THERMOCHEMICAL PROPERTIES OF PHOSPHORUS COMPOUNDS

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Introduction

Although most of the detailed thermochemistry reported in the literature refers to carbon compounds, the compounds of phosphorus and sulphur have more recently been the subject of considerable thermochemical investigation, yielding information on the strengths of chemical bonds.

Naturally occurring phosphorus compounds possess molecules in which the atom is four-co-ordinate; however, synthesis can provide us with molecules which have three, four, five, and even six-co-ordinated phosphorus. In molecules which contain three-co-ordinated phosphorus, the hybrid orbitals are nearer to sp^3 than p^3, owing to the participation of a lone pair of electrons.[1] This is the situation in compounds such as phosphorus trichloride or trialkyl phosphites. However, the most abundant are the four-co-ordinated compounds of phosphorus, the molecules of which have four σ sp^3 bonds together with different amounts of additional π-bonding involving the $3d_{x_2y_2}{}^-$ and $3d_{z_2}$ orbitals of the central atom and depending upon the orbitals of the attached atoms.[2,3] The overall geometry of these compounds is tetrahedral and the group is represented by PR_4^+, $POCl_3$, $OP(OR)_3$, or PO_4^{3-}. In the well known condensed phosphates, linking of the phosphorus tetrahedra uses essentially this latter type of bonding though with modifications involving opening of the bond angles.[3]

The use of d orbitals is also involved in compounds having a five-co-ordination where the σ bonds may be considered to be hybrids of sp^3d character[4] and occur for example in the trigonal bipyramid of phosphorus pentachloride. Finally, six-co-ordination involving the use of two d orbitals in the hybrid occurs,[5] for example, in the octahedral PCl_6^- ion.

In consideration of the structural characteristics of the compounds of phosphorus much use has been made of bond lengths and bond angles.[5] Less reference has been made to bond energies to support these findings and it is one of the purposes of the present review to indicate how far thermochemical data are available and can be used to provide a coherent picture of the binding in phosphorus compounds. The further practical

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[1] Gillespie and Nyholm, *Quart. Rev.*, 1957, **11**, 339.
[2] Jaffé, *J. Phys. Chem.*, 1954, **58**, 185.
[3] Cruikshank, *J.*, 1961, 5486.
[4] Craig and Magnusson, *J.*, 1956, 4895.
[5] Van Wazer, "Phosphorus and its compounds," Interscience, New York, 1958.

use of thermochemical values as a first stage in the provision of thermodynamic data for phosphorus compounds is obvious. Enthalpy measurements are usually required to provide adequate data for equilibrium calculations, since direct free-energy measurements are often extremely difficult.

Comparatively little combustion calorimetry has been carried out to obtain the thermochemical data which are available for phosphorus compounds. There are certain experimental difficulties in this technique, compared with the combustion of carbon compounds, due to the corrosive nature of the products and to the determination of the state of hydration of the phosphorus oxides formed in the bomb. The problem of incomplete combustion, however, appears to be no greater with phosphorus compounds than with many organic molecules, provided that an excess of oxygen is employed. To date, no combustion measurements on phosphorus compounds with high-precision rotating-bomb calorimeters have been reported, and much of the thermochemical information has been derived from reaction calorimetry. These indirect techniques raise the attendant problems of side reactions, making for an overall standard of accuracy in phosphorus thermochemistry which is lower than for the best measurements on, for example, carbon compounds.

Thermochemical Reference States

In common with some other elements the thermochemical standard state for phosphorus is not the most stable allotropic modification but that most commonly used in practice, *i.e.*, white phosphorus in the α modification which we will designate $P_4(\alpha)$.

The values of the enthalpy changes on passing from one allotropic modification to another, necessary for the standardisation of many thermochemical measurements, have recently been discussed by Rodewald.[6] These (Table 1) are largely obtained from vapour pressure measurements which, together with specific heat data, enable values to be calculated for the heats of transition from solids at 25° to the hypothetical ideal gas at one atmosphere and 25°. For the transition from white to red amorphous, not discussed by Rodewald, the heats of sublimation at 300° have been taken from the reports by the Tennessee Valley Authority.[7] An auxiliary value for this transition at 25°, obtained from direct combustion measurements, is also given.[8] The value for interconversion of the two forms of white phosphorus has been re-examined by Rodewald;[6] it is obtained by an extrapolation to zero pressure of Bridgman's high-pressure transitions,[9] and, unlike the other measurements, refers to −77°.

[6] Rodewald, *Helv. Chim. Acta*, 1960, **43**, 878.

[7] Tennessee Valley Authority, Chemical Engineering Report on Phosphorus, No. 8, 1950.

[8] Holmes, *Trans. Faraday Soc.*, 1962, **58**, 1916.

[9] Bridgman, *Phys. Rev.*, 1914, **3**, 126, 153.

TABLE 1. *Enthalpy changes for transition from one allotropic modification of phosphorus to another.*

	$\Delta H°$ (kcal./mole of P_4)	
$P_4(\alpha) \rightarrow P_4(\beta)$	−3·8	(−76·8°)
$P_4(\alpha) \rightarrow$ 4P (red triclinic)	−16·6	
$P_4(\alpha) \rightarrow$ 4P (red amorphous)	−6·2 (ref. 7);	−7·0 (ref. 8)
$P_4(\alpha) \rightarrow$ 4P (black)	−24·7	
$P_4(\alpha) \rightarrow P_4$ (liquid)	+0·6	

The heat of atomisation of $P_4(\alpha)$ derived by Cottrell,[10] which supersedes the value quoted by the National Bureau of Standards,[11] has been revised here, using the heat of sublimation for white phosphorus of 14 kcal./mole (Table 2).

TABLE 2. *Heat of atomisation of* $P_4(\alpha)$.

Reaction	$\Delta H°$ (kcal./4 P atoms)
P_4 (cryst.) $\rightarrow P_4$ (gas)	14·0
P_4 (gas) $\rightarrow 2P_2$	54·5
$2P_2$ (gas) $\rightarrow$ 4P (gas)	233·6
$\frac{1}{4}P_4(\alpha) \rightarrow$ P atoms	$\Delta H_f°$(P,g) = 75·5 kcal./P

Oxides of Phosphorus

Phosphoric Oxide, P_4O_{10}.—The classical work of Giran[12] on the oxidation of phosphorus has remained unchallenged since 1903. Giran protected phosphorus by treating it with carbon dioxide and then measured its heat of combustion by conventional bomb techniques. The combustion product was identified as P_4O_{10} of a mainly amorphous nature and the value of $\Delta H_f°$ estimated for crystalline P_4P_{10}, by additional measurements of heats of solution of the different oxides, was −720·0 kcal./P_4O_{10}.

A recent investigation,[8] using an adiabatic bomb calorimeter, of the combustion of both white phosphorus protected by thin layers of Perspex, and red phosphorus has revealed a small difference from Giran's results, and the value for $\Delta H_f°$ found for crystalline hexagonal P_4O_{10} is −713 kcal./mole.

