84. *The Thermochemistry of Organic Phosphorus Compounds. Part II.* Ester and Anilide Formation from Halides, and Combustion of the Anilides.*

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In continuation of the work reported in Part I * reaction calorimetry has been extended to cover ester formation from tervalent and quinquevalent phosphorus halides and also anilide formation from alkylphosphonic dihalides. Heats of combustion of the anilides have also been determined. The combined data have permitted the compilation of a table of " average bond-energy " terms from which it is possible to make an approximate estimate of heats of formation or reaction of most compounds in the organophosphorus field.

This work continues that reported in Part I,* in order to obtain sufficient data to permit the compilation of a table of average bond-energy terms to be used to estimate heats of formation or reaction of organic compounds containing phosphorus. Reaction calorimetry has been extended to include ester formation from tervalent and quinquevalent phosphorus halides and alcohols in the presence of a tertiary base, and also the formation of anilides from alkylphosphonic dihalides. None of the reactions, however, gave direct information on the carbon–phosphorus bond. Considerable difficulty was experienced in the application of usual methods of combustion calorimetry to phosphorus compounds, the majority

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* Part I, *J.*, 1955, 2485.

being hygroscopic liquids which gave erratic results suggestive of incomplete burning. An exception was, however, found in the dianilides; they are non-hygroscopic solids, and although the precision achieved was well below that of the most refined modern techniques, results were sufficiently consistent to provide, with those from reaction calorimetry useful data to estimate (1) the heats of formation of the alkylphosphonic dihalides and (2) the average bond-energy term to be assigned to the carbon–phosphorus bond.

EXPERIMENTAL

Preparation of Compounds.—Purification of phosphorus trichloride and preparation and purification of methyl- and ethyl-phosphonic dichlorides were effected as already described.[1] Methyl- and ethyl-phosphonic dianilides were prepared by treating the appropriate alkylphosphonic dichloride with excess of aniline, dissolving the product in benzene, and washing the solution with dilute hydrochloric acid. The anilides were recrystallised first from benzene–chloroform and then aqueous alcohol: *methylphosphonic dianilide* had m. p. 158° (Found: C, 63·2; H, 6·3. $C_{13}H_{15}ON_2P$ requires C, 63·4; H, 6·1%), and *ethylphosphonic dianilide*, m. p. 147° (Found: C, 64·6; H, 6·7. $C_{14}H_{17}ON_2P$ requires C, 64·5; H, 6·6%).

Reaction Calorimetry.—The Dewar-vessel calorimeter and procedure were as in earlier work.[1] Samples were filled into glass ampoules in a glove-box through which dry air or dry nitrogen was passed. Phosphorus trichloride was esterified in *cyclo*hexane (sodium-dried) with dimethylaniline ("AnalaR" dried over KOH) as the tertiary base. These conditions were not satisfactory for esterification of alkylphosphonic halides; dioxan ("AnalaR" sodium-dried) with triethylamine was found to be most suitable. Triethylamine was purified by recrystallisation of the hydrochloride; the purified product was dried by distillation over barium oxide.

Absolute alcohol was dried by distillation after refluxing with magnesium turnings and iodine; *iso*propanol ("AnalaR") was distilled over aluminium *iso*propoxide.

The heat of anilide formation was also measured in *cyclo*hexane in which both the anilides and the aniline hydrochloride produced in the reaction were insoluble, thus minimising the work of measuring heats of solution. Ethylphosphonic dichloride, being a liquid at room temperature, was introduced undiluted, but methylphosphonic dichloride, a solid, gave more consistent results when added as a concentrated solution in benzene. Aniline was distilled over zinc dust and dried (KOH).

Heats of solution were measured in the apparatus used for the main reactions. It was also necessary to determine the heats of formation of the base hydrochlorides; in the case of aniline and dimethylaniline the heats of hydrolysis of the salts in aqueous sodium hydroxide were measured. Erratic results were obtained by this technique for triethylamine hydrochloride, but the necessary results were satisfactorily obtained by breaking an ampoule containing a weighed amount of standard hydrochloric acid into an aqueous solution of triethylamine.

