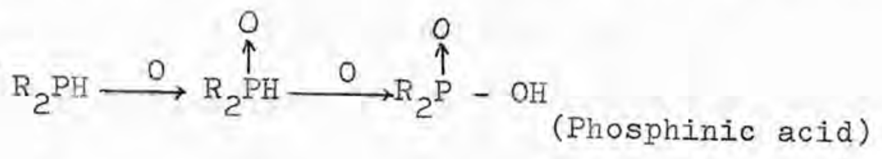
$$2RPX_2 + LiAlH_4 \longrightarrow 2RPH_2 + LiAlX_4$$
$$4R_2PX + LiAlH_4 \longrightarrow 4R_2PH + LiAlX_4$$

The primary phosphines are oxidised easily in the air to give primary phosphine oxides which subsequently on further oxidation produce a mixture of phosphonous and phosphonic acids according to the equations:



$$RPH_2 \xrightarrow{O} R\text{-}\overset{O}{\overset{\uparrow}{P}}H_2 \xrightarrow{O} R\text{-}\overset{O}{\overset{\uparrow}{P}}\text{-}OH \qquad \text{(Phosphonous acid)}$$
$$R\text{-}PH_2 \xrightarrow{2O} R\text{-}\underset{O}{\underset{\downarrow}{P}}{<}^{OH}_{OH} \qquad \text{(Phosphonic acid)}$$

Similarly secondary phosphines are also oxidised by air. Unlike primary phosphines only one compound, namely phosphinic acid, is formed and the stages may be written as:



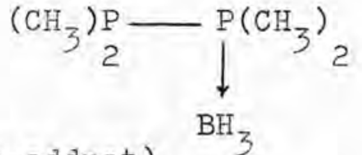
$$R_2PH \xrightarrow{O} R_2\overset{O}{\overset{\uparrow}{P}}H \xrightarrow{O} R_2\overset{O}{\overset{\uparrow}{P}} - OH \qquad \text{(Phosphinic acid)}$$

The primary and secondary phosphines on condensation with the corresponding halo substituted derviatives produce organophosphorus compounds, containing P-P bonds.

$$2RPCl_2 + 2RPH_2 \longrightarrow (RP)_4 + 4HCl$$

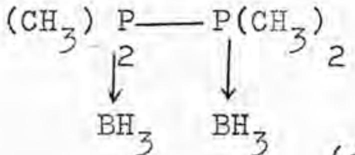
$$R_2PCl + R_2PH \longrightarrow R_2P - PR_2 + 2HCl$$

The former is known as a cyclotetraphosphine and the latter is known as a biphosphine. The ultraviolet, infrared as well as X-ray powder patterns of cyclotetra phenyl phosphine have been published. Both the phosphorus atoms in the biphosphine[13-14] have an unshaired pair of electrons and are thus able to give two different types of adducts with Lewis acids, namely the mono-adduct and the di-adduct. Both types have been isolated with tetra methyl biphosphine as the Lewis base and borane as the acid.



$$(CH_3)_2P - P(CH_3)_2 \rightarrow BH_3$$

(mono-adduct)



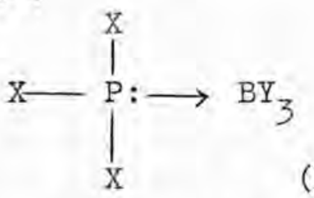
$$BH_3 \leftarrow (CH_3)_2P - P(CH_3)_2 \rightarrow BH_3$$

(di-adduct)

Similarly phosphine also forms addition compounds with boron trifluoride at low temperature to give a product $H_3P \cdot BF_3$ [15]. Boron trichloride and boron tribromide also form 1:1 adduct with phosphine. Diborane[16] readily reacts with phosphine to give an addition compound having the formula $B_2H_6\ 2PH_3$ or perhaps $H_3B\ PH_3$. When this product is dissolved in liquid ammonia a white solid results with the approximate composition $B_2H_6\ PH_3\ NH_3$ which might be a double compound of the mixture of $H_3B\cdot PH_3$ and $H_3B\ NH_3$. Phosphine also forms complexes with anhydrous aluminium halides[17]. The compounds are similar to the compounds of phosphine and boron halides. In other words, probably phosphorus donates a pair of its electrons to the aluminium so that both the phosphorus and the aluminium are present as sp^3 hybrids.

Compounds of Phosphorus Trihalides with Lewis Acids

Various aspects of the chemistry of the phosphorus trihalides such as Lewis basicity, structures and some metathetical reactions have been examined. They form an extensive series of co-ordination compounds with Lewis acids, especially boron halides where the usual explanation for the stability of the addition compounds is also based on the donation of unshaired pair of electrons from the phosphorus to other elements involved in the adduct :



$$X - \underset{\substack{|\\X}}{\overset{\substack{X\\|}}{P}}: \longrightarrow BY_3$$

(X and Y are halogen atoms)

The donor behaviour of the phosphorus atom depends [18] upon the electronegativity of the halogen substituents. Thus PCl_3[19] and PBr_3[19] form 1:1 addition compounds with

BBr_3 while PF_3 appears to have no donor property. Cross halogenation (exchange of halogen atoms between phosphorus and boron atoms) occurs in PCl_3 adducts with BBr_3 and BI_3 resulting in the formation of volatile boron trichloride, although both $I_3B\ PBr_3$[20] and $BBr_3\ PI_3$[21] are stable towards heat and their compositions remain unaltered even after heating at 100°. In an infrared study, Cowley and Cohen[22] were also unable to detect cross halogenation in $BBr_3\ PI_3$. The crystalline individuality of the adducts has been established by determining their X-ray patterns.

Compounds of Phosphorus Pentahalides with Lewis Acids

With Lewis bases (L:) reacting with Lewis acids (MX_5) the obvious product is that in which a co-ordinate bond is formed between L: and M by the donation of the lone pair of electrons into the vacant orbital of M and therefore, M increases its co-ordination number from 5 to 6 (i.e. trigonal bipyramidal going to octahedral co-ordination). Thus $PCl_5\ BCl_3$ complex is an example of this class. This has been established by X-ray analysis.[23] There is also another series of addition compounds in which the metal atom probably exhibits octahedral configuration corresponding to d^2sp^3 hybridization in the anion. This group of compounds includes $3PX_5\ MX_3$(M= Bi, Sb and As).

Phosphorus pentachloride is also capable of forming complexes with other metal halides which themselves are potential Lewis acids. The compound PCl_5 $AlCl_3$[23] is an example of this class and has been formulated as PCl_4^+ $AlCl_4^-$ both in the solid state or in solution in nitrobenzene. Transference number studies show that the amount of phosphorus increases in the catholyte and decreases in the anolyte with the aluminium varying inversely. This means that phosphorus is in the cation and aluminium in the anion so that the ionic formulation of the addition compound is probably PCl_4^+ $AlCl_4^-$. Similar studies indicate that PCl_5 $FeCl_3$ addition compound has an ionic structure PCl_4^+ $FeCl_4^-$. The addition compounds of the type PX_5 MX_3 (M= Bi, Cr, Tl) appear to be similar to aluminium trichloride and iron trichloride adducts with phosphorus pentahalide. Probably for all these compounds phosphorus is present as PX_4^+ cation and the metal in the anion exhibiting tetrahedral co-ordination corresponding to sp^3 hybridization.

Compounds of Phosphoryl Halides with Lewis Acids

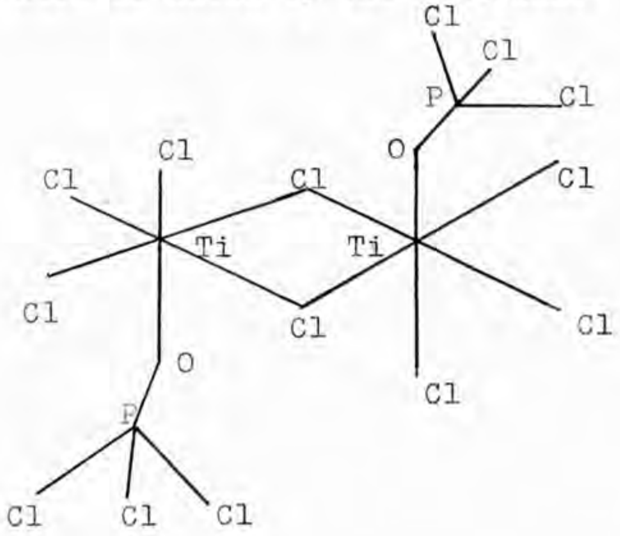
When phosphoryl halide is the donor, the addition may take place either by halogen atom or oxygen atom acting as an electron donor. Considerations of the available experimental data do not clearly indicate whether it is the oxygen or the halogen atom donating electrons, or whether in some cases, it is the one and in other cases, the other. A number of addition compounds[24-30] of phosphoryl halide with metal halides have been discovered. The adducts are $POCl_3$ $AlCl_3$, $POCl_3$ $AlBr_3$, $POCl_3$ $SbCl_3$ and $POCl_3$ MX_4 (M= Ti, Sn, Te). A phase diagram study[31] shows that 1:1 compound is formed between BF_3 and POF_3. Both $POCl_3$ and $POBr_3$ form addition compounds with BCl_3 and BBr_3. There are two possible structures for these compounds, they can be either POX_2^+ BX_4^- or $X_3PO \rightarrow BX_3$. It has been postulated[27] previously that the phosphoryl chloride - boron chloride complex is ionic species. This argument is based on changes in P-Cl and P-O frequencis and there being no B-O frequency in the spectrum. The infrared spectra of $POCl_3$ BCl_3 and $POCl_3$ BF_3 complexes have been recorded by Waddington and Klanberg[29].

They found no B-Cl stretching frequency in the spectrum of $POCl_3$ BF_3 and so no BF_3Cl^- anion can be present. Furthermore, a peak assigned to B-O stretching mode is found too close to that in the diethylether-boron trifluoride complex. The presence of a frequency at $1190cm^{-1}$ which could not occur in $POCl_2^+$ BCl_4^- is a strong evidence in favour of $Cl_3PO \rightarrow BCl_3$. They found that P-O frequencies are hardly shifted at all from that of unco-ordinated phosphoryl chloride. This was in marked contrast to the behaviour of phosphoryl chloride adducts with stannic chloride and titanic chloride prepared by Sheldon and Tyree[32] who found the frequency was lowered as much as $75cm^{-1}$. The infrared spectra of some other compounds like $Ph_2POCl\ BCl_3$ and $Ph_3PO\ BCl_3$ have been examined by Peach and Waddington[33]. They suggested that the structures are all oxygen co-ordinated and not ionic. There was only a slight change in P-Cl frequencies in the adduct. If there was a change in hybridization, a greater change infrequency would be expected as indicated by the following table :

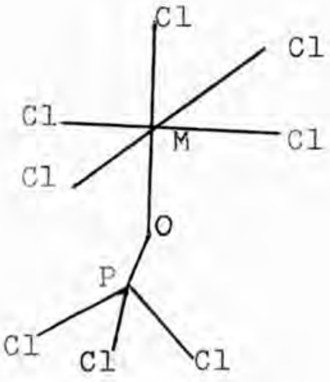
Compound	Frequency[33] (cm^{-1})
PCl_4^+ (sp^3)	584, 650
PCl_5 g(sp^3d)	465, 592
PCl_6^- (d^2sp^3)	447

The frequencies associated with B-Cl bonds in all these complexes were higher than those found for tetrachloro borates (660 and 700 cm^{-1}) and were within broad ranges found for boron trichloride adducts[34] (690 -813cm^{-1}) The infrared and Raman spectra of some phosphoryl halide-metal halide complexes have been studied in their solid state, by Goubeau et al.[30] The addition occurs through the oxygen atom of the phosphoryl halides and the interaction between the halide and phosphoryl chloride decreases with increasing atomic weight.

X-ray determinations[35-38] have been carried out on some molecules such as $POCl_3$ MCl_5 (M=Sb, Nb, and Ta). The compounds were found to be of similar types. The crystal structure of phosphoryl chloride - titanium chloride adduct has been investigated from X-ray crystallography. The structure is built up of dimeric molecules with the double chlorine bridges between the two titanium atoms of the dimer, $(POCl_3\ TiCl_4)_2$. The co-ordination around titanium atom is octahedral. The oxygen atom in phosphoryl chloride functions as donor atom as shown by the diagrams:



$(POCl_3\ TiCl_4)_2$ adduct

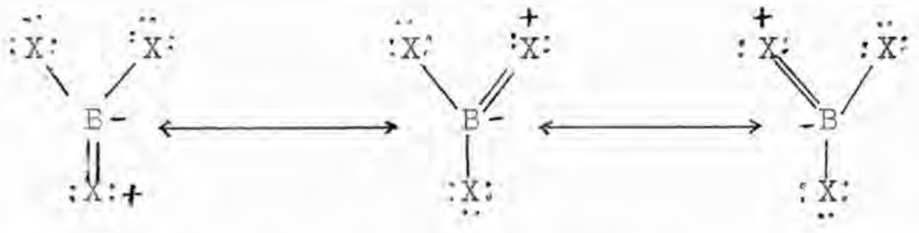


$POCl_3$ MCl_5
(M= Nb, Sb)

Similarly, $PO(CH_3)_3SbCl_5$ is a molecular solid where the structure is also oxygen co-ordinated.

Boron Halides as Lewis Acids

For many years it was thought that BF_3 was a stronger Lewis acid than BCl_3. Such an assumption may be rationalized on (i) electronegativity grounds, fluorine being the most electronegative halogen and its electron withdrawing tendancy making the B atom electrophilic and (ii) steric grounds, BF_3 molecule being smallest in the boron trihalide series. Also very many more complexes of BF_3 were known than the other trihalides mainly due to its extensive use as a catalyst.[39] However, it was shown by Brown and Holmes[40] calorimetrically that the order of Lewis acidity is $BBr_3 > BCl_3$. Cook,[41] using a spectroscopic method, has extended this order to include boron iodide and shown this order is consistent with that of Holmes and established further as $BI_3 > BBr_3 > BCl_3$. This has also been checked by Cowley and Cohen[22] and also by Stone[42]. The electronegativities of halogens decrease with increasing atomic weight. On the basis of the inductive effect, the strongest acid would have been expected to be boron trifluoride followed by chloride and bromide in order. The order $BI_3 > BBr_3 > BCl_3 > BF_3$ was explained by Holmes in terms of resonance stabilization. The marked shortening of boron-fluorine bond distances observed in boron fluoride led Pauling[43] to suggest that the structures of the following types must contribute strongly to boron trifluoride:



The ability to form double bonds appear to decrease sharply in the heavier elements. Resonance of this type should be of less importance in the case of chloride and still smaller importance in the bromide. Therefore, resonance interactions are sufficiently greater so as to reverse the trend expected from relative inductive effect of different groups. This has been supported by Cotton and Leto's calculation[54].

Thermochemistry of some Phosphorus Compounds

The thermochemistry of several phosphorus compounds has been the subject of several investigations and has yielded information on the strengths of chemical bonds. The thermochemistry of inorganic phosphorus halides has been reported in the earlier literature[44]. Recently the thermochemistry of some phosphorus halides has been studied by Finch et. al.[45] In cases of phosphorus tri-iodide and phosphorus pentabromide, new values for the standard enthalpies of formation have been suggested. Neale et. al.[46] have measured the heats of hydrolysis of phosphorus trichloride and oxychloride. The latter results have been checked by Skinner et.al.[47] The heats of hydrolysis of liquid PCl_3, PBr_3, $POCl_3$ and crystalline $POBr_3$ have been measured, from which the respective heats of formation have been derived. These workers have also calculated the mean bond dissociation energies of $\bar{D}$ (P-Cl) and $\bar{D}$ (P-Br) and P-O bond dissociation energies in the oxyhalides.

The heats of reaction of the trihalides, pentahalides and oxyhalides were determined by hydrolyzing the halides in the reaction calorimeter. The heats of the reaction were then equated to the difference between the heats of formation of the products of the reaction and the sum of the heats of formation of the reactants:

$$\Delta H = \sum \Delta H^{\circ}_{f} \text{ (products)} - \sum \Delta H^{\circ}_{f} \text{ (reactants)}$$

Knowing all but one of the heats of formation, the unknown heats of formation of the phosphorus halides were determined in their standard states.

Gas dissociation energies[48] of several phosphorus compounds have been determined which may be represented by the equation :

$$APR_3 \longrightarrow A + PR_3$$

The results of D(P = O) of phosphoryl compounds are shown in the following table :

Compound	D(P=O) K.Cal.mole^{-1}
POF_3	129.8
$POCl_3$	127.5
$POBr_3$	124.9

Here in the cases of phosphoryl halides; fluroide, chloride and bromide, D(P=O) decreases from 129.8 through 127.5 to 125 K.Cal. which shows that with the decrease of electronegativity from 3.9 (F), through 3.0 (Cl) to 2.8 (Br), D(P=O) decreases. But in compounds containing P=S linkages, D(P=S) is almost independent of the particular halogen group. This is possibly because the electronegativity difference between phosphorus (2.1) and sulphur (2.5) is very much smaller than between phosphorus (2.1) and oxygen (3.5), leading to a very little $\overset{-}{S} - \overset{+}{P}$ dipole and a lesser tendency to back co-ordination to the phosphorus from the halogen atoms. The thermochemistry of some other phosphorus compounds such as oxides of phosphorus, phosphorus acid, metal phosphides, phosphonium compounds, covalent inorganic hydrides and sulphides have been reviewed by Hartley et.al.[49]

The thermochemistry of some organo phosphorus compounds has also been studied in a combustion calorimeter[50]. The compounds studied have been triethyl phosphate, triphenyl phosphine and triphenyl phosphine oxide.

The compounds were oxidised in excess of oxygen to give phosphoric acid, carbon dioxide and water. The combustions refer to the reactions :

$$PPh_3(C) + 23O_2(g) \longrightarrow H_3PO_4(C) + 18CO_2(g) + 6H_2O(liq)$$

$$OPPh_3(C) + 22.5O_2(g) \longrightarrow H_3PO_4(C) + 18CO_2(g) + 6H_2O(liq)$$

$$OP(OEt)_2(liq) + 9O_2(g) \longrightarrow H_3PO_4(C) + 6CO_2(g) + 6H_2O(liq)$$

The mean bond dissociation energy of the molecule PPh_3 in the gas phase, $PPh_3(g) \longrightarrow P(g) + 3Ph(g)$, is given by the thermochemical equation,

$$3\bar{D}(P\text{-}Ph) = \Delta H_f^o(P,g) + 3\Delta H_f^o(Ph,g) - \Delta H_f^o(PPh_3,g)$$

Similarly, the heat of dissociation of the molecule $OPPh_3$ in the gas phase $OPPh_3(g) \longrightarrow O(g) + PPh_3(g)$, is given by the thermochemical equation ,

$$D(O = PPh_3) = \Delta H_f^o(PPh_3,g) + \Delta H_f^o(O,g) - \Delta H_f^o(OPPh_3,g)$$

Finally the mean bond dissociation energy $\bar{D}(P\text{-}Ph)$ and the bond dissociation energy $D(O{=}PPh_3)$ were derived.

The main products of the combustion[55] of trimethyl phosphine in oxygen are also phosphoric acid, carbon dioxide and water. The reaction refers to the equation.

$$P(CH_3)_3(l) + 6\tfrac{1}{2}O_2 \longrightarrow H_3PO_4(C) + 3H_2O(l) + 3CO_2(g)$$

The heat of formation of trimethyl phosphine has been determined from which the energy of dissociation of the carbon - phosphorus bond has been calculated by Long et. al.[55]

Scope of The Present Investigation

It was intended to investigate the thermochemistry of some donor- acceptor complexes, namely phosphorus (lll or V) halide - boron halide and phosphoryl halide - boron halide types. The purpose was to determine the heats of formation of the compounds which might be useful in estimating and discussing donor - acceptor bond strengths. The infrared spectra of phosphoryl halide - boron halide complexes were determined in non-polar solvents to see if there is a change of structures on going into solution. Similarly, compounds containing mixed halogen atoms were studied cryoscopically to see if there is any dissociation of complexes in benzene solution.

The values of enthalpies of solution of phosphorus tetraiodide in CS_2 has been found to be endothermic[45] where as the result reported in the earlier literature was exothermic. The latter value was in error possibly because of the reaction of phosphorus tetra iodide with oxygen or sulphur. It has been proved by Finch et. al.[45] that in the absence of precautions to remove oxygen, dissolution was also exothermic due to the formation of a polymer with oxygen. Therefore, the heat of formation of phosphorus tetraiodide determined previously is also open to some suspicion (determined from the same source by the same synthetic procedure). Therefore, by using a new degradative method, the value of $\Delta H^{o}_{f}P_2I_4(C)$ has been redetermined.

Considerable interest attaches to phenyl phosphorus halides which are precursors in the syntheses of a large number of phenyl phosphorus compounds. Reorganization of halogen atoms[51-53] between phosphorus halides, phosphoryl halides and thiophosphoryl halides is well known and such scrambling reactions have received considerable attention. In the case of dihalophosphine only one compound can be formed and the system is very suitable as a model for which kinetic and energetic data can be obtained quite easily. It was, therefore, of interest to investigate compounds of the type C_6H_5PXY (where X and Y are two different halogen atoms). The thermochemistry of some phenyl phosphorus dihalides and diphenyl phosphorus halides were also studied as there are no thermodynamic data in the literature.

CHAPTER 11

Thermochemistry of Phosphoryl Halide-Boron Halide Complexes

The literature on compounds in which the phosphoryl trihalides act as donor molecules is extensive and is most controversial[27-30] where the acceptor molecule is a boron trihalide. The existence of ionic forms, eg. $POX_2^+ BX_4^-$, rather than the generally accepted covalent form, with the donation through the oxygen, is still possible in the light of the existing data. The main techniques previously applied to these compounds have been vibrational spectroscopy, phase diagram studies and the kinetics of active halogen exchange[56-57]. In this investigation, using standard thermochemical methods the strength of donor-acceptor bond has been estimated to ascertain whether the magnitude is within accepted limits of such bonds.

Results

The compounds studied were $POCl_3$ BCl_3 (l), $POCl_3$ BBr_3 (ll), $POBr_3$ BCl_3 (lll) and $POBr_3$ BBr_3 (lV), all of which are solid at room temperature. For compounds (l) and (lV) the hydrolysis is :

$$POX_3\ BX_3(C)+(n+6)H_2O(liq) = [H_3PO_4+H_3BO_3+6HX]\,n\ H_2O$$
$$\Delta H(obs)\ (X=Cl,Br)$$

and for (ll) and (lll) is

$$POX_3\ BY_3(c)+(n+6)H_2O(liq) = [H_3PO_4+H_3BO_3+3HX+3HY]\,n\ H_2O$$
$$\Delta H(obs)\ (X,Y = Cl,\ Br)$$

Hence,

$$\Delta H_f^o POX_3\ BX_3(c) = \Delta H_f^o H_3PO_4\ nH_2O + \Delta H_f^o H_3BO_3\ nH_2O + 6\Delta H_f^o HX\ nH_2O - 6\Delta H_f^o\ H_2O(liq) - \Delta H(obs)\ (X)$$

and

$$\Delta H_f^o POX_3\ BY_3(c) = \Delta H_f^o\ H_3PO_4\ nH_2O + \Delta H_f^o\ H_3BO_3\ nH_2O + 3\Delta H_f^o\ HX\ nH_2O + 3\Delta H_f^o\ HY\ nH_2O - 6\Delta H_f^o\ H_2O(liq) - \Delta H(obs)(X\ Y)$$

The hydrolyses occured without undue violence, reaction being complete for (1) and (111) within 6 minutes and for (11) and (1V) within 3 minutes. The detailed description of the calorimeter is given in the experimental section.

Ancillary Data

The ancillary thermodynamic data were taken from the following sources:

Compound	ΔH_f^o (k.cal $mole^{-1}$)	ΔH^o_{Soln}(k.cal $mole^{-1}$)	Source
H_3PO_4	$- 305.7 \pm 0.3$	$- 2.65 \pm 0.1$	Holmes[58]
H_3BO_3	$- 261.7 \pm 0.3$	$+ 5.24 \pm 0.05$	Gunn [59]

The standard heats of formation of liquid water, and aqueous solutions of HCl and HBr are taken from the National Bureau of Standards Circular 500.[60] The latter two data have recently been reassessed by Johnson et.al.[61] and Sunner et. al.[62] The value of Sunner et. al.[62] has been used for calculation. All data are expressed in terms of therochemical calorie defined by 1 cal = 4.1840 abs. joule. The heats of mixing of H_3PO_4, H_3BO_3 and HX are ignored.

Discussion

From the standard enthalpies of formation of the adducts, it is possible to derive the thermodynamic functions defined by the following equations (ss = standard state) :

$$POX_3(ss) + BY_3(ss) = POX_3\ BY_3(c) \qquad \Delta H^{o}$$

$$POX_3(g) + BY_3(g) = POX_3\ BY_3\ (c) \qquad \Delta H$$

Using the ancillary data from Table 2, these data are shown in table 3.

Making the assumption that the crystal sublimation energies are substantially constant, then ΔH is a measure of donor-acceptor binding (assuming that donation is through O). On this basis, $POCl_3$ is a stronger donor than $POBr_3$, and BBr_3 a stronger acceptor than BCl_3 in one case only.

