285. *Thermochemistry of Organophosphorus Compounds. Part II.* Triethyl Phosphate, Tripropylphosphine Oxide, and Tributylphosphine Oxide.*

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Values are reported for the heats of oxidation by hydrogen peroxide (dissolved in methanol) of tripropylphosphine and of tributylphosphine to the phosphine oxides. The heat of oxidation of triethyl phosphite to phosphate, measured similarly, was appreciably higher than the heat given by reaction of triethyl phosphite with aqueous (5%) hydrogen peroxide; in the latter, however, it seems that the oxidation is in competition with hydrolysis.

The thermal data have been used to derive the dissociation energies $D(O{=}PPr_3) \sim 138{\cdot}3$ kcal./mole, $D(O{=}PBu_3) \sim 137{\cdot}2$ kcal./mole, and $D[O{=}P(OEt)_3] \sim 150{\cdot}8$ kcal./mole. Comment is made on the apparent variability in the $O{=}PR_3$ bond dissociation energies with changes in the atom or group R, and some of the factors that may be responsible for these variations are discussed.

THE trialkylphosphines are readily oxidized to their corresponding oxides by various oxidizing agents; *e.g.*, Davies and Jones [1] mention specifically nitric acid, potassium permanganate, peracetic acid, and hydrogen peroxide. The last seemed most suitable for the present studies, as its heat of formation is already well established, and the reactions $R_3P + H_2O_2 \longrightarrow R_3PO + H_2O$ take place rapidly at room temperature in methanol. The oxidation of triethyl phosphite to phosphate by hydrogen peroxide in methanol also takes place readily, and appeared suitable for thermochemical study.

EXPERIMENTAL

Compounds.—Tri-*n*-propylphosphine and tri-*n*-butylphosphine were prepared according to Davies and Jones [1] and Davies, Pearse, and Jones,[2] by reaction of phosphorus trichloride with the appropriate Grignard reagents. The crude products were fractionally distilled under reduced (nitrogen) pressure, through an 8" gauze-packed column. The tri-*n*-propylphosphine

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* Part I, *J.*, 1955, 3936.

[1] Davies and Jones, *J.*, 1929, 33.

[2] Davies, Pearse, and Jones, *J.*, 1929, 1262.

fraction (b. p. 74—75°/6·5 mm.) and the tri-*n*-butylphosphine fraction (b. p. 110—111°/10 mm.) were retained, redistilled *in vacuo*, and collected and sealed in thin glass ampoules. Triethyl phosphite was prepared as described in Part I. Tri-*n*-propylphosphine oxide was made by oxidation of the phosphine with hydrogen peroxide in methanol; the resulting solution was fractionally distilled, and the fraction (b. p. 262°/750 mm.) retained. Tri-*n*-butylphosphine oxide was prepared similarly (b. p. 293—296°/745 mm.). Both oxides are colourless solids at room temperature, and are very hygroscopic.

Calorimeter.—The calorimeter was that described in Part I. The oxidation reactions were carried out by breaking ampoules, containing known weights of reactant, into 750 c.c. of methanol in which a small amount of hydrogen peroxide was dissolved. The resulting temperature rise was followed by the change in resistance of a shielded thermistor element. A slow stream of nitrogen (saturated with methanol vapour) was maintained during each experiment in the head-piece fitting the Dewar vessel, to prevent oxidation by air; also the methanol was alternately degassed and saturated with nitrogen, until rid of dissolved oxygen, before use in the calorimeter. The hydrogen peroxide consumed was determined volumetrically: a known excess of ceric ammonium sulphate solution was added to aliquot samples of the initial methanol–hydrogen peroxide solution and of the final calorimeter contents: the excess of ceric ion was back-titrated against ferrous ammonium sulphate solution, ferroin being used as indicator. The ferrous ammonium sulphate solution was standardized against potassium dichromate solution.

Units.—All heat quantities are given in units of the thermochemical calorie, defined as 1 cal. ≡ 4·1840 abs. joule. The experiments were performed at 25°.