As an analytical check on reactions with aniline and esterification in the presence of dimethylaniline, the base hydrochlorides were filtered off and titrated against sodium hydroxide with phenolphthalein as indicator. In reactions involving triethylamine the hydrochloride was recovered and estimated by titration of chloride ion. All reactions were carried out at 22—23°.

Combustion Calorimetry.—The calorimeter and jacket which were made of chromium-plated copper were similar to those described by Dickinson.[2] The stainless-steel bomb (300 ml. capacity) was of the standard B.T.L. Type (L.F.A. 6330). Temperature was measured by a mercury-in-glass thermometer of range 21—27° graduated to 0·01° and calibrated to 0·001°. All combustions were carried out in 30 atm. of oxygen, with the bomb containing 10 ml. of water. The water equivalent of the apparatus was assessed by repeated combustion of benzoic acid obtained from the Bureau of Analysed Samples Ltd.; results were reproducible to within ±0·1%.

Considerable difficulty was encountered in the choice of a crucible. Silica was first used but there was evidence of attack by the phosphoric acid produced; nickel, fused alumina, and fused zirconia were also tried and rejected. Platinum was finally adopted; it appeared to be unattacked chemically although there was evidence of physical change (development of cracks) after repeated use. The samples were fused in the crucible before being weighed, the amount taken being such as to give ΔT within 0·1° of that in the benzoic acid calibration. Combustion

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[1] Neale and Williams, *J.*, 1954, 2156; 1955, 2485.

[2] Dickinson, *Nat. Bur. Stand. Bull.*, 1915, **17**, 189.

was started with the calorimeter at 22·00°; the final temperature was approximately that of the thermostat (25°). Washburn corrections were not applied.

In the preliminary experiments the combustion products were analysed for ortho-, pyro-, and meta-phosphoric acid; results showed that 93—96% was present as orthophosphoric acid. As the error involved in treating the whole as the last acid would not exceed 0·3—0·4 kcal. under the worst conditions it was decided to determine only total phosphoric acid; Wilson's quinoline-phosphomolybdate method [3] was used. Nitric acid in the bomb was also determined by the phenoldisulphonic acid method.

Latent heats of vaporisation were estimated from vapour-pressure data except where published information was available. Subsidiary thermochemical data used in deriving heats of formation and average bond-energy terms were taken from the National Bureau of Standards Circular 500 (Feb. 1952).

Results.—(a) *Esterification of phosphorus trichloride with alcohols in the presence of dimethylaniline* (*solvent,* cyclo*hexane*) :

$$PCl_3\ (liq.) + 3ROH\ (soln.) + 3Ph\cdot NMe_2\ (soln.) \longrightarrow P(OR)_3\ (soln.) + 3Ph\cdot NMe_2,HCl\ (solid) \quad . \quad (1)$$

Approximately 4 moles of alcohol and 4 moles of base were taken for each mole of phosphorus trichloride. Results were as follows :

(i) Ethyl alcohol

Wt. of PCl_3 (g.)	Moles of solvent per mole of PCl_3	$\Delta H_{obs.}$ (kcal.)
1·0281	610	−89·6
0·9302	680	−90·5
0·5705	1100	−91·0
	Mean	−90·4

(ii) *iso*Propyl alcohol

Wt. of PCl_3 (g.)	Moles of solvent per mole of PCl_3	$\Delta H_{obs.}$ (kcal.)
0·8610	730	−90·7
0·7701	820	−90·4
0·6315	1000	−91·2
	Mean	−90·8

Recovery of dimethylaniline hydrochloride as determined by titration with standard alkali varied between 98 and 99% of theoretical; no correction was applied to $\Delta H_{obs.}$ on this account.