For an absolute comparison of donor-acceptor binding, the energy $D(B \leftarrow O)$ of the donor-acceptor bond is required. To derive this it is necessary to estimate the sublimation energies of the crystalline adducts. As an approximation we put this equal to the sum of the component sublimation energies $[\Delta H(C \longrightarrow g)]$, ie.

$$\Delta H\ (POX_3\ BY_3\ C \rightarrow g) = \Delta H\ (POX_3 C \rightarrow g) + \Delta H\ (BY_3\ C \rightarrow g)$$

The crystal structures[63-64] of both BCl_3 and B_2Cl_4 are such that the molecules are planar and mutually parallel. Making the assumption that the intermolecular forces in these two crystals are similar in character we may write:

$$\Delta H\ (BCl_3\ C \rightarrow g) = \Delta H\ (B_2Cl_4\ C \rightarrow g)\ \frac{M(BCl_3)}{M(B_2Cl_4)}$$

where, M is the molecular weight. Using Moore's[65] datum for the sublimation energy of B_2Cl_4, we have $\Delta H\ (BCl_3\ C \rightarrow g) \sim 9.5$ k.cal mole^{-1}. Interpolating a corresponding datum for BBr_3 from the data for BCl_3 and BI_3[66], the approximate adduct sublimation energies have been derived. Combining these data with :

$$-\Delta H = \Delta H\ (POX_3\ BY_3\ C \rightarrow g) + D(B \leftarrow O)$$

we derive the over all donor-acceptor bond energy $D(B \leftarrow O)$. (See Table 4)

Such estimates of the bond-dissociation energy include the re-organization energies Er(A) and Er (D) respectively of the donor (D) and acceptor (A) molecules. This is summarised in the energy diagram :

$$\begin{tikzcd}
POX_3\ (g) + BY_3\ (g) \arrow[rr, "Er\ (D) + Er\ (A)"] & & POX_3^*\ (g) + BY_3^*\ (g) \\
& X_3PO\ BY_3\ (g) \arrow[ul, "D(B \leftarrow O)"] \arrow[ur, "D^*"'] &
\end{tikzcd}$$

D^* is essentially the bond dissociation energy as defined by Szwarc and Evans[67] with each product molecule in a similar structural and electronic state to those in the complex. Since $D^* = D\ (B \leftarrow O) + [Er(A) + Er(D)]$ values may be calculated if estimates of Er(D) and Er(A) are available. Reliable calculations[54] of the latter exist (BCl_3, 30.3 ; BBr_3, 26.2 k.cal mole^{-1}). No estimates of Er(D) are available, but it is reasonable to assume that Er(D) $\ll$ Er(A), since little structural change occurs in $POX_3^* \longrightarrow POX_3$ transformation in contrast to the change from tetrahedral (sp^3) to planar (sp^2) in the boron trihalides. Further differences in Er(D) ie. Er ($POCl_3$) -Er($POBr_3$) may still more reasonably be neglected, and hence significant ΔD^* values may be computed. Appropriate values are in Table 4. The differences in D(B←O) and in D^* between (1) and (111) and between (11) and (1V) are both positive and are not within the assigned error. Hence $POCl_3 > POBr_3$ is the confirmed order of Lewis basicity. It is accepted that the order of Lewis acidity of the boron halides[40] is $BCl_3 < BBr_3$, and this is confirmed by the differences in D(B←O) between (1) and (11) but appears to be reversed when $POBr_3$ is the donor [ie. from (111) and (1V)] . This may be ascribed to enhanced steric interactions in (1V) or, more probably, to the fact that the data are not sufficiently sensitive for the trend to be real. The donor-acceptor bond strengths are approximately an order of magnitude less than the normal B - O bond[68] strength (~120 k.cal), and this is the same ratio that was noted by Skinner[69]. Hence our evidence is consistent with covalent bonding but does not exclude an ionic formation.

There is the possibility that in the mixed halogen complexes, (11) and (111), halogen exchange between phosphorus and boron might occur. Using active chlorine Herber[57] studied the exchange in $POCl_3\ BCl_3$. He found that exchange is rapid (complete within approx. 1min. at 0°) in excess $POCl_3$, but no exchange occurs in an excess of BCl_3. He concludes that an ionic formation is not possible, since the formation of BCl_4^- would lead to an immediate exchange in view of the kinetic equivalence of the Cl in BCl_4^-. On this basis it has been suggested that in $POCl_3$ rich systems the observed rapid halogen exchange between the two components occurs by the mechanism:

$$POCl_3 \rightleftharpoons POCl_2^+ + Cl^-$$

$$Cl^- + Cl_3^*BO\ PCl_3 \rightleftharpoons \left[Cl_4^*\ B\ POCl_3\right] \rightleftharpoons Cl^{*-} + Cl_3B\ OPCl_3$$

where * signifies a radioactive species.

The bracketed reaction intermediate may be regarded as an activated complex configuration in which two chlorine atoms are both partially bonded to the central atom at one of the regular tetrahedron positions.

This explains why exchange occurs in $POCl_3$ rich systems (the dielectric constants of $POCl_3$ and BCl_3 are 13.9 and 1.0 respectively). Hence in the syntheses, care was taken to maintain an excess of boron halide to avoid the interconversion $POCl_3\ BBr_3 \rightleftharpoons POBr_3\ BCl_3$.

TABLE 1

Compound	T(^{0}C)	N	ΔHobs	ΔH_f^o(T)	
$POCl_3\ BCl_3$ (1)	25.3	7470	-122.5	-271.9	-271.2±1.0* K.cal mole^{-1}
	25.2	7550	-123.5	-270.9	
	25.1	9790	-122.9	-271.6	
	25.3	5270	-123.1	-271.4	
	25.1	4790	-124.1	-270.4	
$POCl_3\ BBr_3$ (11)	25.1	5088	-127.6	-234.4	-234.3±1.8* K.cal mole^{-1}
	25.1	6399	-127.5	-234.4	
	25.0	5056	-126.2	-235.7	
	25.0	10281	-129.3	-232.7	
	25.0	6230	-126.0	-235.9	
	25.0	6590	-128.8	-233.2	
$POBr_3\ BCl_3$ (111)	25.1	9082	-134.7	-227.3	-227.4±0.8* K.cal Mole^{-1}
	25.1	9002	-134.0	-228.0	
	25.2	10065	-134.9	-227.1	
	25.2	8895	-134.8	-227.2	
	25.2	7053	-134.8	-227.2	
	25.3	10379	-134.3	-227.7	
$POBr_3\ BBr_3$ (1V)	25.0	16103	-151.7	-177.6	-178.7±1.8* K.cal mole^{-1}
	25.0	21317	-149.0	-180.2	
	24.9	10986	-152.3	-177.0	
	24.7	17771	-149.1	-180.1	

* Errors were calculated as the square root of the sum of the constituent errors.

TABLE 2

	$POCl_3$	$POBr_3$	BBr_3	BCl_3	
ΔH_f^o (298) (g)	60 -134.3	b (-94.9)	74 -49.3	a, 72 -96.7	K·Cal mole^{-1}
ΔH_f^o (298) (l)	a,47 -143.8	b (-106.6)	a,73 -57.5	59 -102.3	
ΔH_f^o (298) (c)	71 -147.1	a,47 -110.1	* (-62.1)	* (-106.2)	

a, Standard state data. b, Estimate (See ref. 47)
* Estimate (See text). Other references refer to source ΔH (transition).

TABLE 3

	$POCl_3$ BCl_3 (1)	$POCl_3$ BBr_3 (11)	$POBr_3$ BCl_3 (111)	$POBr_3$ BBr_3 (1V)	
ΔH^o	-30.7	-33.1	-20.6	-10.1	K.cal mole^{-1}
ΔH	-40.2	-50.8	-35.0	-33.7	

(The uncertainty in these data is approximately ± 2 K.cal)

TABLE 4

	ΔH (C→g)	D (B←O)	ΔD	D*	ΔD*
$POCl_3$ BCl_3 (1)	22.3	17.9	-7.6	48.2	-3.5
$POCl_3$ BBr_3 (11)	25.3	25.5		51.7	
$POBr_3$ BCl_3 (111)	23.9	11.1	4.2	41.4	8.4
$POBr_3$ BBr_3 (1V)	26.9	6.8		33.0	

(The uncertainty in these data is approximately ± 5 K.cal)

Infrared Spectra of Phosphoryl Halide-Boron Halide Complexes

Considerable, and divergent spectroscopic work on these molecules has been reported. Accumulated evidence for covalent structures stems largely from marked shifts (50-55cm^{-1}) of the (P=O) mode in complexes compared with "free" phosphoryl halide. However, it was suggested by Gerrard[28] that $POCl_3$ BCl_3 in particular exists as $POCl_2^+$ BCl_4^-, on the basis of no apparent (P=O) shift and identification of BCl_4^- bond envelope. Waddington and Klanberg[29] examined $POCl_3$ BF_3 and $POCl_3$ BCl_3 spectroscopically and concluded that the former was definitely covalent and the latter probably so. The evidence was the occurence of a bond at 1190cm^{-1} assigned to a B-O stretching mode and to the inability to locate vibrations characteristic of BCl_4^-. In addition, they observed negligible ν(P=O) shift. A recent spectroscopic study[30] of all complexes studies here reveals a marked (P=O) shift, and a semi-quantitative vibrational analysis provides a strong support for a covalent formation.

Spectra of the complexes were recorded over the range 2000 - 400 cm.$^{-1}$ in carbon disulphide and in cyclohexane (these solvent have very similar dielectric constants). In carbon disulphide solution all complexes show bands at 1300 ± 10 cm^{-1} (P = O stretch) and 1200 ± 10 cm^{-1} (B - O stretch) of varying relative intensity. The spectrum of (1) compares in its salient feature with that obtained by Waddington (mull) but not with that of Goubeau[30]. The spectra of the mixed halogeno complexes, (11) and (111), in cyclohexane appear similar to those of Goubeau[30] (mull). Molecular weight determinations (by cryoscopy in benzene) indicate (Fig 1) that there is no dissociation in a solvent of similar polarity (benzene) to those used for spectroscopic work. A description of the apparatus used for the cryoscopy is given in the experimental section. A full analysis of the spectral data would be of great interest, since, from a knowledge of the force constant of the B-O bond, an estimate of D^*, independent of calorimetric measurement, should be possible. This could then be used to check the assumption that the magnitude of the reorganization energies of the phosphoryl halides is sufficiently low to be neglected.

Vapour Pressure Measurement of $POCl_3$ BCl_3 and its Comparison With the Calorimetric Result

Burg and Ross[70] examined the equilibrium $POCl_3\ BCl_3(c) \rightleftharpoons BCl_3(g) + POCl_3(g)$ by vapour tensimetric method, and, from their result, $\log k = 15.803 - \frac{5714}{T}$, the value of ΔH has been derived to be 26.1 k.cal. $mole^{-1}$. The value reported in the thermochemistry section is 40.2 k.cal. $mole^{-1}$. In order to check the ambiguity of the two results, both experiments were repeated on freshly prepared sample .

The detailed of the vapour pressure measurements have been described in the experimental section. The dissociation pressure of the complex was noted at different temperatures and a straight line (Fig. 2) was obtained when $\log_{10} p$ was plotted against $\frac{1}{T}$. It is interesting to mention that the experimental points of Burg[70] also fall on the same line which proves that the value of ΔH calculated by Burg[70] was correct. The complex was again hydrolysed in the calorimeter and the results are recorded in the following table:

T (^{o}C)	N	$-\Delta H^{o}_{obs}$ (K.cal mole^{-1})	$-\Delta H^{o}_{f}$(K.cal mole^{-1})
24.6	7877	-121.7	-272.8
24.4	9258	-122.8	-271.7
24.4	8772	-122.5	-272.0
24.5	19,263	-121.6	-272.9

Mean $\Delta H^{o}_{f} \doteq -272.3 \pm 1.0$ K.cal mole^{-1}

(cf. ΔH^{o}_{f} (previous sample) $= -271.2 \pm 1.0$ K.cal mole^{-1})

Therefore the heats of formation calculated before was reproducible within ± 0.5% accuracy. The above deviations between the two techniques may be taken as further evidence for the existence of two forms of the complex.

The vapour pressures of the complex and phosphoryl chloride have been plotted against temperatures. The two graphs meet at a point. The temperature of the meeting point (Fig. 3) is about 28°C. This is possibly due to the fact that the complex is stable below this temperature whereas above this temperature, the complex is in metastable state.

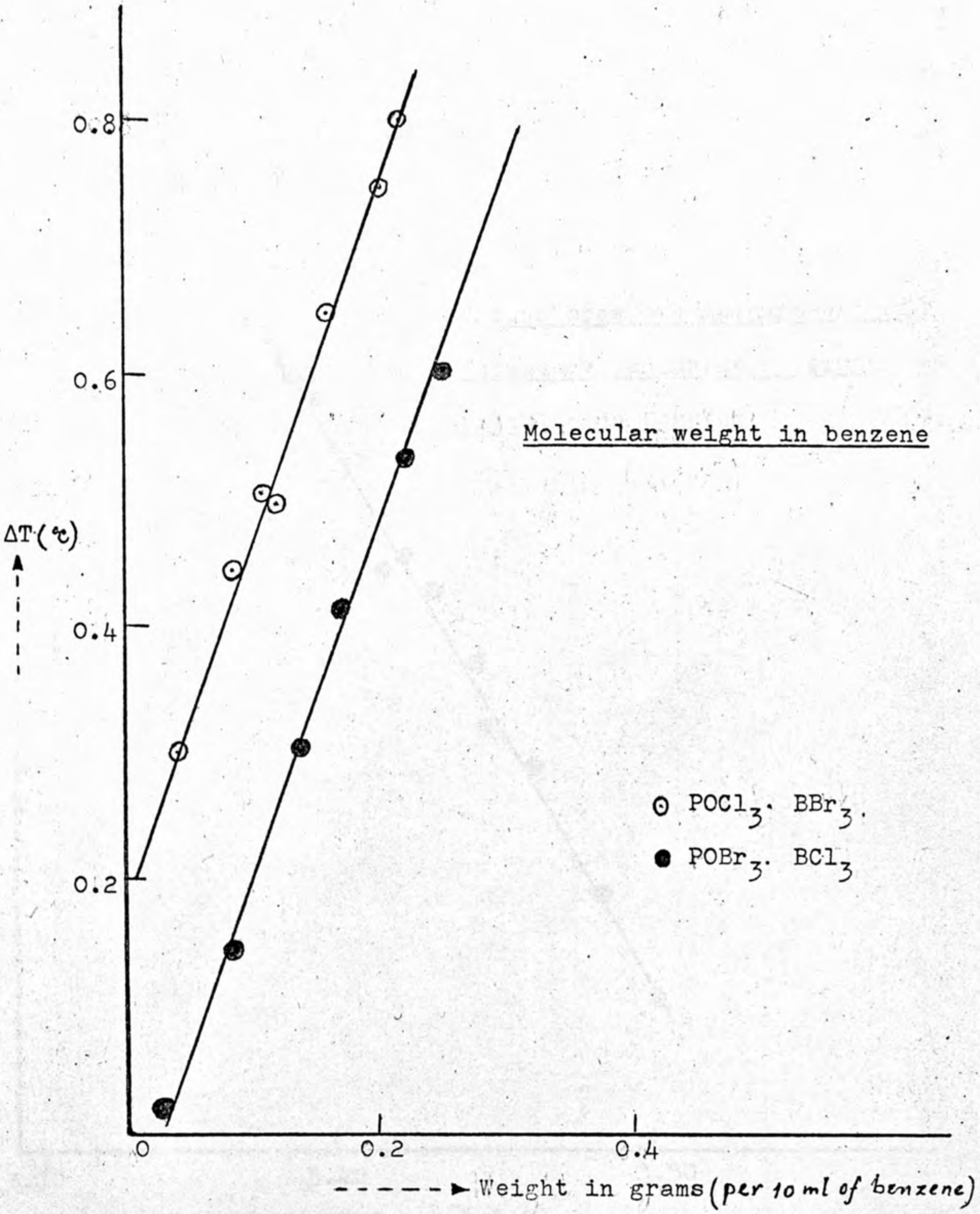

0.8
0.6
0.4
0.2
ΔT (°c)
0
0.2
0.4
Molecular weight in benzene
⊙ POCl3 · BBr3
● POBr3 · BCl3
Weight in grams (per 10 ml of benzene)

FIGURE 1

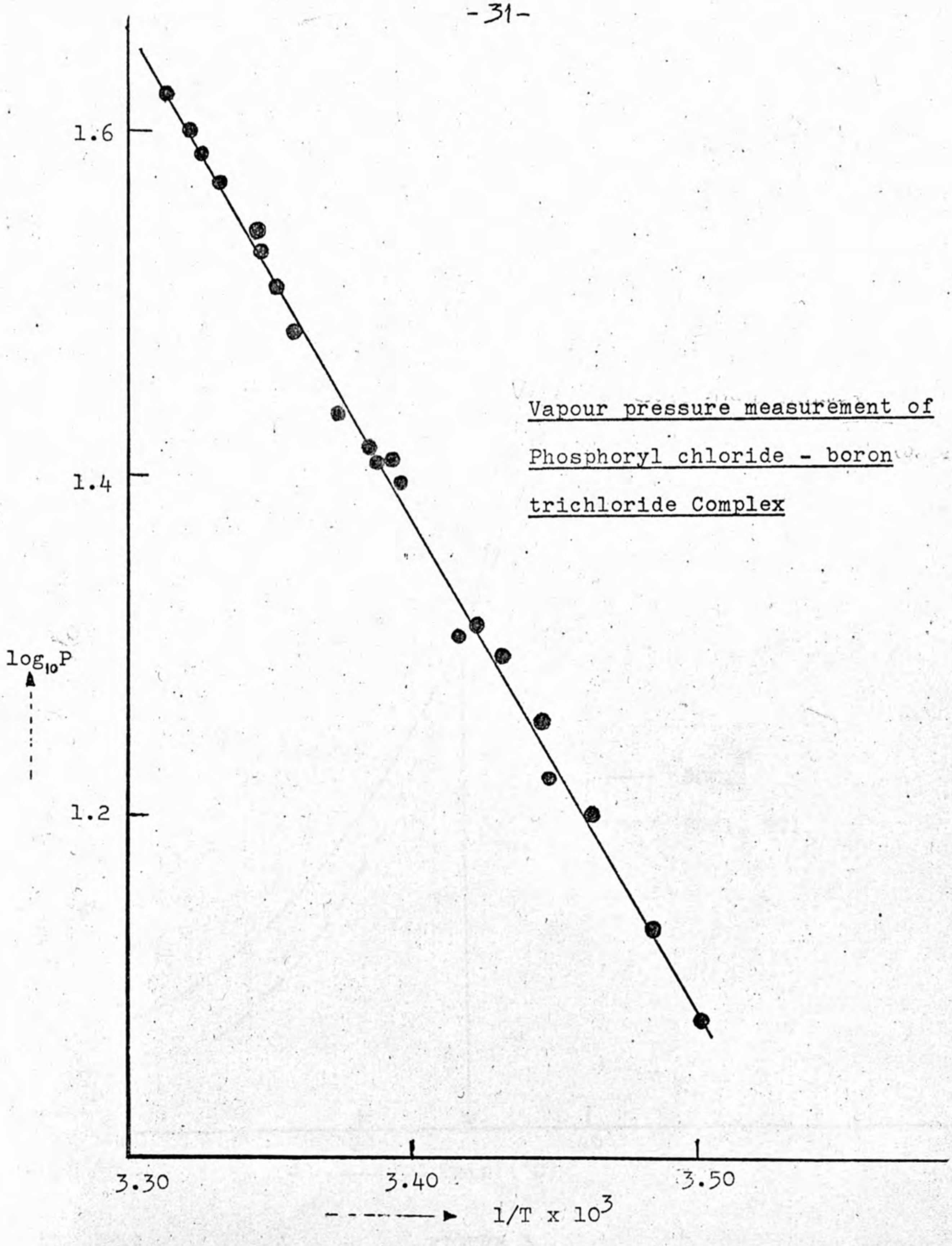

Vapour pressure measurement of
Phosphoryl chloride - boron
trichloride Complex
1.6
1.4
1.2
$\log_{10}P$
3.30
3.40
3.50
1/T x 10^3

FIGURE 2

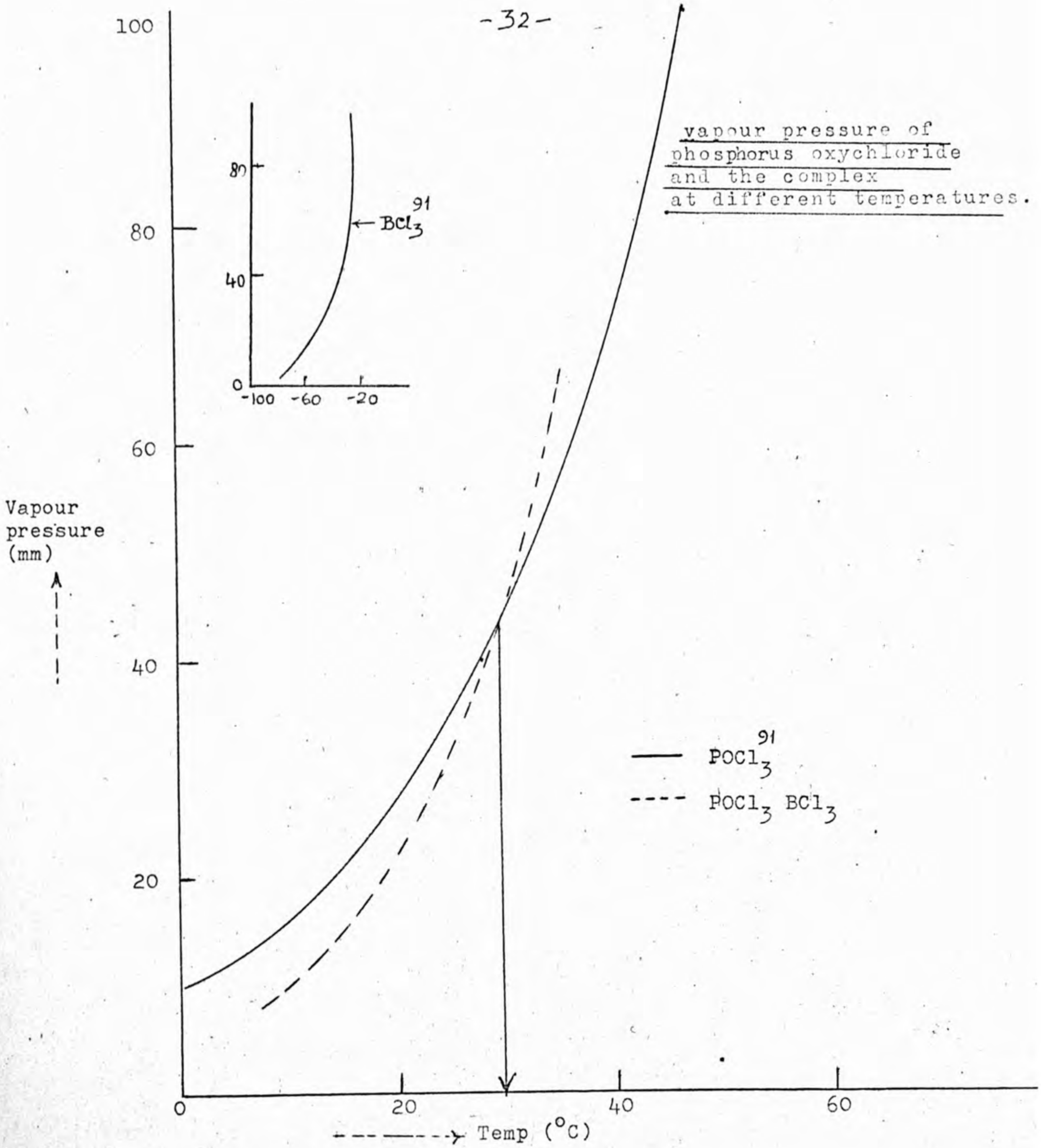

vapour pressure of phosphorus oxychloride and the complex at different temperatures.
100
80
60
40
20
0
20
40
60
Vapour pressure (mm)
Temp (°C)
80
40
0
-100
-60
-20
BCl3 91
POCl3 91
POCl3 BCl3

FIGURE 3

CHAPTER 111

Thermochemistry of Phosphorus Halide-Boron Halide Complexes

The 1:1 complexes formed from borontrihalides and phosphorus trihalides have been studied in connection with their stability with respect to dissociation[19], their halogen exchange reactions and their solid-phase structure[21,22]. Only the complexes involving the heavier halogen atoms are stable with respect to disproportionation or dissociation at room temperature. These complexes are presumably σ bonded from phosphorus to the boron atom. This is in contrast to the phosphoryl halide-boron halides adducts, which have been examined thermochemically (see Chapter 11),where bonding is most probably from oxygen to boron.

Results:

The adducts PI_3 BI_3 (1), PI_3 BBr_3 (11), PBr_3 BI_3(111) and PBr_3 BBr_3 (1V) hydrolyze quantitatively and without undue violence in water according to the equations,

$$PX_3\ BX_3\ (c) + (n+6)\ H_2O\ (1) = [H_3PO_3 + H_3BO_3 + 6HX]\ nH_2O$$

$$PX_3\ By_3\ (c) + (n+6)\ H_2O\ (1) = [H_3PO_3 + H_3BO_3 + 3HX + 3HY]\ nH_2O$$

from which we may write,

$$\Delta H_f^o\ [PX_3\ BX_3\ (c)] = \Delta H_f^o\ (H_3PO_3\ nH_2O) + \Delta H_f^o\ (H_3BO_3\ nH_2O) + 6\Delta H_f^o\ (HX\ nH_2O) - 6\Delta H_f^o\ H_2O\ (1) - \Delta H(obsd)\quad X$$

and,

$$\Delta H_f^o\ [PX_3BY_3(c)] = \Delta H_f^o\ (H_3PO_3\ nH_2O) + \Delta H_f^o\ (H_3BO_3\ nH_2O) + 3\ \Delta H_f^o\ (HX\ nH_2O) + 3\Delta H_f^o\ (HY\ nH_2O) - 6\Delta H_f^o\ H_2O(1) - \Delta H\ (obsd)\quad (X,Y)$$

Ancillary data:

The following ancillary thermodynamic data were used:

Compound	ΔH_f^o (k.cal. mole^{-1})	Source.
H_3BO_3. 1000 H_2O	- 256.5 ± 0.3	Gunn[59]
H_3PO_3 (aq)	- 226.5 ± 0.8	Skinner[75]
$HI \infty H_2O$	- 13.79 ± 0.1	Skinner[76]
HBr. 3000 H_2O	- 29.05 ± 0.09	Sunner et. al[62]

The values ΔH_{diln} (HBr and HI) and ΔH_f^o H_2O (1) are due to Rossini et. al.[60]. The enthalpy of dilution of boric acid is small[77] and that of phosphorous acid is unknown but probably within the assigned error. The heats of mixing of H_3PO_3, H_3BO_3, HBr and HI are ignored.

