327. *Heats of Formation and Bond Energies. Part II.*[1] *Triethyl Phosphate, Triphenylphosphine, and Triphenylphosphine Oxide.*

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Values for the heats of combustion of triphenylphosphine, triphenylphosphine oxide, and triethyl phosphate to crystalline orthophosphoric acid, carbon dioxide, and water are reported. These data are used to calculate $\Delta H_f°(PPh_3, c) = +54\cdot3 \pm 2\cdot3$; $\Delta H_f°(OPPh_3, c) = -15\cdot6 \pm 3\cdot0$; and $\Delta H_f°[OP(OEt)_3, liq] = -297\cdot5 \pm 1\cdot3$ kcal./mole. From these values the *mean* bond dissociation energy $\bar{D}$(P–Ph) = 71·3 ± 4, and the bond dissociation energy $D(O{=}PPh_3)$ = 128·4 kcal./mole, are derived.

Few heats of combustion of organophosphorus compounds have been reported, and recent values are confined to trimethyl-[2] and triethyl-phosphine.[3] In this paper the heats of combustion of the three compounds named in the title are reported.

In the combustion of trimethylphosphine, Long and Sackman[2] initiated burning by using a magnesium fuse, which, however, introduced analytical and thermal complications. The combustions now reported were carried out without using a large auxiliary fuse, for, although combustion was incomplete, a procedure was adopted to analyse to a sufficient accuracy the contents of the bomb after combustion. The uncertainties associated with the heats of combustion can be attributed mainly to non-homogeneity of the final phosphoric acid solution, a limitation inherent in using a static bomb technique.

The heats of combustion were sought to derive a *mean* dissociation energy for the phosphorus–carbon bond, and also to supplement information about the heats of oxidation of tervalent phosphorus compounds.[1] Previously, some of these heats have been measured directly by reaction calorimetry, but the results were open to question because of assumptions made about the chemistry of the oxidation reactions.[4]

Experimental

Preparation of Materials.—" B.D.H. Thermochemical Standard " benzoic acid was used. Triphenylphosphine and its oxide (L. Light and Co. Ltd.) were recrystallised from absolute ethanol to m. p. 79·0° and 152·0°, respectively. Kosolapoff[5] gives 79° and 153°, respectively. Triethyl phosphate (Tennessee Eastmann Co.), distilled through a 6″ Fenske column, had b. p. 91·0°/10·7 mm. (Kosolapoff[5] gives 90°/10 mm.).

Combustion Calorimetry.—Combustions were made in a twin-valve bomb (the Parr Instrument Co., Moline, Illinois, U.S.A.) which together with the subsidiary apparatus has been described previously.[6] The liquid triethyl phosphate was sealed in thin glass ampoules. The solid triphenyl compounds were compressed into pellets. All combustions were initiated by a platinum wire and cotton-thread fuse, and for the liquid an additional fuse of oil. The bomb was charged with oxygen to an initial pressure of 30 atm., and with 3 ml. of water. Each sample was fired at 25°.

Analysis.—After each combustion the bomb gases were analysed for carbon dioxide, to an accuracy of ±0·02%. The bomb washings were filtered from the solid residue. In the combustion of triphenylphosphine and its oxide this residue contained traces of carbon and unburnt compound. By weighing and extraction with ether, the separate weights of these were determined. In the combustion of triethyl phosphate it was possible to recover only carbon. Four aliquot parts of the bomb washings were treated as follows: one was titrated with 0·1N-sodium hydroxide solution, with thymolphthalein as indicator, to give the total phosphorus acids and nitric acid; a second was treated with acetic acid, hydrochloric acid, and mercuric chloride, but in no case was mercurous chloride precipitated, showing the absence of

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[1] Part I, Fowell and Mortimer, *J.*, 1959, 2913.
[2] Long and Sackman, *Trans. Faraday Soc.*, 1957, **53**, 1606.
[3] Lautsch, *Chem. Tech.* (*Berlin*), 1958, **10**, 419.
[4] Chernick and Skinner, *J.*, 1956, 1401.
[5] Kosolapoff, " Organo-phosphorus Compounds," Wiley, New York, 1950.
[6] Fletcher, Mortimer, and Springall, *J.*, 1959, 580.

phosphorous acids; a third was analysed for orthophosphoric acid by the quinoline phosphomolybdate method [7] to an accuracy of $\pm 0{\cdot}1\%$; a fourth was boiled with nitric acid to convert any condensed acids into the ortho-acid, and the total phosphoric acids found, but in no case were any condensed phosphoric acids found. The quantity of phosphate recovered corresponded closely to the theoretical amount formed, as calculated from the recovery of carbon, carbon dioxide, and unburnt compound.

