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Brief Communications

Thermochemistry of heteroatomic compounds

19.* Enthalpies of combustion and formation for alkylphosphines in different phase states

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The enthalpies of combustion (ΔH_{comb}) of 13 primary, secondary, and tertiary alkylphoshines in the condensed state were calculated using the equation $\Delta H_{\text{comb}} = -860.7 - 107.0N$, where N is the number of valent (bond-forming) electrons. This equation can be used for the calculation of enthalpies of combustion and formation of phosphoric acid esters.

Key words: phosphines, phosphites, enthalpy of combustion, enthalpy of formation.

Data on thermochemistry of formation of alkylphosphines (R_2PH, R_3P), which are widely used as complex-forming agents and efficient mediators responsible for metal transport in living beings, are virtually lacking in literature. The enthalpies of formation of some primary phosphines RPH_2 have previously[2] been estimated by the molecular mechanics method. In this work, the enthalpies of combustion (ΔH_{comb}) of the phosphorus(III) compounds available from literature are used to calculate the heats of formation ($\Delta H^\circ{}_{\text{f}}$/kJ mol^{-1}) of alkylphosphines for the condensed and gas phases.

The complete combustion of the compounds of tri- and tetracoordinated phosphorus occurs in an oxygen atmosphere *via* the same scheme[3]

$$[R_{(3-n)}PH_n \text{ or } R'_3P{=}O] + O_2 \longrightarrow$$
$$\longrightarrow x\,CO_2(g) + y\,H_2O(liq) + z\,H_3PO_4(s), \qquad (1)$$

where n, x, y, and z are stoichiometric coefficients; R = Alk, Ph; R′ = Alk, RO, NHR″. The $\Delta H^\circ{}_{\text{f}}$ values for CO_2(g) (−395.5 kJ mol^{-1}), H_2O(liq) (−285.8 kJ mol^{-1}), and H_3PO_4(s) (−1279.0 kJ mol^{-1}) are available from the reference book.[3]

The enthalpy of combustion of organic compounds in the condensed state can be characterized[4] by the following equation:

$$\Delta H_{\text{comb}} = a + bN, \qquad (2)$$

where N is the number of bond-forming (valent) electrons, and a and b are coefficients.

Lone electron pairs (LEPs) are ignored in the calculation. For example, one LEP is ignored in compounds having trivalent nitrogen (≡N:) and phosphorus (≡P:) atoms, while two LEPs are ignored in compounds containing oxygen atoms (:O:—). A similar approach is used for other molecules containing heteroatoms (for example, S or As).

For instance, the total number of electrons for a methanol molecule Me—O—H is considered to be six; this number is obtained by the sum of four electrons of the C atom, four electrons of four H atoms, and two electrons

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* For Part 18, see Ref. 1.

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of the O atom excluding four electrons of two LEPs of oxygen, which are not involved in combustion.[4]

Only six values for enthalpies of combustion of liquid and solid derivatives of tricoordinated phosphorus can be found in the literature[3] (for Ph_3P two values are available).

Compound	$-\Delta H_{comb}$/kJ mol^{-1}
Me_3P (**1**)	3194.9±4.6
Et_3P (**2**)	5176.0±12.5
Ph_3P (**3**)	10309.4±19.2, 10299±12.5
Pentaphenylphosphol (**4**)	18198.3±28.4
9-Phenyl-9-phosphafluorene (**5**)	9982.2±16.7

Based on these data, we calculated a dependence similar to Eq. (2)

$$\Delta H_{comb} = (-860.7\pm41.8) - (107.0\pm0.5)N, \quad (3)$$

$r = 0.999$, $S = 49.2$, $n = 6$.

It turned out that ΔH_{comb} for the P^{III} derivatives can be described by the same parameter N as organic molecules (including those containing a heteroatom).[4] Based on the standard deviation S in Eq. (3), we suggest that thus calculated enthalpies of combustion of the organic phosphorus compounds have an error of at least ±7—10%.

The enthalpies of vaporization of alkylphosphines, which have previously[5] been determined in our earlier work, made it possible to estimate the enthalpies of formation of all phosphines in the gas phase. The calculated enthalpies of combustion and formation of some alkylphosphines are presented in Table 1.

To confirm that Eq. (3) can be used for the determination of enthalpies of combustion of tricoordinated phosphorus derivatives bearing phosphorus-containing bonds other than P—C bonds (P—O, P—N, or P—S), we calculated the enthalpies of combustion to compute the enthalpies of formation (see Table 1) of methyl and ethyl phosphites in the condensed (*i.e.*, liquid) state, *viz.*, $(MeO)_3P$ (**14**) and $(EtO)_3P$ (**15**) known from the literature.[3]

It turned out that for compounds **14** and **15** in the condensed state the enthalpies of formation are equal to −750.2 and −868.1 kJ mol^{-1}, respectively, and the difference with the earlier published[3] values exceeds 7—9 kJ mol^{-1}, which, in our opinion, is comparable with errors of determination of $\Delta H°_f$ of these experimental values obtained by the reaction calorimetry method.

Table 1. Thermochemical characteristics (in kJ mol^{-1}) of tertiary, secondary, and primary alkylphosphines

Compound	N	$-\Delta H_{comb}$(liq)	$-\Delta H°_f$^{a} liquid phase^c	$-\Delta H°_f$^{a} gas phase	ΔH_{vap}^{b}
Me_3P (**1**)	22	3194.9 ^{d}	122.2	93.7	28.5
Et_3P (**2**)	40	5176.0 ^{d}	190.8	149.7	41.1
Pr_3P (**6**)	58	7066.7	344.7	290.5	54.2
Bu_3P (**7**)	76	8992.7	461.9	391.3	70.6
Et_2PH (**8**)	28	3856.7	147.5	112.2	35.3
Pr_2PH (**9**)	40	5140.7	226.7	182.5	43.6
Bu_2PH (**10**)	52	6424.7	304.7	251.7	53.0
$EtPH_2$ (**11**)	16	2572.7	68.9	44.0	24.9
$PrPH_2$ (**12**)	22	3214.7	108.2	78.6	29.6
$BuPH_2$ (**13**)	28	3856.7	147.5	112.5	35.0

Note. N is the number of bond-forming (valent) electrons; ΔH_{comb}, $\Delta H°_f$, and ΔH_{vap} are the enthalpies of combustion, formation, and vaporization, respectively.

[a] Calculated from ΔH_{comb}.

[b] The data in Ref. 5.

[c] Calculated by Eq. (3).

[d] The data obtained by the combustion method.[3]

Thus, when it is difficult to directly determine enthalpies of combustion and formation of substances, reliable thermochemical parameters can be calculated by the correlation that takes into account the number of valent electrons.

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