Discussion

The enthalpy changes of the reactions

PX_3 (s.s) +BY_3 (s.s) = PX_3 BY_3 (c) ΔH^o

PX_3 (g) + BY_3 (g) = PX_3 BY_3 (c) ΔH_1

may be derived using the ancillary thermodynamic data[78-82,45] in the Table 2. Before considering the thermodynamic stability of the adducts, there is evidence[20] that PBr_3BI_3 and PI_3BBr_3 are discrete compounds and cross halogenation does not occur at ambient temperature. Molecular weight determinations indicate that there is no dissociation in benzene (Fig. 1.)

As a first approximation, if the differences between the entropy changes (ΔS^o) are ignored, then relative values of ΔH^o measure the thermodynamic stability of the adducts with respect to dissociation into free donor and acceptor.

An alternative method of considering stability, or relative donor-acceptor power, is to estimate the strength of the donor-acceptor bond. This calculation requires the adduct sublimation enthalpies for which a reasonable assumption is:-

$\Delta H\ (c \rightarrow g,\ PX_3\ BY_3) = \Delta H\ (c \rightarrow g,\ PX_3) + \Delta H\ (c \rightarrow g,\ BY_3)$

Two different estimates of the bond dissociation energy of each adduct are given by the equations

$D(X_3P - BY_3) = -\Delta H\ (c \rightarrow g,\ PX_3\ BY_3) - \Delta H_1$

$D^*(X_3P^* - BY_3^*) = D(X_3P - BY_3) + Er(PX_3) + Er(BY_3)$

where asterisk signifies the molecule in its molecular electronic and molecular hybridization state and Er is the reorganization energy[67].

It has been shown (Chapter 11) that the inclusion of Er in a discussion of donor-acceptor properties of phosphoryl halide-boron halide systems does not significantly affect the conclusions. Hence we shall consider D rather than D* in the subsequent discussion.

Corroboratory evidence for $D(I_3P - BI_3)$ comes from a recent estimate[83] of 16 k cal, for this datum derived from a vibrational analysis of the adduct.

Using the data in Table 3 and analogous data for phosphoryl halide-boron halide complexes, the following order of donor ability with respect to a fixed acceptor may be formulated. Relative donor power (or Lewis basicity) with respect to

(a) BCl_3 is $POCl_3 > POBr_3$ ($> PBr_3 > PCl_3$)

(b) BBr_3 is $PI_3 > POCl_3 > POBr_3 \sim PBr_3$ ($> PCl_3$)

and,

(c) BI_3 is $PBr_3 > PI_3$

Relative acceptor power (or Lewis acidity)with respect to

(d) PCl_3 is ($BBr_3 > BCl_3$)

(e) PBr_3 is $BI_3 > BBr_3$ ($> BCl_3$)

(f) $POBr_3$ is $BCl_3 > BBr_3$

(g) $POCl_3$ is $BBr_3 > BCl_3$

and

(h) PI_3 is $BBr_3 > BI_3$.

The data in the parentheses are deducted from Holmes description of the stabilities with respect to dissociation of the adducts "PCl_3 BCl_3", "PBr_3 BCl_3" and "PCl_3 BBr_3." The order of acceptor power of boron trihalides relative to organic bases, both in solution[40] and in the gas phase[84], has been established as, $BF_3 < BCl_3 < BBr_3$ and extended to include $BBr_3 < BI_3$ by Cook[41] (this latter work relative to xanthone and by frequency shifts in the vibrational spectrum). This order is followed in (d), (e), and (g) but reversed in (f) and (h). Also, orders of the donor power are self consistent except for (c). The anomalous complexes are $POBr_3$ BBr_3, $POBr_3$ BCl_3, PI_3 BBr_3 and PI_3 BI_3. It is readily seen that PI_3 BI_3 is the most sterically hindered with respect to halogen-halogen interaction (or F and B strain)[85] of the PX_3 BY_3 series. Further, the PO B angle in the POX_3 BY_3 complexes is considerably expanded from the tetrahedral angle[86] and examination of the molecular models reveals that $POBr_3$ BBr_3 is considerably more sterically strained, with respect to PO B angle distortion than $POBr_3$ BCl_3. This explanation is not entirely satisfactory in that the $POCl_3$ complexes exhibit the usual order. However, with the present limited evidence, it is probably the most realistic.

TABLE 1

Compound	N	T°C	ΔHobs(X)	$\Delta H_f^o(T)$
	10.692	24.7	-111.2	
PI_3 BI_3 (1)	10,985	24.8	-112.3	-44.1 ± 1.2^b
	13,271	24.8	-110.7	
	12,539	25.0	-111.7	
	11,801	24.8	-110.6	
			Mean-111.3 ± 0.85^a	
PBr_3 BBr_3(1V)	8,177	24.7	-132.1	-115.1
	5,031	24.7	-134.6	-112.5
	11,913	24.6	-133.2	-114.1
	11,880	24.6	-134.4	-112.9
	6,253	25.0	-133.5	-113.7
	7,342	25.0	-132.1	-115.1
				Mean$=-113.9 \pm 1.5^b$
			ΔHobs(X,Y)	
PI_3 BBr_3(11)	14,469	24.6	- 64.5	-137.1
	10,874	24.8	- 62.4	-139.1
	6,806	24.8	- 62.5	-138.9
	4,334	24.7	- 62.3	-139.0
	7,871	24.9	- 63.6	-137.9
	6,946	24.8	- 63.0	-138.4
				Mean$=-138.4 \pm 1.3^b$
PBr_3 BI_3(111)	5,716	24.5	-110.8	- 90.6
	6,915	24.7	-111.4	- 90.0
	10,419	24.8	-111.2	-90.3
	12.025	24.9	-110.4	- 90.2
	17,174	25.0	-110.7	- 90.9
	16,402	24.8	-112.6	- 89.0
				Mean$= - 90.3 \pm 1.4^b$

N = mole ratio of water to adduct.

a, In this case, ΔH obs was averaged rather than ΔH^o_f because the values of N were sufficiently close for only one value of ΔH^o_f ($HX\ nH_2O$) to be used.

c, The error in ΔH obs was taken as the range; this was then combined with the errors in ancillary data to give the root of sum of the squares as the overall error.

TABLE 2

	PI_3	PBr_3	BI_3	BBr_3
ΔH^o_f (g)	-7.05 ± 1.7^g	-30.7 ± 1.5^i	4.7 ± 1.0^a	-48.8 ± 0.22
ΔH^o_f (l)		$\underline{-41.7 \pm 2.0}^c$		$\underline{-57.0 \pm 0.2}$
ΔH^o_f (c)	$\underline{-11.45 \pm 0.85}^f$	-45.2 ± 2.5^d	-10.8 ± 0.8^b	-61.6 ± 2.0^e

a, ΔH (c→g) BI_3 due to Teinsuv[79], b, Data from ref. 8o modified using current ΔH^o_f [HI (aq)] data, c, ΔH (l→g PBr_3) due to Van Driel at. al.[81], estimated using Watson's equation[82]. d, Assuming ΔH(c→l PBr_3) = ΔH(c→l $POBr_3$). e, See Chapter 11 . f, Data from reference 45 modified using current ΔH^o_f [HI (aq)] data. g, ΔH(c→g PI_3) = ΔH(c→l) + ΔH (l→g), latter term extrapolated from vaporization data[81] for PBr_3 and PCl_3 and former term put equal to ΔH[45] (Soln, PI_3 in CS_2). h, Appropriate errors have been assigned where estimates are involved. Underlineddata are in standard state. i, Reference 78.

TABLE 3

	PI_3 BI_3	PI_3 BBr_3	PBr_3 BI_3	PBr_3 BBr_3
ΔH^o	-21.8 ± 1.7	-69.9 ± 1.6	-37.8 ± 2.5	-15.2 ± 2.5
ΔH_1	-55.8 ± 2.3	-96.6 ± 2.1	-64.3 ± 2.3	-34.4 ± 2.1
$\Delta H\ (c \rightarrow g)$	$34.0(\pm 2.0)^*$	$31.3(\pm 2.0)^*$	$30.0(\pm 2.0)^*$	$27.3(\pm 2.0)^*$
D (P-B)	21.8 ± 3.1	65.3 ± 2.9	34.3 ± 3.0	$7.1\ (\pm 2.9)$

* An arbitrary error of ± 2.0 k cal. $mole^{-1}$ is assigned to this datum.

Thermochemistry of Diphosphorus Tetraiodide

The reaction which has been studied for the determination of heat of formation of P_2I_4 (c) is

$$P_2I_4\ (c) + I_2\ (CS_2 Soln) \rightleftharpoons 2PI_3\ (CS_2\ Soln) \text{ --- } \Delta H \text{ obs} \quad (1)$$

The heat of formation of P_2I_4 (c) has been calculated from the following thermochemical equation:

$$\Delta H_f^o\ P_2I_4(c) = 2\Delta H_f^o\ PI_3(CS_2\ Soln) - \Delta H_f^o\ I_2(CS_2 Soln) - \Delta H obs \qquad (2)$$

The reaction has been studied in the presence of excess iodine. Because of the equilibrium, the reaction was investigated at different molar ratios of P_2I_4 to I_2. The experiments gave the same result indicating that equation (1) had moved to R.H.S. The observed heat change was determined either by breaking an ampoule of P_2I_4 (c) into a solution of iodine in carbon disulphide or by breaking an ampoule of iodine (c) into the soluton of P_2I_4 in carbon disulphide.

ie. $P_2I_4\ (CS_2Soln) + I_2(c) \rightleftharpoons 2PI_3\ (CS_2Soln) \quad \Delta H'_{obs}$ (3)
This has recently[89] been shown from nuclear magnetic resonance studies that P - P bond in P_2I_4 is broken when the reaction is carried out with iodine in carbon disulphide and the reaction is very rapid which eleminates the possible existence of P_2I_4 in the presence of free iodine.

Before use in the calorimeter, carbon disulphide was shaken successively with mercury and aqueous potassium permanganate followed by the purification by distillation immediately before use. A stream of oxygen-free nitrogen was continuously bubbled for half an hour into the freshly distilled carbon disulphide to remove dissolved oxygen; this was then used in the calorimeter. It was noticed that unless this precaution is taken, anomalous results were obtained. This supports the evidence of Baudler and Fricke[88] who have reported the results on the relatively rapid reaction of diphosphorus tetraiodide with oxygen to form a polymer of approximate composition $[P_3I_2O_6]_n$. The vapour space above the liquid was also flushed with nitrogen.

The ancillary thermodynamic data (at 298.15°K) have been taken from the following sources:

Compound	ΔH_f^o(k cal. mole^{-1})	ΔH_s^o(k cal. mole^{-1})	Source
PI_3 (c)	- 11.45	+ 6.0	Finch et.al.*[45]
I_2 (c)	- 0.00	+ 5.0	Rossini et.al.[60]

* For details, see PX_3 - BX_3 section.

Table 1 summarises the values of ΔH_f^o P_2I_4(c) and we report a new value of ΔH_f^o P_2I_4(c) which is -17.5 ± 0.4 k cal. mole^{-1} as against the very old datum[44] of -19.8 k cal. mole^{-1} reported in the literature.

TABLE 1

T(^{o}C)	N	N^1	$+\Delta H^o$obs (K cal. mole^{-1})	$-\Delta H_f^o$ (k cal. mole^{-1})
24.5	1572	1.4	1.65	17.55
24.6	1219	1.0	1.75	17.65
24.7	1459	1.6	1.86	17.76
24.6	1593	1.8	1.43	17.33
24.2	1065	3.2	1.84	17.74
24.7	1200	3.7	1.68	17.58
24.7	1085	3.3	1.75	17.65
24.8	1775	5.1	1.65	17.55
24.6	1194	18.1	1.86	17.76
24.8	1565	23.6	1.57	17.47
24.7	860	13.2	1.48	17.38
24.9	1083	16.6	1.67	17.57
24.8	928	5.8	1.40	17.30
25.0	1024	4.0	1.35	17.25

ΔH_f^o P_2I_4(c)$=-17.5\pm0.4$ k cal mole^{-1}

N = mole ratio of solvent to compound

N^1 = mole ratio of iodine to compound

The last three results of the table 1 denote the values of ΔHobs when I_2(c) was broken under P_2I_4 in carbon disulphide solution.

Estimation of E (P-P)

The strength of phosphorus-phosphorus bond in diphosphorus tetraiodide can be estimated by considering the following thermochemical cycle and in the calculation it has been assumed that E(P-I) in PI_3 = E(P-I) in P_2I_4.

$$\begin{tikzcd}
P_2I_4(g) \arrow[rr, "4E(P\text{-}I) + E(P\text{-}P)"] & & 2P(g) + 4I(g) \\
& 2P(\text{white}) + 2I_2(c) \arrow[ul, "\Delta H^o_f(g)"] \arrow[ur, "2\Delta H^o_f P(g) + 4\Delta H^o_f I(g)"'] &
\end{tikzcd}$$

Hence,

$$E(P\text{-}P) = 2\Delta H^o_f P(g) + 4\Delta H^o_f I(g) - \Delta H^o_f(g) - 4E(P\text{-}I)$$

The numerical values and sources of the standard enthalpy data used in the calculation have been recorded in the Table 2.

TABLE 2

Compound	Process	Datum (k cal. $mole^{-1}$)	Source
P_2I_4	Sublimation	+ 30 (estimate)	Hartley et.al[49]
P(g)	Formation	+ 75.5	"
E(P-I)	–	44.0	"
$\Delta H^o_f(I)$	Gaseous	+ 25.537	Janaf[78]

On the basis of the above results, the value of E(P-P) has been calculated to be 64.5 k cal. $Mole^{-1}$. The estimated values of E(P-P) due to Hartley et. al.[49] for the compounds P_4, P_2H_4 and P_2I_4 are 50, 52 and 67 k cal. $mole^{-1}$ respectively. Considering the values of E(P-P) in P_4 and P_2H_4, the present value of E(P-P) in the case P_2I_4 is not unreasonable where the error is probably of the order of ± 4 k cal. $mole^{-1}$ because of the estimated value of heat of sublimation of P_2I_4.

Thermochemistry of Phosphorous Acid

The values of ΔH^o_f H_3PO_3(c), as have been obtained by different workers, have been tabulated by Hartley et.al,[49] and differ considerably with one another. These determinations depended[49] either on the oxidation of aqueous phosphorous acid to aqueous phosphoric acid or by the aqueous hydrolysis of phosphorus trichloride. In view of these differences in values, it was decided to redetermine the values of ΔH^o_f H_3PO_3(c) on recrystallized sample (99.6% pure) of phosphorous acid (the purity was checked by the acidimetric method). The oxidation reaction has been carried out in the presence of excess bromine so that the solution always contains excess tribromide ion. The reaction may be represented by the following equation:

$$H_3PO_3(c) + 3Br_2(l) + H_2O(l) = \left[H_3PO_4 + 2Br_3^- + 2H^+\right]nH_2O \quad \Delta^oH \text{ obs}$$

This has recently been shown by Barter et. al.[90] that during the oxidation of alcohols and ethers by bromine, bromide ion produced in the reaction converted bromine into chemically inert and more strongly absorbing Br_3^- in the solution.

The standard enthalpy of formation follows from the following equation:

$$\Delta H^o_f\ H_3PO_3(c) = \Delta H^o_f\ H_3PO_4(aq) + 2\Delta H^o_f\ Br_3^-(aq) + 2\Delta H^o_f\ H^+(aq)$$
$$- 3\Delta H^o_f\ Br_2(aq) - \Delta H^o_f\ H_2O\ (liq) - \Delta Hobs$$

The ancillary thermodynamic values ie. heat of formation and heat of solution of phosphoric acid as well as heat of formation of liquid water are given in the Chapter 11. The other values have been recorded in the following table:

Compound	ΔH_f^o (k cal. mole^{-1})	Source
Br_2 (aq)	- 1.1	Rossini et. al.[60]
Br_3^- (aq)	-31.2	"
H^+ (aq)	- 0.00(by defination)	"

Table 1 summarises the values of ΔH_f^o H_3PO_3 (c)

TABLE 1

T (^oC)	N	N^1	$-\Delta H^o$obs (k cal. mole^{-1})	$-\Delta H_f^o$ H_3PO_3(c) (k cal. mole^{-1})
24.5	2216	7.5	67.4	231.75
24.9	2217	9.6	67.3	231.85
24.7	2645	9.0	68.4	230.75
24.7	1914	6.5	67.8	231.35
24.7	5981	20.3	67.6	231.55
24.9	4182	14.2	68.5	230.60
24.5	7282	25.8	68.4	230.75
24.5	3935	24.5	67.8	231.35
				Av = -231.2 ± 0.7 k cal. mole^{-1}

N = mole ratio of water to compound

N^1 = mole ratio of bromine to compound

Thermochemistry of PCl_5 BCl_3 Complex

The compound PCl_5 BCl_3 has been studied by X-ray crystallography and, in addition, the infrared spectrum has been recorded. Here phosphorus is probably present as PCl_4^+ cation and boron in the anion (BCl_4^-) exhibiting tetrahedral co-ordination corresponding to sp^3 hybridization although a covalent formation where the phosphorus exhibits octahedral configuration corresponding to d^2sp^3 hydridization is not excluded. In the case of phosphoryl chloride-boron chloride complex (see Chapter 11) it is possible that both ionic and covalent forms exist simultaneously in the equilibrium. The value of ΔH obtained by vapour tensimetric method was much smaller than the value obtained by the calorimetric method. It was, therefore, intended to investigate $PCl_5\ BCl_3$ complex by the above mentioned techniques in order to verify whether the compound exists simply in one form or both the forms remain simultaneously in the equilibrium as before.

The compound hydrolyses according to the following equation:

$$PCl_5\ BCl_3(c) + (n+7)\ H_2O = \left[H_3PO_4 + H_3BO_3 + 8HCl\right]_{\Delta H^o obs}\ n\ H_2O$$

Hence we have derived a value of $\Delta H_f^o\ PCl_5\ BCl_3(c)$ from the following equation:

$$\begin{aligned}\Delta H_f^o\ PCl_5\ BCl_3(c) &= \Delta H_f^o\ H_3PO_4\ n\ H_2O + \Delta H_f^o\ H_3BO_3\ n\ H_2O \\ &\quad + 8\Delta H_f^o\ HCl\ n\ H_2O - 7\Delta H_f^o\ H_2O(liq) - \Delta H\ obs\end{aligned}$$

The ancillary thermodynamic data for calculating the above equation have been described in the Chapter 11. Table 1 lists the observed enthalpies of aqueous hydrolysis (ΔH obs). The heat of mixing of H_3PO_4, H_3BO_3 and HCl are ignored.

TABLE 1

T (^{o}C)	N	$-\Delta H^{o}$obs (k cal. mole^{-1})	$-\Delta H^{o}_{f}$ (k cal. mole^{-1})
24.9	26,290	155.3	251.2
25.0	25,555	155.3	251.2
24.9	14,985	154.1	252.4
25.1	15,354	153.4	253.1
24.8	30,105	155.4	251.1
24.9	39,271	155.2	251.3
24.5	19,867	155.0	251.6
24.6	20,151	156.1	250.4

Av = -251.5 ± 1.8 (k cal. mole^{-1})

From the standard enthalpy of formation of the adduct the thermodynamic functions which defined by the following equations,have been calculated:

$PCl_5(c) + BCl_3(g) = PCl_5\ BCl_3(c)$ ΔH^{o}

$PCl_5(g) + BCl_3(g) = PCl_5\ BCl_3(c)$ ΔH

The ancillary thermodynamic data for the calculation of the above functions have been recorded in the following table:

	BCl_3*	PCl_5 (due to Hartley et. al.[49])	
ΔH^{o}_{f} (298) (g)	-96.7	-95.35	k cal. mole^{-1}
(l)	-102.3	-	
(c)	-106.2	-110.7	

* See Chapter 11.

The values of ΔH^{o} and ΔH have been found to be -44.1 and -59.5 k cal. mole^{-1}respectively. In order to check this, the dissociation pressures of the compounds were measured at various temperatures. The details of the vapour pressure measurements have been given in the experimental section. The resulting dissociation pressure which determine the equation (1), $\log_{10} P\text{mm} = 3.0625 - \frac{621.1}{T}$ (where, $T^{\circ}K$) are tabulated in the Table 2.

TABLE 2

t ($^{\circ}$C)	Pmm(obsd)	Pmm(calcd from equation 1)
28.4	10.3	10.01
32.5	10.8	10.58
37.2	11.4	11.49
40.3	12.0	12.00
43.1	12.42	12.54
45.0	12.85	12.82
49.5	13.60	13.67
52.2	14.00	14.24
54.3	14.50	14.62
60.2	15.86	15.87

On the assumption that the vaporization is represented by the equation, $PCl_5\ BCl_3(c) \rightleftharpoons PCl_5(g) + BCl_3(g)$, the pressure temperature relationship has been converted to $\log_{10} K_{atm} = 2.574 - \frac{1241}{T}$, from which we derive $\Delta H = 5.5$ k.cal. mole^{-1}. Like phosphoryl chloride-boron trichloride complex, $PCl_5\ BCl_3$ complex also shows a similar behaviour ie. ΔH obtained by the calorimetric method is much higher than that of the value obtained by the vapour tensimetric method. The plots of vapour pressures of the complex and phosphorus pentachloride (Fig.3) against temperature show that the vapour pressure of phosphorus pentachloride is less than the vapour pressure of the complex over the investigated temperature range. It is distinctly possible that the complex is unstable at 25°C. However a good straight line for $\log_{10}$ Pmm vs $\frac{1}{T}$ indicates (Fig.2) that possibly the complex is metastable over the temperature range at about 80°C. Hence the results obtained from PCl_5 BCl_3 complex cannot be regarded as definitive.

It may be mentioned that Chernyanev et. al.[101] have measured the vapour pressure of the complex at higher temperatures, eg. from 112 to 173°C. The plot of $\log_{10}P$ against $\frac{1}{T}$ shows a straight line but our results do not agree with their results and the value of ΔH calculated from their values is 23.0 k cal. mole^{-1} as against our value of 5.5 k cal. mole^{-1} at lower temperatures. Even at higher temperatures the value of ΔH calculated was much smaller than those obtained from calorimetric results. (eg. ΔH° and ΔH are -44.1 and-59.5 k cal. mole^{-1})

