LETTERS
TO THE EDITOR

Thermochemistry of Heteroatomic Compounds: XXIV.¹ Calculation of the Formation Enthalpy of 2-Methoxy-2-oxo-1,3,2-dioxaphospholane

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Received November 9, 2007

DOI: 10.1134/S1070363209060346

The ethers of phosphorus acid are important for biochemical processes, however their thermochemistry has been studied insufficiently. We have shown [2] that combustion enthalpy (ΔH_{comb}) of phosphorus(III)-containing compounds can be calculated on the basis of the number of bond-forming (valence) electrons N in a molecule, excluding number (c) of lone electron pairs (LP) of heteroatoms: oxygen ($c = 2$), nitrogen or phosphorus ($c = 1$), etc. [Eq. (1)].

$$\Delta H_{\text{comb}} = -860.7 - 107.0 (N - c_{\text{LP}}). \quad (1)$$

The values of combustion enthalpies of some ethers of phosphorus acid have been published [3, 4]: (EtO)₃PO (I) -4114.5 ± 10.9 , (PrO)₃PO (II) -6075.2 ± 21.3 , (BuO)₃PO (III) -7974.3 ± 11.3 , (PhO)₃PO (IV) -9247.8 ± 6.0 kJ mol⁻¹. Using these data we derived the dependence (2):

$$\Delta H_{\text{comb}} = (-283.6 \pm 35.9) - (106.8 \pm 0.6)(N - c_{\text{LP}}), \quad (2)$$

$r = 0.999, S_0 = 20.4, n = 4.$

With Eq. (2) we calculated the value of combustion enthalpy (-2024.1 ± 10.1 kJ mol⁻¹) of liquid 2-methoxy-2-oxo-1,3,2-dioxaphospholane (V) and with the Eqs. (3) and (4) the value of its formation enthalpy ($\Delta H_f^0 = -1013.4 \pm 10.1$ kJ mol⁻¹).

where n, x, y, z are stoichiometric coefficients.

$$\Delta H_{\text{comb(hydr)}} = \sum \Delta H_{\text{tr}}^0(\text{product}) - \sum \Delta H_{\text{tr}}^0(\text{reagents}). \quad (4)$$

The enthalpies of formation for CO₂ (g) = -395.5 , H₂O (l) = -285.8 , H₃PO₄ (s) = -1279.0 kJ mol⁻¹ were taken from the handbook [3].

On the basis of the determined earlier experimental value of hydrolysis enthalpy ($\Delta H_{\text{hydr}} = -123.4 \pm 3.3$ kJ mol⁻¹) of this cyclic phosphate [5] can be calculated the value of ΔH_f^0 [-1016.7 ± 3.3 kJ mol⁻¹, Eqs. (4) and (5)], which matches well the above calculated value.

The values of ΔH_f^0 for the water solutions of phosphorus acid, methanol and ethylene glycol were calculated from the data in [3, 6].

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¹ For communication XXIII, see [1].