The value recommended for the heat of sublimation of this oxide, when corrected to 25°, is 24—25 kcal./mole,[7] giving the value of $\Delta H_f°(P_4O_{10},g)$ as −688 kcal./mole. The values due to Giran[12] for the heats of transition of the modification of P_4O_{10}(c) are subject to uncertainty since the structures of his solid phases were not clearly defined: The heats of transition reviewed by the Tennessee Valley Authority are also open to some

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[10] Cottrell, "The Strengths of Chemical Bonds," 2nd edn., Butterworths, London, 1958.

[11] National Bureau of Standards, Thermochemical Data, Circular 500.

[12] Giran, *Ann. Chim. Phys.*, 1903, **30**, 203.

suspicion since the heat of sublimation of the most stable O′ form appears to be less than that of the O form.

Phosphorus Oxide, P_4O_6.—A recalculation of Koerner and Daniels's[13a] indirect combustion results gives $\Delta H_f^{\circ}(P_4O_6,c) = -527$ kcal./mole.

A recent direct measurement[13b] of the heat of combustion of P_4O_6 to P_4O_{10} gives $\Delta H_f^{\circ}(P_4O_6,c) = -392$ kcal./mole. The heat of sublimation at 25° is 16—17 kcal./mole.

Phosphorus Acids

The available data are summarised in the following tables.

A. *Phosphoric acid.*

Compound	Method of measuring ΔH_f°	ΔH_f° (kcal./mole)	State	Ref.
HPO_3	Dissolution of P_4O_{10}(c)	−224·8	cryst.	12
	and H_3PO_4(c) in water	−234·6	aq.	12
H_3PO_4	Hydrolysis of HPO_3	−306·2		12
	Oxidation of $P_4(\alpha)$ with Br_2 and HIO_3(aq.)	−306·2	cryst.	14, 16
	Hydrolysis of P_4O_{10}(c)	−305·7	cryst.	8
	Experimental heats of fusion	−302·6	liq.	15*b*
	Experimental heats of dilution	−308·3	aq.	8, 15*a*

B. *Phosphorous Acid.*

Compound	Method of measuring ΔH_f°	ΔH_f° (kcal./mole)	State	Ref.
(a)	Oxidation of H_3PO_3(aq.)	−228·8	aq.	14, 16
	to H_3PO_4(aq.)	−232·2	aq.	14, 11
(b)	Hydrolysis of PCl_3, taking $\Delta H_f^{\circ}(PCl_3,l) = -74·4$ kcal./mole	−227·1	aq.	17, 18
(c)	Using $\Delta H_f^{\circ}(H_3PO_4,aq.)$ (Table A) in calculation (b)	−226·0	aq.	Recalc. this work.

Pseudo-metallic and Ionic Phosphorus Compounds

Metal Phosphides.—Elemental phosphorus combines exothermally with many metals at elevated temperatures to form binary phosphides. Direct measurement of heats of reaction and, more frequently, studies of dissociation vapour pressure, have yielded approximate high-temperature heats of formation for some transition-metal phosphides (Table 3).

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[13] (*a*) Koerner and Daniels, *J. Chem. Phys.*, 1952, **20**, 113; (*b*) Hartley and McCoubrey, *Nature*, 1963, **198**, 476.

[14] Thomsen, "Thermochemische Untersuchungen," Vols. I—IV, Leipzig, 1882—1886.

[15] (*a*) Egan and Luff, *J. Phys. Chem.*, 1961, **65**, 523; (*b*) Egan and Wakefield, *J. Phys. Chem.*, 1957, **61**, 1500.

[16] Bichowsky and Rossini, "The Thermochemistry of Chemical Substances," Reinhold, New York, 1936.

[17] Neale and Williams, *J.*, 1954, 2156.

[18] Charnley and Skinner, *J.*, 1953, 450.

TABLE 3. *Heats of formation of transition-metal phosphides.*

Molecule	ΔH_f° (kcal./mole)	Ref.	Molecule	ΔH_f° (kcal./mole)	Ref.
Fe_2P	−36·0	7, 19	TiP	−63·4	21
Fe_3P	−40·0	"	MnP	−23·0	22
Ni_3P	−53·0	"	Na_3P	−30·0	23, 24
Cu_3P	−36·4	"	Mg_3P_2	−118·0	25, 26
Au_2P_3	−24·1	"	Ca_3P_2	−120·5	26
GeP	−6·0	20	Sr_3P_2	−160·0	27
SiP	−15·0	20	Zn_3P_2	−53·4	28
InP	+26·0	20	Cd_3P_2	−24·4	29

It is instructive to attempt to place a limit on the electron affinity of P^{3-}, employing for this purpose the heat of formation for Na_3P (a "favourable" case for yielding an approach to an ionic lattice). Using this value in a conventional Born–Haber cycle,

$$E_{P\rightarrow P^{3-}} = \Delta H_f^\circ(Na_3P, \text{ cryst.}) + 3\Delta H_f^\circ[Na(a)] + 3I_{Na\rightarrow Na^+} + \Delta H_f^\circ[P(a)] - U,$$

we obtain a value $E_{P\rightarrow P^{3-}} = -460$ kcal./mole. In this summation, the lattice energy U has been calculated by the method of Kapustinskii,[30] using for P^{3-} the crystal radius for 2·12 Å given by Pauling.[31,32]

Since a truly ionic crystal of Na_3P must be less stable than the actual crystal formed, the true electron affinity must be equal to or more negative than the above, provided that the value chosen for the lattice energy is correct.

An alternative procedure is to assume that the electron affinity can be calculated by the method of Glockler,[33] shown by Baughan[34] to give reasonable accuracy for N^{3-}. If the ionisation-potential data of Edlèn[35] are used in this calculation, $E_{P\rightarrow P^{3-}}$ is found to be −228 kcal./mole, and a lattice energy calculated from the above equation is lower than that calculated from Kapustinskii's model, implying that the ionic radius of

[19] "FIAT" Report on German Science 1939—1945, ed. Klemm, Inorg. Chem. Part II, 1948, pp. 71—90.

[20] Weiser, *J. Phys. Chem.*, 1957, **61**, 513.

[21] Shchukarev, Morozova, and Li, *Zhur. obshchei Khim.*, 1959, **29**, 2465.

[22] Shchukarev, Morozova, and Stolyarova, *Zhur. obshchei Khim.*, 1961, **31**, 1773.

[23] Morozova, Bolshakova, and Lukinykh, *Zhur. obshchei Khim.*, 1959, **29**, 3144.

[24] Lowe and Topley, Albright & Wilson Ltd., unpublished data.

[25] Shchukarev, Ariya, and Lakhtin, Vestnik, Leningrad Univ., 1953, **2**, 121.

[26] Shchukarev, Morozova, and Li, *Zhur. obshchei Khim.*, 1959, **29**, 3142.

[27] Shchukarev, Morozova, and Kan, *Zhur. obshchei Khim.*, 1957, **27**, 1289.

