Thermochemistry of Heteroatomic Compounds: Some Thermodynamic Aspects of Combustion and Formation of Carbohydrates of Different Structures

Vitaly Ovchinnikov

Tupolev Kazan National Researching Technical University, St-K, Marks 10, 420111 Kazan, Tatarstan/Russia
E-Mail: chem_vvo@mail.ru

Abstract

The linear equation of a general view $\Delta Y^o = i \pm f (N - g)$, where $\Delta Y^o$ can be a free energy or heat of combustion or formation, entropy and the heat of capacity, parameters, $i$ and $f$ are correlation factors, describing the interdependence between thermodynamic functions of sugars and their numbers ($N$) of valence electrons except the numbers of lone electron pairs ($g$) of heteroatoms in them, has been applied for calculation of sugars of a various structure. The obtained results can be used for an estimation of the energy transfer in living systems by the means of phosphorus containing sugars like adenosine-triphosphate (ATP).

Keywords: Sugar, Carbohydrate, Combustion, Formation, Free Energy, Heat, Entropy, Heat Capacity

1. Introduction

The interest of biochemists to the definition and analysis of thermodynamic functions of carbohydrates a various structure does not weaken during many tens years till this time (Corbridge, 1980 and Haynie, 2008). It is established, that metabolism processes of carbohydrates are carried out via the formation of phosphorus-containing esters. The significance of phosphorus-containing sugars in biochemical processes it is possible to explain from the energetic and structural positions (Stepanenko, 1977). Nucleoside-diphosphosugars (NDFS) are good donors of the sugar rests from the thermodynamic points of view. According to Kochetkov and co-authors (Kochetkov et al, 1967) the hydrogen bonds formation inside NDFS leads to the twist conformation, which promotes its interaction with enzyme and help to conduct biochemical reaction. Taking into account the presented results only it is possible to make some analysis of the thermochemical properties of sugars of the different structure.

2. Results and Discussion

The combustion process of heteroatomic compounds corresponds to Eq. 1 in general (Cox & Pilcher, 1970)

$$C_aH_bN_cO_dP_e + nO_2 \rightarrow aCO_2 + b/2 H_2O + d/2 N_2 + eH_3PO_4 + \Delta Y^o$$……..1

Where $a, b, c, d, e$ are stoichiometric coefficients, and $\Delta Y^o$ is a change of functions: the free energy, enthalpy or entropy at the standard conditions

Earlier it has been shown (Kharasch & Sher, 1925; Ovchinnikov, 2006; 2011 and 2012) that the magnitudes of the heats of combustion for organic compounds ($\Delta H^f$) can be calculated effectively within the limits of the one-factorial regression analysis i.e. at the construction of a various correlation equations between the values obtained earlier experimentally heats of combustion of compounds and a number of participating in them bond-forming, valence electrons (Eq. 2):

$$\Delta H^f = i \pm f (N - g)$$……………………………………...2

Where parameters $i$ and $f$ are a correlation factors. They characterize structurally-thermal contributions in the heats of combustion and "sensitivity" of valence electrons $N$ in molecule, from which the number ($g$) lone pair electrons of heteroatoms in a various functional groups is

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subtracted. So, for elements of IVA group of Periodic table g is 0, for VA groups g is 1, for VI group g is 2 (Ovchinnikov, 2012)

Similarly Eq. 3 can be presented for the characteristic of other thermodynamic functions, such as the free energy of combustion and formation, entropy and heat capacity

\[ \Delta Y^o = i \pm f (N - g) \] ……………………………………….3

2.1. Free Energies of Combustion and Formation

The values of the free energy of combustion (\(\Delta_G^o\)) and formation (\(\Delta_f^o\)) in the condensed phase carbohydrates such as \(\alpha-D\)-galactose -I, \(\alpha-D\)-glucose -II, \(\alpha-D\)-lactose -III, \(\alpha-D\)-saccharose -IV, \(\alpha-D\)-fructose -V for a long time are known in the literature (Metzler et al, 2001). The heats of combustion of all phosphorus-containing carbohydrates (XIII-XXVIII) have been calculated with the use of dependence (Eq. 7). The contribution acidic phosphorylic groups (-75.3 kJ mol\(^{-1}\)) has been considered at calculation of values \(\Delta_f^p\).

