

THE THERMOCHEMISTRY OF SOME ORGANO-PHOSPHORUS COMPOUNDS

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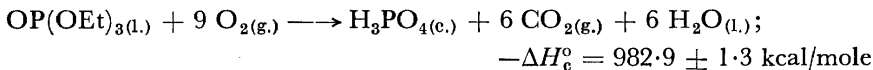
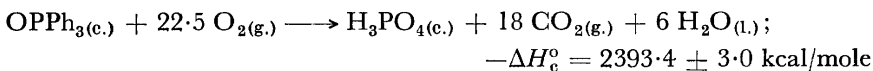
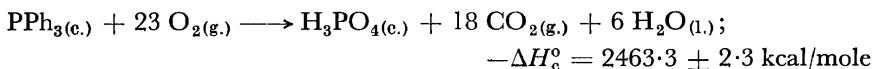
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DETERMINATION OF HEATS OF FORMATION

In recent years a certain amount of thermochemical data has been accumulated for organo-phosphorus compounds. The data have been obtained by measuring heats of reaction by two general methods:

- (a) combustion calorimetry, involving degradative oxidation; and
- (b) reaction calorimetry, where the heats of such reactions as hydrolysis, aminolysis, and partial oxidation have been measured.

As examples of degradative oxidation, we may mention the following combustion reactions, the heats of which have been measured recently¹:



From these heats of combustion, the heats of formation of the organo-phosphorus compounds may be calculated in terms of the heat of formation of crystalline orthophosphoric acid, taken as² -306.2 kcal/mole, and the generally accepted values for carbon dioxide and water². The values obtained are

$$\Delta H_f^\circ(\text{PPh}_3(\text{c.})) = +54.3 \pm 2.3 \text{ kcal/mole};$$

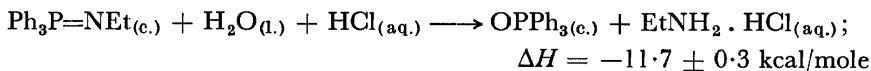
$$\Delta H_f^\circ(\text{OPPh}_3(\text{c.})) = -15.6 \pm 3.0 \text{ kcal/mole};$$

$$\text{and } \Delta H_f^\circ(\text{OP}(\text{OEt})_3(\text{l.})) = -297.5 \pm 1.3 \text{ kcal/mole}$$

After the combustions, the phosphoric acid was, in fact, in aqueous solution, so that a correction for the heat of solution was necessary. These combustions were made in a static bomb, and as a result the concentration of phosphoric acid probably varied considerably in different parts of the bomb, leading to the comparatively large error of ± 0.1 per cent, associated with the heats of combustion. This error could be reduced very considerably by using a rotating bomb technique.

A number of organo-phosphorus compounds undergo reactions which can be studied conveniently in a simple reaction calorimeter. An example

of such a reaction, the heat of which has been measured recently³, is the hydrolysis of the phosphinimine, $\text{Ph}_3\text{P}=\text{NEt}$,

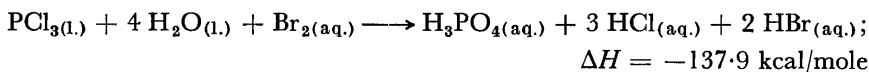


In this case the heat of formation of the phosphinimine

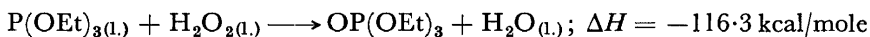
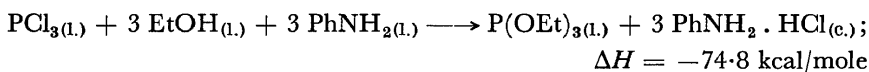
$$\Delta H_f^\circ(\text{Ph}_3\text{P}=\text{NEt}_{(\text{c.})}) = +27.0 \pm 3.5 \text{ kcal/mole}$$

is calculated from the heat of formation of triphenylphosphine oxide, which is known from the combustion data, in terms of the heat of formation of orthophosphoric acid.