[28] Kavelis, *Vilniaus Univ. Mokslo Darbai. Chem.*, 1959, **28**, 110.

[29] Shchukarev, Morozova, and Bortnikova, *Zhur. obshchei Khim.*, 1958, **28**, 3289.

[30] Kapustinskii, *Quart. Rev.*, 1956, **10**, 283.

[31] Pauling, *J. Amer. Chem. Soc.*, 1927, **49**, 770.

[32] Sherman, *Chem. Rev.*, 1932, **11**, 151.

[33] Glockler, *Phys. Rev.*, 1934, **46**, 111.

[34] Baughan, *Trans. Faraday Soc.*, 1959, **55**, 736, 2025.

[35] Edlèn, *J. Chem. Phys.*, 1960, 33, 98.

P^{3-} is larger than that estimated by Pauling.[31] The true value for the electron affinity probably lies between these limits.

Phosphonium Compounds.—Values of $\Delta H_f{}^\circ$ available for the compounds $PH_4Cl(c)$[11,36,37] $PH_4Br(c)$, and $PH_4I(c)$ are −42·5, −29·5, and −15·8 kcal./mole, respectively.[11] These solids have much higher dissociation pressures than the corresponding ammonium salts at the same temperature; at room temperatures the chloride and bromide are gaseous, with a high proportion of phosphine and hydrogen chloride in equilibrium.[36,38]

The enthalpies of formation have been used, in conjunction with calculated lattice energies, by Wendlandt[37] to calculate the approximate value of the heat of protonation, ΔH°, in the step:

$$PH_3(g) + H^+(g) \rightarrow PH_4{}^+(g)$$

A mean value is 209 kcal./mole, which gives $\Delta H_f{}^\circ(PH_4{}^+,g)$ as 159 kcal./mole.

By an examination of the individual steps contributing to the relative base strengths of $NH_4OH(aq.)$ and $PH_4OH(aq.)$ in the "typical" cycles shown in the annexed scheme, we can see that the difference in the heats of protonation of phosphine and ammonia in the gas phase (209 and 207 kcal./mole, respectively) is small, so that the major factor determining the low base strength of PH_4OH is the smaller value of the heat of hydration of the $PH_4{}^+$ tetrahedron which may be taken to be approximately 0·4 Å larger than $NH_4{}^+$ (since the P–H bond is 0·4 Å longer than N–H in these ions) and will consequently have a heat of hydration about 20 kcal./mole less, as estimated from Eley and Evans's data.[39]

$$\begin{tikzcd}
NH_3(g) & + & H_2O(g) \arrow[r, "\Delta H^\circ + D_{H_2O} + I_H + E_{OH^-}"] & NH_4{}^+(g) \arrow[d, "\Delta H_{solu.}"] & + & OH^-(g) \arrow[d, "\Delta H_{solu.}"] \\
NH_3(aq.) \arrow[u, "-\Delta H_{solu.}"] & + & H_2O(l) \arrow[u, "\Delta H_{vap.}"'] & NH_4{}^+(aq.) \arrow[l, "-\Delta H_{dissocn.}"] & + & OH^-(aq.)
\end{tikzcd}$$

Inorganic Phosphates.—The structure of these compounds ranges from the highly ionic metal compounds to the mixed oxide "pseudo silica" lattices of the group III elements. Major interests has been centred on the

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[36] Johnson, *J. Amer. Chem. Soc.*, 1912, **34**, 877.
[37] Wendlandt, *Science*, 1955, **122**, 831.
[38] Smith and Calvert, *J. Amer. Chem. Soc.*, 1914, **36**, 1363.
[39] Eley and Evans, *Trans. Faraday Soc.*, 1938, **34**, 1093.

phosphates of groups I and II and heats of formation of phosphates have been obtained by Meadowcroft and Richardson[40] by measuring heats of hydrolysis in hydrochloric acid to give chlorides of known heat of formation and phosphoric acid. The values of ΔH_f° for the orthophosphates Na_3PO_4, Li_3PO_4, $Zn_3(PO_4)_2$, and $Ca_3(PO_4)_2$ are, respectively, −462·6, −502·6, −694·5, and −984·5 kcal./mole.

A method[5] of representing the enthalpy changes involved in the formation of inorganic phosphates of different structure is illustrated in the following schematic sequences:

$$P_4O_{10}(c) + 6M_2O \xrightarrow{\Delta H_1} (4/3)[(MPO_3)_3, (c)] + 4M_2O \xrightarrow{\Delta H_2} 2M_4P_2O_7, (c)$$

$$+ 2M_2O \xrightarrow{\Delta H_3} 4M_3PO_4, (c)$$

The heat balance in these reactions can conveniently be summarised as

$$4(4 - x)\,\Delta H_f^\circ(\text{Phosphate, c}) = \Delta H_f^\circ(P_4O_{10}, c) + 2x\,\Delta H_f^\circ(M_2O, c) + \sum_x \Delta Hx$$

$$x = 1,2,3.$$

where x is the number of M–O bonds per phosphorus atom. The quantity ΔHx represents the "excess heat" on mixing the oxides to form a phosphate. The amount of heat release for the addition of $2M_2O$ and formation of four P–O groups is highest on passing from the fully covalent P_4O_{10} to the tri-metaphosphate. Such an effect may be due to the sum of changes involving the lattice energies, differences in the electron affinities of the oxygen atoms, and covalent binding energies in the individual ions due to changes in π bonding.

TABLE 4. *Enthalpy changes in the formation of inorganic phosphates.*

Oxide	ΔH_f° (oxide)	ΔH_1	ΔH_2	ΔH_3
$H_2O(l)$	−68·3	− 56·2	− 26·6	−12·2
$ZnO(c)$	−83·2	−112·4	−51·7	−16·1
$Na_2O(c)$	−99·4	−256·0	−164·6	−113·0
$Li_2O(c)$	−142·4	−201·4	−119·9	−114·2
$CaO(c)$	−151·9	−156·0	−118·2	−64·8

All values are in kcal./formula weight.

Phosphate Minerals.—The following recent values are recommended for the enthalpies of formation of apatites:[41,42,43] $[Ca_3(PO_4)_2]_3,CaF_2(c)$,

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[40] Meadowcroft and Richardson, *Trans. Faraday Soc.*,

[41] Gottschel, *J. S. African Chem. Inst.*, 1958, **11**, 45.

[42] Egan, Wakefield, and Elmore, *J. Amer. Chem. Soc.*, 1956, **78**, 1811.

[43] Jacques, *J.*, in the press.

−3296 kcal./mole; $[Ca_3(PO_4)_2]_3,Ca(OH)_2(c)$, −3231 kcal./mole; and $[Ca_3(PO_4)_2]_3,CaCl_2(c)$, −3172 kcal./mole.

