The Thermochemistry of Organic Phosphorus Compounds. Part I. Heats of Hydrolysis and Oxidation.

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In order to obtain data on the heats of formation of organic phosphorus compounds for which the usual methods of combustion calorimetry proved unsatisfactory, a number of typical reactions have been studied in a simple Dewar vessel calorimeter. Although the information thus obtained does not necessarily permit the direct computation of heats of formation, it does enable approximate values to be assigned for " average bond-energy terms " which can be used to estimate heats of formation or reaction. The present paper deals with hydrolytic and oxidative reactions.

THIS investigation was undertaken to obtain preliminary values for the heats of formation of some simple organic compounds of phosphorus. Comparatively little work has been done on the thermochemistry of phosphorus and, with the exception of methylphosphonic acid reported by Thompson (*J.*, 1952, 3292) after the commencement of this work, no organophosphorus compounds have been studied hitherto.

One reason for this lack of data is the difficulty, experienced by both Thompson and ourselves, of securing complete combustion and of determining the precise stoicheiometry of the bomb reaction with phosphorus compounds. We were therefore compelled to resort for the most part to reaction calorimetry, for which purpose we were able to find a number of convenient reactions, but the data obtained were of course dependent on the heats of formation accepted for the parent substances, phosphorous acid, orthophosphoric acid, and phosphorus trichloride and oxychloride. The values given in " Selected Values of Chemical Thermodynamic Properties " (National Bureau of Standards, Circular 500) are based on determinations carried out some eighty years ago and only in the case of orthophosphoric acid are more recent data available, confirming the earlier work. In a note (*J.*, 1952, 4535) we gave revised values for the two chlorides, and these results were supported reasonably well by the independent work of Charnley and Skinner (*J.*, 1953, 450) carried out at about the same time.

In this work, the N.B.S. Circular 500 values were used for heats of formation of phosphorous and phosphoric acids but in view of the uncertainty regarding the former, the heat of formation of the trichloride was redetermined by simultaneous hydrolysis and

oxidation, thus enabling $\Delta H_f°(H_3PO_4)$ rather than $\Delta H_f°(H_3PO_3)$ to be used in the computation. This work has also been published by us (*J.*, 1954, 2156).

This paper reports the heats of hydrolysis of several phosphorus halides and other compounds, and the heats of oxidation of some compounds of tervalent phosphorus. The data obtained are used to derive heats of formation, where possible, and values for the relevant " average bond energies " (cf. Cottrell and Sutton, *Quart. Reviews*, 1948, **2**, 260). In a later paper it is intended to report similar data on heats of esterification and anilide formation, and heats of combustion of some anilides formed from phosphorus halides.

EXPERIMENTAL

Preparation of Compounds.—(i) Methyl and ethylphosphonic dichlorides : by hydrolysis of the complex of the appropriate alkyl chloride with phosphorus trichloride and aluminium chloride (Kinnear and Perren, *J.*, 1952, 3437). (ii) Tri*iso*propyl phosphite : by Ford-Moore and Perry's method (*Org. Synth.*, **31**, 111). (iii) Diethyl hydrogen phosphite : by esterification of the trichloride in the absence of base (McCombie, Saunders, and Stacey, *J.*, 1945, 380). (iv) Ethyldichlorophosphine : by treatment of tetraethyl-lead with phosphorus trichloride (Kharasch, Jensen, and Weinhouse, *J. Org. Chem.*, 1949, **14**, 429). (v) Tetraethyl pyrophosphate : treatment of the silver salt of diethyl hydrogen phosphate with diethyl chloro-phosphonate (details of this preparation will be published later). (vi) Diethyl phosphoro-fluoridate : by Saunders and Stacey's method (*J.*, 1948, 695).

The method used for the preparation of *iso*propyl methylphosphonochloridate will be published later.

All materials were purified by repeated distillation under reduced pressure, the tervalent phosphorus compounds being distilled under nitrogen. Purity was checked by hydrolysis and acidimetry for the halides and the pyrophosphate, and by reaction with iodine buffered with bicarbonate for the phosphite esters. Refractive indices agreed well with published data where available (see below) and infrared spectra gave no evidence of impurity except for tri*iso*propyl phosphite where a trace of phosphate was indicated. In the latter case purity was assessed at 98·5% ; all other compounds came within the range 99·0—99·8% purity.