Units and Auxiliary Quantities.—The heats of combustion are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs. J. The energy equivalent of the calorimeter was determined by combustion of a sample of benzoic acid, having $-\Delta U_b = 6{\cdot}3181 \pm 0{\cdot}0007$ kcal./g. The following values were used for thermal corrections. The heat evolved in the formation of 0·1N-nitric acid from nitrogen, oxygen, and water was taken [8] as 13·81 kcal./mole. The heat evolved in the combustion of cotton fuse was taken [9] as 3·88 kcal./g. of cotton used. The heat evolved in the combustion of oil of empirical formula $CH_{1{\cdot}878}$ was determined as 10·949 kcal./g. of oil used. The heat evolved in the solution of crystalline phosphoric acid to give a 1·0N-solution was taken as 2·9 kcal./mole of phosphoric acid.[10] The heat of combustion of carbon to carbon dioxide was taken as 8·11 kcal./g. of carbon.

Results.—The results of the combustion experiments are given in Tables 1, 2, and 3, in which the symbols have the following meanings: E_s = energy equivalent of the uncharged calorimeter system; E_c = contribution from the contents of the bomb after combustion to the total energy equivalent; ΔR_c = overall change in resistance of the platinum-resistance thermometer proportional to the corrected temperature rise; q_i = heat of combustion of cotton fuse; q_o = heat of combustion of kindling oil; q_n = heat evolved by formation of nitric acid; q_c = heat correction for unburnt carbon (soot); q_p = heat correction for the solution of crystalline phosphoric acid; q_w = heat correction to standard states (Washburn corrections), at 25°, calculated according to Prosen; [7] $\bar{s}$ = overall standard deviation to be applied to the mean heat of combustion:

$$\bar{s} = \sqrt{[(\bar{s}E)^2 + (\bar{s}B)^2 + (\bar{s}\Delta U_c{}^\circ)^2]}$$

where $\bar{s}E$ = standard deviation of energy equivalent, $\bar{s}B$ = standard deviation in the accepted value for the heat of combustion of benzoic acid, and $\bar{s}\Delta U_c{}^\circ$ = standard deviation in $\Delta U_c{}^\circ$. Further, CO_2 obs : calc. = the proportion of carbon dioxide recovered to that calculated for complete combustion of the sample.

The mass of sample burned in each experiment was calculated from the mass of carbon dioxide and carbon formed on combustion, the cotton fuse and oil being assumed to have burned completely. This mass was also found, though slightly less accurately, from recovery of orthophosphoric acid.

The combustions refer to the reactions:

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

$$OPPh_3(c) + 22{\cdot}5O_2(g) \longrightarrow H_3PO_4(c) + 18CO_2(g) + 6H_2O(liq)$$

$$OP(OEt)_3(liq) + 9O_2(g) \longrightarrow H_3PO_4(c) + 6CO_2(g) + 6H_2O(liq)$$

The standard deviations associated with the standard heats of combustion are between $\pm 0{\cdot}09$ and 0·13%. The major contribution to this uncertainty probably lies in non-homogeneity of the products of combustion, especially of the phosphoric acid solution. This uncertainty would probably be reduced by using a rotating-bomb technique.

Using the $\Delta H_f{}^\circ$ values at 25°: H_2O(liq), $-68{\cdot}3174$; CO_2(g), $-94{\cdot}0518$; H_3PO_4(c), $-306{\cdot}2$ kcal./mole (ref. 10), we calculate the following heats of formation at 25°:

$$\Delta H_f{}^\circ(PPh_3,\ c) = +54{\cdot}3 \pm 2{\cdot}3;\ \Delta H_f{}^\circ(OPPh_3,\ c) = -15{\cdot}6 \pm 3{\cdot}0;$$

$$\Delta H_f{}^\circ[OP(OEt)_3,\ liq] = -297{\cdot}5 \pm 1{\cdot}3 \text{ kcal./mole.}$$

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[7] Wilson, *Analyst*, 1951, **76**, 55.