Use can also be made of the above data, together with that obtained for some silicate materials, to calculate the energetics of a typical phosphorus furnace reaction of commerce. The specific-heat value of Britske and Veselovskii[44] and of this laboratory, enable the heat change at 1500°K to be calculated for the reaction:

$$[Ca_3(PO_4)_2]_3,CaF_2(c) + 8SiO_2 + 15C \longrightarrow$$

$$[3CaO{\cdot}2SiO_2{\cdot}CaF_2]\ (c) + 6CaSiO_3\ (c) + 15CO(g) + (3/2)P_4(g)$$

ΔH is found to be + 1016 kcal./mole of fluorapatite, illustrating the very considerable energy requirement of this process.

Covalent Inorganic Compounds

Diatomic Compounds.—The bond-dissociation energies of several diatomic phosphorus species which occur at high temperatures have been measured spectroscopically; these are PN (164 kcal./mole),[45] PC (138), PO (140). The uncertainties attached to these, however, are probably ± 20 kcal./mole.[10]

Hydrides.—The value of $\Delta H_f{}^\circ(PH_3,g)$ quoted by Cottrell,[10] is 0 ± 2 kcal./mole, assessed from a number of scattered values. Recently, using a measurement of the heat of explosive decomposition to the elements in the presence of stibine, Gunn and Greene[46] obtained a value of +1·3 kcal./mole; they have also obtained a value of $\Delta H_f{}^\circ$ for $P_2H_4(g)$ of +5 kcal./mole.

Halides.—Reliable thermal data on the halides of phosphorus are still very incomplete and in some cases depend on early and unchecked investigations (Table 5).

Sulphides.—Despite the considerable commercial interest in these compounds, which are used to make oil additives and insecticides, very few thermochemical data are available in the literature.

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[44] Britske and Veselovskii, *Izvest. Akad. Nauk S.S.S.R.*, *Otdel. tekh. Nauk*, 1937, **4**, 479.

[45] Huffman, Tarbutton, Elmore, Cate, Walters, and Elmore, *J. Amer. Chem. Soc.*, 1954, **76**, 6239.

[46] Gunn and Greene, *J. Phys.*, *Chem.*, 1961, **65**, 779.

TABLE 5. *Phosphorus halides.*

Compound	Method of measuring $\Delta H_f°$	$\Delta H_f°$ (kcal./mole)	State	Ref.
PCl_3	Oxidation with Br_2 using $\Delta H_f°(H_3PO_4,aq.)$ $-308·3$ kcal./mole	−73.3	liq.	17
	Latent heat of vaporisation of 7·8 kcal./mole	−65·5	gas	18
PBr_3	Hydrolysis to H_3PO_3(aq.) using $\Delta H_f°(H_3PO_3, aq.)$ $-226·0$ kcal./mole	−40·5	liq.	18
	Latent heat of vaporisation of 11·6 kcal./mole	−28·9	gas	18
PI_3	Reaction of I_2 with phosphorus in CS_2 soln.	−10·9	cryst.	47
	Reaction of $PI_3 + 6KOH \rightarrow K_3PO_3(aq.) + 3H_2O + 3KI$	−10·5	cryst.	48
PF_3	Recalc. assuming quantitative reaction, *viz.*, $PF_3+6KOH \rightarrow KPO_3(aq.)+3H_2O+3KF(aq.)$	−221·0	gas	49
$POCl_3$	Hydrolysis of liquid to H_3PO_4(aq.) using $\Delta H_f°(H_3PO_4, aq.)$ $-308·3$ kcal./mole	−143·2	liq.	18, 50
	Latent heat of vaporisation 9·22 kcal./mole	−134·0	gas	51
	Latent heat of sublimation 12·4 kcal./mole	−146·4	cryst.	51
$POBr_3$	Hydrolysis to H_3PO_4(aq.) using $\Delta H_f°(H_3PO_4, aq.)$ $-308·3$ kcal./mole	−109·0	cryst.	18
	Latent heat of sublimation 15·0 kcal./mole	−94·0	gas	18
POF_3	Calc. from $PF_3(g.) + \frac{1}{2}O_2 \rightarrow POF_3(g.)$, using $\Delta H_f°(PF_3, g)$ above	−292	gas	52
PCl_5	1. By hydrolysing to H_3PO_4. 2. By reaction: $PCl_3(l) + Cl_2(g) \rightarrow PCl_5/(c)$ (Original data revised by Nat. Bur. Stand.)	−110·7	cryst.	11
	Using latent heat of sublimation 15·35 kcal./mole	−95·35	gas	11
PBr_5	Hydrolysis to H_3PO_4(aq.) [No correction for the new value of $\Delta H_f°(H_3PO_4$ aq.)]	−66·0	cryst.	11
	Heat of sublimation 13 kcal./mole	−53·0	gas	11
P_2I_4	Estimated heat of sublimation 30 kcal./mole	−19·8	cryst.	11
		~+10·0	gas	53
$PO(NCO)_3$	Combustion, using estimated $\Delta H_{vap.} = 13·4$ kcal./mole	−172.0	liq.	54
		−158·6	gas	55, 56

[47] Ögier, *Compt. rend.*, 1881, **92**, 83.
[48] Berthelot, *Ann. Chim. Phys.*, 1878, **3**, 207.
[49] Berthelot, *Ann. Chim. Phys.*, 1885, **6**, 358.
[50] Neale and Williams, *J.*, 1952, 4535.
[51] Ott and Giauque, *J. Amer. Chem. Soc.*, 1960, **82**, 1308.
[52] Ebel and Bretscher, *Helv. Chim. Acta*, 1929, **12**, 450.
[53] Rice, "Electronic Theory of Chemical Bonding," McGraw-Hill, New York, 1940.
[54] Jacques and Paddock, Albright & Wilson Ltd., unpublished results.
[55] Forbes and Anderson, *J. Amer. Chem. Soc.*, 1940, **62**, 762.
[56] Anderson, *J. Amer. Chem. Soc.*, 1942, **64**, 1757.

Recent investigations[57] using differential thermal analysis (d.t.a.) have provided useful data from which approximate values of $\Delta H_f{}^\circ$ have been obtained.

A study of the size of the exothermic peak in the reaction:

$$4P(red) + 3S(l) \xrightarrow{200\text{—}260^\circ} P_4S_3(l)$$

together with heats of fusion lead to $\Delta H_f{}^\circ(P_4S_3,c) = -32$ kcal./mole, no heat capacity corrections from 230° to 250° having been made. The only other value for this compound in the literature is that of Treadwell and Beeli,[58] which is extremely ambiguous since it is not clear which reference states are used.

The alternative routes to P_4S_7 formation:

$$P_4S_3(c) + 4S(rhombic) \rightarrow P_4S_7(c) \text{ and } 4P(red) + 7S(l) \rightarrow P_4S_7(l)$$

have also been studied by d.t.a., and heats of fusion measured by the same technique lead to $\Delta H_f{}^\circ(P_4S_7,c.) \sim -72$ and -70 kcal., respectively.