	B. p. (M. p.)	n_D^{25}
Methylphosphonic dichloride	86°/44 mm. (33°)	—
Ethylphosphonic dichloride	65°/5 mm.	1·4630
Diethyl phosphorofluoridate	63°/12 mm.	1·3724
Diethyl hydrogen phosphite	77°/17 mm.	1·4064
Tri*iso*propyl phosphite	43°/1 mm.	1·4080
*iso*Propyl methylphosphonochloridate	47°/3 mm.	1·4280
Ethyldichlorophosphine	112°/760 mm.	—
Tetraethyl pyrophosphate	110°/0·05 mm.	1·4176

Procedure.—The calorimeter was of the Dewar-vessel type described previously (*loc. cit.*) ; it was calibrated electrically. The samples were contained in glass ampoules which were broken under the surface of the liquid ; they were filled in a glove-box through which dry air was circulated (dry nitrogen was used when handling tervalent phosphorus compounds). All measurements were carried out between 22° and 23°.

Hydrolytic reactions were carried out in distilled water where possible, but in a few cases, noted below, aqueous sodium hydroxide was necessary. For the oxidation of phosphite esters, a variety of oxidants was examined but only (i) aqueous hydrogen peroxide and (ii) a solution of iodine buffered with bicarbonate were suitable. Oxidation of ethyldichlorophosphine was carried out in benzene containing sulphuryl chloride.

Analysis of Products.—In the hydrolysis reactions, the products were determined acidimetrically, and results agreed well with analyses on the original compounds, *i.e.*, reactions were >99% quantitative. For the oxidation reactions it was necessary to have the oxidant present in large excess and an accurate assessment of the amount consumed was impracticable ; however, a check was made by means of separate non-calorimetric runs in which the ratio of sample to oxidant was greater, an increased time being allowed for completion of the reaction.

Heats of solution, and heats of neutralisation of acids where relevant, were determined in the same apparatus as used for the main investigation. Latent heats of vaporisation were estimated from vapour-pressure plots, except where published information on latent heat was already available.

Subsidiary thermochemical data used in deriving heats of formation (ΔH_f°) and average bond energies were taken from National Bureau of Standards, Circular 500.

Estimates of Error.—Purely calorimetric errors have been assessed in the course of calibration; they are not greater than $\pm 1 \cdot 0\%$. Errors due to impurity in materials and to side reactions are probably less than 1% for the hydrolytic experiments but may be 2% in the oxidation studies. Latent heat estimates are in some cases very approximate but errors are unlikely to be greatly in excess of one kcal.

Results.—R = moles of solvent per mole of sample.

(a) *Hydrolysis of alkylphosphonic dichlorides in water*: $R \cdot POCl_2 + 2H_2O(l.) \longrightarrow R \cdot PO(OH)_2(aq.) + 2HCl(aq.).$

		(i) Me·POCl$_2$ (c.)					(ii) Et·POCl$_2$ (l.)		
Wt. (g.)	R	ΔH, obs. (kcal.)	Wt. (g.)	R	ΔH, obs. (kcal.)	Wt. (g.)	R	ΔH, obs. (kcal.)	Wt. (g.)	R	ΔH, obs. (kcal.)

Wt. (g.)	R	ΔH, obs. (kcal.)	Wt. (g.)	R	ΔH, obs. (kcal.)	Wt. (g.)	R	ΔH, obs. (kcal.)	Wt. (g.)	R	ΔH, obs. (kcal.)
0·7839	4700	−47·2	0·8191	4500	−47·1	0·6808	6000	−49·4	0·7730	5300	−49·6
0·6670	5500	−46·7	0·5751	6400	−46·9	0·5455	7500	−49·0	1·0795	3800	−49·5
				Mean	−47·0					Mean	−49·4

ΔH (soln.) Me·PO(OH)$_2$ = <0·1. $\qquad\qquad\qquad$ ΔH (soln.) Et·PO(OH)$_2$ = <0·1.

Heats of formation of the halides cannot be derived directly from the above, but the data can be reduced to :

(i) ΔH_f°Me·POCl$_2$(c.) − ΔH_f°Me·PO(OH)$_2$ (c.) = 103·8 kcal./mole.

(ii) ΔH_f°Et·POCl$_2$(l.) − ΔH_f°Et·PO(OH)$_2$ (c.) = 106·2 kcal./mole.