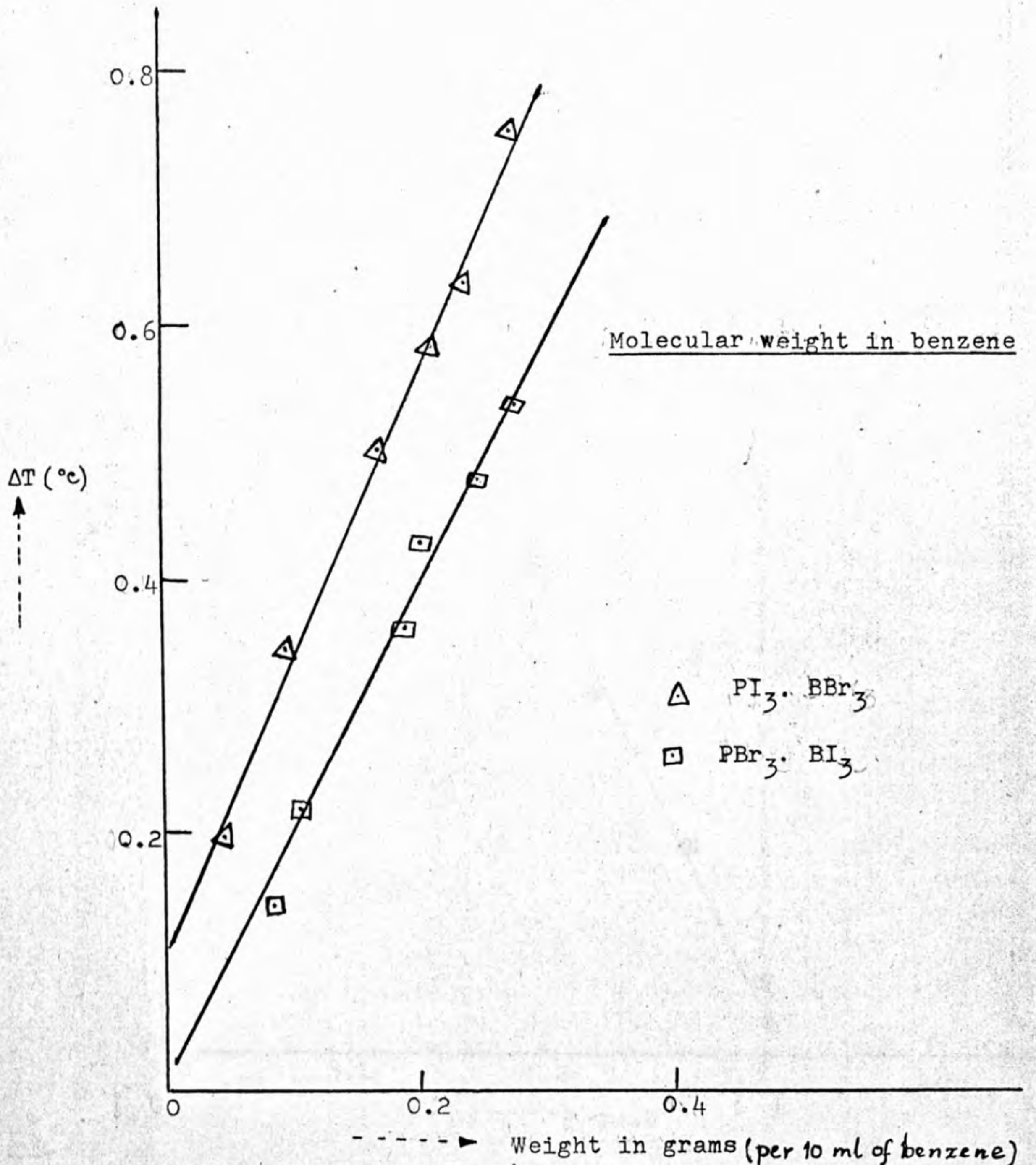
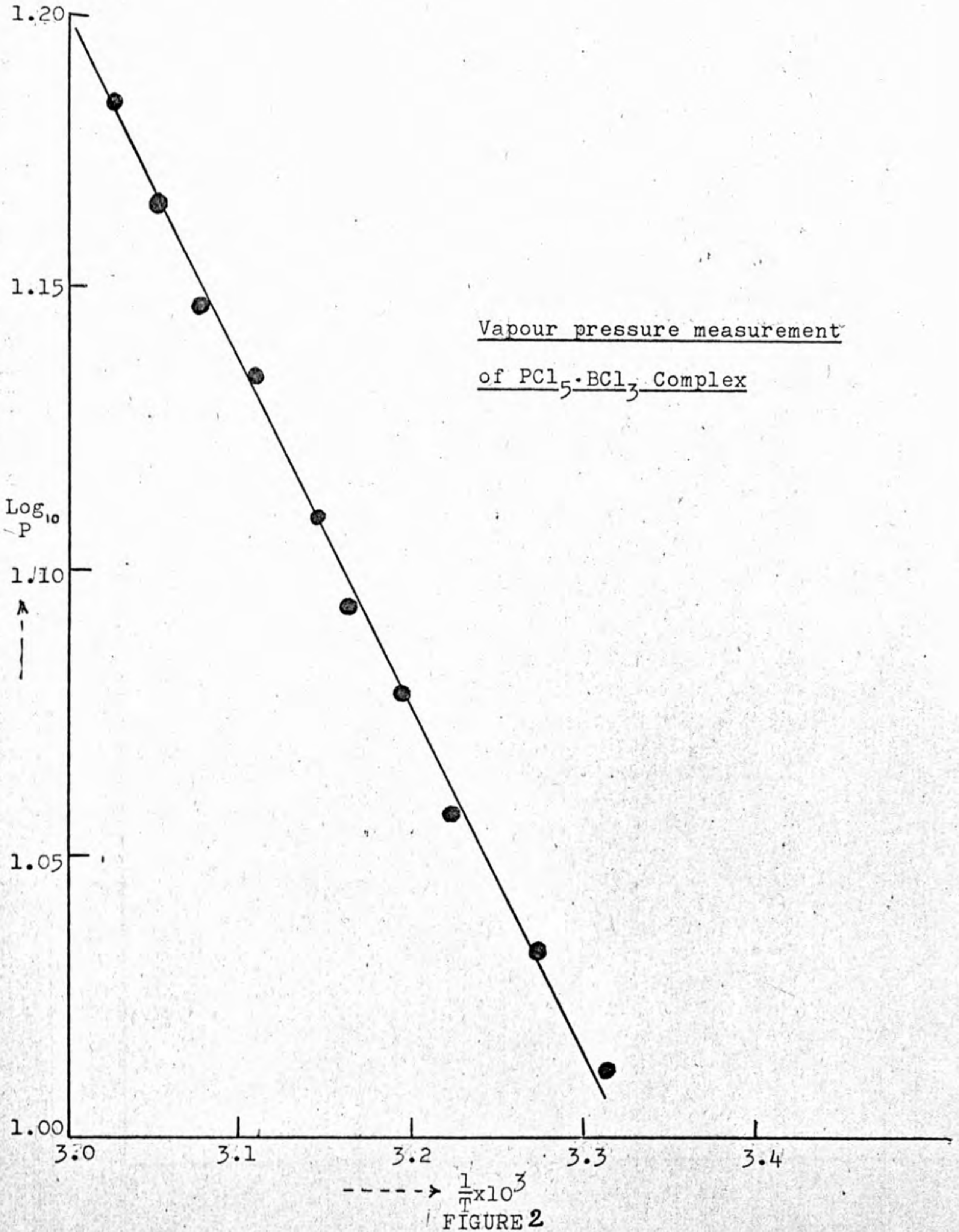
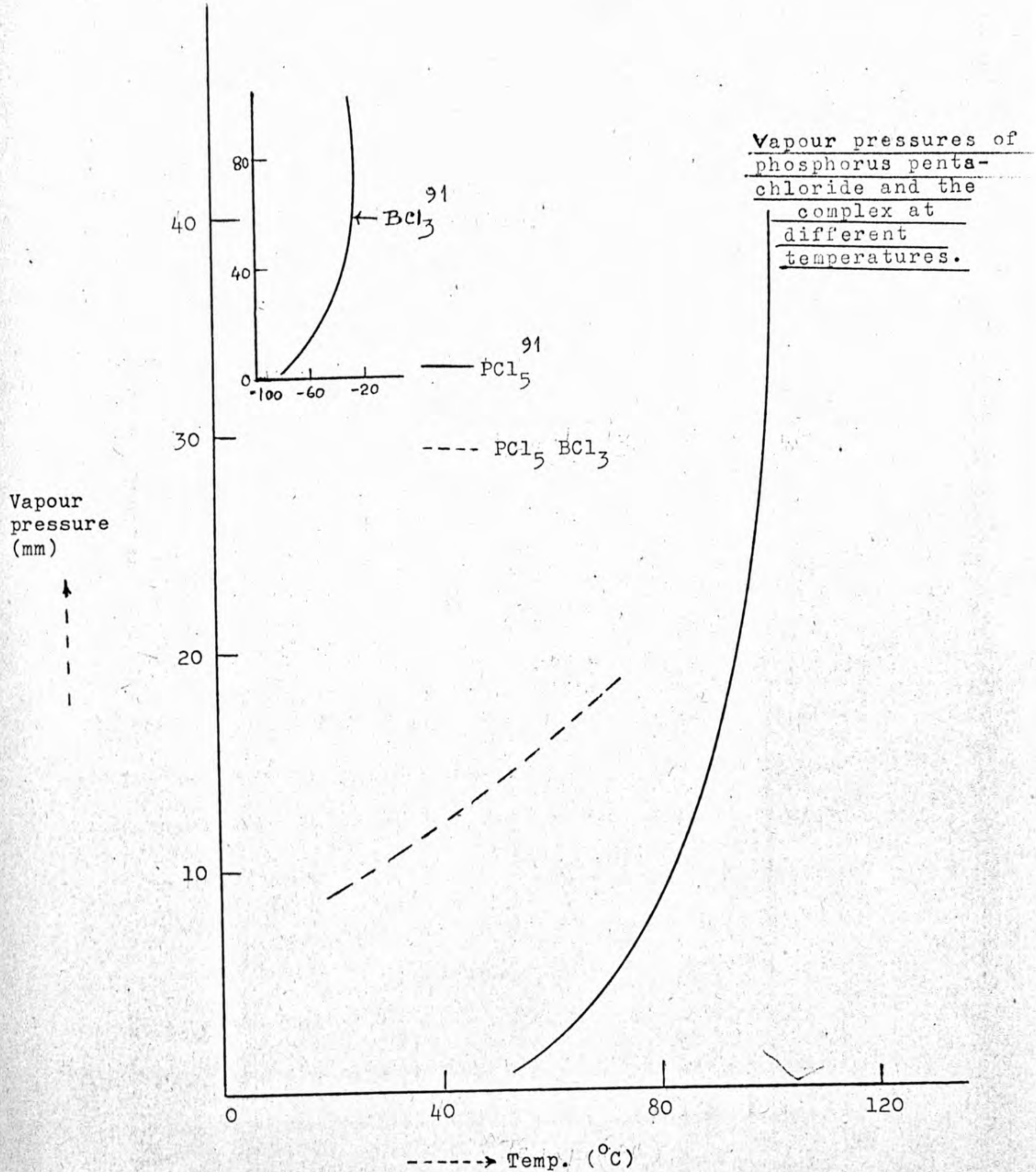

Molecular weight in benzene
ΔT (°c)
0.8
0.6
0.4
0.2
0
0.2
0.4
Weight in grams (per 10 ml of benzene)
△ $PI_3 . BBr_3$
⊡ $PBr_3 . BI_3$

FIGURE 1



Vapour pressure measurement of $PCl_5 \cdot BCl_3$ Complex

FIGURE 2



Vapour pressures of phosphorus pentachloride and the complex at different temperatures.

FIGURE 3

CHAPTER 1V

Phenyl phosphorus halides have been synthesised by different procedures and this has been described in the introductory chapter. There are no quantitative physical data on the reaction of the halides with themselves or with water. We report the first measurement of heat of hydrolysis before obtaining standard enthalpies of formation.

Thermochemistry of Phenyl Phosphorus Dihalides

The reaction investigated was:

$$PhPX_2(liq) + (n+2)H_2O(liq) = [PhPO_2H_2 + 2HX]\ nH_2O \quad \Delta Hobs$$

from which,

$$\Delta H_f^o PhPX_2(liq) = \Delta H_f^o PhPO_2H_2\ nH_2O + 2\Delta H_f^o HX\ nH_2O - 2\Delta H_f^o H_2O(liq) - \Delta Hobs$$

The standard enthalpy of formation of phenyl phosphonous acid is not yet available, hence we derive $[\Delta H_f^o PhPX_2(liq) - \Delta H_f^o PhPO_2H_2(c)]$. It has been suggested[87] that the aqueous hydrolysis of phosphonous chlorides does not proceed unambiguously according to the above equation, and does not proceed to completion, and the solution contains phenyl phosphine. The hydrolyses were performed over a wide concentration range when variation of heat evolved with concentration would indicate an equilibrium; there was no significant variation in ΔHobs. Although the hydrolysate was contaminated with phenyl phosphine (detected by odour), the concentration and hence the extent of side reaction, was small, as post hydrolysis analysis indicated 100% recovery of both the halide and phenyl phosphonous acid. The results are in the Table.1. The ancillary thermodynamic data for HCl and HBr have been described in Chapter 11. A very approximate estimate of $\Delta H_f^o PhPO_2H_2(c)$ can be obtained by considering the enthalpy change in the reaction

$PhH(g) + H_3PO_3(g) = PhPO_2H_2(g) + H_2O(g)$

in terms of bond energies, mostly taken from Hartley et.al.[49] Combining with the relevant standard enthalpies of formation, $\Delta H_f^o PhPO_2H_2(c) = 130 \pm 10$ k cal. mole^{-1}, from which we have $\Delta H_f^o PhPCl_2(liq) \sim -30$ and $\Delta H_f^o PhPBr_2(liq) \sim -8$ k cal. mole^{-1}.

TABLE 1

Compound	T(°C)	N	-ΔHobs (k cal. mole^{-1})
$PhPCl_2$	24.6	1967	42.6
	24.6	1026	41.8
	24.8	995	41.9
	24.8	1983	42.4
	24.8	1781	42.0
			Av: 42.1 ± 0.6
$PhPBr_2$	24.9	1973	41.6
	25.0	2512	41.3
	24.7	1512	42.3
	24.8	1163	41.3
	25.6	2148	42.2
	24.9	2829	41.9
			Av: 41.7 ± 0.5

$PhPO_2H_2(c) + nH_2O = PhPO_2H_2\ nH_2O \qquad \Delta H soln$

TABLE 1 (cont.)

Compound	T(^{o}C)	N	-ΔHobs (k cal. mole^{-1})
$PhPO_2H_2$	24.8	780	1.53
	24.6	832	1.48
	25.0	1090	1.29
	24.7	964	1.31
	24.9	629	1.56
	24.6	877	1.35
	24.9	881	1.52
			Av: 1.43 ± 0.2

N = mole ratio of water to compound

$[\Delta H_f^o PhPCl_2(liq) - \Delta H_f^o PhPO_2H_2(c)] = 100.3 \pm 0.6$ k cal. mole^{-1}

$[\Delta H_f^o PhPBr_2(liq) - \Delta H_f^o PhPO_2H_2(c)] = 121.7 \pm 0.5$ k cal. mole^{-1}

Thermochemistry of Diphenyl Phosphorus Halides

Diphenyl phosphorus halides hydrolyze in water to give initially a compound of the formula Ph_2POH and aqueous hydrogen halides. It is known[12] that the compound Ph_2POH is unstable and easily disproportionates to give insoluble diphenyl phosphinic acid and diphenyl phosphine according to the equation:

$$2Ph_2P - OH = Ph_2PO_2H + Ph_2PH$$

In order to avoid the contamination of hydrolysate by diphenyl phosphine aqueous hydrogen peroxide was used as calorimetric fluid so that the reaction proceeded completely according to the eqation:

$$Ph_2PX(liq) + H_2O_2(aq) = Ph_2PO_2H\ (c) + HX(aq)$$

from which,

$$\Delta H_f^oPh_2PX(liq) = \Delta H_f^oPh_2PO_2H(c) + \Delta H_f^oHX(aq) - \Delta H_f^oH_2O_2(aq) - \Delta Hobs$$

The hydrolyses were carried out in different concentration ranges in order to see whether there is any equilibrium and in both the cases there was no significant variation in observed heat change. The extent of side reactions were also very small, as post-hydrolysis analysis of the reaction indicated 99.7% recovery of diphenyl phosphinic acid. The standard enthalpy of formation of crystalline diphenyl phosphinic acid is not known and hence we have derived the expression: $[\Delta H_f^oPh_2PX(liq) - \Delta H_f^oPh_2PO_2H(c)]$. The ancillary thermodynamic data, ie. heats of formation of aqueous hydrochloric and hydrobromic acid for the calculation of the above functions have been given in the Chapter 11. The heat of formation of aqueous hydrogen peroxide due to Rossini et. al.[60] is -45.68 k cal. mole^{-1} at $N = \propto$. The heat of dilution[94] of H_2O_2 from 50 H_2O to $\propto H_2O$ is only 0.003 k cal. mole^{-1}. It is assumed that the heat of mixing of the products is negligible. The results have been recorded in the Table 1.

TABLE 1

$N^1 = 188.8$

Compound	T°C	N	$-\Delta$Hobs (k cal. mole^{-1})
Ph_2PCl	24.5	2441	21.5
	24.4	2732	21.1
	24.3	2661	21.2
	24.0	1580	22.3
	24.5	1865	22.4
	24.5	2988	22.2
	24.3	4061	22.05
			Av= 21.8 ± 0.7 k cal. mole^{-1}
Ph_2PBr	24.1	4742	21.0
	24.0	2605	20.3
	24.6	3978	20.0
	24.7	2597	21.3
	24.6	1906	20.5
	24.6	2473	21.5
	24.7	2307	21.2
	24.9	2493	21.3
	24.5	2402	20.0
			Av= 20.8 ± 0.8 k cal. mole^{-1}

N = mole ratio of water to compound

N^1 = mole ratio of water to hydrogen peroxide.

$[\Delta H^o_f Ph_2PCl(liq) - \Delta H^o_f Ph_2PO_2H(c)] = 27.5 \pm 0.7$ k cal. mole^{-1}

$[\Delta H^o_f Ph_2PBr(liq) - \Delta H^o_f Ph_2PO_2H(c)] = 37.4 \pm 0.8$ k cal. mole^{-1}

Infrared Spectra of Halophosphines

The infrared spectra of phenyl phosphorus dihalides and diphenyl phosphorus halides over the range 4000 to 400 cm^{-1} have been recorded. The bands from 1300 cm^{-1} to 400 cm^{-1} have been shown in the figures (1-5). The other bands at higher wave numbers have been recorded in the following table:

PhPF$_2$	PhPCl$_2$	PhPBr$_2$	Ph$_2$PCl	Ph$_2$PBr
1338(m.sh)	1278(v.w)	1306(v.w)	1303(v.w)	1303(v.w)
1443(s.sh)	1300(m.sh)	1338(v.w)	1324(v.w)	1324(v.w)
1546(m.sh)	1330(m.sh)	1438(s.sh)	1438(s.sh)	1425(s.sh)
1820(v.w)	1478(s.sh)	1481(w.sh)	1480(m.sh)	1486(m.sh)
2442(v.w)	1580(v.w)	1581(w.sh)	1582(v.w)	1580(w.sh)
3060(w)	3130(m.sh)	3048(m.sh)	3043(m.sh)	3045(m.sh)

w=weak, m=medium, s=strong, sh=sharp, v=very.

Far Infrared Spectra of Phenyl Phosphorus Dibromide and Dihpenyl Phosphorus Bromide

The spectrum of phenyl phosphorus dibromide was run over the range 450 to 100 cm^{-1} as a liquid film on a far infrared spectrometer constructed in this department. Bands near 388 and 409 cm^{-1} were observed and tentatively assigned to P-Br stretching modes. Similarly a broad band near 294±2 cm^{-1} in the case of diphenyl phosphorus bromide may be assignable due to P-Br stretching modes.

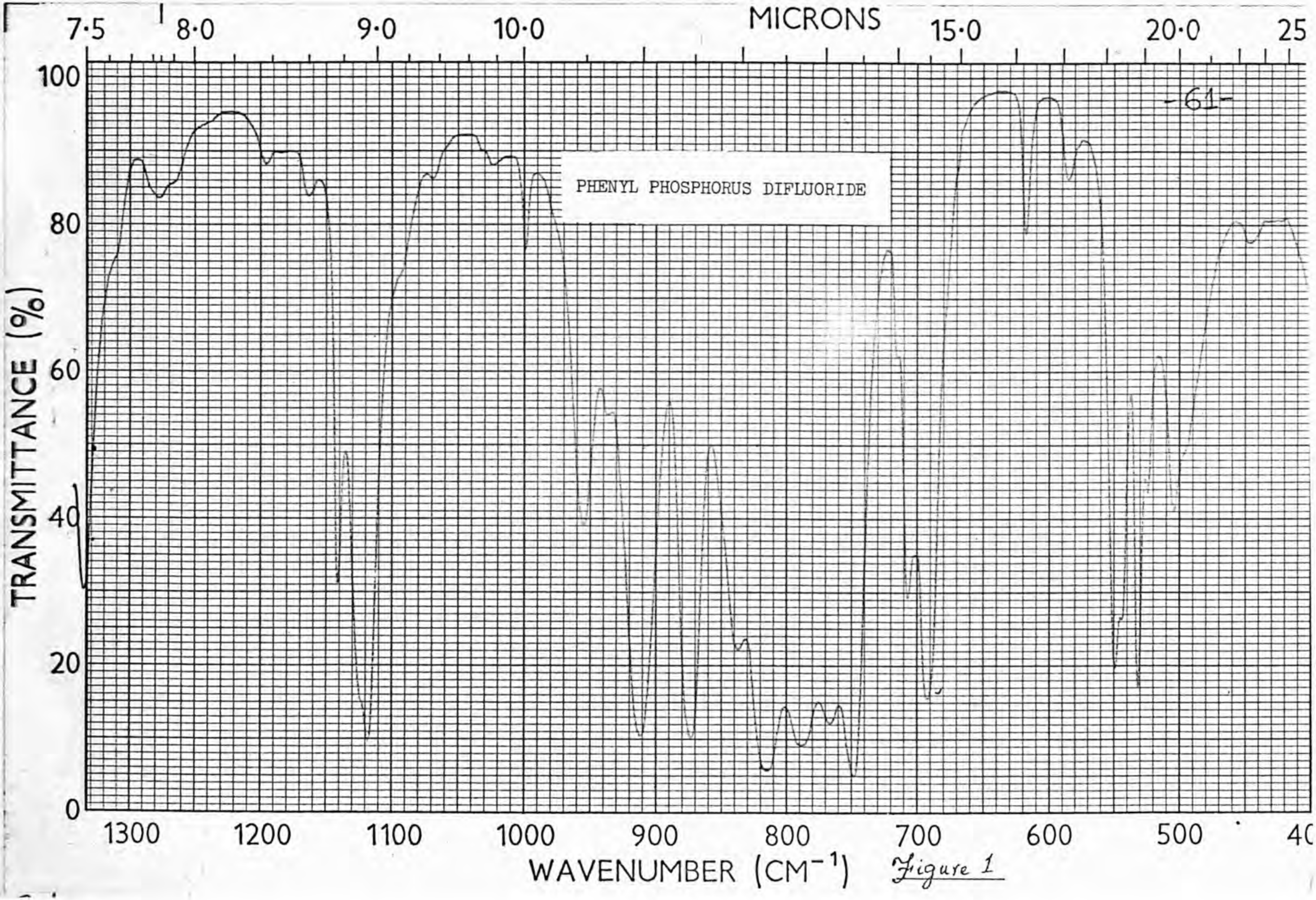

MICRONS
7·5
8·0
9·0
10·0
15·0
20·0
25
TRANSMITTANCE (%)
100
80
60
40
20
0
PHENYL PHOSPHORUS DIFLUORIDE
1300
1200
1100
1000
900
800
700
600
500
40
WAVENUMBER (CM^{-1})

Figure 1

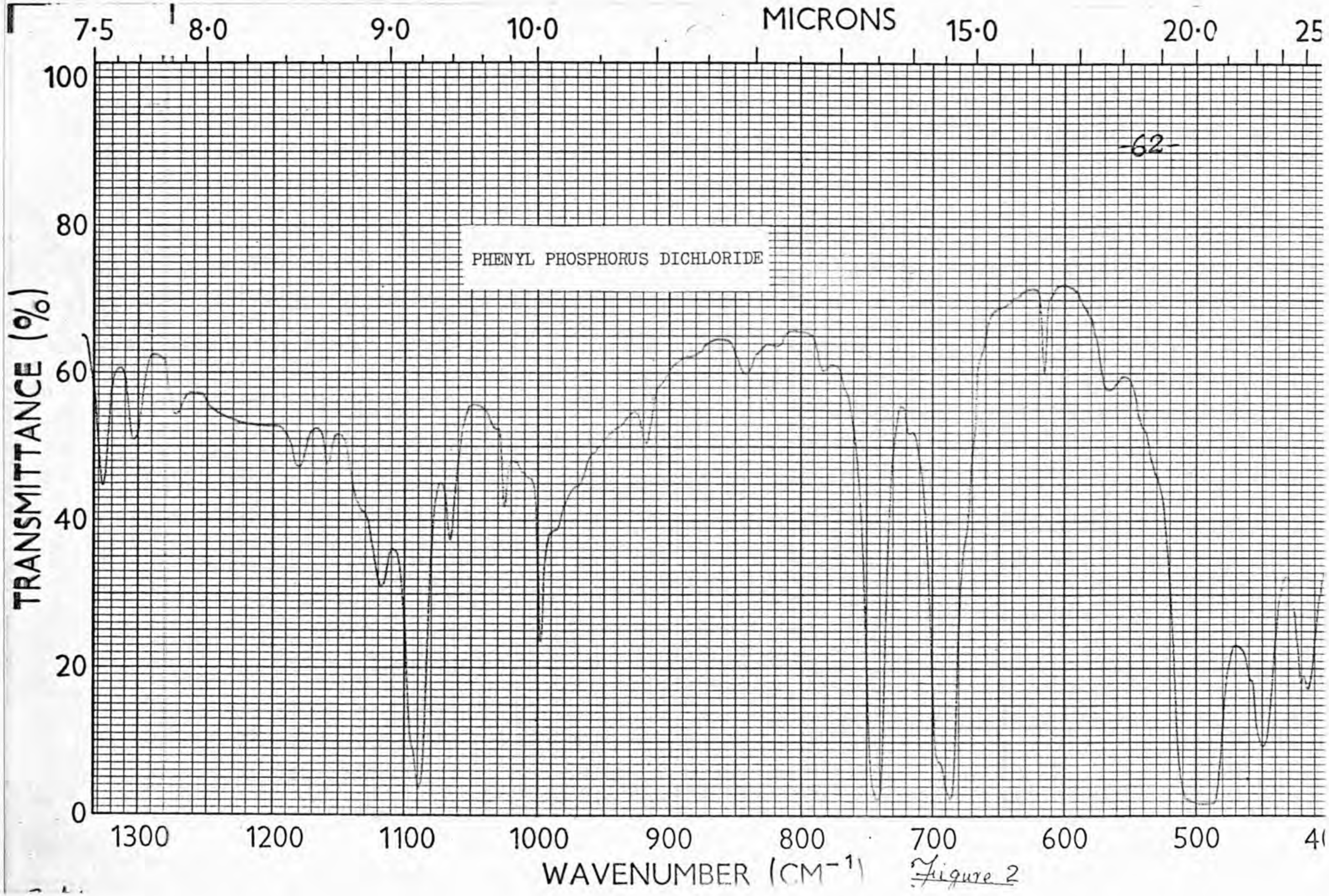

MICRONS
7·5
8·0
9·0
10·0
15·0
20·0
25
TRANSMITTANCE (%)
100
80
60
40
20
0
PHENYL PHOSPHORUS DICHLORIDE
1300
1200
1100
1000
900
800
700
600
500
4(
WAVENUMBER (CM⁻¹)