From this, the reaction;

$$P_4S_5(c) + 2S(l) \rightarrow P_4S_7(c)$$

has been used to derive $\Delta H_f{}^\circ(P_4S_5,c) \sim -50$ kcal. (For structure, cf. ref. 59)

Finally, reactions:

$$4P(red) + 10S(l) \rightarrow P_4S_{10}(l)$$

and $$P_4S_7(c) + 3S(l) \rightarrow P_4S_{10}(c)$$

give $\Delta H_f{}^\circ(P_4S_{10},c) \geqslant -87$ and $\Delta H_f{}^\circ(P_4S_{10},l) \geqslant -68$ kcal./mole.

Organic Phosphorus Compounds

A number of workers have used standard thermochemical methods to measure enthalpies of formation of organophosphorus compounds. This work has been summarised in Table 6 in which the types of measurement used are illustrated. It is also apparent from this Table that vapour pressure data, necessary for the accurate evaluation of gaseous enthalpies and bond strengths, are often quite inadequate.

A few calorimetric measurements, not recorded in the Table, have been made to evaluate dissociation energies $D(P{=}O)$ or $D(P{=}S)$; these do not yield values of enthalpies of formation directly.

Calculation of the Strength of Chemical Bonds from Enthalpies of Formation

It is easy to deduce mean bond energies $\bar{E}$ in simple molecules such as PCl_3, PH_3, and P_4O_6, where only one kind of bond is involved, by simple subdivision of the enthalpy change on forming the gaseous compound from the constituent atoms (see Table 7).

[57] Jacques, Albright & Wilson, Ltd., unpublished results.
[58] Treadwell and Beeli, *Helv. Chim. Acta*, 1935, **18**, 1161.
[59] van Houten and Wiebenga, *Acta. Cryst.*, 1957, **10**, 156.

TABLE 6. *Enthalpies of formation of organophosphorus compounds.*

Compound	Standard state	$\Delta H_f°$ (kcal./mole)	Calorimetric method	$\Delta H_{trans.}$ (kcal./mole)		Method of obtaining $\Delta H_{trans.}$	$\Delta H_f°(g.)$ (kcal./mole)	Ref.
$(MeO)_3P$	l	−175·0	Reaction alcohol + PCl_3	l→g	9·0	Estimated	−166·0	60
$(EtO)_3P$	l	−203·5	"	l→g	10·0	Vap. press.	−193·5	61
"		−204·1						60
$(Pr^iO)_3P$	l	−235·0	"	l→g	11·0	" "	−224·0	61
$(EtO)_3PO$	l	−297·8	Oxidation of phosphite in soln.	l→g	12·2	" "	−285·6	62
"		−296·7	"		12·2	" "	−284·5	63
"	l	−297·5	Combustion	l→g	12·2	" "	−285·3	64
$(Pr^iO)_3PO$	l	−323·9	Oxidation of phosphite in soln.	l→g	13·0	Estimated	−310·9	63
Me_3P	l	−30·1	Combustion	l→g	6·92	Vap. press.	−23·2	65
Me_3PO	c	−115·1	Oxidation of phosphite in soln.	c→g	12·0	Vap. press.	−103·0	66
Ph_3P	c	+54·3	Combustion	c→g	18·1	Estimated	+72·4	64
Ph_3PO	c	−15·6	"	c→g		"	+3·5	64
$(Me_2N)_3PO$	l	−127·6	Reaction: $POCl_3$ + Me_2NH	l→g	13·5	Vap. press.	−114·1	63
$Ph_3P{:}NEt$	l	+27·0	Hydrolysis in HCl	l→g	13·0	" "	+40·0	66
$Me_3P{:}NEt$	l	−36·6	"	l→g	12·0	" "	−24·6	66

TABLE 6.—*continued.*

Compound	Standard state	ΔH_f° (kcal./mole)	Calorimetric method	$\Delta H_{\text{trans.}}$ (kcal./mole)	Method of obtaining $\Delta H_{\text{trans.}}$	ΔH_f°(g.) (kcal./mole)	Ref.
$(PNCl_2)_3$	c	−194·1	Combustion	c→g 18·2	Vap. press.	−175·9	67
$(PNCl_2)_4$	c	−259·2	,,	c→g 23·1	,, ,, and ΔH_{fusion}	−236·1	67
$PN[cyclo(C_6H_{11}O)_2]_3$	c	−582·0	,,				68
$(PNPh_2)_4$	c	+40·7	,,				68
$(PNMe_2)_3$	c	−125·1	,,				68
$Me{\cdot}PO(NHPh)_2$	c	−86·6	,,				61
$(Et{\cdot}PO)NHPh_2$	c	−89·6	,,				61
$MePOCl_2$	c	−148·8	Reaction: $RO{\cdot}PCl_2$ + $PhNH_2$ in solution	c→g 14·9	Latent heat of fusion and vap. press.	−133·9	61
$EtPOCl_2$	l	−147·3	,,	l→g 10·2	Vap. press.	−137·1	61
$(Me_2N)_3P$	l	—45·0	Reaction PCl_3 + Me_2NH	l→g ~13	Estimated	—32·0	63*b*
$(Et_2N)_3P$	l	—66·8	Reaction PCl_3 + Et_2NH	l→g 14·5	Vap. press.	—52·3	63*a*

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[60] Chernick, Skinner, and Mortimer, *J.*, 1955, 3936.

[61] Neale, Williams, and Moores, *J.*, 1956, 422.

[62] Chernick and Skinner, *J.*, 1956, 1401.

[63] (*a*) Claydon and Mortimer, *J.*, 1962, 3212; (*b*) Hartley, Albright & Wilson Ltd., unpublished results.

[64] Bedford and Mortimer, *J.*, 1960, 1622;

[65] Long and Sackman, *Trans. Faraday Soc.*, 1957, **53**, 1606.

[66] Claydon, Fowell, and Mortimer, *J.*, 1960, 3284.

[67] Hartley, Paddock and Searle, *J.*, 1961, 430.

[68] Bedford and Mortimer, *J.*, 1960, 4649.

TABLE 7. *Bond energies in phosphorus compounds.*

Bond	$\bar{E}$ (kcal./mole)	Molecule	Bond	E (kcal./mole)	Molecule
P–H	77	PH_3	P–I	44	PI_3
P–F	117	PF_3	P–O	86	P_4O_6
P–Cl	76	PCl_3	P–P	50	P_4
P–Br	62	PBr_3			

In more complex molecules, where several kinds of bond are introduced, we are often faced with the problem of allotting an arbitrarily assigned energy to one bond, in order to estimate the strength of a second type of bond. One possible way, for example in the case of phosphorus oxychloride, is to apply the value of $\bar{E}$(P–Cl) from phosphorus trichloride in order to calculate a dissociation energy "D" for P=O, according to equation (1)

$$D(P{=}O)\,(POCl_3) = \Delta H_f^a(POCl_3) - 3\bar{E}(P{-}Cl)\,(PCl_3) \quad (1)$$

or, alternatively, and more directly, from the equation

$$D(P{=}O)\,(POCl_3) = -\Delta H_f{}^\circ(Cl_3PO),g) + \Delta H_f{}^\circ(PCl_3),g) + \Delta H_f{}^\circ\,(O,g) \quad (2)$$

Similarly, in tervalent compounds such as $P(CH_3)_3$, $P(OEt)_3$, $P(NEt_2)_3$, it is possible to evaluate the mean bond dissociation energies $\bar{D}$(P–C), $\bar{D}$(P–O), and $\bar{D}$(P–N) by assuming a value for the heat of formation of the groups CH_3, OEt, and NEt_3; these latter are obtained *directly* from the enthalpies of dissociation of parent compounds (*e.g.*, $CH_4 \rightarrow CH_3 + H$). The values of $\bar{D}$ so obtained may be equated with mean bond energies only *if there is no change in energy* in the groups CH_3 etc. when they are "transplanted" from their parent molecule to the phosphorus-centred compounds. Bond energies calculated on this assumption are given in Table 8.