(b) *Hydrolysis of* iso*propyl methylphosphonochloridate in water* : (Pr^{i}O)MePOCl(l.) + H$_2$O(l.) $\longrightarrow$ (Pr^{i}O)MePO·OH(aq.) + HCl(aq.).

Wt. (g.)	0·6047	0·6689	1·0260	0·6498	
R	7200	6500	4200	6700	
ΔH, obs. (kcal.)	−30·0	−29·3	−30·0	−28·7	Mean −29·5

ΔH (soln.) (Pr^{i}O)MePO·OH = − 5·5 kcal.
ΔH_f° (Pr^{i}O)MePO·Cl (l.) − ΔH_f°(Pr^{i}O)MePO·OH (l.) = 52·4 kcal.

(c) *Hydrolysis of diethyl phosphorofluoridate in aqueous sodium hydroxide* (0·5N) : (EtO)$_2$POF(l.) + 2NaOH(aq.) $\longrightarrow$ (EtO)$_2$PO·ON·ONa(aq.) + NaF(aq.) + H$_2$O(l.).

Wt. (g.)	0·8400	0·8650	1·1857	1·2012	
R	5200	5100	3700	3600	
ΔH, obs. (kcal.)	−46·4	−46·1	−47·2	−46·9	Mean −46·6

Heat of reaction of diethyl hydrogen phosphate with aqueous NaOH = − 22·0 kcal.
ΔH_f°(EtO)$_2$POF(l.) − ΔH_f°(EtO)$_2$PO·OH(l.) = +0·9 kcal.

(d) *Hydrolysis of tetraethyl pyrophosphate in aqueous sodium hydroxide* (0·5N) : (EtO)$_2$PO·O·PO(OEt)$_2$(l.) + 2NaOH(aq.) $\longrightarrow$ 2(EtO)$_2$PO·ONa(aq.) + H$_2$O(l.).

Wt. (g.)	1·8975	1·5970	2·5271	1·9360	
R	4200	5000	3200	4100	
ΔH, obs. (kcal.)	−58·1	−58·1	−58·1	−58·6	Mean −58·2

ΔH_f° (EtO)$_2$PO·O·PO(OEt)$_2$ (l.) − 2ΔH_f° (EtO)$_2$PO·OH (l.) = 82·5 kcal.

(e) *Oxidation of tri*iso*propyl phosphite to phosphate with neutral aqueous hydrogen peroxide* (5%) : (Pr^{i}O)$_3$P(l.) + H$_2$O$_2$(aq.) $\longrightarrow$ (Pr^{i}O)$_3$PO(aq.) + H$_2$O(l.).

Wt. (g.)	1·3022	0·8343	1·1167	
R	4400	6900	5200	
ΔH, obs. (kcal.)	−103·1	−104·5	−103·2	Mean −103·6

ΔH (soln.) (Pr^{i}O)$_3$PO = − 3·6 kcal.
ΔH_f° (Pr^{i}O)$_3$P (l.) − ΔH_f° (Pr^{i}O)$_3$PO (l.) = 77·4 kcal.

(f) *Oxidation of ethyldichlorophosphine with sulphuryl chloride in benzene* : EtPCl$_2$(l.) + SO$_2$Cl$_2$(benzene) $\longrightarrow$ Et·POCl$_2$(benzene) + SOCl$_2$(benzene).

Wt. (g.)	0·9855	0·8877	0·6384	0·7413	
R	750	840	1160	1000	
ΔH, obs. (kcal.)	−40·8	−40·1	−40·7	−40·9	Mean −40·6

ΔH (soln.) Et·POCl$_2$ in benzene = < 0·1 kcal.
ΔH (soln.) SO$_2$Cl$_2$ in benzene = < 0·1 kcal.
ΔH (soln.) SOCl$_2$ in benzene = − 0·6 kcal.

Using the values for $\Delta H_f°SOCl_2$ and $\Delta H_f°SO_2Cl_2$ given in *J.*, 1954, 2156, we get :
$\Delta H_f°EtPCl_2(l.) - \Delta H_f°Et·POCl_2(l.) = 74·8$ kcal.