Figure 2

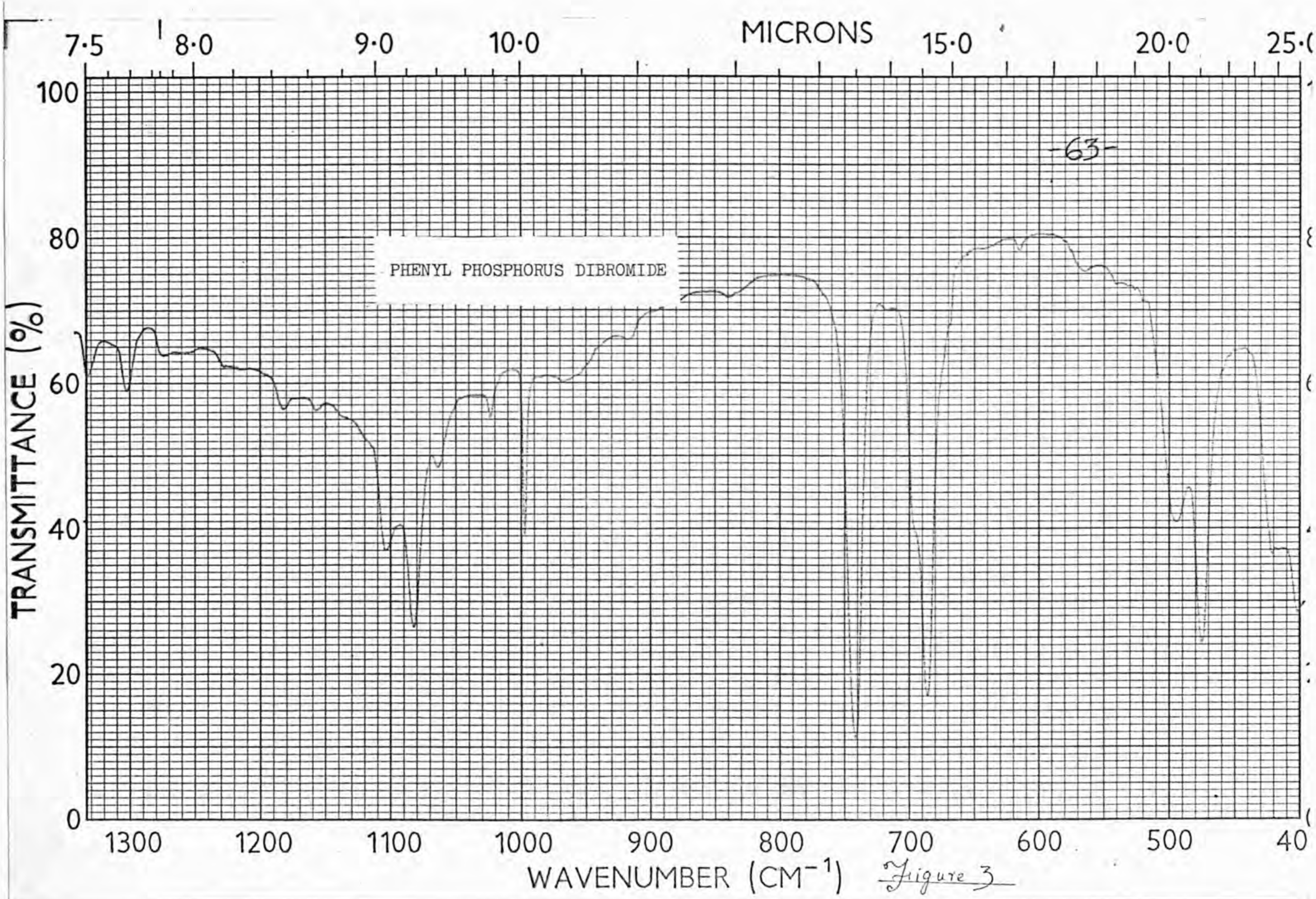

MICRONS
7·5
8·0
9·0
10·0
15·0
20·0
25·0
PHENYL PHOSPHORUS DIBROMIDE
TRANSMITTANCE (%)
100
80
60
40
20
0
1300
1200
1100
1000
900
800
700
600
500
400
WAVENUMBER (CM⁻¹)

Figure 3

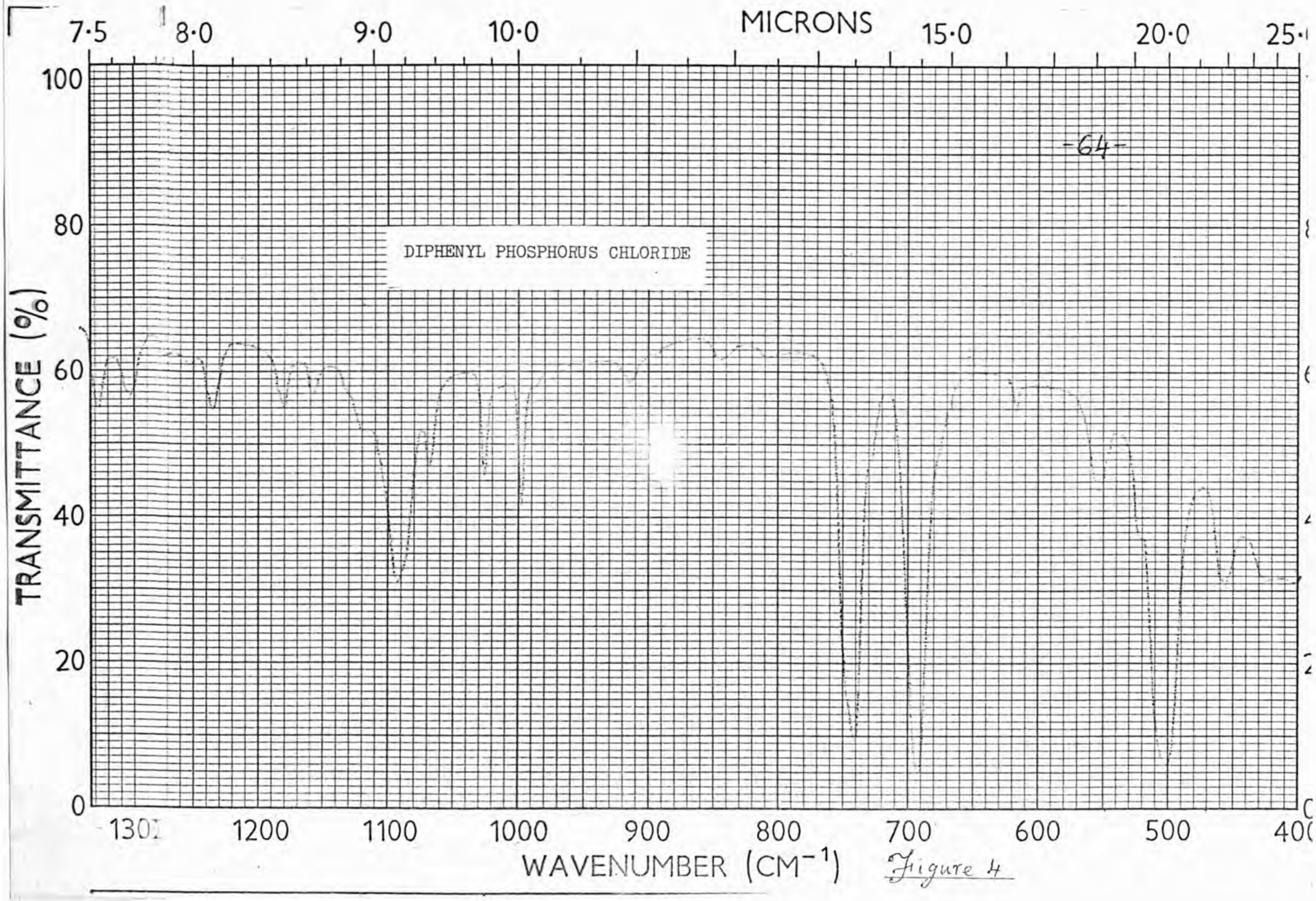

DIPHENYL PHOSPHORUS CHLORIDE
MICRONS
7·5
8·0
9·0
10·0
15·0
20·0
25·
TRANSMITTANCE (%)
100
80
60
40
20
0
130
1200
1100
1000
900
800
700
600
500
40
WAVENUMBER (CM^{-1})

Figure 4

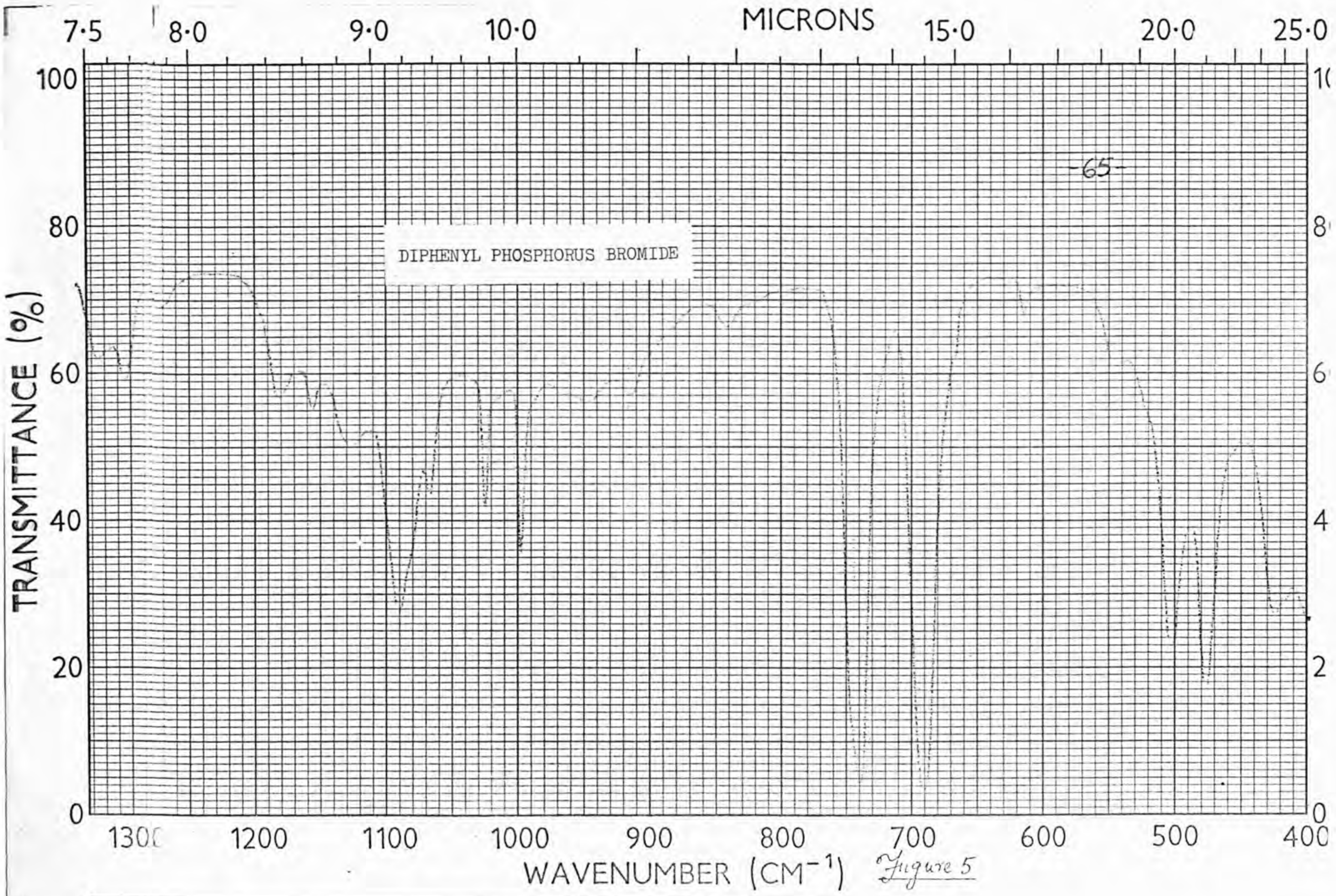
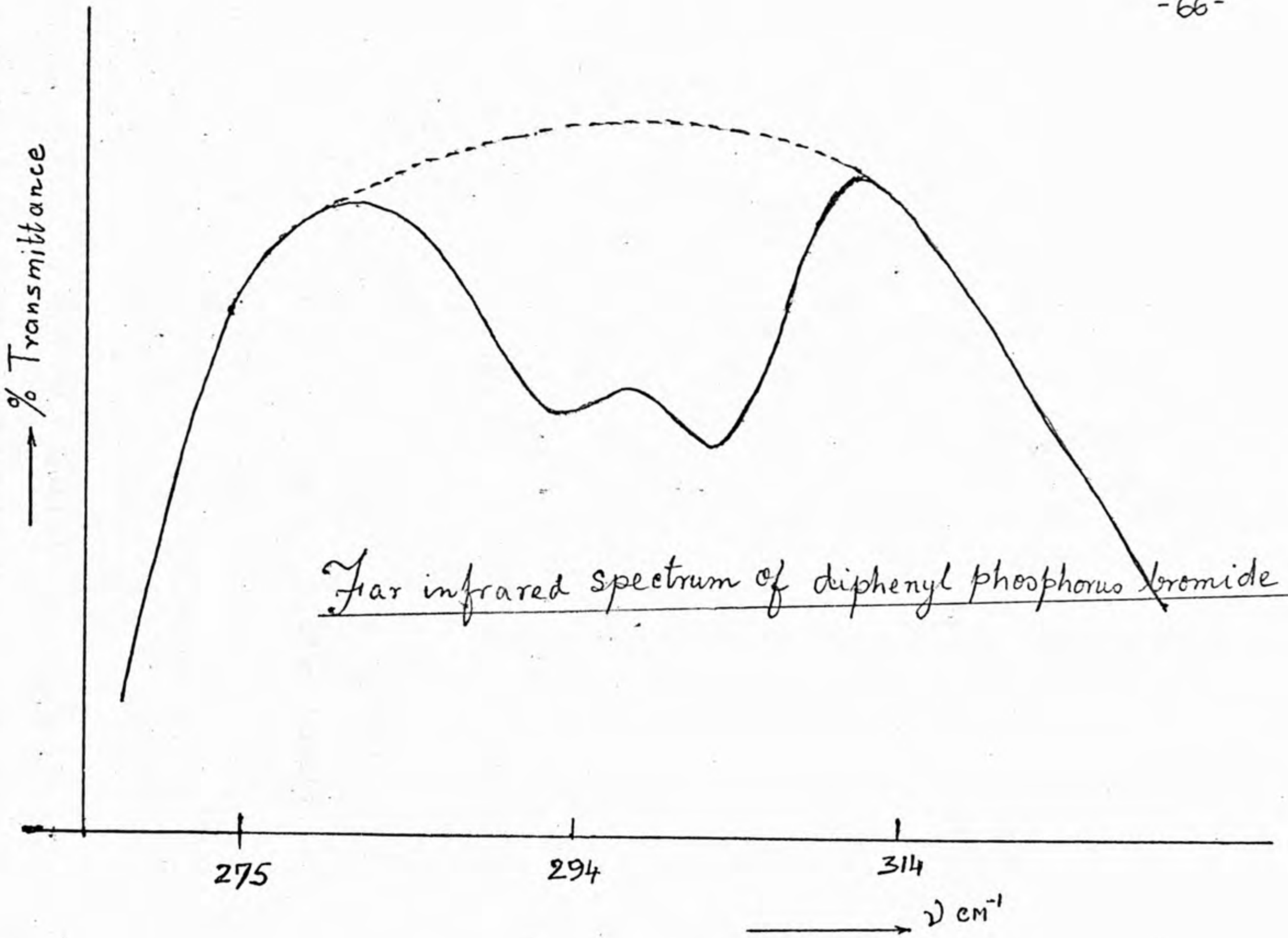

DIPHENYL PHOSPHORUS BROMIDE
MICRONS
7·5
8·0
9·0
10·0
15·0
20·0
25·0
TRANSMITTANCE (%)
100
80
60
40
20
0
WAVENUMBER (CM^{-1})
1300
1200
1100
1000
900
800
700
600
500
400

Figure 5



Far infrared spectrum of diphenyl phosphorus bromide

Figure 6

Existence of Phenyl Phosphorus Chloride Bromide:

The existence of C_6H_5PClBr has been proved from two independent experiments.

(a) Nuclear magnetic resonance measurements (^{31}P). these were made with liquid samples of phenyl phosphorus dichloride, phenyl phosphorus dibromide and a 1:1 (mole) mixture. Results are shown in the Figure 7; values of the chemical shifts, relative to 85% phosphoric acid and as external standard are as follows:

$C_6H_5PCl_2$: -161 ± 1 p.p.m.
C_6H_5PClBr : -158 ± 1 p.p.m.
$C_6H_5PBr_2$: -152 ± 1 p.p.m.

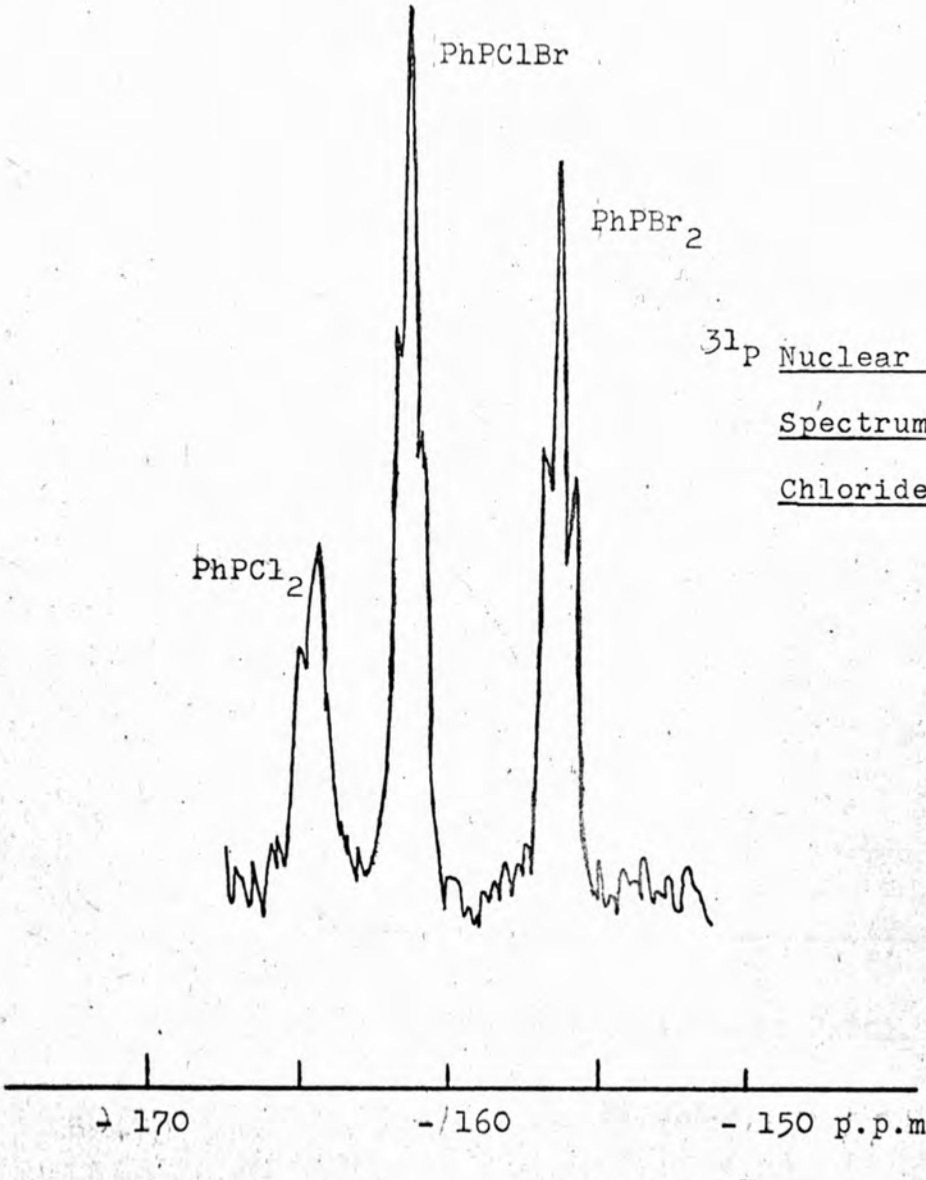
(no diamagnetic susceptibility correction applied)

The value obtained for the dichloride agrees with literature values (-161.6,[92] -166 ± 1[93]). Peak area and signal pattern remained constant over a period of time, and a sharp band at 158 p.p.m. is readily assignable to C_6H_5PClBr.

(b) Cryoscopic measurements. - these were made in a magnetically stirred cryometer using a miniature platinum resistance thermometer as temperature sensing element. Results are summarised in Figure 8; despite several attempts no eutectic could be found, though the maximum at a 1:1 mole ratio of the halide was reproducible within ± 1%. The details about the cryoscopic measurements have been described in the experimental section.

Existence of Phenyl Phosphorus Chloride Fluoride:

An attempt was also made to prove the existence of C_6H_5PClF from the study of nuclear magnetic resonance. The 1:1 mixture of $C_6H_5PCl_2$ and $C_6H_5PF_2$ showed no positive evidence for C_6H_5PClF. The spectra of $C_6H_5PCl_2$ and $C_6H_5PF_2$ were re-recorded. The value of chemical shift with respect to 85% phosphoric acid was -161 p.p.m. in the case of $C_6H_5PCl_2$ which is in agreement with the previous value. Similarly $C_6H_5PF_2$ also showed a triplet along with a quintuplet due to the presence of $C_6H_5PF_4$. This is probably because $C_6H_5PF_2$ disproportionates to give $C_6H_5PF_4$ and $(C_6H_5P)_4$ (see experimental section). On standing for few days even at -20°, a solid substance appeared and the presence of phosphobenzene in the sample has also been proved by analysis (see experimental section). Therefore the mixture, in fact, is not in equimolecular ratio due to the instability of the compound. The experiment was repeated in a different instrument(Perkin Elmer Ltd.), where there was positive evidence for $C_6H_5PCl_2$, $C_6H_5PF_4$ and $C_6H_5PCl_{4-n}Fn$ (where n = 1, 2, 3) in the mixture. In this case also, it failed to show signal for C_6H_5PClF.



^{31}P Nuclear magneticresonance Spectrum of phenylphosphorus Chloride bromide.

FIGURE 7

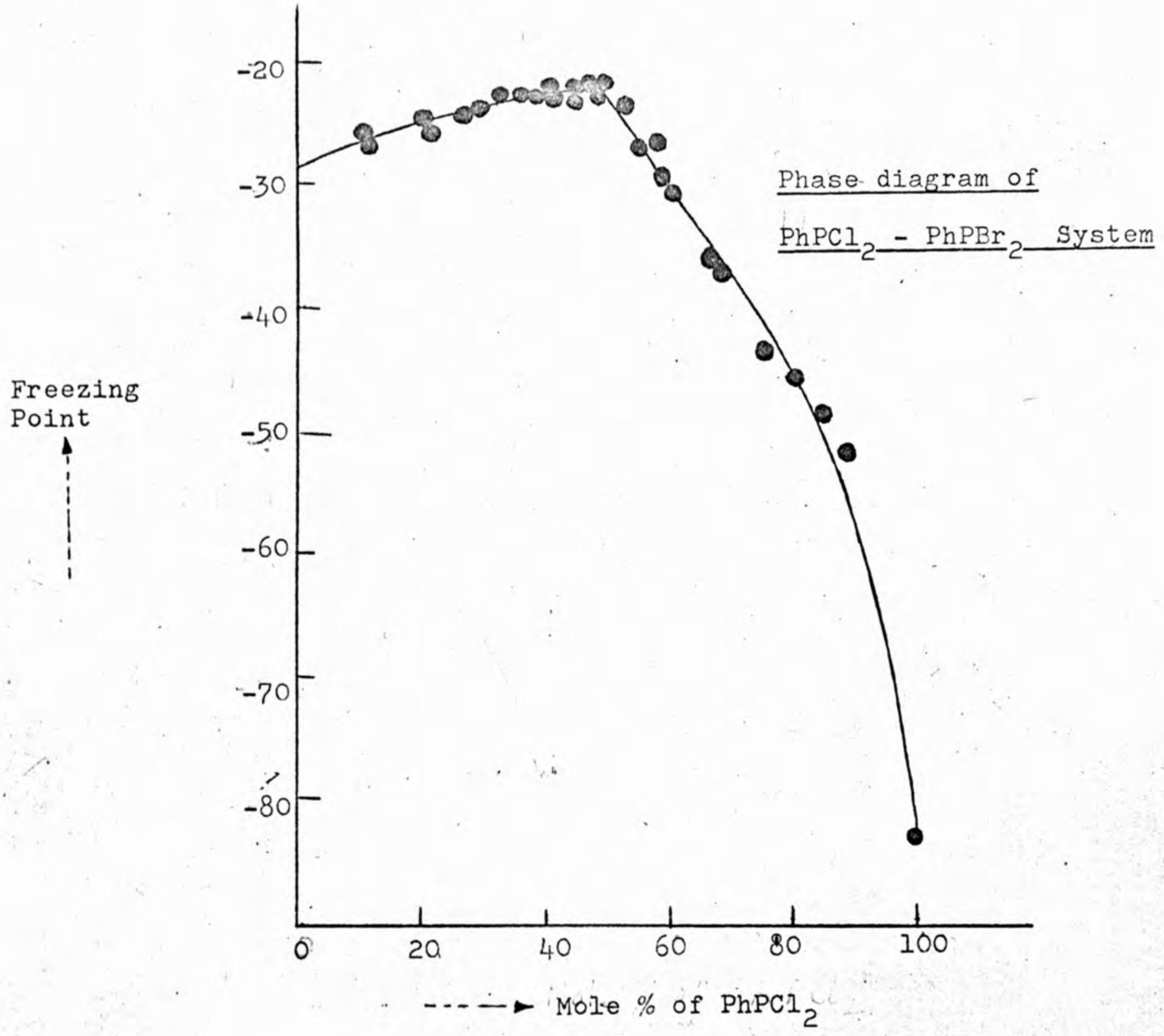

Phase diagram of
PhPCl$_2$ - PhPBr$_2$ System
Freezing Point
-20
-30
-40
-50
-60
-70
-80
0
20
40
60
80
100
Mole % of PhPCl$_2$

FIGURE 8

CHAPTER V

Syntheses

Phosphoryl Halide - Boron Halide Complexes

Phosphoryl Chloride- Boron Trichloride. This complex was synthesised by the method of Frazer et. al.[27]. This involves adding phosphoryl chloride to boron trichloride dissolved in dry methylene chloride at -80°. This solvent was used to crystallise the compound, m.p. 72 - 75° (lit[28]., 70 - 71°) (Found: B, 4.0; Cl, 78.4. Calc for BCl_6OP: B, 4.0; Cl, 78.6%).

Phosphoryl Chloride-Boron Tribromide. A similar procedure to the above was used to synthesise this adduct, m.p. 126 - 129° (lit[30]., 128°) Found: B, 2.7; Br, 60.5; Cl, 26.8%; M (cryoscopy in benzene), 400. Calc, for BBr_3Cl_3PO: B, 27; Br, 59.6; Cl, 26.4%; M, 404.3).

Phosphoryl Bromide-Boron Tribromide. A similar procedure to the above was used to synthesise this adduct, m.p. 152 - 154° (lit[30]. 150 - 154° or 150°) (Found: B, 2.1; Br, 88.9; Calc. for BBr_6PO: B, 2.0; Br, 89.4%).