TABLE 8. *Bond dissociation energies in phosphorus compounds.*

Bond	Compound	Mean dissociation energy $\bar{D}$ (kcal./mole)	Bond	Compound	Mean dissociation energy $\bar{D}$ (kcal./mole)
P–O	$(MeO)_3P$	91	P–C	$(Me)_3P$	65
	$(EtO)_3P$	92		$(Ph)_3P$	71
	$(Pr^iO)_3P$	92	P–N	$(Et_2N)_3P$[63a]	67
				$(Me_2N)_3P$[63b]	70

The method of allocating fixed, arbitrary values to the energies of certain bonds and of certain transferable groups (such as methyl and ethoxy), in order to calculate enthalpies of formation in more complex molecules, may be criticised on the grounds that no account has been taken of energy changes due to structural reorganisation within the attached groups or bonds (*e.g.*, changes in co-ordination on passing from PCl_3 to $POCl_3$), and of changes in electron hybridisation and overlap in the "transferred bonds" caused by the introduction of electrophilic or nucleophilic substituents (*e.g.*, the possible electron-attracting influence of the phosphoryl P=O on the P–Cl or P–Me groups on passing from Cl_3P to $Cl_3P{=}O$, etc.

An attempt has been made below to overcome these difficulties in a fairly rational manner. Instead of transferring unchanged bond and group energies from a known to an unknown molecule, a correcting factor should be applied, which makes allowance for the changed environment. For this purpose, we can use external physical evidence about changes in bond length, vibration frequency, or force constant of the transferred bond, obtained from infrared, Raman, and *X*-ray experiments. It is first necessary, however, to attempt a correlation between these physical properties and bond energies in cases where little ambiguity exists about the energy terms.

In Tables 9 and 10 data are given for series of compounds containing the P=O grouping.

TABLE 9. *Stretching frequencies and force constants in phosphoryl and thiophosphoryl compounds.*

Compound	*D*(P=O) or *D*(P=S) (kcal./mole)	Phosphoryl or thiophosphoryl stretching frequency (cm.$^{-1}$)	P=O stretching force constant md/Å
P_4O_{10}	138^{13b}	1400^{69}	11·0
F_3PO	130*	1415^{70}	11·4
Cl_3PO	128*	1292^{70}	10·0, 9·6
Br_3PO	125*	1260^{70}	9·6
Me_3PO	139^{66}	1170^{71}	8·2
Pr_3PO	138^{62}	1166^{72}	—
Bu_3PO	137^{62}		—
Ph_3PO	128^{64}	1195^{73}	—
$(EtO)_3PO$	$151^{64,62}$	1272^{74}	—
$(PrO)_3PO$	146^{63b}	1264^{72}	—
$(Me_2N)_3PO$	139^{63b}	1206^{72}	—
$(Et_2N)_3PO$	156^{63a}		
$(EtO)_3PS$	$90{\cdot}6^{75}$	608^{76}	—
Pr_3PS	$91{\cdot}6^{75}$	$\sim 550^{76}$	—
Bu_3PS	$91{\cdot}5^{75}$	$\sim 550^{76}$	—

* Recalculated from the original results (Table 5) using up to date values for $\Delta H_f^{\circ}(PX_3)$.

[69] Brederode and Gerding, *Rec. Trav. chim.*, 1948, **67**, 677.

[70] Siebert, *Z. anorg. Chem.*, 1954, **275**, 210.

[71] Daasch and Smith, *J. Chem. Phys.*, 1951, **19**, 22.

[72] Chapman and Thirlwell, Albright & Wilson Ltd., unpublished results.

[73] Cotton, Barnes, and Bannister, *J.*, 1960, 2199.

[74] Bellamy and Beecher, *J.*, 1952, 475.

[75] Chernick, Pedley, and Skinner, *J.*, 1957, 1851.

[76] Popov, Kabachnik, and Mayants, *Russ. Chem. Rev.*, 1961, **30**, 362.

TABLE 10. *Stretching force constants for phosphorus–halogen bonds.*

Molecule	P–Hal bond length r_0 (Å)[5]	P–Hal stretch force constant m. dynes/Å	Molecule	P–Hal bond length r_0 (Å)[5]	P–Hal stretch force constant m. dynes/Å
PF_3	1·55	4·9[77]	F_3PO	1·52	6·2[70]
PCl_3	2·04	2·1[78]	Cl_3PO	1·99	2·45[70] 2·90[79]
PBr_3	2·23	1·6[78]	Br_3PO	2·06	2·1[70]

From Table 9 it can be seen first, that the values of D(P=O) obtained by applying equations 1 or 2 are apparently unrelated to the force constants for P=O stretching.[72] Since the force constant is essentially a measure of the strength of the bond *at equilibrium*, and "isolated" from the influence of other dynamic oscillators in the system, while D(P=O) includes the environmental influences, mentioned above, and is related to a difference of equilibrium states, this situation is not surprising.

Secondly, within one homologous series (*e.g.*, trialkyl phosphates, phosphoryl halides) there seems to be a direct relationship between the values of D(P=O) and the phosphoryl stretching frequency.

Finally, however, in the phosphoryl halides increased electronegativity of the attached halogen has apparently strengthened the P=O bond, whereas in the trialkyl and trialkoxy-derivatives even higher values of the P=O bond energies are found despite the lower electronegativity of the attached groups; the phosphoryl stretching frequency reflects the expected changes in P=O strength more readily than does D(P=O).

From Table 10 can also clearly be seen the influence of adding the phosphoryl P=O grouping to the phosphorus trihalides; in each case, the introduction of P=O has led to shortening and strengthening of the phosphorus–halogen bonds. Increases in P–N stretching frequencies have also been observed on passing from compounds such as $(Me_2N)_3P$ to $(Me_2N)_3PO$.

An Arbitrary Method of Assigning Bond Energies.—In view of the changes in length and force constant which occur in P–X bonds on passing from PX_3 to POX_3 compounds, it is clear that the value of D(P=O) must be related not only to the energy of formation of a P=O bond but also to changes in bonding energy which occur throughout the molecules. In order to assign the proportions of energy associated with different bonds, it is necessary to adopt hypothetical standards of binding.