A useful intermediate in the reaction calorimetry of phosphorus compounds is phosphorus trichloride. The heat of formation of this is known from the heat of hydrolysis, carried out under oxidizing conditions, to orthophosphoric acid⁴, *viz.*,



The heat of formation of triethyl phosphate has been determined, in terms of that of phosphorus trichloride, from measurements of the heats of the following reactions, in which phosphorus trichloride is esterified to triethyl phosphite⁵, which is then oxidized to triethyl phosphate⁶:



From these data, the value $\Delta H_f^\circ(\text{OP}(\text{OEt})_{3(\text{l.})}) = -297.8 \pm 3.0 \text{ kcal/mole}$ is derived, which is in close agreement with that obtained by combustion calorimetry.

Other thermochemical data for organo-phosphorus compounds include $\Delta H_f^\circ(\text{P}(\text{NEt}_2)_{3(\text{l.})}) = -66.8 \pm 2.5 \text{ kcal/mole}$, obtained by measuring the heat of reaction of phosphorus trichloride with diethylamine, in which the amino-phosphine is formed⁷. Also the heats of combustion of some phosphonitrilic compounds have been determined, and the heats of formation derived⁸: $\Delta H_f^\circ((\text{PNPh}_2)_4_{(\text{c.})}) = +40.7 \pm 11.5 \text{ kcal/mole}$ and $\Delta H_f^\circ((\text{PNMe}_2)_3_{(\text{c.})}) = -125.2 \pm 2.7 \text{ kcal/mole}$.

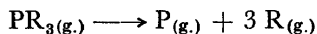
All these heats of formation are based on the heat of formation of orthophosphoric acid. This is derived from the work of Thomsen⁹, in 1882, the overall accuracy of which it is difficult to assess: some independent measurements by Giran¹⁰, in 1903, confirm Thomsen's value, so that it might be accepted with some confidence. However, it would seem advisable to redetermine the value with the advantage of modern thermochemical methods.

DISSOCIATION ENERGIES

The heats of formation may be used to find the strength of the bonding between phosphorus and other atoms. A measure of this, for trivalent

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phosphorus compounds of the type PR_3 , is the mean bond dissociation energy $D_m(\text{P}-\text{R})$. This is defined as one-third of the heat of the gas-phase reaction



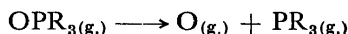
in which the compound is dissociated into phosphorus atoms and atoms or radicals R. Table 1 shows some mean bond dissociation energies, together with the heats of formation used in the calculations.

Table 1. Mean bond dissociation energies in PR_3 , based on¹³ $\Delta H_f^\circ(\text{P}(\text{g.})) = 75.3$ kcal/g-atom

Compound	$\Delta H_f^\circ(\text{PR}_3(\text{g.}))$ (kcal/mole)	Ref.	$\Delta H_f^\circ(\text{R}(\text{g.}))$ (kcal/mole)	Ref.	$D_m(\text{P}-\text{R})^*$ (kcal/mole)
PCl_3	- 66.6	4	+ 28.94	13	76.2
PBr_3	- 29.7	11	+ 26.7	13	61.7
$\text{P}(\text{OEt})_3$	- 194.1	1, 4	- 8.1	14	81.7
$\text{P}(\text{NEt}_2)_3$	- 52.3	7	+ 34.9	*	77.4
PMe_3	- 23.2	12	+ 32.5	14	65.3
PPh_3	+ 72.4	1	+ 70	14	71.0

* Calculated from $\Delta H_f^\circ(\text{Et}_2\text{NH}(\text{g.})) = -17.0$ kcal/mole, assuming¹⁵ $D(\text{Et}_2\text{N}-\text{H}) = D(\text{H}_2\text{N}-\text{H}) = 104$ kcal/mole.

The heats of dissociation of the phosphoryl compounds to the trivalent phosphorus compounds, $D(\text{P}=\text{O})$, represented by the following equation, are especially interesting:



In some cases the heat of the reverse process, that is oxidation of the PR_3 molecule, has been measured. Otherwise these dissociation energies can be calculated from differences between the heats of formation of OPR_3 and PR_3 molecules.

It has been suggested⁶ that the OPR_3 molecule should be regarded as a tetrahedral structure $\bar{\text{O}}-\overset{+}{\text{P}}\text{R}_3$, modified by back co-ordination from the $2p_x^2$ and $2p_y^2$ orbitals of O^- to the vacant $3d_\pi$ orbitals of P^+ , thus giving $\bar{\text{O}}-\overset{+}{\text{P}}$ triple bond character, with the further possibility of back co-ordination to P from the R atoms or groups, if these have donor electrons. For convenience, we shall continue to designate the dissociation energy of the bond $D(\text{P}=\text{O})$, though bearing in mind this additional π -bonding.