Results.—(a) *Oxidation of tri-*n*-propylphosphine.* The methanol–hydrogen peroxide solution contained 1·7 ml. of hydrogen peroxide (110-vol.) per l. of methanol. Nine measurements of the heat of oxidation of propylphosphine were made; the purity of the phosphine, determined from the hydrogen peroxide consumption, was 97—99%. The observed heats of reaction ($\Delta H_{\text{obs.}}$) refer to the equation:

$$\text{PPr}_3\ (\text{liq.}) + \text{H}_2\text{O}_2{,}4{\cdot}7\text{H}_2\text{O}\ (\text{methanol soln.}) \longrightarrow \text{OPPr}_3 + 5{\cdot}7\text{H}_2\text{O}\ (\text{methanol soln.}) \quad . \quad (1)$$

A representative selection from the values of $\Delta H_{\text{obs.}}$ is given in Table 1; the values are based on the hydrogen peroxide consumed, and not on the weight of phosphine used. The limits of error to be attached to the mean $\Delta H_{\text{obs.}}$ we estimate at *ca.* ±2 kcal./mole, arising from possible errors of *ca.* 1% in the volumetric analysis, and errors of similar order in the calorimetry.

TABLE 1. *Heat of oxidation of tri-*n*-propyl phosphine.*

PPr_3 (mmoles)	H_2O_2 used (mmoles)	Purity (%) of PPr_3	$-\Delta H_{\text{obs.}}$ (kcal./mole)	PPr_3 (mmoles)	H_2O_2 used (mmoles)	Purity (%) of PPr_3	$-\Delta H_{\text{obs.}}$ (kcal./mole)	
4·161	4·095	98·4	107·9	4·420	4·367	98·8	108·2	Mean value, $\Delta H_{\text{obs.}}$
3·710	3·629	97·8	109·3	4·289	4·177	97·4	106·9	= − 108·1

The heat of solution of solid tri-*n*-propylphosphine oxide in methanol * was measured separately, $\Delta H_{\text{soln.}} = -1{\cdot}32$ kcal./mole. The heat of solution of hydrogen peroxide (110-vol.) in methanol was barely distinguishable (at the concentrations used in the oxidation studies) from that of water in methanol. Accordingly, we may obtain, for the idealized reaction:

$$\text{PPr}_3\ (\text{liq.}) + \text{H}_2\text{O}_2\ (\text{liq.}) \longrightarrow \text{OPPr}_3\ (\text{c.}) + \text{H}_2\text{O}\ (\text{liq.}) \quad . \ . \ . \ . \ . \ . \quad (2)$$

$\Delta H = -106{\cdot}8\ (\pm 2)$ kcal./mole. Accepting the values, ΔHf° (H_2O, liq.) $= -68{\cdot}3$ kcal./mole, and ΔHf° (H_2O_2, liq.) $= -45{\cdot}7$ kcal./mole (N.B.S. Tables, Circular 500), we have from eqn. (2) the *difference* $\Delta Hf^\circ(\text{OPPr}_3,\ \text{c.}) - \Delta Hf^\circ(\text{PPr}_3,\ \text{liq.}) = -84{\cdot}2\ (\pm 2)$ kcal./mole.

(b) *Oxidation of tri-*n*-butylphosphine.* Six measurements of the heat of oxidation of tributylphosphine were made, from which the mean value $\Delta H_{\text{obs.}} = -107{\cdot}0$ kcal./mole resulted. The determinations of purity, from the hydrogen peroxide consumption, were less consistent than in the tripropylphosphine oxidations, although all (except one) were 97—100% pure. We accordingly assign slightly larger error limits (±3 kcal./mole) to $\Delta H_{\text{obs.}}$ in the present case.

The heat of solution of tri-*n*-butylphosphine oxide in methanol was measured separately, $\Delta H_{\text{soln.}} = -1{\cdot}29$ kcal./mole. Hence, for the idealized reaction,

$$\text{PBu}_3\ (\text{liq.}) + \text{H}_2\text{O}_2\ (\text{liq.}) \longrightarrow \text{OPBu}_3\ (\text{c.}) + \text{H}_2\text{O}\ (\text{liq.}) \quad . \ . \ . \ . \quad (3)$$

$\Delta H = -105{\cdot}7\ (\pm 3)$ kcal./mole, and the *difference* ΔHf° (OPBu_3, c.) $-$ ΔHf° (PBu, liq.) $= -83{\cdot}1$ (± 3) kcal./mole.