For the reaction of dimethylaniline hydrochloride with aqueous sodium hydroxide (0·2N) :

$$Ph\cdot NMe_2,HCl\ (solid) + NaOH\ (aq.) \longrightarrow Ph\cdot NMe_2\ (liq.) + NaCl\ (aq.) + H_2O\ (liq.) \quad . \quad (2)$$

$\Delta H_{obs.} = -5{\cdot}8$ kcal./mole, whence $\Delta H_f^\circ(Ph\cdot NMe_2,HCl) = \Delta H_f^\circ(Ph\cdot NMe_2) - 47{\cdot}6$ kcal. Heats of solution in *cyclo*hexane (in kcal./mole) were as folows : Dimethylaniline, +1·7; ethyl alcohol, +4·7; *iso*propyl alcohol, +4·2; triethyl phosphite, +1·5; tri*iso*propyl phosphite, +0·8. Substituting the above data in equation (1), we get : $\Delta H_f^\circ[P(OEt)_3]$ (liq.) = −203·5 kcal./mole, and $\Delta H_f^\circ[P(OPr^i)_3]$ (liq.) = −235·0 kcal./mole.

With allowance for both calorimetric and chemical errors these values are probably reliable to within ±2·0 kcal.

(b) *Esterification of alkylphosphonic dichlorides with alcohols in the presence of triethylamine* (*solvent, dioxan*) :

$$R\cdot POCl_2 + 2R'OH\ (soln.) + 2Et_3N\ (soln.) \longrightarrow R\cdot PO(OR')_2\ (soln.) + 2Et_3N,HCl\ (solid) \quad . \quad (3)$$

3—4 Moles of alcohol and base were used for each mole of $R\cdot POCl_2$. The results are given below.

(i) R = Me, R′ = Et

Wt. of $R\cdot POCl_2$ (g.)	Moles of solvent per mole of $R\cdot POCl_2$	ΔH_{obs} (kcal.)
0·8760	870	−89·2
0·9851	770	−89·4
0·6322	1200	−90·1
0·7480	1000	−88·5
	Mean	−89·3

(ii) R = Et, R′ = Pr^i

Wt. of $R\cdot POCl_2$ (g.)	Moles of solvent per mole of $R\cdot POCl_2$	$\Delta H_{obs.}$ (kcal.)
0·8167	1000	−93·7
0·8596	975	−93·5
0·6885	1200	−94·0
0·7405	1100	−92·8
	Mean	−93·5

Recovery of triethylamine hydrochloride as determined by estimation of chloride was 97·8—98·6% of theoretical; values of $\Delta H_{obs.}$ were not corrected for this. The reaction of triethylamine with aqueous hydrochloric acid :

$$Et_3N\ (aq.) + HCl\ (aq.) \longrightarrow Et_3N,HCl\ (aq.) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

whence $\Delta H_f^\circ(Et_3N,HCl) = \Delta H_f^\circ(Et_3N) - 60{\cdot}3$ kcal.

[3] Wilson, *Analyst*, 1951, **76**, 65.

Heats of solution (kcal./mole) in dioxan were as follows: triethylamine, +1·0; ethyl alcohol, +1·5; *iso*propyl alcohol, +1·6; diethyl methylphosphonate, +0·6; di*iso*propyl ethylphosphonate, +0·4. Substituting the above data in equation (3)we get: $\Delta H_f°$[Me·$POCl_2$] (cryst.) − $\Delta H_f°$[Me·PO(OEt)$_2$] (liq.) = +97·1 kcal., and $\Delta H_f°$ [Et·$POCl_2$] (liq.) − $\Delta H_f°$ [EtPO(OPr^i)$_2$] (liq.) = +121·1 kcal. These values are probably reliable to within ±2·0 kcal.