Such standards may be found in the molecules P_4O_6 and P_4O_{10}. The first of these contains twelve single P–O bonds of length about 1·66 Å. According to our recent re-measurement[13b] of $\Delta H_f^\circ(P_4O_6)$ the energy of the single bonds in this molecule is 86 kcal./mole. The "single" bonds in

[77] Wilson and Polo, *J. Chem. Phys.*, 1952, **20**, 1716.
[78] Howard and Wilson, *J. Chem. Phys.*, 1934, **2**, 630.
[79] Hariharan, *J. Ind. Inst. Sci.* 1956, **38***A*, 16.

P_4O_{10}, however, are of length 1·60 Å and the double bonds of length 1·40 Å and it has been suggested by Cruikshank that, of the two π bonds available to each phosphorus atom surrounded by oxygen, one π bond is available to P=O and $\frac{1}{3}$ π bond is available to each P–O.

Acceptance of such a distribution would allow us to ascribe the difference between $\bar{D}$(P=O) and $\bar{E}$(P–O), which is 52 kcal./mole, to the change in phosphorus hybridisation from "sp^3)" to $sp^3(\pi^2)$. Further, if we accept as an approximation that the σ binding energy of the P–O bonds of P_4O_{10} is substantially the same as that in P_4O_6 then we may set the 52 kcal./mole equal to the binding energy of two π bonds (such an approximation is probably more nearly correct in the case of phosphorus than it would be in the case of carbon).

Allocation of the π bonds as suggested by Cruikshank gives the *in situ* binding energy of P=O in P_4O_{10} as $(86 + 26) = 112$ kcal./mole and that of each P–O as $(86 + 26/3) = 94{\cdot}7$. The *in situ* binding energy of P=O we have chosen to call ϵ(P=O).

The P=O bond in P_4O_{10} is unique among such bonds in its length, 1·40 Å, and in the magnitude of the stretching frequency associated with it, 1400 cm.$^{-1}$. In the case of trialkyl phosphates, $(RO)_3PO$, for example, Cruikshank has suggested that the π-bond content of the P=O is about 0·8 with each of the P–O bonds having a contribution of 0·4π-bond. This effect should be reflected in the length and the force constants of the bond. Here, as for other phosphates, length or force constant data are not freely available. However, the nature of the P=O stretching vibration is such that it is substantially independent of other vibrations in the molecules and to a reasonable degree of approximation, we can set ν^2(P=O) proportional to the stretching force constant. This being so, we may establish a scale of *in situ* bond energies for P=O in a range of molecules by means of the equation:

$$\epsilon(\mathrm{P{=}O}) = \bar{E}(\mathrm{P{-}O})_{\mathrm{tervalent}} + E(\pi)$$

where the π-bond energy, $E(\pi)$, may be calculated with reference to that in P_4O_{10} by means of the arbitrary relation:

$$E(\pi) = [\nu^2\mathrm{cm.}^{-1}/(1400\ \mathrm{cm.}^{-1})^2].26$$

in which we suggest that changes in the force constants of P=O bonds are due entirely to changes in the π bond character.

In principle it would be desirable to be able to calculate *in situ* bond energies for P–X bonds in molecules POX_3 by an extension of the above arguments but this is largely precluded by the absence of force-constant data and by difficulty of establishing a norm for π bonding in P–X systems. An alternative arrangement is to evaluate ϵ(P=O) by the above and to assume that

$$D(\mathrm{P{=}O}) - \epsilon(\mathrm{P{=}O}) = E'_{\pi}(\mathrm{P{-}X})/3$$

where $E'\pi(\text{P–X})$ represents the partial π bond energy attaching to the P–X bonds in POX_3.

The quantity $\bar{\epsilon}(\text{P–X})$ may then be calculated to be

$$\epsilon(\text{P–X}) = \bar{E}(\text{P–X})_{\text{tervalent}} + E'_{\pi}(\text{P–X})$$

Values of $\epsilon(\text{P=O})$ for POF_3, $POCl_3$, and $POBr_3$ are found to be 112, 108·5, and 107 kcal./mole, making $\bar{\epsilon}(\text{P–F}) = 123$, $\bar{\epsilon}(\text{P–Cl}) = 82{\cdot}5$, and $\bar{\epsilon}(\text{P–Br}) = 68$ kcal./mole.

An approximate value for the large π bonding contribution to $\bar{\epsilon}(\text{P–N})$ in the phosphoramidates can also be calculated in this way. Assuming that $\bar{E}(\text{P–N})$ in the phosphoramidite is taken as a mean of the observed 71 and 67 kcal./mole, and that $D(\text{P=O})$ in the phosphoramidates is a corresponding mean of 139 and 156 kcal./mole, then since $\nu \sim 1200 \text{cm.}^{-1}$, $\epsilon(\text{P=O})$ is $\sim$105 kcal./mole and $\bar{\epsilon}(\text{P–N})$ in these latter compounds is $\sim$83 kcal./mole.

For the case of tri alkylphosphates and phosphites a slightly more elaborate calculation is possible. The values of $\bar{D}(\text{P–OR})$ in the trialkyl phosphites, derived assuming standard enthalpies of formation for the alkoxy-radicals, are about 92 kcal./mole. These values, which are 6 kcal. greater than $\bar{E}(\text{P–O})$ in P_4O_6, probably reflect changes in the nominal σ bonding of phosphorus due to bonding of alkyl groups.

To estimate $\bar{\epsilon}(\text{P–O})$ in the trialkyl phosphates it is necessary to evaluate $\epsilon(\text{P=O})$, which can as a first approximation be set equal to $\bar{E}(\text{P–O}) + E\pi = (86 + 21)$ kcal./mole, the π bond energy being that of a bond of 0·8π-order or $\nu \sim 1270$ cm.$^{-1}$. This leaves 42 kcal./mole as $[D(\text{P=O} - \epsilon(\text{P=O})]$ which is obviously greater than the 1·2π-bond energy (31 kcal./mole) properly belonging to the three P–O bonds. The difference of 11 kcal./mole must be due to changes in the energy of the σ bond hybrids on passing from sp^3 to $sp^3(\pi^2)$.

From a final allocation of the phosphorus oxygen bonding energies in trialkyl phosphates, $\epsilon(\text{P=O}) = (86 + 21 + \frac{11}{4}) = 110$ kcal./mole, and $\bar{\epsilon}(\text{P–O}) = (92 + 10{\cdot}5 + \frac{11}{4}) = 105{\cdot}5$ kcal./mole.

