658. *Heats of Formation and Bond Energies. Part III.* Trimethylphosphine Oxide,* N-*Ethyltrimethylphosphine Imine, and* N-*Ethyltriphenylphosphine Imine.*

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The heats of hydrolysis of *N*-ethyltrimethylphosphine imine to trimethylphosphine oxide, and of *N*-ethyltriphenylphosphine imine to triphenylphosphine oxide have been measured in dilute hydrochloric acid solution. A value is also reported for the heat of oxidation by hydrogn peroxide (dissolved in methanol) of trimethylphosphine to trimethylphosphine oxide.

These thermal data have been used to calculate $\Delta H_f^\circ(\text{Me}_3\text{PO, c}) = -115{\cdot}1 \pm 2$ kcal./mole, $\Delta H_f^\circ(\text{Me}_3\text{P=NEt, liq}) = -36{\cdot}6 \pm 2{\cdot}5$ kcal./mole, and $\Delta H_f^\circ(\text{Ph}_3\text{P=NEt, c}) = +27{\cdot}0 \pm 3{\cdot}5$ kcal./mole. From these heats of formation the dissociation energies are derived: $D(\text{Me}_3\text{P=O}) = 139{\cdot}3 \pm 3$ kcal./mole, $D(\text{Me}_3\text{P=NEt}) \sim 97$ kcal./mole, and $D(\text{Ph}_3\text{P=NEt}) \sim 125$ kcal./mole. Comparison is made between $D(\text{Me}_3\text{P=O})$ and other $\text{R}_3\text{P=O}$ bond dissociation energies, and comment is passed on the variability of $D(\text{R}_3\text{P=NEt})$ with changes in the group R.

In Parts I and II of this series [1,2] the heats of formation of some organophosphorus compounds were reported, and it was shown that the heat of dissociation, $D(\text{R}_3\text{P=O})$, of the phosphoryl compound R_3PO to the tervalent compound PR_3 varies with the nature of the group R. This dissociation energy increases slightly along the series R = Br, Cl, F, and to a greater extent along the series R = F, OR′, NR'_2, falling to a lower value for R = alkyl or phenyl.

In order to extend this information, dissociation energies $D(\text{R}_3\text{P=NR})$ were sought, corresponding to the gas-phase dissociation $\text{R}_3\text{P=NR} \longrightarrow \text{R}_3\text{P} + \text{NR}$. Two compounds for which a knowledge of the heat of formation would be valuable are *N*-ethyltrimethylphosphine imine, and *N*-ethyltriphenylphosphine imine, since the dissociation energies $D(\text{Me}_3\text{P=NEt})$ and $D(\text{Ph}_3\text{P=NEt})$, which could be derived from these heats of formation, might be compared with the corresponding values of $D(\text{Me}_3\text{P=O})$ and $D(\text{Ph}_3\text{P=O})$. A value for $D(\text{Ph}_3\text{P=O})$ is known, and $D(\text{Me}_3\text{P=O})$ can be obtained from the heat of formation of trimethylphosphine oxide.

These compounds are suitable for thermochemical study since they are hydrolysed quickly, in 0·01N-hydrochloric acid at room temperature, according to the reaction $\text{R}_3\text{P=NEt} + \text{H}_2\text{O} + \text{HCl} \longrightarrow \text{R}_3\text{PO} + \text{EtNH}_3\text{Cl}$, and the heats of these reactions have been measured.

Of the heats of formation required to calculate the heats of formation of the phosphine

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* Part II, *J.*, 1960, 1622.

[1] Fowell and Mortimer, *J.*, 1959, 2913.

[2] Bedford and Mortimer, *J.*, 1960, 1622.

imines, all are available from the literature except that of trimethylphosphine oxide. In order to obtain this in terms of the known heat of formation of trimethylphosphine, the heat of oxidation of trimethylphosphine by hydrogen peroxide was measured. This oxidation takes place rapidly, at room temperature in methanol, according to the scheme $Me_3P + H_2O_2 \longrightarrow Me_3PO + H_2O$.

EXPERIMENTAL

Compounds.—Trimethylphosphine was prepared by a modification of Hibbert's procedure[3] for the triethyl compound, suggested by Long and Sackman,[4] from phosphorus trichloride and methylmagnesium iodide, in ether under an atmosphere of nitrogen. It was isolated as the crystalline complex $[AgI,PMe_3]_4$, which was dried over phosphorus pentoxide. Trimethylphosphine was regenerated by heating the complex *in vacuo*, and was further purified by distillation.