[8] Prosen, " Experimental Thermochemistry," Interscience, New York, 1956, Chap. 6.

[9] Coops, Jessup, and van Nes, *op. cit.*, Chap. 3.

[10] National Bureau of Standards, Circular 500, Washington, 1952.

TABLE 1. *Triphenylphosphine*; *M*, 262·275.

Expt.	1	2	3	4	5
Wt. * of sample (g.)	0·564620	0·622456	0·524790	0·531634	0·562501
ΔR_c (ohm)	0·13197	0·14544	0·12237	0·12419	0·13167
CO_2 obs.: calc. (%)	99·87	99·16	99·56	99·64	99·82
Wt. of carbon (g.)	0·00014	0·00330	0·00174	0·00085	0·00038
q_i (cal.)	5·4	5·8	5·3	5·1	5·1
q_n (cal.)	0·3	0·3	0·3	0·3	0·3
$-q_c$ (cal.)	1·1	26·8	13·8	6·9	3·1
q_p (cal.)	6·0	6·6	7·3	5·7	5·4
q_w (cal.)	2·0	2·2	1·9	1·9	2·0
E_c (cal./ohm)	6·9	7·6	6·4	6·5	6·9
$-\Delta U_c^\circ$ (kcal./mole)	2456·1	2468·2	2456·1	2459·2	2461·7

Mean 2460·3 (standard deviation of mean ±2·3)

* All weights *in vacuo*. $E_s = 40{,}120{\cdot}0$ cal./ohm and $\bar{s}E = \pm 0{\cdot}025\%$ apply to all combustions. $\bar{s}\Delta U_c^\circ = \pm 0{\cdot}09\%$; $\bar{s} = \pm 0{\cdot}09\%$; $\Delta n\boldsymbol{R}T = -3{\cdot}0$ kcal./mole; $-\Delta H_c^\circ = 2463{\cdot}3 \pm 2{\cdot}3$ kcal./mole.

TABLE 2.

Triphenylphosphine oxide; *M*, 278·275.

Expt.	1	2	3	4
Wt.* of sample (g.)	0·331010	0·633325	0·503030	0·716490
ΔR_c (ohm)	0·07024	0·13533	0·10750	0·15205
CO_2 obs.: calc. (%)	98·24	99·40	99·71	98·83
Wt. of carbon (g.)	0·00100	0·00119	0	0·00353
q_i (cal.)	6·2	6·2	6·3	5·9
q_o (cal.)				
q_n (cal.)	0·3	0·3	0·3	0·3
$-q_c$ (cal.)	8·1	9·7	0	28·6
q_p (cal.)	3·3	6·4	5·1	7·2
q_w (cal.)	1·1	2·4	2·0	2·8
E_c (cal./ohm)	3·8	7·3	5·8	8·1
$-\Delta U_c^\circ$ (kcal./mole)	2399·5	2390·9	2385·3	2387·1

Mean $-\Delta U_c^\circ$ 2390·7 (standard deviation of mean ±3·0)

$\bar{s}\Delta U_c^\circ = \pm 0{\cdot}13\%$; $\bar{s} = \pm 0{\cdot}13\%$; $\Delta n\boldsymbol{R}T = -2{\cdot}7$ kcal./mole; $-\Delta H_c^\circ = 2393{\cdot}4 \pm 3{\cdot}0$ kcal./mole.

TABLE 3.