Values of $D(\text{P}=\text{O})$ for a number of phosphoryl compounds are shown in Table 2. The variation in these dissociation energies reflects changes in the strength of both the phosphoryl bond, as suggested by the shift in Raman frequency and infra-red wavelength of this bond on changing the R groups, and also in the strength of the P-R bonds.

In the series (a) OPBr_3 , OPCl_3 , OPF_3 , it is seen that $D(\text{P}=\text{O})$ increases with increasing electronegativity of R. Along the series (b) OPF_3 , $\text{OP}(\text{OEt})_3$, $\text{OP}(\text{NEt}_2)_3$, there is also an increase in $D(\text{P}=\text{O})$, which is unexpected in terms of electronegativity. A possible explanation is that back co-ordination from the R groups to the phosphorus atom is increased in $\bar{\text{O}}-\overset{+}{\text{P}}\text{R}_3$, as compared with PR_3 , causing a strengthening of the P-R

bonds in the phosphoryl compound, which will be included in $D(\text{P}=\text{O})$. It is known that the power to back co-ordinate is greater for nitrogen than oxygen, which is greater, in turn, than that for chlorine¹⁶. This effect would seem to offset any reduction in $D(\text{P}=\text{O})$ due to the decrease in electronegativity along the series fluorine, oxygen, nitrogen.

Table 2. Gas-phase dissociation energies (in kcal/mole): $\text{APR}_3 \rightarrow \text{A} + \text{PR}_3$

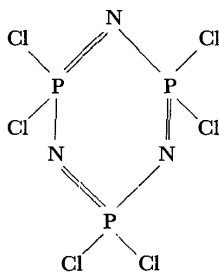
Basis of estimate	$D(\text{P}=\text{O})$	Ref.
(a) ΔH oxidation PF_3 to OPF_3	129.8	20
$\Delta H_f^\circ \text{PCl}_3$ and OPCl_3	127.5	4
$\Delta H_f^\circ \text{PBr}_3$ and OPBr_3	124.9	11
(b) ΔH oxidation PF_3 to OPF_3	129.8	20
$\Delta H_f^\circ \text{P}(\text{OEt})_3$ and $\text{OP}(\text{OEt})_3$	150.7	1, 5, 6
$\Delta H_f^\circ \text{P}(\text{NEt}_2)_3$ and $\text{OP}(\text{NEt}_2)_3$	160*	7
ΔH oxidation PPr_3 to OPPr_3	138.3	6
$\Delta H_f^\circ \text{PPh}_3$ and OPPh_3	128.4	1
	$D(\text{P}=\text{S})$	
(c) ΔH oxidation $\text{P}(\text{OEt})_3$ to $\text{SP}(\text{OEt})_3$	81.6	21
ΔH oxidation PPr_3 to SPPr_3	82.6	21

* $\Delta H_f^\circ(\text{OP}(\text{NEt}_2)_3(\text{g.}))$ estimated from bond energy data, see Ref. 7.

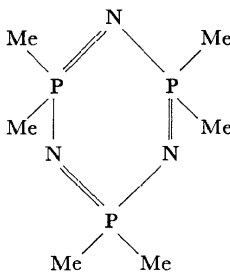
Although there are fewer data available for the thiophosphoryl compounds (c), the variation in $D(\text{P}=\text{S})$ appears to be considerably less than $D(\text{P}=\text{O})$ in phosphoryl compounds. This is expected, since the smaller electronegativity difference between sulphur and phosphorus, than between oxygen and phosphorus, will make the bonding in thiophosphoryl compounds less susceptible to the nature of the R groups.

BOND ENERGIES IN PHOSPHONITRILIC COMPOUNDS

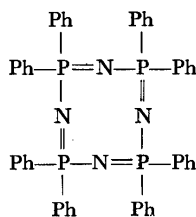
The thermochemistry of the phosphonitrilic compounds shown below is best interpreted in terms of bond energies. The heat of formation of (I) has been given by Paddock and Searle¹⁷ as -178.1 ± 3 kcal/mole, from some preliminary measurements; the heats of formation of (II) and (III) have been referred to previously⁸. From these figures it is possible to calculate the sum of the bond energies in the "ring unit", $E(\text{R}_2\text{P}=\text{N}-\text{P})$.