(g) *Oxidation of diethyl hydrogen phosphite with iodine in the presence of bicarbonate* :
$(EtO)_2P·OH(l.) + KI_3(aq.) + 3KHCO_3(aq.) \longrightarrow$
$(EtO)_2PO·OK(aq.) + 3KI(aq.) + 3CO_2(aq.) + 2H_2O(l.)$

Wt. (g.)	1·1464	0·7065	0·9133	0·9160	
R	3300	5500	4200	4200	
ΔH, obs. (kcal.)	−56·7	−57·2	−57·4	−56·7	Mean −57·0

Heat of reaction of diethyl hydrogen phosphate with aqueous KOH : −22·4 kcal./mole.
$\Delta H_f°(EtO)_2P·OH(l.) - \Delta H_f°(EtO)_2PO·OH(l.) = 81·5$ kcal.

DISCUSSION

Although it is not possible to derive heats of formation directly from the data recorded above, the information is useful in permitting the computation of " average bond-energy " terms from which heats of formation can be estimated when used in conjunction with similar data on other phosphorus bonds (to be reported in a subsequent paper). Ideally such quantities should be derived from the heats of formation of molecules containing only one type of bond PX_n, when

$$\bar{D}(P–X) = Q_f(a)PX_n/n$$

where $Q_f(a)PX_n$ is the heat of formation of the compound in the gaseous state from normal gaseous atoms. For tervalent phosphorus such data are available in the case of the halides and phosphine :

$\bar{D}$(P–F) 117 kcal.[1] $\bar{D}$(P–Cl) 76·3 kcal.[2] $\bar{D}$(P–Br) 61·7 kcal.[3] $\bar{D}$(P–H) 76·3 kcal.[4]

[1] Berthelot, *Ann. Chim. Phys.*, 1885, **6**, 358.   [2] Neale and Williams, *J.*, 1954, 2156.   [3] Charnley and Skinner, *J.*, 1953, 450; Neale and Williams, *loc. cit.*   [4] Nat. Bur. Stand., Circular 500 (1952).

A compound such as phosphorus pentachloride does not afford similar information for quinquevalent phosphorus, as the polar and equatorial bonds are known to differ (cf. bond lengths) and in any case its structure (trigonal bipyramid) is such that data obtained from it could not be applied to compounds containing the phosphoryl (P=O) bond, which have a tetrahedral structure. The first step in deriving average bond-energy terms for quinquevalent organic phosphorus compounds is therefore to determine the quantity to be allowed for the phosphoryl bond.

Estimates of bond energy in the P=O bond, based on thermochemical measurements involving the formation of the latter, must necessarily be empirical, as they embody not only the valency promotion energy but also any change resulting from strengthening of other bonds in the molecule. Since the bonds in tervalent phosphorus compounds are probably formed from the p orbitals, and those in the phosphoryl compounds from hybridised orbitals, the latter would be expected to be the stronger. A number of estimates of the phosphoryl bond energy are possible both from previously published data and from those recorded above; in all cases the phosphoryl compound is compared directly with the corresponding tervalent compound :

Basis of estimate	D(P=O) (kcal.)	Source of information
$\Delta H_f°$ P_4O_6 and P_4O_{10}	115	Koerner and Daniels, *J. Chem. Phys.*, 1952, **20**, 113, and private communication
$\Delta H_f°$ PCl$_3$ and POCl$_3$	127·5	Neale and Williams, *J.*, 1952, 4535; 1954, 2156
ΔH oxidation of PF$_3$	129·8	Ebel and Bretscher, *Helv. Chim. Acta*, 1929, **12**, 450
ΔH oxidation of (Pr^{i}O)$_3$P	134·1	Present paper, (e) above
ΔH oxidation of EtPCl$_2$	131·0	Present paper, (f) above

More recently Skinner (private communication) has determined the heat of oxidation of triethyl phosphite with hydrogen peroxide in ethanol; his results indicate a value exceeding 140 kcal. for D(P=O). Although the phosphoryl bond energy probably varies to some

extent, it is evident from bond-length data in the case of phosphorus halides that the effect is partly due to strengthening of the P–Cl bond :

	PCl_3 [a]	$POCl_3$ [b]
P–Cl	2·04 Å	1·99 Å

[a] Kisliuk and Townes, *Phys. Rev.*, 1950, **78**, 347. [b] Williams, Gordy, and Sheridan, *J. Chem. Phys.*, 1952, **20**, 164.