Extension of the Argument to Cyclic P–N Compounds.—The value of $\bar{\epsilon}(\text{P–X})$ so calculated may now be used to calculate other hypothetical *in situ* bond energies, in four-co-ordinated phosphorus compounds. A particularly interesting example of this application is to the phosphonitrilic compounds, in which force constant data and bond lengths suggest a close analogy between the P–X bonds and those in the corresponding X_3PO molecules, despite the differences in the $p\pi$–$d\pi$ bonding orbitals involved. The values of $\bar{\epsilon}(\text{P–O})$, $\bar{\epsilon}(\text{P–C})$, and $\bar{\epsilon}(\text{P–Cl})$ are used to estimate the value of $\bar{\epsilon}(\text{P–N})$ in the phosphonitrilic compounds from the known heats of formation as in the following example:

$$[\text{PN(cyclo-}C_6H_{11}O)_2]_3(g) \xrightarrow{\Delta H_1} \tfrac{3}{4}P_4(\alpha) + \tfrac{3}{2}N_2(g) + 36C(g) + 33H_2(g) + 30_2$$

$$\xrightarrow{\Delta H_2} 3P + 3N + 6\ (\text{cyclo-}C_6H_{11}O)(g)$$

$$\Delta H_1 + \Delta H_2 = 6\bar{\epsilon}(P\text{–}O) + 6\ (P\text{–}N)$$

where $-\Delta H_1$ is the measured $\Delta H_f°(g)$ for the phosphonitrilic compounds, and ΔH_2 is the sum of the heats of formation of the constituent atoms[10] and radicals. Table 11 illustrates this effect.

TABLE 11. *Binding energies in cyclic phosphorus–nitrogen compounds.*

	$\Delta H_f°(g)$	Assumed $\bar{\epsilon}(P\text{–}X)$	Radical X $\Delta H_f°(g)$	$\bar{\epsilon}(P\text{–}N)$ (kcal./mole)
$(PNCl_2)_3$	−176	82·5	+28·9	70
$(PNCl_2)_4$	−236	82·5	+28·9	70
$[PN(OC_6H_{11})_2]_3$	−562	106·0	−5·8	76
$(PNPh_2)_4$	+59	79·0	+66·9	74
$(PNMe_2)_3$	−105	76·0	+32·0	68

These may be compared with the P–N single bond energies given in Table 8. The values of $\bar{\epsilon}(P\text{–}N)$ in these rings are surprisingly small, particularly compared to the value of 83 kcal. derived for the phosphoramidates. This suggests that the gain of π-bond de-localisation energy can only be obtained at the expense of σ-bond repulsion effects.

Phosphorus Sulphides.—Phosphorus sulphur compounds are similar in certain ways to phosphorus oxygen compounds and we may derive some value of the effective change of binding energy due to π bond formation in P_4S_{10}.

Estimation of P–P and P–S bonds.—The values of $\Delta H_f°$ for $P_2H_4(g)$ and $P_2I_4(g)$ can be used in conjunction with the above values of $\bar{E}(P\text{–}H)$ and $\bar{E}(P\text{–}I)$ to give values of $\bar{E}(P\text{–}P)$ of 52 and 67 (using the questionable value for the heat of sublimation of P_2I_4 of 30 kcal./mole). Alternatively, using the value for $\bar{E}(P\text{–}P)$ in P_4 as 50 kcal./mole we can derive a value of $\bar{E}(P\text{–}S)$ in P_4S_5 to be 52·4 kcal./mole, on the basis of the reported structure given by van Houten, *et al.*[59]

If we assume that the P–S σ bond energy is 52 kcal./mole (cf. above) then the energy in eight effective π bonds (two per P atom) is calculable from the approximate heat of atomisation −880 kcal./mole for $P_4S_{10}(g)$ by subtracting from it the energy of sixteen σ bonds. This gives a difference of 50 kcal./mole, or about 6 kcal/π-bond.

The values of $D(P{=}S)$ in organic thiophosphates are about 90 kcal./mole,[75] very much greater than $\bar{E}(P\text{–}S)$, and it is plausible to assume, as in the case of organic phosphates, that the $\bar{E}(P{=}S)$ is about $(52 + 6)$ kcal./mole, and that the difference of 32 kcal./mole is, as in the phosphates, due to partial π binding effects arising in the three RO–P bonds and to changes in the overall σ binding on passing to the "quinquevalent" compound.

Double Bonds to Phosphorus.—Consideration of the preceding thermochemical values shows that the increase in binding, resulting from the formation of a formal "double bond" in phosphorus compounds, appears to be accompanied by smaller energy changes than is the case for the well known carbon compounds. No precise interpretation of this finding has been reported and it seems likely that several causes contribute to produce the effect.

The π bonds formed by phosphorus make use of d_π orbitals which give most favourable binding when the central phosphorus atom is rendered effectively positive by the attachment of electronegative groups to it. As we have seen above, these electronegative groups, attached by formal single bonds to the phosphorus, require a considerable fraction of the two orbitals available for binding, making a formal double bond less strong than a full ($\sigma + \pi$) combination. However, even when allowance for this is made, π binding effects remain small in comparison to the calculated orbital overlap effects.

Caldow and Coulson[80] suggested that the contribution of the coulombic term to binding energy is much higher than is usually assumed. If this is so, the repulsion effects due to the lone pair in tervalent phosphorus and the sensitivity of the phosphorus hybrid orbitals in the quinquevalent state to electrostatic influences may both reflect in the difference term from which the effective π-bonding energies have been deduced.

Again, it is by no means certain that comparisons with carbon are fully relevant since the concomitant changes of σ binding which occur on passing from sp^3 to $sp^2(p_\pi)$ in the case of carbon may make more difference to the net binding energy than the change in σ energy involved on passing from sp^3 (lone pair), to $sp^3(d_\pi{}^2)$ in phosphorus.

At present no completely relevant quantitative theory on binding energies in phosphorus compounds has been published, and it seems scarcely profitable to try to discuss these effects further here.

The Bond Energies in Pentahalides.—Values of $\Delta H_f{}^\circ$ in the gaseous pentahalides may be used to evaluate $\bar{E}$(P–Hal) in these compounds, dividing the heats of atomisation by five. In this way a value of 63·0 kcal./mole for $\bar{E}$(P–Cl) and of 52 kcal./mole for $\bar{E}$(P–Br) are calculated. It seems clear from the differences in bond length and stretching force constant in PCl_5[81] that the equatorial bonds ($k = 2{\cdot}89$ md/Å) are much stronger than the axial bonds ($k = 1{\cdot}8$ md/Å) in the trigonal bipyramidal structure. The force constant for the equatorial bonds is closely similar to that in phosphorus oxychloride, and if we assume that the energy value of these three bonds are $\bar{\epsilon}$(P–Cl) 82·5 kcal./mole then the average value for the axial bond is about 34 kcal./mole.

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[80] Caldow and Coulson, *Trans. Faraday Soc.*, 1962, **58**, 633.
[81] Cotton, *J. Chem. Phys.*, 1961, **35**, 228.

In the case of phosphorus pentabromide information on the force constants yields only an average value. The value of $\bar{E}$(P–Br) in this compound however, is considerably less than in the tribromide and the situation is probably very similar to that in phosphorus pentachloride. The binding in these compounds involves the assumed hybrid sp^3d and, as discussed above, it has been shown by Craig *et al.*[4,82] that the full participation of the *d* orbitals requires the attachment of highly electronegative groups to the phosphorus. It is unfortunate that no accurate data have been published for phosphorus pentafluoride.

[82] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.