(c) *Reaction between alkylphosphonic dichlorides and aniline* (*solvent*, cyclo*hexane*):

$$R{\cdot}POCl_2 + 4Ph{\cdot}NH_2\ (soln.) \longrightarrow R{\cdot}PO(NHPh)_2\ (solid) + 2Ph{\cdot}NH_2{,}HCl\ (solid) \quad . \quad (5)$$

The calorimeter filling was approximately 0·5M with respect to aniline. The results are given below.

(i) R = Me

Wt. of Me·$POCl_2$ (g.)	Moles of solvent per mole of Me·$POCl_2$	ΔH_{obs} (kcal.)
0·7676	760	−71·6
0·6204	940	−71·9
0·5849	1000	−71·9
0·6227	940	−71·8
	Mean	−71·8

(ii) R = Et

Wt. of Et·$POCl_2$ (g.)	Moles of solvent per mole of Et·$POCl_2$	$\Delta H_{obs.}$ (kcal.)
1·0917	590	−72·5
0·6697	970	−73·6
0·5116	1260	−72·4
0·7196	900	−72·1
	Mean	−72·7

Extraction of the precipitates with water and titration with sodium hydroxide (phenolphthalein) gave 1·99—2·01 moles of aniline hydrochloride per mole of R·$POCl_2$.

For the reaction of aniline hydrochloride with aqueous sodium hydroxide (0·2N):

$$Ph{\cdot}NH_2{,}HCl\ (solid) + NaOH\ (aq.) \longrightarrow Ph{\cdot}NH_2\ (liq.) + NaCl\ (aq.) + H_2O\ (liq.) \quad . \quad (6)$$

ΔH, obs. = −3·2 kcal./mole, whence $\Delta H_f°$(Ph·NH_2,HCl) = −42·9 kcal./mole. The heat of solution of Me·$POCl_2$ in benzene was +3·6; and that of aniline in *cyclo*hexane, +3·8 kcal./mole. The heat of mixing of benzene and *cyclo*hexane is shown by Baud[4] to be negligible for the present purpose.

Applying the above data to equation (5), we have: $\Delta H_f°$(Me·$POCl_2$) (cryst.) − $\Delta H_f°$ [Me·PO(NHPh)$_2$] (cryst.) = −62·2 kcal., and $\Delta H_f°$(Et·$POCl_2$) (liq.) − $\Delta H_f°$[Et·PO(NHPh)$_2$] (cryst.) = −57·7 kcal. ± 1·0 kcal. in each case.

(d) *Combustion of methylphosphonic dianilide*: The heat of combustion (mean of six measurements) was −1857 kcal./mole (standard deviation ±3·0 kcal.). 99·2—100·8% of the theoretical H_3PO_4 was recovered, and 12·2—16·5% (mean 14%) of the available nitrogen was found to be present as HNO_3.

The approximate concentration of aqueous nitric acid in the bomb was 0·14M. The necessary correction for the formation of HNO_3,aq. from N_2 (g.), O_2 (g.), and H_2O (liq.) being +13·8 kcal./mole of HNO_3, the corrected heat of combustion is $\Delta U_R = -1857 + (2 \times 0{\cdot}14 \times 13{\cdot}8) = -1853$ kcal./mole.

The complete reaction may now be expressed as:

$$C_{13}H_{15}ON_2P\ (cryst.) + 17\tfrac{1}{2}O_2\ (g.) \longrightarrow 13CO_2\ (g.) + N_2\ (g.) + 6H_2O\ (liq.) + H_3PO_4\ (aq.) \quad . \quad (7)$$

As the reaction results in a decrease of 3·5 gaseous molecules we have:

$$\Delta U_R = \Delta H + 3{\cdot}5\boldsymbol{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Therefore ΔH = −1855 kcal./mole.