N-Ethyltrimethylphosphine imine was prepared by a slight modification of the method used by Staudinger[5] for the preparation of *N*-ethyltriethylphosphine imine. Ethyl azide, prepared according to Dimroth,[6] was distilled under nitrogen into dried light petroleum and this solution was siphoned into one of trimethylphosphine in light petroleum at −10°. On warming to room temperature nitrogen was evolved, after which the petroleum was removed by distillation. The remaining *N*-ethyltrimethylphosphine imine was distilled through a 6 in. Fenske column. It had b. p. 56°/10 mm. The preparation of this compound has not been recorded previously.

N-Ethyltriphenylphosphine imine was prepared by the same method but from triphenylphosphine. It was recrystallised from light petroleum and had m. p. 95°. Staudinger[5] gives 90°. Our higher m. p. was due to small amounts of triphenylphosphine oxide, m. p. 140°, which is very difficult to remove. Allowance for this impurity was made in the thermochemical measurements described below.

The trimethylphosphine and *N*-ethyltrimethylphosphine imine were distilled *in vacuo* into thin, weighed glass ampoules. Ampoules of solid *N*-ethyltriphenylphosphine imine were filled in an atmosphere of dry air and then evacuated. Despite this precaution varying amounts of hydrolysis occurred before the ampoules were evacuated.

The depression of freezing point of cyclohexane due to *N*-ethyltrimethylphosphine imine was measured and the molecular weight calculated from it corresponded to a monomeric formula. The unsubstituted triphenylphosphine imine, $Ph_3P{=}NH$, is also a monomer in solution,[7] and it was assumed that this is also the case with *N*-ethyltriphenylphosphine imine.

The vapour pressure of *N*-ethyltrimethylphosphine imine was measured and is given by the equation $\log_{10} p$ (mm.) $= -A/T + B$, where $A = 3217$ and $B = 11{\cdot}05$. The derived latent heat of vaporisation (liquid to vapour), given by $\Delta H_{\text{vap.}} = 4{\cdot}57 \times 10^{-3}$ kcal./mole, is $14{\cdot}7 \pm 0{\cdot}1$ kcal./mole. The latent heats of sublimation of trimethylphosphine oxide and *N*-ethyltriphenylphosphine imine were estimated as 12 ± 1 and 18 ± 2 kcal./mole, respectively.

Calorimeter.—The heats of reaction were measured in calorimeters which have been described previously.[8,9] The hydrolyses were carried out in a cylindrical, silvered Dewar vessel (capacity 300 ml.) encased in a brass can; for the oxidation a larger spherical, silvered Dewar vessel (capacity 1 l.) with a long neck was used. Both vessels were immersed in a thermostat at 25·000° ± 0·005°. Temperature measurements were made from the resistance change of a thermistor element. The calorimeter was calibrated electrically by the substitution method.

The oxidation of trimethylphosphine was carried out by breaking an ampoule of the compound into a solution of methanol containing 1·0—2·0 ml. of hydrogen peroxide (110-vol.) per litre, a slight excess for the quantity of trimethylphosphine. The hydrolyses of the phosphine imines were carried out in 0·01N-hydrochloric acid solution.

Units.—Heat quantities are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs. joule.

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[3] Hibbert, *Ber.*, 1906, **39**, 160.
[4] Long and Sackman, *Trans. Faraday Soc.*, 1957, **53**, 1606.
[5] Staudinger and Hauser, *Helv. Chim. Acta*, 1921, **4**, 861.
[6] Dimroth and Wislicenus, *Ber.*, 1905, **38**, 1573.
[7] Appel and Hauss, *Angew. Chem.*, 1959, **71**, 626.
[8] Pedley, Skinner, and Chernick, *Trans. Faraday Soc.*, 1957, **53**, 1612.
[9] Mortimer and Skinner, *J.*, 1952, 4331.

Results.—In the table, ΔH_1, ΔH_2, and ΔH_3 refer to the heats of the reactions (1), (2), and (3), respectively.

$$Me_3P{=}NEt\ (liq) + H_2O\ (liq) + HCl\ (5000H_2O) \longrightarrow Me_3PO\ (soln) + EtNH_3Cl\ (soln) \quad (1)$$

$$Ph_3P{=}NEt\ (c) + H_2O\ (liq) + HCl\ (5000H_2O) \longrightarrow Ph_3PO\ (c) + EtNH_3Cl\ (soln) \quad (2)$$

$$Me_3P\ (liq) + H_2O_2\ (soln) \longrightarrow Me_3PO\ (soln) + H_2O\ (soln) \quad . \quad (3)$$

A volumetric estimation of the amount of hydrochloric acid consumed in reactions (1) and (2) showed that for *N*-ethyltrimethylphosphine imine 98—100% of the calculated quantity was used, whilst for *N*-ethyltriphenylphosphine imine the amount varied from 63 to 83% of the calculated quantity. It was assumed that the sample of *N*-ethyltriphenylphosphine imine was contaminated only with triphenylphosphine oxide. This was shown to have no heat effect since it is insoluble in the reaction mixture. The ΔH values are based on the amount of hydrochloric acid used. A volumetric estimation of the unused hydrogen peroxide showed that 100 ± 1% of that required by the weight of trimethylphosphine was consumed.

