Thermochemistry of Heteroatomic Compounds. Calculation of Combustion and Formation Enthalpy of some Phosphorylated Sugars and Aminoacids

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A new approach is suggested for the calculation of combustion enthalpies of three-coordinated phosphorus organic derivatives in the condensed state (scheme A) on the basis of the equation $\Delta H'_{comb} = a + b\,N$, in which a and b are constants and N is a number of valence, bond-forming electrons in the researching molecules [1]

$R_3P(liq\ or\ sol) + n\ O_2 \rightarrow x\ CO_2\ (gas) + y\ H_2O\ (liq) + z\ H_3PO_4\ (sol)$ (A)

n, x, y, z are stoichiometric coefficients, and R is Alk, Ar.

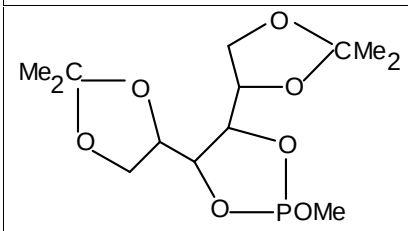
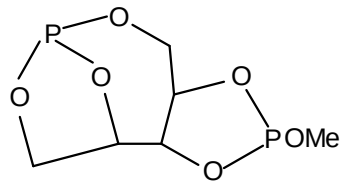
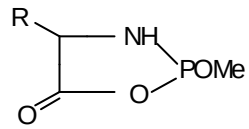
The formation enthalpies (ΔH^o_f) of liquid phosphorus derivatives accordingly to the mentioned above equation and Hess-low [$\Delta H'_{comb} = \Sigma\ \Delta H^o_f$ (products) - $\Sigma\ \Delta H^o_f$ (reactants)] have been calculated. The gaseous formation enthalpies of P(III)-compounds (in kJ mol^{-1}), receiving on the basis of mannite, ribite, glycine and alanine (see Table), were calculated with the use of their vaporization enthalpies: $\Delta H_{vap} = 4.26 + 9.37\,{}^1X^s + 0.87\mu^2$. Last equation includes in itself the solvation topological index of the first order and a dipole moment of molecule, obtained by molecular mechanics method [2,3].

Necessary to note, that the calculated combustion enthalpies in condensed phase

it is difficult to suppose as a final values. It is only the intermediate stage on the way to the obtaining of real magnitudes, which are required for the bond energy (E_b) calculations [$\Sigma E_b \approx \Sigma\ \Delta H^o_f$(all atoms) - ΔH^o_f(molecule, gas)]. All $\Delta H'_{comb}$ values need in the addition in enthalpy of combustion of correction contributions (w_i) for such structural fragments of molecules as there are in simple and complex ethers, amines, multiple bonds and cycles of different size with a phosphorus atom in their composition. Ultimately the suggested in the top of abstract equation has a next form:

$$\Delta H_{comb} = \Delta H'_{comb} + \Sigma\ w_i\ .$$

Table. Structural ($^1X^s$ and μ, D) and calculated thermochemical parameters (kJ mol^{-1}) ethers of phosphoric acid

Formula	$^1\chi^S$ (μ)	- $\Delta H'_{comb}$ (±0.005%)	- ΔH_{vap} (±0.05%)	- ΔH^o_f (±0.055%)	
				liq, sol	gas
	11.085 (1.0)	7922.7 ±39.6	109.0 ±5.4	1723.8 ±39.6	1614.9 ±44.9
	8.089 (1.0)	3428.7 ±17.1	80.9 ±4.0	2062.1 ±17.1	1981.2 ±21.6
R=H 	4.105 (4.3)	2358.7 ±11.8	41.5 ±2.1	529.6 ±11.8	488.1 ±13.9
R=Me	4.526 (4.3)	3000.7 ±15.0	44.7 ±2.2	567.0 ±15.0	522.3 ±17.2

References

[1] Ovchinnikov V.V., Lapteva L.I., Kireev M.G., Russian Chem. Bulletin, 2004, No 8. P. 1693-1694.

[2] Ovchinnikov V.V., Khazieva L.R., Lapteva L.I., Konovalov A.I., Russian Chem. Bulletin, 2000, Vol. 49, No 1. P. 33-38.

[3] Ovchinnikov V.V., Phosphorus, Sulfur, and Silicon. 2004. Vol. 179, N 1. P.115-151.