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* The methanol contained a little water—to comply with the conditions represented by eqn. (1).

(c) *Oxidation of triethyl phosphite.* Preliminary measurements on the heat of oxidation of triethyl phosphite were carried out with *aqueous* hydrogen peroxide as oxidant. The experimental conditions were essentially the same as those described by Neale and Williams.[3] The heat of oxidation, when 5% aqueous hydrogen peroxide was used, was found to be $\Delta H = -99{\cdot}2$ kcal./mole.

However, in aqueous hydrogen peroxide, the oxidation of ethyl phosphite takes several minutes to approach completion, owing to the slowness of the solution of the phosphite in water. The possibility that some triethyl phosphite might be lost during this time through competing hydrolytic reactions could not be disregarded. The secondary ester, which is formed by hydrolysis, exists in the keto-form, $H{\cdot}PO(OEt)_2$, with the phosphorus atom already in the quinquevalent state, so that it is not readily oxidized. Hence it may be that the heat measured when using aqueous hydrogen peroxide is composite, in part arising from the phosphite $\longrightarrow$ phosphate oxidation, and in part from hydrolysis of the tertiary phosphite.

Arbuzov[4] and Arbuzov, Zoroastrova, and Rizpolozhenskii[5] have stated that triethyl phosphite is stable in pure water, but is hydrolysed quite rapidly in the presence of dilute acids. Two experiments were carried out to ascertain whether or not hydrolysis occurred in the calorimeter under the conditions of the aqueous oxidation experiments. First, a sample of triethyl phosphite was broken into 750 ml. of aqueous hydrochloric acid, in the calorimeter, and the time–resistance graph was plotted for 2 hr. afterwards. There was an initial rapid resistance change, followed by a much slower one, after which the plot straightened out; the overall heat change was of the order 17 kcal. per mole of triethyl phosphite added. In the second experiment a similar sample of triethyl phosphite was broken into 750 ml. of conductivity water. In this case the resistance change occurred more slowly, but the overall change after 2 hr. was again similar ($\Delta H = -17$ kcal./mole). The heat evolved is appreciably larger than to be expected from a mere heat of solution effect, and indicates that hydrolysis occurs both in acid and in neutral solution, although less rapidly in the latter.

Because of the possible complications due to hydrolysis in the aqueous oxidations, the oxidation by hydrogen peroxide in methanol was chosen for further study. Since triethyl phosphite is easily soluble in methanol, the reaction occurs far more rapidly in this medium, and it was now possible to use very dilute hydrogen peroxide. The procedure was that described for the oxidation of tripropylphosphine. In most cases, samples of phosphite were broken into methanol–hydrogen peroxide solution containing an excess of peroxide (relative to added phosphite), and the amount of peroxide used was estimated volumetrically. The reverse procedure (excess of phosphite into peroxide) was followed in a few cases. Finally, some experiments were done using dry methanol (dehydrated with magnesium methoxide) in which a small amount of 90% hydrogen peroxide was dissolved; these may conveniently be termed " water-free " conditions.

Nine experiments were made in the calorimeter, the first four with a sample of ethyl phosphite which was made without special precautions against atmospheric oxidation. Subsequent infrared analysis of this batch sample showed it to contain *ca.* 5% of impurity (ethyl phosphate); correspondingly, with samples from this batch, the hydrogen peroxide consumed was found to be low (94—96%) on the weight of phosphite taken. A second batch, prepared under nitrogen, gave purity figures of 98—100% on hydrogen peroxide consumption, and the infrared analysis confirmed less than 2% of ethyl phosphate as impurity. A selection from the results obtained is given in Table 2.

TABLE 2. *Oxidation of triethyl phosphite.*

$P(OEt)_3$ (mmoles)	Purity (%) from H_2O_2 used	$-\Delta H_{obs.}$* (kcal./mole)	Comments
6·330	96·3	116·3	Excess of 30% H_2O_2 in methanol
5·476	98·2	116·1	,, ,,
4·986	100	115·9	,, ,,
5·103	100	115·4	" Water-free "
5·928	100	117·8	H_2O_2 (30%) added to excess of phosphite

Mean $\Delta H_{obs.} = -116{\cdot}3$ kcal./mole.