Heats of solution were also measured for the following compounds in the mixed solvents in which they were formed in the reactions: Me_3PO (c) in [HCl, $EtNH_3Cl$], −4·1; Me_3PO (c) in [methanol, H_2O_2], +1·59; Ph_3PO (c) in [HCl, $EtNH_3Cl$], in which it appears to be insoluble, 0·0 kcal./mole. The heat of solution of hydrogen peroxide (110-vol.) in methanol has been found to be barely distinguishable (at the concentrations used in the oxidation study) from that of water in methanol,[10] so that ΔH_3 can be taken as referring to the reaction

Heats of hydrolysis and oxidation.

$Me_3P{=}NEt$ (g.)	0·2775	0·2072	0·1922	0·1391	0·2190
HCl used (%)	98·1	99·6	98·8	98·9	99·4
$-\Delta H_1$ (kcal./mole)	51·1	52·8	52·2	50·9	51·7
			Mean ΔH_1 = −51·7 ± 0·5 kcal./mole		
$Ph_3P{=}NEt$ (g.)	0·5890	0·7444	0·4213	0·4008	0·6747
HCl used (%)	81·1	75·7	83·0	73·7	63·3
$-\Delta H_2$ (kcal./mole)	12·3	12·0	11·9	10·8	11·5
			Mean ΔH_2 = −11·7 ± 0·5 kcal./mole		
Me_3P (g.)	0·3391	0·3235	0·6827		
H_2O_2 used (%)	99·0	—	101		
$-\Delta H_3$ (kcal./mole)	106·9	106·3	107·2		
			Mean ΔH_3 = −106·8 ± 1·0 kcal./mole.		

$$Me_3P\ (liq) + H_2O_2\ (liq) \longrightarrow Me_3PO\ (soln) + H_2O\ (liq)$$

The following heats of formation are used: $\Delta H_f^\circ(H_2O,\ liq) = -68{\cdot}32$; $\Delta H_f^\circ(HCl,\ 5000H_2O) = -39{\cdot}97$; $\Delta H_f^\circ(EtNH_3Cl,\ aq) = -77{\cdot}4$;[11] $\Delta H_f^\circ(Me_3P,\ liq) = -30{\cdot}1 \pm 1{\cdot}1$;[4] $\Delta H_f^\circ(Ph_3PO,\ c) = -15{\cdot}6$;[2] $\Delta H_f^\circ(H_2O_2,\ liq) = -44{\cdot}87$ kcal./mole.[12]

From these values and the heats of reaction we calculate $\Delta H_f^\circ(Me_3PO,\ c) = -115{\cdot}1 \pm 2$; $\Delta H_f^\circ(Me_3P{=}NEt,\ liq) = -36{\cdot}6 \pm 2{\cdot}5$; and $\Delta H_f^\circ(Ph_3P{=}NEt,\ c) = +27{\cdot}0 \pm 3{\cdot}5$ kcal./mole, and incorporating the latent heats given previously, we find values of −103 ± 3, −21·9 ± 2·6, and +45 ± 5 kcal./mole, respectively, for the heats of formation of the gaseous compounds.

DISCUSSION

The heat of dissociation of the molecule R_3PA (where A = O or NEt) in the gaseous phase, $R_3PA\ (g) \longrightarrow R_3P\ (g) + A\ (g)$, is given by the thermochemical equation

$$D(R_3P{=}A) = \Delta H_f^\circ(R_3P,\ g) - \Delta H_f^\circ(R_3PA,\ g) + \Delta H_f^\circ(A,\ g)$$

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

[11] National Bureau of Standards, Circular 500, Washington, D.C., 1952.

[12] Giguère, Morisette, Olmos, and Knop, *Canad. J. Chem.*, 1955, **33**, 804; Giguère, Liu, Dugdale, and Morrison, *ibid.*, 1954, **32**, 117.