(I)



(II)



(III)

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This is simply done by taking one-third of the heat of formation of the compounds (I) and (II) from the atoms, or one-quarter of the heat of formation of (III). Now it is unlikely that the bond energies (or group energies where $R = \text{Me}$ or Ph) of the P-R bonds (or groups) in the phosphonitrilic molecules will be less than in the corresponding PR_3 compounds, and the indications of the preceding section are that the bond energies will be slightly greater in the phosphonitrilics. Substituting the values for $E(\text{P-R})$, derived from PR_3 molecules, in the ring unit gives a *maximum* value for the sum of the single and double phosphorus-nitrogen bond energies, $E(\text{P=N-P})$. These values are shown in *Table 3*.

Table 3. Bond energies in phosphonitrilic compounds (in kcal/mole). $E(\text{P-R}) = \frac{1}{3}\Delta H_f^\circ(\text{PR}_3(\text{g.}))^*$

Compound	$\Delta H_f^\circ(\text{g.})$	$E(\text{R}_2\text{P=N-P})$	$E(\text{P-R})$	$E(\text{P=N-P})$
$(\text{PNCl}_2)_3$	- 178.1	305.4	76.2	153
$(\text{PNMe}_2)_3$	- 107.1	878.3	360.0	158
$(\text{PNPh}_2)_4$	+ 58.7	2745.1	1286.8	172

*The heat of formation of the gaseous compound from the atoms.

It would be interesting to compare $E(\text{P=N-P})$ with the sum $E(\text{P=N}) + E(\text{P-N})$, the single and double bond energies, found in other molecules, since it has been suggested that these inorganic "aromatic" molecules will have a resonance energy¹⁸.

Values for the bond energy of the phosphorus-nitrogen double bond, $E(\text{P=N})$ can be calculated from the heats of formation of the gaseous phosphinimines $\text{Me}_3\text{P=NEt}$ and $\text{Ph}_3\text{P=NEt}$. These have been given⁸ as -21.9 ± 2.6 , and $+45.0 \pm 5$ kcal/mole, respectively. Assuming that the bond energies of the groups Me_3P and Ph_3P are the same in the phosphinimines as in the trivalent compounds trimethylphosphine and triphenylphosphine, the bond energies are calculated as $E(\text{P=N}) = 69.7$ kcal/mole in trimethylphosphinimine, and $E(\text{P=N}) = 98.4$ kcal/mole in triphenylphosphinimine. It is interesting to note the large difference, of 28.7 kcal/mole, between these two values.

For the phosphorus-nitrogen single bond, we have the value $E(\text{P-N}) = 66.8$ kcal/mole, calculated from the heat of formation of gaseous trisdiethylaminophosphine, $\text{P}(\text{NEt}_2)_3$. Since we have used $E(\text{P-R})$ values derived from trivalent PR_3 molecules to calculate the bond energy of the ring unit $E(\text{P=N-P})$, and also to derive $E(\text{P=N})$ values, it seems reasonable to use this value for $E(\text{P-N})$ found in a trivalent compound. Thus, the sum $E(\text{P=N}) + E(\text{P-N})$ is calculated as 136.5 kcal/mole, when the phosphorus atom in the phosphinimine is methyl-substituted; and 165.2 kcal/mole when it is phenyl-substituted.

The values of $E(\text{P=N-P})$ in the corresponding phosphonitrilic compounds are 158 and 173 kcal/mole, so that the "resonance" energy of the ring unit is 21 kcal/mole for the methyl-substituted compound and 7 kcal/mole for the phenyl-substituted compound. Hence, the resonance energy of the six-membered ring system, $(\text{PNMe}_2)_3$, is ~ 60 kcal/mole, and of the eight-membered ring system, $(\text{PNPh}_2)_4$, is ~ 28 kcal/mole.

Here, as in the calculation of all resonance energies, the values depend upon the choice of the standard, non-resonating compound with which the resonance structure is compared. In these cases it is the phosphinimines which are taken as the reference compounds, despite the fact that there is probably considerable electron delocalization involving the phosphorus $3d$ -electrons and the π -electrons of the phenyl groups.

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