The correct dilution to be allowed for the phosphoric acid is complicated by the fact that 85% was in the 10 ml. of water in the bomb (concentration *ca.* 0·5M), the remainder being in about 0·5 ml. of liquid in the crucible (concentration *ca.* 2M). We have therefore taken an average value of $\Delta H_f°$(H_3PO_4) (aq.) = −309·0 kcal./mole. Substituting this value and those for CO_2 (g.) and H_2O (liq.) given in N.B.S. Circular 500 (1952), in equation (7), we obtain:

$$\Delta H_f°[Me{\cdot}PO(NHPh)_2]\ (cryst.) = -86{\cdot}6\ kcal./mole$$

which when applied to the result on the formation of anilide from dihalide [(c) above] gives

$$\Delta H_f°[Me{\cdot}POCl_2]\ (cryst.) = -148{\cdot}8\ kcal./mole.$$

(e) *Combustion of ethylphosphonic dianilide.* The heat of combustion (mean of seven measurements) was −2016 kcal./mole (standard deviation ±1·5 kcal.).

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[4] Baud, *Bull. Soc. chim. France*, 1915, **17**, 329.

99·5—101·2% of the theoretical H_3PO_4 was recovered.

13·0—15·4% (mean 14%) of the available nitrogen was found to be present as HNO_3. The heat of combustion, corrected for nitric acid formation, is therefore $\Delta U_R = -2012$ kcal./mole.

$$C_{14}H_{17}ON_2P \text{ (cryst.)} + 19O_2 \text{ (g.)} \longrightarrow 14CO_2 \text{ (g.)} + N_2 \text{ (g.)} + 7H_2O \text{ (liq.)} + H_3PO_4 \text{ (aq.)} \quad (9)$$

Hence $$\Delta U_R = \Delta H + 4{\cdot}0RT \quad (10)$$

$\Delta H = -2014{\cdot}3$ kcal./mole and ΔH_f°[Et·PO(NHPh)$_2$] (cryst.) $= -89{\cdot}6$ kcal./mole.

This value, substituted in the result on the formation of anilide from dihalide, gives: ΔH_f°(Et·POCl$_2$) (liq.) $= -147{\cdot}3$ kcal./mole.

DISCUSSION

The procedure followed in deriving bond-energy terms from the experimental data is the same as that used earlier.[1b] Some explanation is, however, necessary regarding the values assumed for the heats of formation of alkyl and ester groups. In so far as the identity of a group is not changed in a reaction the value assumed for its heat of formation is to some extent immaterial, but a consistent procedure is obviously desirable. Charnley, Mortimer, and Skinner [5] used values for the radicals R· and RO· when calculating the more fundamental parameter—the "bond-dissociation energy"—but the number of radicals for which such data are available is very limited. We have followed the simple if somewhat empirical method of estimating values for alkyl and ester groups from the parent hydrocarbon or alcohol respectively:

$$Q_f(\text{a})\text{R} = Q_f(\text{a})\text{RH} - \bar{D}(\text{C–H})$$
$$Q_f(\text{a})\text{OR} = Q_f(\text{a})\text{ROH} - \bar{D}(\text{O–H})$$

$\bar{D}$(C–H) and $\bar{D}$(O–H) being derived from methane and water.

On this basis the average bond-energy term for the P–OR link in tervalent phosphorus esters can be derived directly from the heats of formation of the tertiary esters given above:

$$\bar{D}(\text{P–OR}) = \tfrac{1}{3}Q_f(\text{a})[(\text{RO})_3\text{P}] - Q_f(\text{a})\text{OR}$$

	ΔH_f° (liq.) (kcal.)	Heat of vapn. (kcal.)	$\bar{D}$(P–OR) (kcal.)
(EtO)$_3$P	−203·5	10·0	91·9
(Pr^{i}O)$_3$P	−235·0	11·0	92·3

Similarly the P–OR link in quinquevalent phosphorus compounds can be evaluated from the results on the esterification of the alkylphosphonic dihalides [(b) above]:

$$\bar{D}(\text{P–OR}) = \tfrac{1}{2}\{Q_f(\text{a})[\text{R}'{\cdot}\text{PO(OR)}_2] - Q_f(\text{a})[\text{R}'{\cdot}\text{POCl}_2]\} - Q_f(\text{a})\text{OR} + \bar{D}(\text{P–Cl})$$