* Corrected for the heat of solution in methanol of the water contained in the 30% H_2O_2 added.

The heat of solution of liquid ethyl phosphate in methanol was measured separately and

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[3] Neale and Williams, *J.*, 1955, 2485.

[4] Arbuzov, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 291.

[5] Arbuzov, Zoroastrova, and Rizpolozhenskii, *Izvest. Akad. Nauk, S.S.S.R.*, 1948, 208.

found to be small ($\Delta H_{\text{soln.}}$ = 0·1 kcal./mole); for ethyl phosphite in methanol, $\Delta H_{\text{soln.}}$ = 1·0 kcal./mole. Thus, for the idealized reaction,

$$\mathrm{P(OEt)_3\,(liq.) + H_2O_2\,(liq.) \longrightarrow OP(OEt)_3\,(liq.) + H_2O\,(liq.)} \quad . \quad . \quad . \quad . \quad (4)$$

the heat of reaction is unchanged from $\Delta H_{\text{obs.}}$ of Table 2, and the difference ΔHf°[OP(OEt]$_3$, liq.] − ΔHf°[P(OEt)$_3$, liq.] = −93·7 kcal./mole. The limits of error in $\Delta H_{\text{obs.}}$ we estimate at *ca.* ±2 kcal./mole. With the value given in Part I, ΔHf°[P(OEt)$_3$, liq.] = −204·1 kcal./mole, we obtain ΔHf°[OP(OEt)$_3$, liq.] = −297·8 kcal./mole.

DISCUSSION

The heat of dissociation of a molecule OPR$_3$ in the gaseous phase, OPR$_3$(g.) $\longrightarrow$ O(g.) + PR$_3$(g.), is given by the thermochemical equation :

$$D(\mathrm{O{=}PR_3}) = \Delta Hf^\circ[\mathrm{PR_3,\ g.}] - \Delta Hf^\circ[\mathrm{OPR_3,\ g.}] + \Delta Hf^\circ[\mathrm{O,\ g.}] \quad . \quad . \quad . \quad . \quad (5)$$

For the molecules R = OEt, the heats of vaporization of both PR$_3$ and OPR$_3$ have been reported : [6] $\Delta H_{\text{vap.}}$[P(OEt)$_3$] = 10·0 kcal./mole, $\Delta H_{\text{vap.}}$[OP(OEt)$_3$] = 12·0 kcal./mole, so that we obtain ΔHf°[P(OEt)$_3$, g.] − ΔHf°[OP(OEt)$_3$, g.] = 91·7 kcal./mole. As the value ΔHf°(O, g.) = 59·1 kcal./mole is well established (N.B.S. Tables, Circular 500), eqn. (5) then gives the value D[O=P(OEt)$_3$] = 150·8 kcal./mole.

Heats of vaporization for propyl- and butyl-phosphine and -phosphine oxide have not been reported, but, from the boiling points and Trouton's constant the difference in the heats of vaporization of the phosphine oxides and the phosphines may be estimated at *ca.* 2 kcal./mole. The heats of fusion of the phosphine oxides are also undetermined; an estimate of *ca.* 3 kcal./mole cannot be seriously in error, however. Thus we may derive D(OP=Pr$_3$) ~ 138·3 kcal./mole, and D(O=PBu$_3$) ~ 137·2 kcal./mole; these values may be unreliable within limits of *ca.* ±4 kcal./mole, allowance being made for possible errors in the thermochemistry, coupled with the assumptions made in respect of the heats of vaporization and fusion.

The O=P$\leqslant$ dissociation energies now reported are higher than those in the phosphorus oxyhalides,[7] and it seems that D(O=PR$_3$) values may vary appreciably with changes in the atom or group R. We are unable to give a detailed explanation for the apparent variability in O=PR$_3$ bond dissociation energies, but the problem is not easy, since the dissociation process is accompanied by a change in the valency state of the phosphorus atom, so that some reorganization in the PR$_3$ part of the OPR$_3$ molecule is likely to occur on dissociation.

