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SHORT COMMUNICATIONS

Calculation of Enthalpy of Formation of Methyl-α-D-glucopyranosido-4',6'-cyclophosphate from Its Enthalpy of Combustion

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The enthalpy of formation of phosphorus-containing carbohydrates are necessary for the calculation of bond energy governing the biological activity of these compounds. One of the ways to obtain these data is the calorimetry of combustion, frequently experimentally difficult task for organophosphorus glycosides. We showed [1–4] that enthalpy of combustion of heteroatomic compounds (P, As, Sb, Bi), like that of various classes of organic molecules [5] can be simply and reliably calculated based on bonding (valent) electrons (*N*) in the molecule without taking into account the number of the lone electron pairs (*c*LEP).

$$\Delta H_{\text{comb}} = a + b\,(N - c\text{LEP}). \qquad (1)$$

We calculated a similar equation (2) based on the published [6] data on enthalpy of combustion (ΔH_{comb}, kJ mol^{-1}) of 17 cyclic ethers, sugars, and number of electrons (*N*–*c*LEP) of tetrahydrofuran (–2505.8, 22), 1,3-dioxolane (–1705.0, 14), 1,3-dioxane (–2331.9, 20), 2-Me-1,3-dioxane (–2959.0, 26), 4-Me-1,3-dioxane (–2979.1, 26), 2-methoxytetrahydropyran (–3633.8, 32), α-D-xylose (–2339.0, 20), D-ribose (–2334.2, 20), α-D-glucose (–2805.0, 24), L-sorbose (–2804.6, 24), D-mannose (–2813.0, 24), D-galactose (–2803.7; 24), α-Me-glucofuranoside (–3552.1, 30), α-D-Me-glucopyranoside (–3522.1, 30), β-D Me-glucopyranoside (–3518.0, 30), sucrose (–5643.4, 48), and β-lactose (–5629.5, 48).

$$\Delta H_{\text{comb}} = (15.7 \pm 37.2) - (117.2 \pm 1.3)\,(N - C\text{LEP}) \qquad (2)$$

$$r\ 0.999,\ S_{\circ}\ 47.2,\ n\ 17.$$

In order to test the applicability of the latter equation for the calculation of the combustion enthalpy of nucleosides of different structure and with various spatial substituents we calculated ΔH_{comb} of identical in the empirical formula ($C_{12}H_{24}O_{12}$) α-lactose and β-maltose monohydrates (–5609.9 ± 28.0 kJ mol^{-1}). The divergence from the published data (–5668.0 ± 1.0 and –5692.4 ± 0.5 [6]) in both cases did not exceed 1.4%.

According to equation (2) we calculated the combustion enthalpy of methyl-α-D-glucopyranosido-4',6'-cyclophosphate $C_7H_{13}O_8P$ (–3500.1±17.5 kJ mol^{-1}), and with accounting for Scheme (3) and Hess's equation (4) its enthalpy of formation in the condensed phase $\Delta H^{\circ}_{\text{form}}$ = –1962.7± 9.8 kJ mol^{-1}.

$$C_7H_{13}O_8P_{\text{cond}} + 11.5\ O_{2\text{gas}} \rightarrow 7\ CO_{2\text{gas}} + 5\ H_2O_{\text{liq}} + H_3PO_{4\text{solid}} \qquad (3)$$

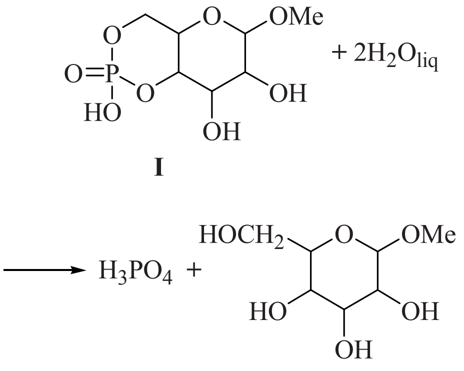
$$\Delta H_{\text{comb/hydr}} = \Sigma\Delta H^{\circ}_{\text{form of products}} - \Sigma\Delta H^{\circ}_{\text{form of reagents}} \qquad (4)$$

The values $\Delta H^{\circ}_{\text{form}}$ for $CO_{2\text{gas}}$ (– 395.5), H_2O_{liq} (–285.8), $H_3PO_{4\text{solid}}$ (–1279.0 kJ mol^{-1}) are taken from the monograph [6].

The experimental exothermal enthalpy of hydrolysis of nucleoside **I** according to Scheme leading to the formation of aqueous phosphoric acid and hydrated α-D-Me-glucopyranoside (**II**) amounts to ΔH_{hydr} = –28.7 ± 0.5 kJ mol^{-1} [7].

To compare the calculated by us value of $\Delta H^{\circ}_{\text{form}}$ of nucleoside **I** it was necessary to calculate the same

Scheme.



I

II

thermochemical parameter in keeping with Scheme. The value $\Delta H^\circ_{\text{form}}$ of H_3PO_4 was –1289.9 kJ mol^{-1} [8], and that of pyranoside **II** in a condensed phase, −1233.4 ± 0.8 kJ mol^{-1} [6]. The application to Scheme (5) of Hess's equation (4) required the evaluation of the value $\Delta H^\circ_{\text{form}}$ of the product of hydration of **II** in the water phase.

The calculated enthalpy value of the water layer of pyranoside **II** by molecular mechanics method $\Delta H_{\text{aq layer}}$ = –29.7 kJ mol^{-1}; this value turned out to be close to the known quantum-chemical estimation of the hydration of riboside rings, ~ –34.3 kJ mol^{-1} [9].

By the summation of the value of enthalpy of formation of compound **II** in the condensed phase and the enthalpy of its hydration we were able to obtain its enthalpy of formation in the water phase: $\Delta H^\circ_{\text{form}}$ (**II**) = $\Delta H^\circ_{\text{form}}$ + $\Delta H_{\text{aq layer}}$ = –1263.1 ± 2.5 kJ mol^{-1}.

The calculation of the enthalpy of formation of methyl-α-D-glucopyranosido-4',6'-cyclophosphate (**I**) by Hess's equation (4)

$$\Delta H^\circ_{\text{form}}(\text{I}) = -\Delta H_{\text{hydr}} + \Delta H^\circ_{\text{form}}(\text{aqueous } H_3PO_4) \\ + \Delta H^\circ_{\text{form}}(\text{II}) - 2\,\Delta H^\circ_{\text{form}}(H_2O_{\text{liq}})$$

gave the value –1952.7 ± 3.0 kJ mol^{-1} in good agreement with the value calculated by us.

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