From $\Delta H_f°(\text{Me}_3\text{P, g}) = -23{\cdot}2$;[2] $\Delta H_f°(\text{O, g}) = 59{\cdot}54$ kcal./mole,[13] and the value for $\Delta H_f°(\text{Me}_3\text{PO, g})$ given above, the dissociation energy $D(\text{Me}_3\text{P=O}) = 139{\cdot}3 \pm 3$ kcal./mole is obtained. This may be compared with $D(\text{Pr}_3\text{P=O}) = 138{\cdot}3 \pm 3$, and $D(\text{Bu}_3\text{P=O}) = 137{\cdot}2 \pm 3$ kcal./mole obtained by Chernick and Skinner[10] using the same experimental method. The values are the same within the experimental errors.

Calculation of $D(\text{R}_3\text{P=NEt})$ requires a value for $\Delta H_f°(\text{NEt, g})$. This is not known but can be calculated in a way suggested by Gowenlock.[14] This is based on a dissociation energy of ethyl azide, corresponding to the process $\text{EtN}_3 \longrightarrow \text{EtN} + \text{N}_2$, for which the value has been given $D(\text{EtN–N}_2) = 39{\cdot}7$ kcal./mole,[15] so that $\Delta H_f°(\text{EtN, g})$ might be obtained from the relation $D(\text{EtN–N}_2) = \Delta H_f°(\text{EtN, g}) + \Delta H_f°(\text{N}_2\text{, g}) - \Delta H_f°(\text{EtN}_3\text{, g})$. Unfortunately, the heat of formation of ethyl azide is unknown. However, Gray[16] has suggested that for the azides the dissociation energy $D(\text{R–N}_3)$ is invariant at ~83 kcal./mole and is independent of the particular alkyl group R. From the relation

$$D(\text{Et–N}_3) = \Delta H_f°(\text{Et, g}) + \Delta H_f°(\text{N}_3\text{, g}) - \Delta H_f°(\text{EtN}_3\text{, g})$$

and taking the values $\Delta H_f°(\text{Et, g}) = 25{\cdot}5$,[17] and $\Delta H_f°(\text{N}_3\text{, g}) = 116$ kcal./mole,[16] we obtain $\Delta H_f°(\text{EtN}_3\text{, g}) = 58{\cdot}5$ kcal./mole, and $\Delta H_f°(\text{EtN, g}) = 98$ kcal./mole.

This value, together with $\Delta H_f°(\text{Ph}_3\text{P, g}) = +72{\cdot}4 \pm 3{\cdot}0$ kcal./mole[2] and the heats of formation of the gaseous phosphine imines, leads to $D(\text{Me}_3\text{P=NEt}) = 96{\cdot}7$, and $D(\text{Ph}_3\text{P=NEt}) = 125{\cdot}4$ kcal./mole. Although it is difficult to ascribe uncertainties to these values, because of the poorly established heat of formation of the radical EtN, the *difference* $D(\text{Ph}_3\text{P=NEt}) - D(\text{Me}_3\text{P=NEt}) = 28{\cdot}7$ kcal./mole probably has an uncertainty of ±8 kcal./mole. By contrast, in the phosphoryl compounds we have $D(\text{Me}_3\text{P=O}) = 139{\cdot}3 \pm 3$ kcal./mole, some 11 kcal./mole *greater* than $D(\text{Ph}_3\text{P=O}) = 128{\cdot}4 \pm 5$ kcal./mole.[2]

The phosphine imines, $\text{R}_3\text{P=NEt}$, can be regarded, like the phosphoryl compounds, as a tetrahedral structure $\text{R}_3\overset{+}{\text{P}}\text{–}\overset{-}{\text{N}}\text{Et}$, modified by back co-ordination from $2p_{x^2}$ and $2p_{y^2}$ orbitals of the $\overset{-}{\text{N}}\text{Et}$ group to the vacant $3d_\pi$ orbitals of $\overset{+}{\text{P}}$, thus giving P–N triple-bond character, with the additional possibility of back co-ordination from the R groups, if these have donor electrons.

An explanation of the different trend in $D(\text{P=O})$ and $D(\text{P=N})$ values may be that, whereas in the phosphoryl compounds the more electronegative phenyl group (electronegativity 2·4[18]) tends to reduce back co-ordination between the phenyl group and the phosphorus atom, with no great strengthening of the P=O bond, yet the less electronegative methyl group (2·1) allows for a bond strengthening between the methyl group and the phosphorus atom, which more than compensates for any loss in the P=O bond strength. In the phosphine imines the P=N bond is strengthened by the electronegative phenyl group to a greater extent than any loss in the phenyl–phosphorus bond strength. Wider variations in $D(\text{P=N})$ than in $D(\text{P=O})$ are perhaps to be expected, with alteration of the R groups, especially where atoms other than carbon are bonded to the phosphorus.

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