Triethyl phosphate; *M*, 182·16

Expt.	1	2	3	4
Wt.* of sample (g.)	0·78927	0·76540	0·75079	0·68982
ΔR_c (ohm)	0·11400	0·10861	0·10522	0·10301
CO_2 obs.: calc. (%)	99·50	92·89	93·88	92·17
Wt. of carbon (g.)	0	0·00263	0·00348	0
q_i (cal.)	8·8	8·7	7·1	8·2
q_o (cal.)	306·0	512·9	410·3	694·1
q_n (cal.)	0·3	0·3	0·3	0·3
$-q_c$ (cal.)	0	21·3	28·2	0
q_p (cal.)	12·1	10·9	11·2	9·7
q_w (cal.)	0·5	0·5	0·5	0·8
E_c (cal./ohm)	10·5	10·3	10·1	9·2
$-\Delta U_c^\circ$ (kcal./mole)	985·0	979·9	980·0	979·5

Mean $-\Delta U_c^\circ$ 981·1 (standard deviation of mean ±1·3,

$\bar{s}\Delta U_c^\circ = \pm 0{\cdot}13\%$; $\bar{s} = 0{\cdot}13\%$. $\Delta n\boldsymbol{R}T = -1{\cdot}8$ kcal./mole; $-\Delta H_c^\circ = 982{\cdot}9 \pm 1{\cdot}3$ kcal./mole.

DISCUSSION

Values for the heats of formation of triphenylphosphine and triphenylphosphine oxide have not been recorded previously. The value obtained here for the heat of formation of triethyl phosphate is close to that given by Chernick and Skinner,[4] *viz.*, $-297{\cdot}8 \pm 3{\cdot}0$ kcal./mole. This was based on a heat of formation of triethyl phosphite, derived from the heat of reaction between phosphorus trichloride and ethanol,[11] and a heat of oxidation of triethyl phosphite by hydrogen peroxide, carried out in methanol. These authors drew attention to an important assumption made in interpreting their results, namely, that hydrogen peroxide was consumed only in accordance with the equation $P(OEt)_3 + H_2O_2 \longrightarrow OP(OEt)_3 + H_2O$, and that small amounts of peroxide $(C_2H_5O)_3PO_2$ were not formed. Within the limits of experimental error, their assumption appears justified thermochemically.

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:

$$3\bar{D}(\text{P–Ph}) = \Delta H_f^\circ(\text{P,g}) + 3\Delta H_f^\circ(\text{Ph,g}) - \Delta H_f^\circ(\text{PPh}_3\text{,g})$$

The heat of sublimation of triphenylphosphine has not been reported, but from m. p. and b. p. a value is estimated, $\Delta H_{\text{sub.}}$: = 18·1 kcal./mole. Incorporating this, we derive

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

$\Delta H_f°(PPh_3,g) = +72{\cdot}4 \pm 2{\cdot}3$ kcal./mole. Taking also the values: $\Delta H_f°(P,g) = 75{\cdot}3$ kcal./g. atom,[12] and $\Delta H_f°(Ph,g) = 70 \pm 3$ kcal./mole, considered by Skinner[13] to be the " best " value, we have then $\bar{D}(P–Ph) = 70{\cdot}6 \pm 4$ kcal./mole. This is 5 kcal./mole stronger than $\bar{D}(P–Me) = 65{\cdot}3 \pm 1{\cdot}4$ kcal./mole in trimethylphosphine.[2] A difference in this direction is to be expected from the possibility of additional bonding involving 3*d* orbitals of the phosphorus atom and the π-orbitals of the benzene ring.

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:

$$D[O{=}PPh_3] = \Delta H_f°(PPh_3,g] - \Delta H_f°(OPPh_3,g) + \Delta H_f°(O,g)$$

The heat of sublimation of triphenylphosphine oxide has not been reported, but from m. p. and b. p. a value is estimated, $\Delta H_{sub.}: = 19{\cdot}1$ kcal./mole. This leads to $\Delta H_f°(OPPh_3,g] = +3{\cdot}5 \pm 3{\cdot}0$ kcal./mole, and with $\Delta H_f°(O,g) = 59{\cdot}54$ kcal./g. atom,[12] then $D(O{=}PPh_3) = 128{\cdot}4 \pm 5{\cdot}5$ kcal./mole. This value may be compared[4] with $D(O{=}PPr_3) = 138{\cdot}3 \pm 4$ and $D[O{=}PBu_3) = 137{\cdot}2 \pm 4$ kcal./mole.

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[12] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 2nd Edition, 1958.
[13] Skinner, Monograph No. 3, 1958, The Royal Institute of Chemistry, London.