Phosphoryl Bromide-Boron Trichloride. The above procedure was used to synthesise this compound, m.p. 115 - 118° (decomp)(Found: B, 2.7; Br, 60.4; Cl, 26.2%; M; (cryoscopy in benzene, 411. Calc. for BBr_3Cl_3PO: B, 2.7; Br, 59.6; Cl, 26.4%; M, 404.3.)

Phosphoryl Bromide. The method of Booth and Seegmiller[5] was used to prepare this compound, b.p. 193 - 195°, m.p. 55 - 56° (lit[5]; b. p. 193°, m. p. 56°) (Found: Br, 84.4, Calc. for Br_3OP: Br, 83.6%)

Phosphorus trihalide - boron trihalide complexes

Materials. Carbon disulfide used as solvent in the syntheses was British Drug Houses AnalaR grade, successively shaken with aqueous potassium permanganate and mercury followed by distillation immediately prior to use. The boron and phosphorus tribromides were supplied by BDH and distilled prior to use. Boron triiodide was supplied by L. Light and Co. and phosphorus triiodide (mp. 60 - 61°, lit.[3], 60.5°) was synthesised by the method of Germann and Traxler[3] and recrystallised from carbon disulfide. Handling was performed in a nitrogen-filled drybox as the compounds are sensitive to both oxidation and hydrolysis.

All complexes were synthesised by mixing equimolar quantities of the boron and phosphorus halides dissolved in carbon disulfide. The adducts were yellow solids (white, in the case of PBr_3BBr_3)and precipitated from carbon disulfide.

Phosphorus Triiodide-Boron Triiodide. This was prepared by the method of Mitchell et. al.[21], and vacuum dried; mp 250°. Calc. for PI_3BI_3: I, 94.8. Found I, 95.7%.

Phosphorus Triiodide-Boron Tribromide. This adduct was prepared by the method of Cowley and Cohen[22] and crystallised from carbon disulfide; mp. 159 - 160°; lit.[22] 160°. Calcd for PI_3BBr_3: Br, 36.2; I, 57.6; M, 662. Found: Br, 37.0; I, 56.5%; M. (by cryoscopy in benzene), 651.

Phosphorus Tribromide-Boron Tribromide. The method of Tarible[95] was used to synthesise this adduct; mp 59 - 61°, lit.[95] 61°. Calcd for PBr_3BBr_3: Br, 91.9. Found: Br, 91.0%.

Phosphorus Tribromide-Boron Triiodide. The methodof Armington et. al.[20], was used to prepare this adduct; mp. 178 - 182°. Calcd. for PBr_3BI_3: Br, 36.2; I, 57.6; M, 662. Found: Br, 37.2; I, 55.7; M, (by cryoscopy in benzene), 646.

PCl_5BCl_3 Complex : This was synthesised[5] by direct combination of boron trichloride and phosphorus pentachloride in a carbon tetrachloride as solvent.

Phosphorus pentachloride (18.0g) was dissolved in carbon tetrachloride (500 ml, dried over anhydrous calcium chloride). This was then filtered to remove insoluble matters. Boron trichloride was then bubbled into it and white precipitate formed. This process was continueduntil the solution was saturated. The precipitate was then filtered off, washed with solvent and then vacuum dried. Found: Cl, 87.3; B, 3.4; Calc for BCl_8P, Cl, 87.1; and B, 3.3%. The compound sublimes[5] completely in the sealed tube above 300° and the vapour is greenish yellow indicating dissociation into chlorine, phosphorus trichloride and boron trichloride.

Phenyl Phosphorus difluoride: This was synthesised by the procedure of Schmutzler[96]. A suspension of AnalaR NaF (50.4g, dried for 5 hours at 600°) in sulfolane (120ml) was made followed by the addition of phenyl phosphorus dichloride (71.6 g) with stirring for approximately 30 min. It was then heated with stirring for an hour at 140 -180°. The compound was then vacuum distilled using a column packed with glass beads and then finally redistilled (bp. 30 - 31°/11 - 12 mm, lit. bp.[96] 30 -31°/ 11mm.) . Immediately after synthesising the compound, the molecular weight was deterimed. (Found: M, 149; Calc. for $C_6H_5F_2P$: M, 146). On standing for one month at 0°, a solid substance precipitated which was filtered and recrystallised from methanol (mp. 150 - 152°; Found: C, 66.6; H, 4.5; P, 28.8; Calc for C_6H_5P: lit mp.[8] = 150°, C, 66.6; H, 4.6; P,28.7%). The results suggest that phenyl phosphorus difluoride is unstable at ordinary temperature and disproportionates according to the equation: $2n\ C_6H_5PF_2 = n\ C_6H_5PF_4 + (C_6H_5P)_n$.

Phenyl Phosphorus Dichloride: Benzene (205g.) was heated with phosphorus trichloride (109g.) under reflux for 30 hours in the presence of anhydrous aluminium trichloride (43g.) in a three-necked flask fitted with a rubber-sealed glass stirrer, thermometer, and a reflux condenser. A stream of nitrogen was passed throughout the course of the reaction and 86% H_3PO_4 (15 ml.) was added with vigorous shaking of the mixture in the dry box. The precipitate was then filtered using glass wool and the excess benzene was removed by distillation. Finally the compound was vacuum distilled and purified by redistillation.

(Yield, 12.5%, b.p. 130°/18 mm; Found: $n_D^{25} = 1.5951$; $d_4^{20} = 1.319$; Cl, 39.8; Calc. for $C_6H_5Cl_2P$; Cl, 39.6%)

Phenyl Phosphorus Dibromide:

(a) Bromination of phenyl phosphine:- phenyl phosphine was first synthesised by the reduction of phenyl phosphorus dichloride by lithium aluminium hydride. Phenyl Phosphorus dichloride (48.9 g.) in ether (125 ml.) was added dropwise with stirring in a flask as described before containing lithium aluminium hydride (10 g.) in ether (200ml.). The repulsive and penetrating odour was noticed from the beginning of the reaction. Stirring was continued for an hour, after which water (26 ml.) was added, and the mixture finally refluxed for 2 hours. The liquid was then filtered and excess solvent was removed by distillation. The residual liquid was then dried over anhydrous calcium chloride, decanted and finally distilled (yield: 53.2%; b.p. 159 - 160°, Found: C, 65.6; H, 6.3; P, 28.2; Calc. for C_6H_7P : , C, 65.45; H, 6.4; P, 28.2%).

A solution of bromine (65 g.) in chloroform (50 ml) was added to a solution of phenyl phosphine (27 g.) in chloroform (70 ml.) as before with stirring. The temperature was maintained below 20°C and a stream of nitrogen was passed during the reaction. The excess chloroform was distilled and the compound was separated by distillation and finally redistilled. (Yield: 22.3%, b.p. 132°/ 13 - 14 mm.; Found: $n_D^{25} = 1.6534$; $d_4^{20} = 1.872$; C, 26.65;

H, 1.8; Br, 59.4; P, 11.5; Calc. for $C_6H_5Br_2P$; C, 26.9, H, 1.9; Br, 59.7; P, 11.6%).

(b) Method of Kuchen and Grunewald[11]: Phenyl phosphorus dichloride (179 g.) was heated with phosphorus tribromide at 100° - 200° for 2 hours. The initial fractions up to 175°, containing both phosphorus trichloride and chlorobromides, were removed at ordinary pressures. The excess phosphorus tribromide was then removed by distillation under vacuum and the compound was separated by distillation. (Yield: 78.3%, b.p. 126 - 128 / 11mm; Found: Br, 59.3: Calc. for $C_6H_5Br_2P$; Br, 59.7%).

(c) Friedel-Crafts reaction: Benzene (78 g.) was added to phosphorus tribromide (271 g.) in the presence of anhydrous aluminium tribromide (26.6 g.). The reaction mixture was then refluxed for 12 hours with a continuous stirring. Air inside the flask was removed by passing a continuous stream of nitrogen. The reaction mixture was then cooled and filtered. The unreacted benzene and fractions boiling up to 175° were removed by distillation at ordinary pressure followed by the removal of phosphorus tribromide at reduced pressure. The compound was then vacuum distilled and purified by redistillation. (Yield: 16.8%; b.p. 132 - 134 / 14 mm; Found: C, 26.7; H, 1.7; Br, 59.2; P, 11.45; Calc. for $C_6H_5Br_2P$; C, 26.9, H, 1.9; Br, 59.7; P, 11.6).

Phenyl Phosphonous Acid: Dichlorophenyl phosphine (1 vol) was added to absolute alcohol (5 vol.) with stirring, subsequently diluted with water (2 vol.) and boiled for 5 to 10 minutes. After that benzene (2 vol.) was added. The excess water and benzene was removed by distillation. The solution was then concentrated and the compound after separation was purified by recrystallisation from benzene (m.p. 85 - 86°, Found: C, 50.8; H, 5.1; Calc. for $C_6H_7O_2P$; C, 50.7; H, 5.0%). The compound after successive recrystallisations showed 99.6% pure which was checked by cerimetric oxidation method.

Diphenyl Phosphorus Bromide: Diphenyl phosphorus chloride used was of commercial grade (Aldrich Chemical Co.) and was purified by distillation (b.p. 178 - 180° / 16 mm, lit[12]. b.p. 183 - 184° / 18 mm.). Diphenyl phosphorus bromide was prepared by equilibrating diphenyl phosphorus chloride with phosphorus tribromide. Diphenyl phosphorus chloride (68.0 g) was heated with phosphorus tribromide(83.4 g) at 100 - 200° for about 2 hours. This was then continuously distilled to remove phosphorus trichloride and phosphorus chloride bromides. The excess phosphorus tribromide was then removed by distillation under reduced pressure and the compound was separated by distillation and finally redistilled. (b.p. 142 - 144 / 38 mm, lit. b.p.[11] 140 - 141 / 35 mm, Found: C, 53.6; H, 3.84; Br, 30.8; Calc for $C_{12}H_{10}BrP$, C, 54.3; H, 3.77; Br, 30.2%).

Experiments and Techniques

(2) Calorimeter: A typical "Dewar vessal" type of calorimeter[100] with its parts (Figs 1 - 4), which was used for the hydrolytic reaction, has been described. The potentiometer was a Tinsley type 3387B used in conjunction with a scal lamp galvanometer (Pye & Co. Ltd) and was accurate to ± 0.00005V. The standard cell used with the potentiometer was a Weston Cadmium cell. The electric timer was supplied by Precision Scientific Co. and was accurate to ± 0.05 sec. The whole calorimeter was monitored with a miniature platinum resistance thermometer (100 ohm. Degussa) coupled to a six inch potentiometric recorder (Elliot) accurate to ± 0.01°C. Samples were weighed on a balance sensitive to ± 0.00005g.

The main principle of calorimetry is to measure the temperature change produced by a known weight of sample undergoing reaction or solution and then to calibrate by introducing a known amount of heat which is electrically measured (the Substitution method). Finally, the temperature change is again measured and so by comparison of the two, the heat change per unit mass may be calculated.

The "Dewar vessal" has ground glass flanges and the flanged top has sockets with ground glass joints. The stirrer was mounted in the central joint, the ampoule breaker in another and both of them via ground glass joints and precision bore tubing so that the central rod could be rotated. The other holes carried the Thermistor (F.23 type, Standard Telephones and Cables) mounted on a B_{10} leak, the heater (made of nichrome wire) for calibration and the platinum resistance thermometer. The remaining hole was available for gas inlet or outlet. The samples were contained in fragile glass ampoules mounted on the end of a prcision rod by rubber bands. The ampouls was broken by rotating into the stirring blades and resistances were recorded against time.

The resistance - temperature relationship of a thermistor may be written:

$$R = A.\ \exp\left(\frac{B}{T}\right) \qquad (1)$$

where R = Resistance in ohms.

T = Temperature in $^{\circ}K$

and, A and B = thermistor constants.

In the endothermic experiment (Fig. 5), the two temperature changes ΔT_1 (reaction temperature change) and ΔT_2 (calibration temperature change) produced by a heater) may be calculated from the equations such as:

$$\Delta T_1 = \frac{B\left\{\text{Log}\ \frac{R_2}{A} - \log \frac{R_1}{A}\right\}}{\log \frac{R_1}{A}\ \ \log \frac{R_2}{A}} \quad (2) \qquad \Delta T_2 = \frac{B\left\{\log \frac{R_3}{A} - \log \frac{R_4}{A}\right\}}{\log \frac{R_3}{A}\ \ \log \frac{R_4}{A}} \quad (3)$$

$$\frac{\Delta T_1}{\Delta T_2} = \frac{\log \frac{R_2}{A} - \log \frac{R_1}{A}}{\log \frac{R_1}{A}\ \ \log \frac{R_2}{A}} \Bigg/ \frac{\log \frac{R_3}{A} - \log \frac{R_4}{A}}{\log \frac{R_3}{A}\ \ \log \frac{R_4}{A}} \qquad (4)$$

For an endothermic reaction (Fig. 5) if it is assumed that $T_1 \sim T_4$ and $T_2 \sim T_3$, then equation (4) reduces to:

$$\frac{\Delta T_1}{\Delta T_2} = \frac{\log \frac{R_2}{R_1}}{\log \frac{R_3}{R_4}} \qquad (5)$$

The error involved when T_1 and T_4 or T_2 and T_3 differ by about 0.3°C by using equation (5) was within ± 0.5%. The observed enthalpy change is:

$$\Delta H\text{obs (Cal g}^{-1}) = \frac{\text{electrical energy (in Joules)} \times \Delta T \text{ reaction}}{\text{J x wt of sample (in g.)} \times \Delta T \text{ calibration}} \qquad (6)$$

Considering the circuit in the Fig. 6, the electrical energy may be calculated in the following manner. The positions A, B, and C are the potential probe points. The potentials recorded experimentally being that across standard V_s and that across smaller component of the potential divider V_H.

$$i = i_1 + i_2 = \frac{V_s}{R_s} \quad \therefore \quad i_1 = \frac{V_s}{R_s} - i_2 = \left[\frac{V_s}{R_s} - \frac{V_H}{R_2}\right]$$

But $V_{R_1} + V_{R_2} = V_R + V_r$

$$V_R = V_{R_1} + V_{R_2} - V_r = \frac{R_1 V_H}{R_2} + V_H - \frac{V_R}{R}\, r$$

So, $$V_R = \left[\frac{R}{r+R}\right] V_H \left[\frac{R_1 + R_2}{R_2}\right] \qquad (7)$$

$$\text{Power} \doteq i_1 V_R = \left[\frac{V_s}{R_s} - \frac{V_H}{R_2}\right]\left[\frac{R}{r+R}\right] V_H \left[\frac{R_1 + R_2}{R_2}\right]$$

$= \left[V_s - \frac{V_H}{10} \right] \text{ x f x } V_H \text{ x } 11$; $\{$where $R_s = 1$ ohm, $R_1 = 100$ ohm, and $R_2 = 10$ ohm.$\}$

So $f = \frac{R}{r+R}$ and Power $= 11\, V_H \left[V_s - \frac{V_H}{10} \right]$ watts

$$\text{Electrical energy} = 11\, V_H \left[V_s - \frac{V_H}{10} \right] t \text{ joules} \qquad (8)$$

The complete expression for the enthalpy change comes out to be;

$$\underset{(\text{k cal.mole}^{-1})}{\Delta H} = \frac{f \text{ x } 11V_1 \left(V_s - \frac{V_H}{10}\right) \text{M.t} \left[\log \frac{R_2}{R_1} \Big/ \log \frac{R_1}{A} \log \frac{R_2}{A} \right]}{10^3 \text{ x J x wx} \left[\log \frac{R_3}{R_4} \Big| \log \frac{R_3}{A} \log \frac{R_4}{A} \right]}$$

f = correction factor, M = molecular weight.

t = time of heating in secs, w = weight of sample in gm.

The resistances R_1, R_2, R_3 and R_4 were calculated by utilising back extrapolation method as has been shown in the Figure 7. The thermal leakage calculated[102] by "equal areas" method is reproducible within 0.5% accuracy. Results have been defined in terms of thermochemical calorie, i.e. 1 thermochemical calorie = 4.1840 abs. Joules.

The precision and accuracy of the calorimeter was checked by two standard reactions: (a) dissolution of potassium chloride in water ΔH ($T = 25^\circ C$, $N = 200$) $= 4.23 \pm 0.03$ (mean of 5 determinations) and (b) neutralisation of tris-(hydroxy methyl) amino methane in 0.1N HCl, ΔH ($T = 25^\circ$, $N = 600$) $= -7.15 \pm 0.05$ (mean of 7 determinations)

The literature data for these reactions are (a) 4.206[97], N = 200, T = 25°C, and (b) -7.104[98], N = 1330, T = 25°C. The experiment (b) was again repeated and the following results were obtained:

T	N	$-\Delta H$(k cal. mole^{-1})
24.9	554	-7.124
25.0	682	-7.102

The detailed calculation of one experiment (PI_3 BI_3Complex) has been shown.

Time (Minutes)	Reaction	Calibration
0	3261.9	3247.8
½	3261.6	3247.9
1	3261.5	3248.1
1½	3261.3	3248.2
2	3261.1	3248.3
2½	3261.0	3248.3
3	3260.5	3248.5
3½	3260.5	3248.7
4	3260.3	3248.8
4½	3260.1	3248.9
5	3260.0	3249.0
5½	3260.0	3240.0---Heater on
6	3259.8	3231.1
6½	3259.5	3224.0
7	3259.2 Ampoule broken	3214.0
7½	3245.1	3205.1
8	3235.5	3197.0
8½	3230.0	3185.0---Heater off
9	3225.0	3173.0
9½	3219.0	3164.5
10	3214.2	3159.9
10½	3212.0	3156.1
11	3211.5	3157.9
11½	3208.4	3158.8
12	3208.0	3159.9
12½	3207.8	3160.9
13	3207.6	3162.2
13½	3207.7	3163.1
14	3207.8	3164.7
14½	3207.9	3165.3
15	3208.0	3165.8

$$\left.\begin{array}{l} R_1 = 3259.5 \text{ ohms.} \\ R_2 = 3206.0 \text{ ohms.} \\ R_3 = 3249.0 \text{ ohms.} \\ R_4 = 3150.5 \text{ ohms.} \end{array}\right\} \quad \text{Calculated by back extrapolation method.}$$

$\Delta T = 0.4775$, $\Delta T^1 = 0.8974$, Since $B_{10} = 1.338 \times 10^2$ and $A = 1.053 \times 10^{-1}$. $f = 0.985$, Power = 2.8264, time = 174 secs. and $w = 0.4446$.

$$\therefore \Delta H = \frac{0.4775 \times 2.8264 \times 174 \times 802.8 \times 0.985}{0.8949 \times 4.184 \times 0.4446 \times 10^3} \text{ k cal./mole}$$

$$= 111.7 \text{ k cal./ mole.}$$

(3) <u>Cryoscopy and Phase Diagram Studies</u>: The cryoscopic measurements were carried out in a cryometer[99] having an automatic magnetic stirring device inside the cell. The temperature inside the cell was determined by means of a platinum resistance thermometer which was calibrated before use at different temperatures varying from +5 to -95° in different slush baths. The liquid was injected into the cell with the help of a repeating syringe (Jencon's Scientific Ltd.) through the side arm of the cryometer which was fitted tightly with a subaseal (made by Griffin and George Co.). Each injection was reproducible within ±1%. The whole apparatus was checked by studying a known system[103], eg. chloroform-mesitylene. A weighed amount of dibromo compound was placed in a cryometer and a known amount of dichloro compound was added from the syringe

and the m.p. of the resulting mixture was determined as before. The experiment was repeated in the reverse manner During the molecular weight determination, the introduction of the complex into the cryometer was done through the side arm in a syringe under nitrogen atmosphere.

(4) Vapour Pressure Measurements: The dissociation pressures were measured in a vapour tensiometer. After placing the sample into the apparatus which already contained mercury in the manometer, the open limbs were connected to a rotary vacuum pump and the apparatus was sealed under vacuum (0.1 mm of Hg). The chamber was then surrounded by a bath which could be maintained at various temperatures. The pressure differences were noted with the help of a cathetometer, the accuracy of which is 0.001 of a mm. The temperature of the bath was accurate to $\pm$ 0.1°C. The reliability of the technique was checked by measurement of vapour tension of water.

(5a) Elemental Analysis: The halogen analyses were carried out by Volhard's technique. In some cases, analyses were performed by silver nitrate titrations, using adsorption indicator. Boron was analysed by acid alkali titrations. Carbon, hydrogen and phosphorus were analysed either by Mr. Bernhardt, Max Planck Institute or Messrs. Weiller and Strauss, Oxford.

(b) Solvents: Benzene and ether were dried over sodium wire. Sulfolane was purified by distillation under vacuum (b.p. 155 - 156°/ 12 - 14 mm. Hg, lit. b.p.[104] 283°/760mm) and then dried over sodium wire. Chloroform (b.p. 60-61°C) was purified by distillation. Methylene chloride, cyclohexane, carbon tetrachloride and chloroform was dried[105] over anhydrous calcium chloride.

(c) Handling: The moisture and water sensitive compounds were handled in nitrogen (oxygen free) filled glove box.

(6) Spectroscopy: Spectra of phosphoryl halide - boron halide complexes were recorded from 2000 - 400 $cm.^{-1}$ on a Unicam SP 100. The spectra of phenyl phosphorus halides were recorded on Perkin-Elmer 337 model and the far infrared spectra of phenyl phosphorus bromides were run as a liquid film on polythene plates on a far infrared spectrometer constructed in this department.

The 31p nuclear magnetic resonance spectra were recorded with a Perkin-Elmer spectrometer at 16.19 Mc/sec using phosphoric acid as external standard.

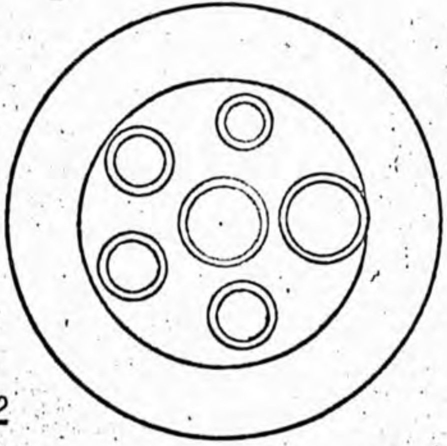


FIGURE 2

FIGURE 3

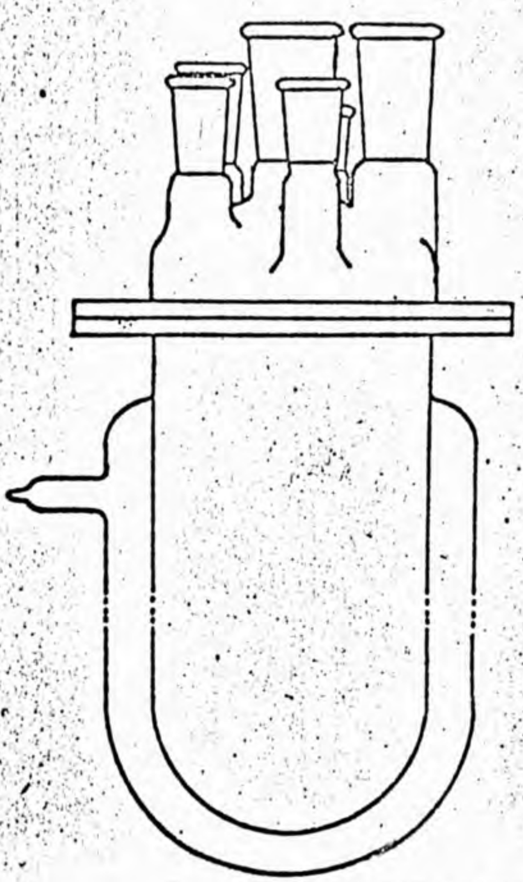
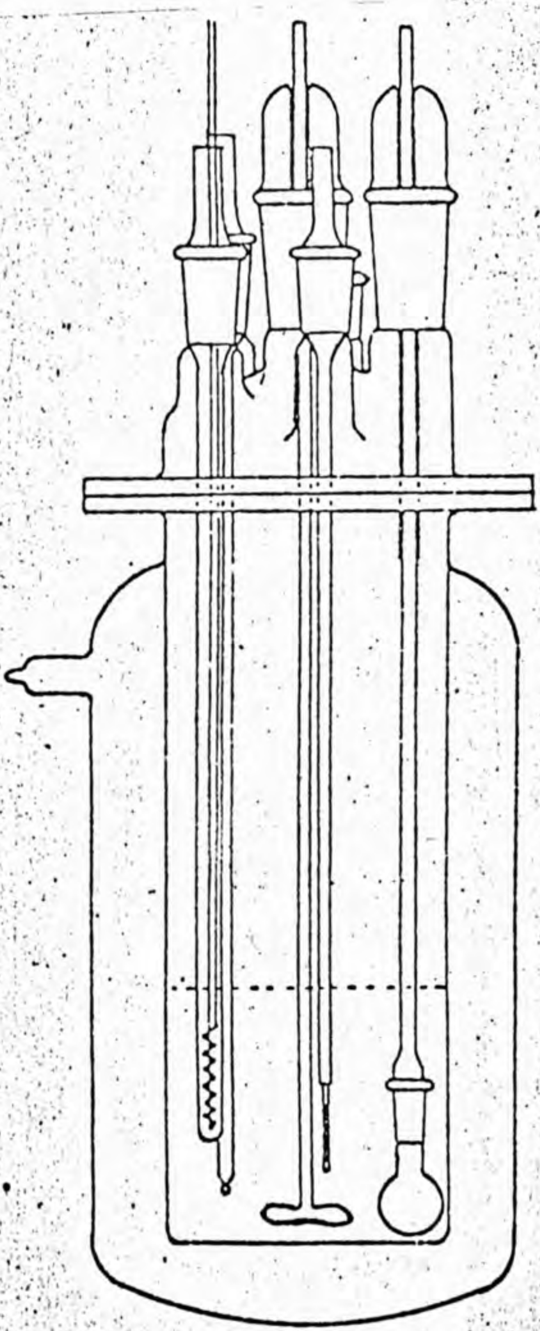


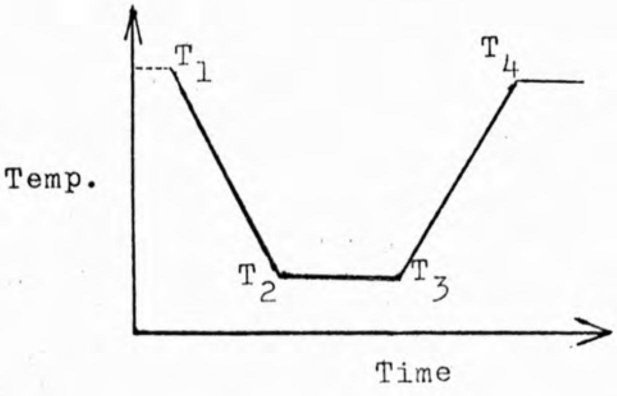
FIGURE 1

Calorimeter and its parts



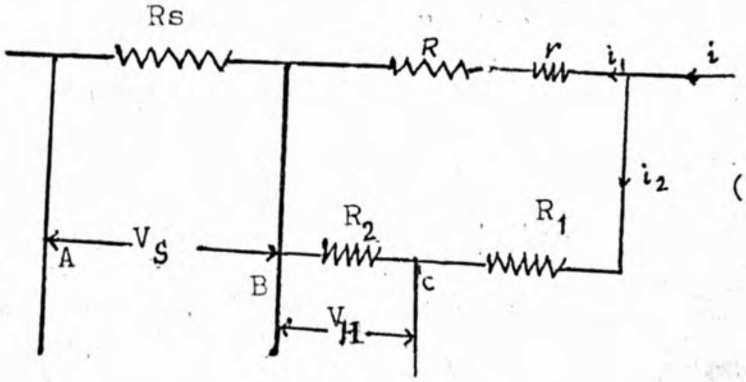
Calorimeter loaded

FIGURE 4

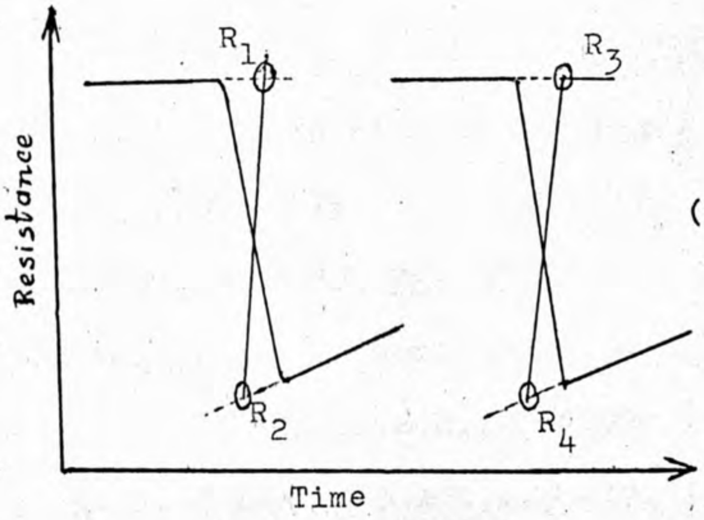


(Fig. 5)

Time - Temperature plot of an endothermic reaction



(Fig. 6)



(Fig. 7)

Resistance - Time plot of an exothermic reaction

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The Thermochemistry of Some Phosphoryl Halide–Boron Halide Complexes

By Arthur Finch, P. J. Gardner, and K. K. Sen Gupta

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The Thermochemistry of Some Phosphoryl Halide–Boron Halide Complexes

By Arthur Finch, P. J. Gardner, and K. K. Sen Gupta

The standard enthalpies of formation of complexes of the general formula POX_3,BY_3(X, Y = Br or Cl) are reported. The nature of the donor–acceptor bond is discussed, and its strength estimated.

