

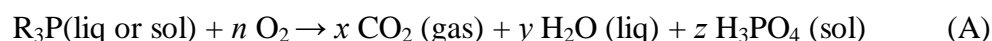
Thermochemistry of Heteroatomic Compounds. Calculation of Combustion and Formation Enthalpy of some Phosphorylated Sugars and Aminoacids

V.V.Ovchinnikov, L.I.Lapteva, N.R.Muzafarov

Kazan State of Architectural-building University

Russia 420043, Kazan, Zelionaya str.1, e-mail: chem._vvo@mail.ru

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 $\Delta H'_{\text{comb}} = a + b N$, in which a and b are constants and N is a number of valence, bond-forming electrons in the researching molecules [1]



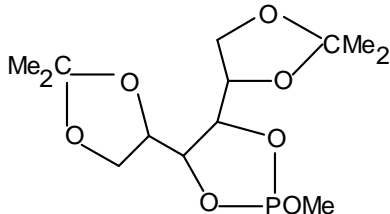
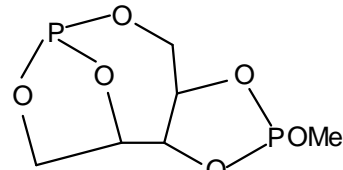
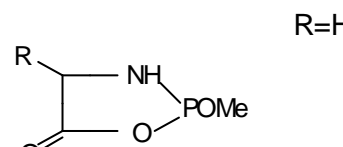
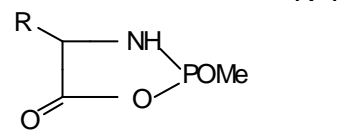
n, x, y, z are stoichiometric coefficients, and R is Alk, Ar.

The formation enthalpies (ΔH°_f) of liquid phosphorus derivatives accordingly to the mentioned above equation and Hess-law [$\Delta H'_{\text{comb}} = \sum \Delta H^{\circ}_f(\text{products}) - \sum \Delta H^{\circ}_f(\text{reactants})$] 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: $\Delta H_{\text{vap}} = 4.26 + 9.37^1 X^s + 0.87\mu^2$. 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 [$\sum E_b \approx \sum \Delta H^{\circ}_f(\text{all atoms}) - \Delta H^{\circ}_f(\text{molecule, gas})$]. All $\Delta H'_{\text{comb}}$ 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:

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

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

Formula	$^1\chi^S$ (μ)	$-\Delta H'_{\text{comb}}$ ($\pm 0.005\%$)	$-\Delta H_{\text{vap}}$ ($\pm 0.05\%$)	$-\Delta H^{\circ}_f$ ($\pm 0.055\%$)	
				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., Kononov 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.