	ΔH_f° (kcal.)	Heat of vapn. (or sublimn.) (kcal.)	$\bar{D}$(P–OR) (kcal.)
Me·POCl$_2$ (cryst.)		14·9	
–Me·PO(OEt)$_2$ (liq.)	+ 97·1	13·5	102·9
Et·POCl$_2$ (liq.)		10·2	
–Et·PO(OPr^i)$_2$ (liq.)	+121·1	14·5	102·4

The bond energy term for the C–P bond in quinquevalent phosphorus compounds can be estimated directly from the values given in (d) and (e) above for the heats of formation of the alkylphosphonic dihalides; the value assumed for $\bar{D}$(P=O) is that used in Part I,[1b] namely, 115·0 kcal.:

$$\bar{D}(\text{C–P}) = Q_f(\text{a})(\text{R}{\cdot}\text{POCl}_2) - Q_f(\text{a})\text{R} - \bar{D}(\text{P=O}) - 2\bar{D}(\text{P–Cl})$$

	ΔH_f° (kcal.)	Heat of vapn. (or sublimn.) (kcal.)	$\bar{D}$(C–P) (kcal.)
Me·POCl$_2$ (cryst.)	−148·8	14·9	80·0
Et·POCl$_2$ (liq.)	−147·3	10·2	80·9

The apparent increase in the bond energy of the P–OR bond in quinquevalent, as compared with tervalent, esters is not necessarily real, as the thermochemical measurements are composite and embody other changes in energy distribution within the molecule. The difference is however quite consistent with the evidence obtained here (see Part I) and at

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[5] Charnley, Mortimer, and Skinner, *J.*, 1953, 1181.

Manchester University [6] that the bond-dissociation energy of the phosphoryl bond appears to be considerably greater in phosphate esters than in phosphonyl halides. This may be due to resonance between the oxygen in P=O and that in P–OR increasing the overall stability of the molecule and thus giving rise to an apparent increase in bond energy in the circumstances of the present measurements.

The average bond energy terms (in kcal.) derived in this investigation are summarised below :

Bond	Tervalent P	Quinquevalent P (containing P=O bond)	Bond	Tervalent P	Quinquevalent P (containing P=O bond)
P–O	—	115·0	P–OH	—	104·5
P–F	117	120·0	P–OR	92·1	102·5
P–Cl	76·3	80·0	P–OP	—	96·0
P–Br	61·7	65·0	P–C	—	80·5
P–H	76·3	78·0			

The reliability of these estimates for predicting heats of formation or reaction can only be tested as other independent thermochemical data become available. A test of their internal consistency is, however, provided by comparing ΔH_f° values calculated from the above table with those obtained directly in the course of experiments :

	$-\Delta H_f^\circ$ (kcal.) :			$-\Delta H_f^\circ$ (kcal.) :	
	calc.	obs.		calc.	obs.
$\mathrm{Me{\cdot}POCl_2}$ (solid)	148·5	148·8	$\mathrm{Me{\cdot}PO(OEt)_2}$ (liquid)	245·5	245·9
$\mathrm{Et{\cdot}POCl_2}$ (liquid)	146·1	147·3	$\mathrm{Et{\cdot}PO(OPr^i)_2}$ (liquid)	268·2	268·4
$\mathrm{Me{\cdot}PO(OH)_2}$ (solid)	250·7	252·6	$\mathrm{P(OEt)_3}$ (liquid)	204·2	203·5
$\mathrm{Et{\cdot}PO(OH)_2}$ (solid)	253·6	253·5	$\mathrm{P(OPr^i)_3}$ (liquid)	234·3	235·0

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[6] Skinner, personal communication.