THE literature on compounds in which the phosphoryl trihalides act as donor molecules is extensive [1] and is most controversial [2-6] where the acceptor molecule is a boron trihalide. The existence of ionic forms,[3,4] *e.g.*, $[POX_2^+][BX_4^-]$, rather than the generally accepted covalent form, with donation through the oxygen, is still possible in the light of the existing data. The main techniques previously applied to these compounds have been vibrational spectroscopy, phase-diagram studies,[7] and the kinetics of active-halogen exchange.[6,8] In this Paper, using standard thermochemical methods, we estimate the strength of the donor–acceptor bond to ascertain whether the magnitude is within the accepted limits of such bonds.

RESULTS

The compounds studied were $POCl_3,BCl_3$ (I), $POCl_3,BBr_3$ (II), $POBr_3,BCl_3$ (III), and $POBr_3,BBr_3$ (IV), all of which are solid at room temperature. For compounds (I) and (IV), the hydrolysis is

$$\begin{aligned} POX_3,BX_3(c) + (n + 6)H_2O(liq) &= [H_3{\cdot}PO_4 + H_3BO_3 \\ &\quad + 6HX]nH_2O \ \Delta H(\text{obs}) \ (X = \text{Cl or Br}) \end{aligned}$$

and for (II) and (III) is

$$\begin{aligned} POX_3,BY_3(c) + (n + 6)H_2O(liq) &= [H_3PO_4 + H_3BO_3 \\ &\quad + 3HX + 3HY]nH_2O \ \Delta H(\text{obs.}) \ (X,Y = \text{Cl,Br}) \end{aligned}$$

$$\begin{aligned} \text{Hence, } \Delta H_f^\circ POX_3,BX_3(c) &= \Delta H_f^\circ H_3PO_4nH_2O \\ &\quad + \Delta H_f^\circ H_3BO_3nH_2O + 6\Delta H_f^\circ HXnH_2O \\ &\quad - 6\Delta H_f^\circ H_2O(liq) - \Delta H(\text{obs.})(X) \end{aligned}$$

$$\begin{aligned} \text{and } \Delta H_f^\circ POX_3,BY_3(c) &= \Delta H_f^\circ H_3PO_4nH_2O \\ &\quad + \Delta H_f^\circ H_3BO_3nH_2O + 3\Delta H_f^\circ HXnH_2O \\ &\quad + 3\Delta H_f^\circ HYnH_2O - 6\Delta H_f^\circ H_2O(liq) \\ &\quad - \Delta H(\text{obs.})(X,Y) \end{aligned}$$

The hydrolyses occurred without undue violence, reaction being complete for (I) and (III) within 6 min., and for (II) and (IV) within 3 mins.

TABLE 1

Compound	T (°c)	N	ΔH(obs.)	$\Delta H_f^\circ(T)$ †
$POCl_3,BCl_3$ (I)	25·3	7470	−122·5	−271·9
	25·2	7550	−123·5	−270·9
	25·1	9790	−122·9	−271·6
	25·3	5270	−123·1	−271·4
	25·1	4790	−124·1	−270·4
$POCl_3,BBr_3$ (II)	25·1	5088	−127·6	−234·4
	25·1	6399	−127·5	−234·4
	25·0	5056	−126·2	−235·7
	25·0	10,281	−129·3	−232·7
	25·0	6230	−126·0	−235·9
	25·0	6590	−128·8	−233·2
$POBr_3,BCl_3$ (III)	25·1	9082	−134·7	−227·3
	25·1	9002	−134·0	−228·0
	25·2	10,065	−134·9	−227·1
	25·2	8895	−134·8	−227·2
	25·2	7053	−134·8	−227·2
	25·3	10,379	−134·3	−227·7
$POBr_3,BBr_3$ (IV)	25·0	16,103	−151·7	−177·6
	25·0	21,317	−149·0	−180·2
	24·9	10,986	−152·3	−177·0
	24·7	17,771	−149·1	−180·1

N = mole ratio of water to compound

$$\left.\begin{aligned} \Delta H_f^\circ \ POCl_3,BCl_3(c) &= -271{\cdot}2 \pm 1{\cdot}0^* \\ \Delta H_f^\circ \ POCl_3,BBr_3(c) &= -234{\cdot}3 \pm 1{\cdot}8^* \\ \Delta H_f^\circ \ POBr_3,BCl_3(c) &= -227{\cdot}4 \pm 0{\cdot}8^* \\ \Delta H_f^\circ \ POBr_3,BBr_3(c) &= -178{\cdot}7 \pm 1{\cdot}8^* \end{aligned}\right\} \text{kcal. mole}^{-1}$$

* Errors were calculated as the square root of the sum of squares of the constituent errors. † The heats of mixing of H_3PO_4,H_3BO_3, and HX are ignored.

The ancillary thermodynamic data for the above calculations were taken from the following sources. The

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standard heats of formation and solution for phosphoric acid (−305·7 ± 0·3 and −2·65 ± 0·10 kcal. mole^{-1}) are those of Holmes,[9] the standard heats of formation and solution for boric acid (−261·7 ± 0·3 and +5·24 ± 0·05 kcal. mole^{-1}) are those recommended by Gunn [10] as " key " data, the standard heats of formation of liquid water, and aqueous solutions of hydrochloric and hydrobromic acid, are from National Bureau of Standards circular 500,[11] the latter two data having recently been reassessed by Johnson *et al.*[12] and Sunner *et al.*,[13] respectively (these data, both at $N = 3000$, are −39·96 and −29·05 kcal. mole^{-1}, respectively). All data are expressed in terms of the thermochemical calorie defined by 1 cal. = 4·1840 abs. joule.

DISCUSSION

From the standard enthalpies of formation of the adducts, it is possible to derive the thermodynamic functions defined by the following equations (ss = standard state):

$$POX_3(ss) + BY_3(ss) = POX_3,BY_3(c) \quad \Delta H^\circ$$

$$POX_3(g) + BY_3(g) = POX_3,BY_3(c) \quad \Delta H$$

Using the ancillary data from Table 2, these data are shown in Table 3.

TABLE 2

	$POCl_3$	$POBr_3$	BBr_3	BCl_3	
$\Delta H_f^\circ(298)$(g)	−134·3 [11]	(−94·9) †	−49·3 [17]	*−96·7* [15]	kcal. mole^{-1}
,, (l)	*−143·8* [14]	(−106·6) †	*−57·5* [16]	−102·3 [10]	
,, (c)	−147·1 [18]	*−110·1* [14]	(−62·1) *	(−106·2) *	

* Estimate (see text). † Estimate (see ref. 14).

Standard-state data are in italics; other references refer to source of ΔH(transition).

TABLE 3

	$POCl_3,BCl_3$ (I)	$POCl_3,BBr_3$ (II)	$POBr_3,BCl_3$ (III)	$POBr_3,BBr_3$ (IV)	
ΔH°	−30·7	−33·1	−20·6	−10·1	kcal. mole^{-1}
ΔH	−40·2	−50·8	−35·0	−33·7	

(The uncertainty in these data is approximately ± 2 kcal.)

Making the assumption that the crystal sublimation energies are substantially constant, then ΔH is a measure of donor–acceptor binding (assuming that donation is through O). On this basis, $POCl_3$ is a stronger donor than $POBr_3$, and BBr_3 a stronger acceptor than BCl_3 in one case only.

For an absolute comparison of donor–acceptor binding, the energy [$D(B \leftarrow O)$] of the donor–acceptor bond is required. To derive this, it is necessary to estimate the sublimation energies of the crystalline adducts. As an approximation, we put this equal to the sum of the component sublimation energies [$\Delta H(c \rightarrow g)$], *i.e.*, $\Delta H(POX_3,BY_3, c \rightarrow g) = \Delta H(POX_3, c \rightarrow g) + \Delta H(BY_3, c \rightarrow g)$. The crystal structures [19,20] of both BCl_3 and B_2Cl_4 are such that the molecules are planar and mutually parallel. Making the assumption that the intermolecular forces in these two crystals are similar in character we may write:

$$\Delta H(BCl_3, c \rightarrow g) = \Delta H(B_2Cl_4, c \rightarrow g)\,\frac{M(BCl_3)}{M(B_2Cl_4)}$$

where M is the molecular weight. Using Moore's datum [21] for the sublimation energy of B_2Cl_4, we have $\Delta H(BCl_3, c \rightarrow g) \sim 9{\cdot}5$ kcal. mole^{-1}. Interpolating a corresponding datum for BBr_3 from the data for BCl_3 and BI_3,[22] we derive approximate adduct sublimation energies. Combining these data with

$$-\Delta H = \Delta H(POX_3,BY_3, c \rightarrow g) + D(B \leftarrow O)$$

we derive the overall donor–acceptor bond energy $D(B \leftarrow O)$ (see Table 4).

Such estimates of the bond-dissociation energy include the reorganisation energies $E_r(A)$ and $E_r(D)$, respectively, of the donor (D) and acceptor (A) molecules. This is summarised in the energy diagram:

$$\begin{tikzcd} POX_3(g) + BY_3(g) \arrow[rr, "E_r(D) + E_r(A)"] & & POX_3^*(g) + BY_3^*(g) \\ & X_3PO,BY_3(g) \arrow[ul, "D(B \leftarrow O)"'] \arrow[ur, "D^*"] & \end{tikzcd}$$

D^* is essentially the bond-dissociation energy as defined

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by Szwarc and Evans,[23] with each product molecule in a similar structural and electronic state to those in the complex. Since $D^* = D(B \longleftarrow O) + [E_r(A) + E_r(D)]$ values may be calculated if estimates of $E_r(D)$ and $E_r(A)$ are available. Reliable calculations[24] of the latter exist (BCl_3, 30·3; BBr_3, 26·2 kcal. mole^{-1}). No estimates of $E_r(D)$ are available, but it is reasonable to assume that $E_r(D) \ll E_r(A)$, since little structural change occurs in the $POX_3^* \longrightarrow POX_3$ transformation, in contrast to the change from tetrahedral (sp^3) to planar (sp^2) in the boron trihalides. Further, differences in $E_r(D)$, *i.e.*, $E_r(POCl_3) - E_r(POBr_3)$ may still more reasonably be neglected, and hence significant ΔD^* values may be computed. Appropriate values are in Table 4. The differences in $D(B \longleftarrow O)$ and in D^* between (I) and (III) and between (II) and (IV) are both positive and are not within the assigned error. Hence, $POCl_3 > POBr_3$ is the confirmed order of Lewis basicity. It is accepted that the order of Lewis acidity of the boron halides[25] is $BCl_3 < BBr_3$, and this is confirmed by the difference in $D(B \longleftarrow O)$ between (I) and (II) but appears to be reversed when $POBr_3$ is the donor [*i.e.*, from (III) and (IV)]. This may be ascribed to enhanced steric interaction in (IV) or, more probably, to the fact that the data are not sufficiently sensitive for the trend to be real. The donor–acceptor bond strengths are approximately an order of magnitude less than the normal B–O bond strength[26] (~120 kcal.), and this is the same ratio that was noted by Skinner.[27] Hence, our evidence is consistent with covalent bonding but does not exclude an ionic formulation.

TABLE 4

	$\Delta H(c \longrightarrow g)$	$D(B \longleftarrow O)$	ΔD	D^*	ΔD^*
$POCl_3,BCl_3$ (I)	22·3	17·9	−7·6	48·2	−3·5
$POCl_3,BBr_3$ (II)	25·3	25·5		51·7	
$POBr_3,BCl_3$ (III)	23·9	11·1	4·2	41·4	8·4
$POBr_3,BBr_3$ (IV)	26·9	6·8		33·0	

(The uncertainty in these data is approximately ±5 kcal.)

Considerable, and divergent, spectroscopic work on these molecules has been reported. Accumulated evidence for covalent (*i.e.*, $B \longleftarrow O$) structures stems largely from marked shifts (50—95 cm.$^{-1}$) of the ν(P=O) mode in the complexes compared with " free " phosphoryl halide.[7] However, it was suggested by Gerrard[3,4] that $POCl_3,BCl_3$, in particular, exists as $POCl_2^+,BCl_4^-$ on the basis of no apparent ν(P=O) shift and identification of the BCl_4^- band envelope. Waddington and Klanberg[2] examined $POCl_3,BF_3$ and $POCl_3,BCl_3$ spectroscopically, and concluded that the former was definitely covalent and the latter probably so. The evidence was the occurence of a band at 1190 cm.$^{-1}$ assigned to a B–O stretching mode and to the inability to locate vibrations characteristic of BCl_4^-. In addition, they observed negligible ν(P=O) shift. A recent spectroscopic[5] study of all the complexes studied here reveals a marked ν(P=O) shift, and a semi-quantitative vibrational analysis provides strong support for a covalent formulation. There is the possibility that in the mixed halogeno-complexes, (II) and (III), halogen exchange between phosphorus and boron might occur. Using active chlorine, Herber[8] studied the exchange in $POCl_3,BCl_3$. He found that exchange is rapid (complete within approx. 1 min. at 0°) in excess $POCl_3$, but no exchange occurs in an excess of BCl_3. He concludes that an ionic formulation is not possible, since the formation of BCl_4^- would lead to immediate exchange in view of the kinetic equivalence of the Cl in BCl_4^-. A mechanism, operative only in a polar solvent and involving pre-dissociation, $POCl_3 \rightleftharpoons POCl_2^+ + Cl^-$, is suggested. This explains why exchange occurs in $POCl_3$-rich systems (the dielectric constants of $POCl_3$ and BCl_3 are 13·9 and 1·0, respectively). Hence, in the syntheses described here, care was taken to maintain an excess of boron halide to avoid the interconversion $POCl_3,BBr_3 \rightleftharpoons POBr_3,BCl_3$. Burg and Ross[28] examined the equilibrium $POCl_3,BCl_3(c) \rightleftharpoons BCl_3(g) + POCl_3(g)$ by a vapour tensimetric method, and from their result, $\log K = 15{\cdot}803 - 5714/T$, we derive $\Delta H = 26{\cdot}1$ kcal. mole^{-1}. This is not in accord with the value reported here (40·2 kcal mole^{-1}) and may be taken as further evidence for the existence of two forms of this complex.

Spectra of the complexes were recorded over the range 2000—400 cm.$^{-1}$ in carbon disulphide and in cyclohexane (these solvents have very similar dielectric constants). In carbon disulphide solution all complexes show bands at 1300 ± 10 cm.$^{-1}$ (P=O stretch) and 1200 ± 10 cm.$^{-1}$ (B–O stretch) of varying relative intensity. The spectrum of (I) compares in its salient features with that obtained by Waddington[2] (mull) but not with that of Goubeau.[5] The spectra of the mixed halogeno-complexes, (II) and (III), in cyclohexane appear similar to those of Goubeau (mull). Molecular weight determinations indicate that there is no dissociation in a solvent of similar polarity (benzene) to those used for the spectroscopic work. A full analysis of the spectral data would be of great interest, since, from a knowledge of the force-constant of the B–O bond, an estimate of D^*, independent of a calorimetric measurement, should be possible. This could then be used to check the assumption that the magnitude of the

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reorganisation energies of the phosphoryl halides is sufficiently low to be neglected.

EXPERIMENTAL

Spectra were recorded from 2000 to 400 cm.$^{-1}$ on a Unicam S.P. 100. The samples were dissolved in dry cyclohexane or carbon disulphide and contained in 0·5-mm. path-length cells with KBr windows. Handling and solution preparation were performed in a nitrogen-filled dry-box.

The calorimeter was of the constant-temperature environment type fully immersed in a thermostat controlled to 25° ± 0·01°. A full description may be found elsewhere.[29] The precision and accuracy of the calorimeter were estimated by two standard reactions, one endothermic and the other exothermic.[30] For the enthalpy of neutralisation of tris(hydroxymethyl)aminomethane (THAM) in excess 0·1N-hydrochloric acid, the mean of seven observations was $-7{\cdot}15 \pm 0{\cdot}05$ kcal. mole^{-1} at 25° and $N = 600$ (lit.,[31] $-7{\cdot}104$ at 25° and $N = 1330$). For the dissolution of potassium chloride in water, the mean of five observations was $4{\cdot}23 \pm 0{\cdot}03$ kcal. mole^{-1} at 25° and $N = 200$ (lit.,[32,33] 4·206 kcal. mole^{-1} at 25° and $N = 200$).

Phosphoryl Chloride–Boron Trichloride. This complex was synthesised by the method of Frazer *et al.*[3]. This involves adding phosphoryl chloride to boron trichloride dissolved in dry methylene chloride at −80°. This solvent was used to crystallise the compound, m. p. 72—75° (lit.,[3,5] 70—71° or 73°) (Found: B, 4·0; Cl, 78·4. Calc. for BCl_6OP: B, 4·0; Cl, 78·6%).

Phosphoryl Chloride–Boron Tribromide.—A similar procedure to the above was used to synthesise this adduct, m. p. 126—129° (lit.,[5] 128°) [Found: B, 2·7; Br, 60·5; Cl, 26·8%; *M* (cryoscopy in benzene), 400. Calc. for BBr_3Cl_3PO: B, 2·7; Br, 59·6; Cl, 26·4%; *M*, 404·3].

Phosphoryl Bromide–Boron Tribromide.—A similar procedure to the above was used to synthesise this adduct, m. p. 152—154° (lit.,[3,5] 150—154° or 150°) (Found: B, 2·1; Br, 88·9. Calc. for BBr_6PO: B, 2·0; Br, 89·4%).

Phosphoryl Bromide–Boron Trichloride.—The above procedure was used to synthesise this compound, m. p. 115—118° (decomp.) [Found: B, 2·7; Br, 60·4; Cl, 26·2%; *M* (cryoscopy in benzene), 411. Calc. for BBr_3Cl_3PO: B, 2·7; Br, 59·6; Cl, 26·4%; *M*, 404·3].

Phosphoryl Bromide.— The method of Booth and Seegmiller [34] was used to prepare this compound, b. p. 193—195°, m. p. 55—56° (lit.,[34] b. p. 193°, m. p. 56°) (Found: Br, 84·4. Calc. for Br_3OP: Br, 83·6%).

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Studies on Phenylphosphorus Dihalides

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Studies on Phenylphosphorus Dihalides

By Arthur Finch, P. J. Gardner, and K. K. Sen Gupta

The standard heats of hydrolysis of phenylphosphorus dichloride and phenylphosphorus dibromide have been determined, and approximate standard heats of formation (−30 and −8 kcal. mole^{-1}, respectively) calculated. The existence of phenylphosphorus chloride bromide (PhPClBr) has been confirmed.

CONSIDERABLE interest attaches to phenylphosphorus halides, $\mathrm{PhPX_2}$, which are precursors in the synthesis of a large number of phenylphosphorus compounds of general formula $\mathrm{PhPR_2}$ (R = alkyl, aryl, alkoxy, etc.). There are no quantitative physical data on the reaction of these halides with themselves or with water, and no thermodynamic data. We report the first measurements of heats of hydrolysis, before obtaining standard enthalpies of formation. Phase diagram and nuclear magnetic resonance studies demonstrated the existence of the mixed halide, PhPClBr, at temperatures up to ambient.

Syntheses.—Phenylphosphorus dichloride was originally prepared by the Friedel–Crafts dichlorophosphination of benzene,[1] and this procedure was adopted initially, but commercial supplies (Aldrich Chemical Co.) were then used.

Phenylphosphorus dibromide was prepared by three methods:

$$\mathrm{PhPCl_2} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{PhPH_2} \xrightarrow{\mathrm{Br_2}} \mathrm{PhPBr_2} \qquad (1)$$[2,3]

$$\mathrm{C_6H_6} + \mathrm{PBr_3} \xrightarrow{\mathrm{AlBr_3}} \mathrm{PhPBr_2} \qquad (2)$$

$$\mathrm{PhPCl_2} \xrightarrow{\mathrm{PBr_3}} \mathrm{PhPBr_2} \qquad (3)$$[4]

Method (3) was by far the easiest and most efficient, and was adopted for bulk syntheses.

Phenylphosphonous acid[5] was prepared by esterification of phenylphosphorus dichloride with ethanol, followed by hydrolysis with water:

$$\mathrm{PhPCl_2} + \mathrm{EtOH} \xrightarrow{\mathrm{H_2O}} \mathrm{PhPO_2H_2}$$

Existence of Phenylphosphorus Chloride Bromide.—Reorganisation of halogen atoms between, *e.g.*, phosphorus halides,[6] phosphoryl halides,[7] and thiophosphoryl halides,[8] is well known, and such scrambling reactions have received considerable attention.[9] In this instance only one compound can be formed, and the system is very suitable as a model for which kinetic and energetic data can be obtained most easily.

Nuclear magnetic resonance measurements (^{31}P) (Figure 1) were made with liquid samples of phenylphosphorus dichloride, phenylphosphorus dibromide, and an equimolar mixture. The chemical shift for the dichloride agrees with literature values ($-161{\cdot}6$,[10] -166 ± 1[11]). Peak area and signal pattern remained

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constant, and a sharp band at −158 p.p.m. is rapidly assignable to PhPClBr.

Cryoscopic measurements were made in a cryometer fitted with a magnetic stirrer[12] using a miniature platinum resistance thermometer. Results are summarised in Figure 2; no eutectics could be found, though the maximum at a 1 : 1 mole ratio of the halide was reproducible within ±1%.

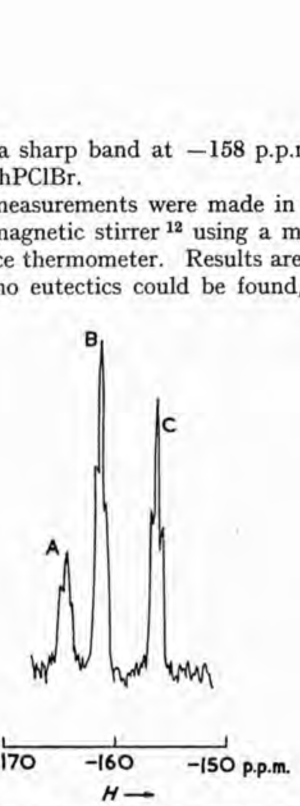

FIGURE 1 ^{31}P Nuclear magnetic resonance spectrum of phenylphosphorus chloride bromide

The chemical shifts (relative to 85% phosphoric acid as external standard; no diamagnetic susceptibility correction applied) are (A) $PhPCl_2$ −161 ± 1 p.p.m., (B) PhPClBr −158 ± 1 p.p.m., and (C) $PhPBr_2$ −152 ± 1 p.p.m.