Although similar bond-length data are not available for the phosphorus esters, it seems likely that the effect is even more marked and in a subsequent paper we shall present evidence, based on the heats of esterification of PCl_3 and $R \cdot POCl_2$ type compounds, which indicates that the P–OR link in quinquevalent compounds is appreciably stronger than in tervalent compounds.

For the practical purpose of setting up a table of average bond-energy terms, however, it is legitimate to regard $D(P=O)$ as constant provided that the experimental data involve only reactions of phosphoryl compounds. In effect this necessitates independent assessments of bond-energy terms for (i) tervalent phosphorus compounds and (ii) quinquevalent (phosphoryl) compounds. The following estimates are made on the assumption of a constant minimum value of $D(P=O) = 115$ kcal. The only justification for adopting this figure (apart from the evidence of Koerner and Daniels) is that bond-length measurements on the phosphorus halides suggest a strengthening of the P–X link in POX_3 as compared with PX_3; if this is so, direct comparison of the heats of formation of phosphorus and phosphoryl halides will give values for $D(P=O)$ which are too high.

The method of deriving the bond-energy terms presents no novelty; it will be self-evident from the example given below the table.

Heat of formation data used	Heat of vaporn. or sublimn. (kcal.)	Reference	Average bond-energy in the phosphoryl molecule (kcal.)	
$POCl_3$	9·5	Neale & Williams, *J.*, 1952, 4535	$\bar{D}$(P–Cl)	80
$POBr_3$	15·0	Charnley & Skinner, *J.*, 1953, 450	$\bar{D}$(P–Br)	65
Me·$POCl_2$–	14·9	Present paper	$\bar{D}$(P–OH)	105
Me·PO(OH)$_2$	11·5	(a) (i) above		
Et·$POCl_2$–	10·2	Present paper,	$\bar{D}$(P–OH)	104
Et·PO(OH)$_2$	12·1	(a) (ii) above		
(Pr^{i}O)MePO·Cl–	14·0	Present paper,	$\bar{D}$(P–OH)	104
(Pr^{i}O)MePO·OH	14·5	(b) above		
(EtO)$_2$POF–	11·0	Present paper,	$\bar{D}$(P–F)	120
(EtO)$_2$PO·OH	10·0	(c) above		
(EtO)$_2$PO·O·PO(OEt)$_2$–	13·1	Present paper,	$\bar{D}$(P–OP)	96
2(EtO)$_2$PO·OH	10·0	(d) above		
P_4O_{10}	17·6	Roth, Meichsner, & Richter, *Arch. Eisenhuttenw.*, 1934, **8**, 239	$\bar{D}$(P–OP)	95
(EtO)$_2$P·OH–	7·0	Present paper,	$\bar{D}$(P–H)	78
(EtO)$_2$PO·OH	10·0	(g) above		

Example :

$$\Delta H_f^\circ \text{Me} \cdot POCl_2(c.) - \Delta H_f^\circ \text{Me} \cdot PO(OH)_2(c.) = 103 \cdot 8 \text{ kcal.}$$

or

$$Q_f \text{Me} \cdot PO(OH)_2(c.) - Q_f \text{Me} \cdot POCl_2(c.) = 103 \cdot 8 \text{ ,,}$$

in the gaseous phase :

$$Q_f \text{Me} \cdot PO(OH)_2(g.) - Q_f \text{Me} \cdot POCl_2(g.) = 107 \cdot 2 \text{ ,,}$$

from atoms :

$$Q_f(a)\text{Me} \cdot PO(OH)_2 - Q_f(a)\text{Me} \cdot POCl_2 = 271 \cdot 6 \text{ ,,}$$

Putting k for the heat of formation from atoms of that part of the molecule common to both, we have

$$Q_f(a)\text{Me} \cdot PO(OH)_2 = k + 2(\text{P–OH}) + 2(\text{O–H})$$

$$Q_f(a)\text{Me} \cdot POCl_2 = k + 2(\text{P–Cl})$$

and $\quad Q_f(a)\text{Me} \cdot PO(OH)_2(a) - Q_f(a)\text{Me} \cdot POCl_2 = 2(\text{P–OH}) + (2 \times 110 \cdot 5) - (2 \times 80 \cdot 0)$

Therefore $271 \cdot 6 = 2(\text{P–OH}) + 61 \cdot 0$ and $\bar{D}(\text{P–OH}) = \frac{1}{2}(271 \cdot 6 - 61 \cdot 0) = 105 \cdot 3$ kcal.