In the cases R = Cl or F, the structural parameters in both PR$_3$ and OPR$_3$ are accurately known from studies in the microwave spectral region,[8] and on dissociation of OPHal$_3$, we now know that the P–Hal bond lengths increase slightly, whilst the Hal–P–Hal angles diminish. Although these changes are not large, they may well involve a reorganization energy of significant magnitude. The structural parameters in PR$_3$ and OPR$_3$, where R = OEt, Pr, or Bu, are not known.

The P=O bond length in OPF$_3$ and in OPCl$_3$ is 1·45 Å,[8c] and is the same as found in the ground-state, $^2\Pi$, of the diatomic PO molecule (r_e = 1·447 Å; Herzberg [9]) for which Gaydon [10] quotes the dissociation energy as 143 ± 12 kcal./mole. This bond length is even shorter than that observed in the ground-state, $^1\Sigma^+$, of the PN molecule (r_e = 1·491 Å), in which it is reasonable to suppose there is a triple bond, P≡N. The formulation O=PHal$_3$, in which the oxygen–phosphorus linkage is represented as a double bond, is thus not altogether satisfactory. We prefer to regard the OPR$_3$ molecule as one in which the tetrahedral structure, $\overset{-}{\mathrm{O}}$–$\overset{+}{\mathrm{P}}\mathrm{R}_3$, is modified by back-co-ordination from the $2p_x{}^2$ and $2p_y{}^2$ orbitals of $\overset{-}{\mathrm{O}}$ to the (vacant) $3d_\pi$ orbitals of P$^+$ (thus giving $\overset{-}{\mathrm{O}}$–$\overset{+}{\mathrm{P}}$ triple-bond character), with the further

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[6] Evans, Davies, and Jones, *J.*, 1930, 1310.

[7] Charnley and Skinner, *J.*, 1953, 450; Neale and Williams, *J.*, 1954, 2156.

[8] (*a*) Gillam, Edwards, and Gordy, *Phys. Rev.*, 1949, **75**, 1014; (*b*) Kisluik and Townes, *J. Chem. Phys.*, 1950, **18**, 1109; (*c*) Williams, Sheridan, and Gordy, *ibid.*, 1952, **20**, 164.

[9] Herzberg, " Molecular Spectra and Molecular Structure, I, Diatomic Molecules," 2nd Edn., Van Nostrand, New York, 1950.

[10] Gaydon, " Dissociation Energies," 2nd Edn., Chapman and Hall, London, 1953.

possibility, in case that R_3 possesses donor electrons, of weaker back-co-ordination to P^+ from the R_3 group (cf. Kimball [11]). The stability of the OPR_3 molecule should, in this event, depend to some extent on the propensity of the atom or group R to act as a donor. Skinner and Smith [12] have previously suggested that the OEt group is more powerful in back-co-ordination than is the Cl atom, and this might be one factor responsible for the increase in $D[O{=}P(OEt)_3]$ over $D(O{=}PCl_3)$. It is, however, difficult to explain in these terms why the bond dissociation energies in the alkylphosphine oxides should be larger than in the phosphorus oxyhalides.

In conclusion, we draw attention to an important assumption made in interpreting most of the results given here, namely, that hydrogen peroxide is consumed *only* in accordance with the equation $R_3P + H_2O_2 \longrightarrow R_3PO + H_2O$. This assumption has not been experimentally verified by us, and objection could be raised against our conclusions on this account. There is the possibility, *e.g.*, that small amounts of phosphine peroxides, R_3PO_2, which have been reported by various workers,[13] are formed, which might analyze as unchanged hydrogen peroxide and thus escape detection. An attempt to eliminate this possibility by some further experiments, in which *excess* of phosphine was added to hydrogen peroxide in methanol was unsuccessful, and the measured heats of reaction under these conditions were not reproducible. In our opinion, the thermochemical results given here need independent verification, possibly by oxidation studies based on some other agent than hydrogen peroxide.

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[11] Kimball, *J. Chem. Phys.*, 1940, **8**, 188.

[12] Skinner and Smith, *J.*, 1954, 2324, 3930.

[13] Jorissen, *Z. phys. Chem.*, 1897, **22**, 35; Engler and Weissberg, *Ber.*, 1898, **31**, 3055; Thompson and Kelland, *J.*, 1933, 1231.