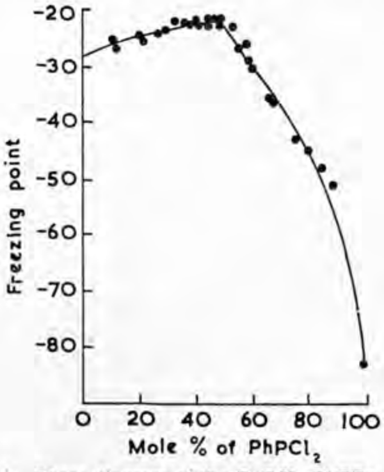

FIGURE 2 Phase diagram of the $PhPCl_2$–$PhPBr_2$ system

Thermochemistry.—The reaction investigated was

$$PhPX_2(liq) + (n + 2)H_2O(liq) = [PhPO_2H_2 + 2HX]nH_2O \ \Delta H_{obs}$$

from which

$$\Delta H_f°PhPX_2(liq) = \Delta H_f°PhPO_2H_2nH_2O + 2\Delta H_f°HXnH_2O - 2\Delta H_f°H_2O(liq) - \Delta H_{obs}$$

The standard enthalpy of formation of phenylphosphonous acid is not yet available, hence we derive $[\Delta H_f°PhPX_2(liq) - \Delta H_f°PhPO_2H_2(c)]$. It has been suggested[13] that the aqueous hydrolysis of phosphonous chlorides does not proceed unambiguously according to the above equation, and does not proceed to completion. The hydrolyses were performed over a wide concentration range when variation of heat evolved with concentration would indicate an equilibrium; there was no significant variation in ΔH_{obs}. Although the hydrolysate was contaminated with phenylphosphine (detected by odour), the concentration, and hence the extent of side-reaction, was small, as post-hydrolysis analysis indicated 100% recovery of halide and phenylphosphonous acid. The results are in the Table. The ancillary thermodynamic data are from the following sources: Sunner *et al.*[14] ($\Delta H_f°$HBr aq), Johnson *et al.*[15] ($\Delta H_f°$HCl aq); National Bureau of Standards Circ. 500 ($\Delta H_f°H_2O$ liq). A very approximate estimate of $\Delta H_f°PhPO_2H_2(c)$ can be obtained by considering the enthalpy change in the reaction

Compound	T (°c)	N	$-\Delta H_{obs}$ (kcal. mole^{-1})
$PhPCl_2$	24·6	1967	42·6
	24·6	1026	41·8
	24·8	995	41·9
	24·8	1983	42·4
	24·8	1781	42·0
			Av. 42·1 ± 0·6
$PhPBr_2$	24·9	1973	41·6
	25·0	2512	41·3
	24·7	1512	42·3
	24·8	1163	41·3
	25·6	2148	42·2
	24·9	2829	41·9
			Av. 41·7 ± 0·5
			ΔH_{soln}
$PhPO_2H_2$	24·8	780	1·53
	24·6	832	1·48
	25·0	1090	1·29
	24·7	964	1·31
	24·9	629	1·56
	24·6	877	1·35
	24·9	881	1·52
			Av. 1·43 ± 0·2

N is the mole ratio of compound to water;
$[\Delta H_f°PhPCl_2(liq) - \Delta H_f°PhPO_2H_2(c)] = 100·3 \pm 0·6$ kcal. mole^{-1};
$[\Delta H_f°PhPBr_2(liq) - \Delta H_f°PhPO_2H_2(c)] = 121·7 \pm 0·5$ kcal. mole^{-1}.

$$PhH(g) + H_3PO_3(g) = PhPO_2H_2(g) + H_2O(g)$$

in terms of bond energies, mostly taken from Hartley *et al.*[16] Combining with the relevant standard enthalpies of formation, $\Delta H_f°PhPO_2H_2(c) = -130 \pm 10$ kcal. mole^{-1}, from which we have $\Delta H_f°PhPCl_2(liq) \sim -30$ and $\Delta H_f°PhPBr_2(liq) \sim -8$ kcal. mole^{-1}. An accurate determination of $\Delta H_f°PhPO_2H_2(c)$ is in progress.

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EXPERIMENTAL

Halogens were determined by Volhard's technique.[17] Benzene and ether were dried over sodium wire. Chloroform was distilled and dried over anhydrous calcium chloride.

Syntheses.—Dichlorophenylphosphine. Benzene (205 g.) was heated with phosphorus trichloride (109 g.) under reflux for 30 hr. in the presence of anhydrous aluminium trichloride (43 g.) in a three-necked flask fitted with a rubber-sealed glass stirrer. A continuous stream of nitrogen was passed during the reaction, and 86% phosphoric acid (15 ml.) was added with vigorous shaking of the mixture in a dry-box. The precipitate was then filtered off using glass wool, the excess of benzene removed by distillation, and the compound vacuum-distilled and redistilled (60·5 g., 12·5%), b. p. 130°/18 mm. (lit.,[1] 90—92°/10 mm.), n_D^{25} 1·5951, d_4^{20} 1·319 (Found: Cl, 39·8. Calc. for $C_6H_5Cl_2P$: Cl, 39·6%).

Dibromophenylphosphine.—(a) Dichlorophenylphosphine (48·9 g.) in ether (125 ml.) was added dropwise with stirring to a flask (as described before) containing lithium aluminium hydride (10 g.) in ether (200 ml.). Stirring was continued for 1 hr., water (26 ml.) added, and the mixture refluxed for 2 hr. The liquid was then filtered, excess of solvent removed by distillation, and the residual liquid dried over anhydrous calcium chloride, decanted, and distilled (16 g., 53·2%); phenylphosphine had b. p. 159—160° (lit.,[2] 160°) (Found: C, 65·6; H, 6·3; P, 28·2. Calc. for C_6H_7P: C, 65·45; H, 6·4; P, 28·2%).

A solution of bromine (65 g.) in chloroform (50 ml.) was added to a solution of phenylphosphine (27 g.) in chloroform (70 ml.), as before with stirring. The temperature was maintained below 20° and a stream of nitrogen was passed during the reaction. The excess of chloroform was distilled off, and the dibromophenylphosphine separated by distillation and finally redistilled (14·5 g., 22·3%), b. p. 132°/13—14 mm. (lit.,[18] 126—128°/11 mm.), n_D^{25} 1·6534, d_4^{20} 1·872 (Found: C, 26·65; H, 1·8; Br, 59·4; P, 11·5. Calc. for $C_6H_5Br_2P$: C, 26·9; H, 1·9; Br, 59·7; P, 11·6%).

(b)[4] Phenylphosphorus dichloride (179 g.) was heated with phosphorus tribromide (271 g.) at 100—200° for 2 hr. The initial fractions, up to 175°, containing both phosphorus trichloride and chloride bromides, were removed at ordinary pressures. The excess of phosphorus tribromide was then removed by vacuum-distillation, and the product separated by distillation (210 g., 78·3%), b. p. 126—128°/11 mm. (Found: Br, 59·3%).

(c) Benzene (78 g.) was added to phosphorus tribromide (271 g.) in the presence of anhydrous aluminium tribromide (26·6 g.). The mixture was refluxed for 12 hr., with continuous stirring and passage of nitrogen, and then cooled and filtered. The unreacted benzene and fractions boiling up to 175° were removed by distillation at ordinary pressure followed by the phosphorus tribromide under reduced pressure. The compound was then vacuum-distilled and redistilled (45·2 g., 16·8%), b. p. 132—134°/14 mm. (Found: C, 26·7; H, 1·7; Br, 59·2; P, 11·45%).

Phenylphosphonous Acid. Dichlorophenylphosphine (1 vol.) was added to absolute alcohol (5 vol.) with stirring, and subsequently diluted with water (2 vol.) and boiled for 5—10 min.; benzene (2 vol.) was then added, and the excess of water and benzene removed by distillation. The solution was concentrated, and the compound, after separation, was recrystallised, m. p. 85—86° (from benzene) (lit.,[5] 86°) (Found: C, 50·8; H, 5·1. Calc. for $C_6H_7O_2P$: C, 50·7; H, 5·0%). After successive recrystallisations it was 99·6% pure (checked by cerimetric oxidation method).

Cryoscopy.—The measurements were carried out in a precision cryometer with a magnetic stirrer in the cell,[12] inside which the temperature was determined with a platinum resistance thermometer calibrated between +5 and −95°. The liquid was inoculated into the cell with a repeating syringe through the side-arm of the cryometer which was fitted tightly with a Subaseal; each injection was reproducible within ±1%. The system was checked with a known mixture, chloroform–mesitylene,[19] which has two eutectics, at 82·5 and 22·5 mole-% of mesitylene. When dihalogenophosphines were used, filling operations were performed in a nitrogen-filled glove-box. A weighed amount of dibromo-compound was placed in the cryometer, a known amount of dichloro-compound added from the syringe, and the m. p. of the resulting mixture determined as before. The experiment was repeated in the reverse manner, and the plot of mole-% of dichlorophenylphosphine against temperature showed a peak at 50% of the two components.

Calorimetry.—The calorimeter[20] was of a constant-temperature type immersed in a bath at 25° ± 0·01°. It was tested by two standard reactions: *(a)* dissolution of potassium chloride in water; $\Delta H(25°, N = 200) = 4·23 \pm 0·03$ (mean of 5 determinations); *(b)* neutralisation of tris-(hydroxymethyl)aminomethane in an excess of 0·1N-hydrochloric acid; $\Delta H(25°, N = 600) = -7·15 \pm 0·05$ (mean of 7 determinations). The literature data are: *(a)* 4·206;[21] 25°, $N = 200$; *(b)* −7·104;[22] 25°, $N = 1330$.

Infrared Spectra.—The spectrum of phenylphosphorus dibromide was run as a liquid film on a far-infrared spectrometer constructed in this department. Bands near 388 and 409 cm.$^{-1}$ were observed, and tentatively assigned to the P–Br stretching modes.

Nuclear Magnetic Resonance.—The ^{31}P magnetic resonance spectra were obtained with a Perkin-Elmer n.m.r. spectrometer at 16·19 Mc./sec., using phosphoric acid as external standard.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Thermochemistry of Some Phosphorus Halide–Boron Halide Complexes

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Received August 18, 1966

The standard enthalpies of formation of four complexes of the general formula $PX_3 \cdot BY_3$ (X, Y = Br or I) are reported. These data are discussed in terms of the strength of the donor–acceptor bond. Estimates of this bond strength are: $PI_3 \cdot BI_3$, 22; $PI_3 \cdot BBr_3$, 65; $PBr_3 \cdot BI_3$, 34 and $PBr_3 \cdot PBr_3$, 7 kcal mole^{-1}.

Introduction

The 1:1 complexes formed from boron trihalides and phosphorus trihalides have been studied in connection with their stability with respect to dissociation,[1] their halogen-exchange reactions,[1] and their solid-phase structure.[2,3] Only the complexes involving the heavier halogen atoms are stable with respect to disproportionation or dissociation at room temperature. These complexes are presumably σ bonded from the phosphorus to the boron atom. This is in contrast to the phosphoryl halide–boron halide adducts, which have also been examined thermochemically,[4] where bonding is most probably from oxygen to boron.

Experimental Section

Materials.—Carbon disulfide used as solvent in the syntheses was British Drug Houses AnalaR grade, successively shaken with aqueous potassium permanganate and mercury followed by distillation immediately prior to use. The boron and phosphorus tribromides were supplied by BDH and distilled prior to use. Boron triiodide was supplied by L. Light and Co. and phosphorus triiodide (mp 60–61°, lit.[5] 60.5°) was synthesized by the method of Germann and Traxler[5] and recrystallized from carbon disulfide. Handling was performed in a nitrogen-filled drybox as the compounds are sensitive to both oxidation and hydrolysis.

Syntheses.—All complexes were synthesized by mixing equimolar quantities of the boron and phosphorus halides dissolved in carbon disulfide. The adducts were yellow solids (white, in the case of PBr_3BBr_3) and precipitated from carbon disulfide.

Phosphorus Triiodide–Boron Triiodide.—This was prepared by the method of Mitchell, *et al.*,[2] and vacuum dried; mp 250°. *Anal.* Calcd for PI_3BI_3: I, 94.8. Found: I, 95.7. Halogen analyses were performed by silver nitrate titrations using adsorption indicators.

Phosphorus Triiodide–Boron Tribromide.—This adduct was prepared by the method of Cowley and Cohen[3] and crystallized from carbon disulfide; mp 159–160°; lit.[3] 160°. *Anal.* Calcd for PI_3BBr_3: Br, 36.2; I, 57.6; mol wt, 662. Found: Br, 37.0; I, 56.5; mol wt (by cryoscopy in benzene), 651.

Phosphorus Tribromide–Boron Tribromide.—The method of Tarible[6] was used to synthesize this adduct; mp 59–61°, lit.[1] 61°. *Anal.* Calcd for PBr_3BBr_3: Br, 91.9. Found: Br, 91.0.

Phosphorus Tribromide–Boron Triiodide.—The method of Armington, *et al.*,[7] was used to prepare this adduct; mp 178–182°. *Anal.* Calcd for PBr_3BI_3: Br, 36.2; I, 57.6; mol wt, 662. Found: Br, 37.2; I, 55.7; mol wt (by cryoscopy in benzene), 646.

Calorimetry.—The calorimeter was of the constant-temperature environment type fully immersed in a thermostat maintained at 25 ± 0.01°. A full description may be found elsewhere.[8] The precision and accuracy of the equipment were checked by two standard reactions, one endothermic and the other exothermic. For the dissolution of potassium chloride in water, ΔH ($N = 200$, $T = 25°$) = 4.23 ± 0.03 kcal mole^{-1} (mean of five determinations), and for the neutralization of tris(hydroxymethyl)aminomethane in excess 0.1 M hydrochloric acid, ΔH ($N = 600$, $T =$

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TABLE I

ENTHALPIES OF HYDROLYSIS AND FORMATION OF PX_3BX_3 AND PX_3BY_3 ADDUCTS (KCAL MOLE^{-1})

Compound	N^a	T, °C	$\Delta H_{\text{obsd}}(X)$	$\Delta H_f{}^\circ{}_T$
PI_3BI_3 (I)	10,692	24.7	−111.2	
	10,985	24.8	−112.3	
	13,271	24.8	−110.7	-44.1 ± 1.2^c
	12,539	25.0	−111.7	
	11,801	24.8	−110.6	
			Mean -111.3 ± 0.85^b	
PBr_3BBr_3 (IV)	8,177	24.7	−132.1	−115.1
	5,031	24.7	−134.6	−112.5
	11,913	24.6	−133.2	−114.15
	11,880	24.6	−134.4	−112.95
	6,253	25.0	−133.5	−113.7
	7,342	25.0	−132.1	−115.1
				Mean -113.9 ± 1.5^c
			$\Delta H_{\text{obsd}}(X, Y)$	
PI_3BBr_3 (II)	14,469	24.6	−64.5	−137.1
	10,874	24.8	−62.4	−139.1
	6,806	24.8	−62.5	−138.9
	4,334	24.7	−62.3	−139.0
	7,871	24.9	−63.6	−137.9
	6,946	24.8	−63.0	−138.4
				Mean -138.4 ± 1.3^c
PBr_3BI_3 (III)	5,716	24.5	−110.8	−90.6
	6,915	24.7	−111.4	−90.05
	10,419	24.8	−111.2	−90.3
	12,025	24.9	−110.4	−90.2
	17,174	25.0	−110.7	−90.9
	16,402	24.8	−112.6	−89.0
				Mean -90.3 ± 1.4^c

[a] N is the mole ratio of water to adduct. [b] In this case, ΔH_{obsd} was averaged rather than $\Delta H_f{}^\circ$ because the values of N were sufficiently close for only one value of $\Delta H_f{}^\circ(HX \cdot nH_2O)$ to be used. [c] The error in ΔH_{obsd} was taken as the spread; this was combined with the errors in the ancillary data to give the root of sum of the squares as the over-all error.

$25°) = -7.15 \pm 0.05$ kcal mole^{-1} (mean of seven determinations). Literature data for these reactions are: ΔH ($N = 200$, $T = 25°$)[9] = 4.206 kcal mole^{-1} and ΔH ($N = 1330$, $T = 25°$)[10] = −7.104 kcal mole^{-1}, respectively. All enthalpies are quoted in terms of the defined thermochemical calorie, 1 cal = 4.1840 abs joules.

Results

The adducts PI_3BI_3 (I), PI_3BBr_3 (II), PBr_3BI_3 (III), and PBr_3BBr_3 (IV) hydrolyze quantitatively and without undue violence in water according to the equation (c = crystal)

$$PX_3BX_3(c) + (n + 6)H_2O(l) = [H_3PO_3 + H_3BO_3 + 6HX]\cdot nH_2O$$

$$PX_3BY_3(c) + (n + 6)H_2O(l) = [H_3PO_3 + H_3BO_3 + 3HX + 3HY]\cdot nH_2O$$

from which we may write

$$\Delta H_f{}^\circ[PX_3BX_3(c)] = \Delta H_f{}^\circ(H_3PO_3\cdot nH_2O) + \Delta H_f{}^\circ(H_3BO_3\cdot nH_2O) + 6\Delta H_f{}^\circ(HX\cdot nH_2O) - 6\Delta H_f{}^\circ[H_2O(l)] - \Delta H_{\text{obsd}}(X)$$

and

$$\Delta H_f{}^\circ[PX_3BY_3(c)] = \Delta H_f{}^\circ(H_3PO_3\cdot nH_2O) + \Delta H_f{}^\circ(H_3BO_3\cdot nH_2O) + 3\Delta H_f{}^\circ(HX\cdot nH_2O) + 3\Delta H_f{}^\circ(HY\cdot nH_2O) - 6\Delta H_f{}^\circ[H_2O(l)] - \Delta H_{\text{obsd}}(X, Y)$$

Ancillary Data.—The following ancillary thermodynamic data were used

$\Delta H_f{}^\circ(H_3BO_3\cdot 1000H_2O) = -256.5 \pm 0.3$ kcal mole^{-1} (ref 11)

$\Delta H_f{}^\circ[H_3PO_3(aq)] = -226.5 \pm 0.8$ kcal mole^{-1} (ref 12)

$\Delta H_f{}^\circ(HI\cdot \infty H_2O) = -13.79 \pm 0.1$ kcal mole^{-1} (ref 13)

$\Delta H_f{}^\circ(HBr\cdot 300H_2O) = -29.05 \pm 0.09$ kcal mole^{-1} (ref 14)

ΔH_{diln}(HBr and HI) and $\Delta H_f{}^\circ[H_2O(l)] = -68.315$ kcal mole^{-1} (ref 15)

The enthalpy of dilution of boric acid is small[16] and that of phosphorous acid is unknown but probably within the assigned error. The heats of mixing of H_3PO_3, H_3BO_3, HBr, and HI are ignored.

Discussion

The enthalpy changes of the reactions

$$PX_3(ss) + BY_3(ss) = PX_3BY_3(c) \qquad \Delta H^\circ$$

$$PX_3(g) + BY_3(g) = PX_3BY_3(c) \qquad \Delta H_1$$

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TABLE II

ANCILLARY THERMODYNAMIC DATA FOR PX_3 AND BY_3 AT 298°K (KCAL MOLE^{-1})[h]

	PI_3	PBr_3	BI_3	BBr_3
$\Delta H_f°(g)$	7.05 ± 1.7[g]	-30.7 ± 1.5[i]	4.70 ± 1.0[a]	-48.8 ± 0.22[i]
$\Delta H_f°(l)$	...	$\underline{-41.7 \pm 2.0}$[c]	...	$\underline{-57.0 \pm 0.2}$[i]
$\Delta H_f°(c)$	$\underline{-11.45 \pm 0.85}$[f]	-45.2 ± 2.5[d]	$\underline{-10.8 \pm 0.8}$[b]	-61.6 ± 2.0[e]

[a] $\Delta H(c \rightarrow g, BI_3)$ due to Tiensuu.[18] [b] Data from ref 19 modified using current $\Delta H_f°[HI(aq)]$ data. [c] $\Delta H(l \rightarrow g, PBr_3)$ due to van Driel and Gerding[20] at ~128°, estimated at 25° using Watson's equation.[21] [d] Assuming $\Delta H(c \rightarrow l, PBr_3) = \Delta H(c \rightarrow l, POBr_3)$. [e] See ref 4. [f] Data from ref 22 modified using current $\Delta H_f°[HI(aq)]$ data. [g] $\Delta H(c \rightarrow g, PI_3) = \Delta H(c \rightarrow l) + \Delta H(l \rightarrow g)$; latter term extrapolated from vaporization data[15,20] for PBr_3 and PCl_3 and former term put equal to $\Delta H(\text{soln}, PI_3 \text{ in } CS_2)$.[22] [h] Appropriate errors have been assigned where estimates are involved. Underlined data are in standard state. [i] Reference 17.

TABLE III

DERIVED THERMODYNAMIC DATA FOR THE ADDUCTS AT 298°K (KCAL MOLE^{-1})

	PI_3BI_3	PI_3BBr_3	PBr_3BI_3	PBr_3BBr_3
$\Delta H°$	-21.8 ± 1.7	-69.9 ± 1.6	-37.8 ± 2.5	-15.2 ± 2.5
ΔH_1[a]	-55.8 ± 2.3	-96.6 ± 2.1	-64.3 ± 2.3	-34.4 ± 2.1
$\Delta H(c \rightarrow g)$[b]	34.0 (±2.0)	31.3 (±2.0)	30.0 (±2.0)	27.3 (±2.0)
$D(P-B)$	21.8 ± 3.1	65.3 ± 2.9	34.3 ± 3.0	7.1 ± 2.9

[a] We thank a referee for drawing our attention to some current ΔH(transition) data from which we calculate alternative values for ΔH_1: PI_3BI_3, −56.4; PBr_3BBr_3, −31.4; PI_3BBr_3, −96.6; and PBr_3BI_3, −61.7, kcal mole^{-1}. [b] An arbitrary error of ±2.0 kcal mole^{-1} is assigned to this datum.

may be derived using the ancillary thermodynamic data[17–22] in Table II (ss = standard state). Before considering the thermodynamic stability of the adducts, there is evidence[7] that PBr_3BI_3 and PI_3BBr_3 are discrete compounds and cross halogenation does not occur at ambient temperature.

As a first approximation, if the differences between the entropy changes ($\Delta S°$) are ignored, then relative values of $\Delta H°$ measure the thermodynamic stability of the adducts with respect to dissociation into free donor and acceptor.

An alternative method of considering stability, or relative donor–acceptor power, is to estimate the strength of the donor–acceptor bond. This calculation requires the adduct sublimation enthalpies for which a reasonable approximation is

$$\Delta H(c \longrightarrow g, PX_3 \cdot BY_3) = \Delta H(c \longrightarrow g, PX_3) + \Delta H(c \longrightarrow g, BY_3)$$

Two different estimates of the bond dissociation energy of each adduct are given by the equations

$$D(X_3P-BY_3) = -\Delta H(c \longrightarrow g, PX_3 \cdot BY_3) - \Delta H_1$$

$$D^*(X_3P^*-BY_3^*) = D(X_3P-BY_3) + E_r(PX_3) + E_r(BY_3)$$

where the asterisk signifies the molecule in its molecular electronic and molecular hybridization state and E_r is the reorganization energy.[23] It has been shown[4] that the inclusion of E_r in a discussion of donor–acceptor properties of the phosphoryl halide–boron halide systems does not significantly affect the conclusions. Hence we shall consider D rather than D^* in the subsequent discussion.

Corroboratory evidence for $D(I_3P-BI_3)$ comes from a recent estimate[24] of 16 kcal for this datum derived from a vibrational analysis of the adduct.

Using the data in Table III and analogous data for phosphoryl halide–boron halide complexes,[4] the following order of donor ability with respect to a fixed acceptor and the converse may be formulated. Relative donor power (or Lewis basicity) with respect to (a) BCl_3 is $POCl_3 > POBr_3$ ($>PBr_3 > PCl_3$), (b) BBr_3 is $PI_3 > POCl_3 > POBr_3 \sim PBr_3$ ($>PCl_3$), and (c) BI_3 is $PBr_3 > PI_3$. Relative acceptor power (or Lewis acidity) with respect to (d) PCl_3 is ($BBr_3 > BCl_3$), (e) PBr_3 is $BI_3 > BBr_3$ ($>BCl_3$), (f) $POBr_3$ is $BCl_3 > BBr_3$, (g) $POCl_3$ is $BBr_3 > BCl_3$, and (h) PI_3 is $BBr_3 > BI_3$. The data in parentheses are deduced from Holmes' description of the stabilities with respect to dissociation of the adducts "PCl_3BCl_3," "PBr_3BCl_3," and PCl_3-BBr_3. The order of acceptor power of boron trihalides relative to organic bases, both in solution[25] and in the gas phase,[26] has been established as $BF_3 < BCl_3 < BBr_3$ and extended to include $BBr_3 < BI_3$ by Cook[27] (this latter work relative to xanthone and by frequency shifts in the vibrational spectrum). This order is followed in (d), (e), and (g) but reversed in (f) and (h). Also, orders of donor power are self-consistent except for (c). The anomalous complexes are $POBr_3BBr_3$, $POBr_3$-BCl_3, PI_3BBr_3, and PI_3BI_3. It is readily seen that PI_3-BI_3 is the most sterically hindered with respect to halogen–halogen interaction (or F and B strain)[28] of the PX_3BY_3 series. Further, the POB angle in the POX_3BY_3 complexes is considerably expanded from

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the tetrahedral angle (probably[29] between 140 and 150°) and examination of molecular models reveals that $POBr_3BBr_3$ is considerably more sterically strained, with respect to POB angle distortion than $POBr_3BCl_3$. This explanation is not entirely satisfactory in that the $POCl_3$ complexes exhibit the usual order. However, with the present limited evidence, it is probably the most realistic.

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