The heats of combustion of phosphorus carbohydrates have been calculated with the combination of equations (1, 8, and 9). The values of \(\Delta_f^p\) for gaseous CO\(_2\), liquid H\(_2\)O and solid H\(_3\)PO\(_4\) (-393.5, 285.8, -1279.0 kJ mol\(^{-1}\)) were taken from the higher mentioned Cox & Pilcher's (1970) monography.

2.2. The Heats of Combustion and Formation

The heats of combustion (\(\Delta_f^p\)) and formation (\(\Delta_f^p\)) values for compounds (I-XII) are known in the literature (Karrer & Floroni, 1923; Clarke & Stegeman, 1939; Skuratov et al, 1957; Ponomarev & Migarskaya, 1960; Desai & Wilhoit, 1970; Gerasimov et al, 1985; Wu et al, 1987 and Gubareva et al, 1991). Their thermochemical parameters directly depend on the number of valence electrons as shown (Eqs. 7 and 8):

\[ \Delta_f^p = (23.5\pm6.0)-(118.1\pm0.2) \] (N g); r 0.999, So 7.1, n12 (I-XII),………………….7

\[ \Delta_f^p = (-264.4\pm31.7)(+40.9\pm0.8) \] (N g); r 0.998, So 25.7, n12 (I-XII)………..8

It is assumed that the heats of combustion and formation for the carbohydrates, containing the phosphate cycles and adenine fragments (XX-XXVIII), were calculated previously (Ovchinnikov & Lapteva, 2011). The values for the same parameters calculated in this work good correspond to the mentioned earlier in the frames of uncertainties (±0.5 %) for calculations.

2.3. Entropy and Heat of Capacity

It was assumed that all thermodynamic data on entropy (\(S^o\)) and heat capacity (\(C_p\)) of carbohydrates, (Miller, 1935; Jack & Stegeman, 1941; Kawaizumi et al, 1981; Domalski & Hearing, 1990; Boerio-Goates, 1991 and Putnam & Boerio-Goates, 1993). These data could be examined in the frame work the given above approach: the interrelation of the chosen thermodynamic function with the number of valence electrons in heteroatomic molecule Eq. 3).

The equations (10 and 11) reflect the dependences of entropy and heat capacity from number valence electrons; they have been calculated similarly.
Table 1a. Thermodynamic Functions (kJ mol⁻¹, J mol⁻¹ K⁻¹) of Carbohydrates at 298.15 K; all Compounds are in The Condensed Phase

<table>
<thead>
<tr>
<th>No Comp.</th>
<th>Compound, Formula, (N-g)</th>
<th>-ΔG° (calc. ±0.5%)</th>
<th>-ΔH° (calc. ±0.5%)</th>
<th>-ΔCp (calc. ±0.5%)</th>
<th>S° (calc. ±0.5%)</th>
<th>Cp (calc. ±0.5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>C₆H₁₂O₆, 24</td>
<td>2865.9</td>
<td>923.5</td>
<td>5204.5</td>
<td>1271.5</td>
<td>205.4</td>
</tr>
<tr>
<td>II</td>
<td>C₆H₁₂O₆, 24</td>
<td>2872.2</td>
<td>917.2</td>
<td>5208.3</td>
<td>1272.8</td>
<td>209.2</td>
</tr>
<tr>
<td>III</td>
<td>C₁₂H₂₂O₁₁, 48</td>
<td>5826.5</td>
<td>1515.2</td>
<td>5652.5</td>
<td>2214.2</td>
<td>(395.7 ±2.0)</td>
</tr>
<tr>
<td>IV</td>
<td>C₁₂H₂₂O₁₁, 48</td>
<td>5789.9</td>
<td>1551.1</td>
<td>5643.5</td>
<td>2221.2</td>
<td>392.4</td>
</tr>
<tr>
<td>V</td>
<td>C₁₀H₁₀O₆, 24</td>
<td>2874.1</td>
<td>915.4</td>
<td>2810.4</td>
<td>1265.6</td>
<td>(201.3 ±1.0)</td>
</tr>
<tr>
<td>VI</td>
<td>C₁₀H₁₀O₆, 20</td>
<td>(2403.3 ±12.0)</td>
<td>(815.9 ±4.1)</td>
<td>2347.6</td>
<td>1049.1</td>
<td>(168.9 ±0.8)</td>
</tr>
<tr>
<td>VII</td>
<td>C₁₀H₁₀O₆, 20</td>
<td>(2403.3 ±12.0)</td>
<td>(815.9 ±4.1)</td>
<td>2338.8</td>
<td>1057.9</td>
<td>(168.9 ±0.8)</td>
</tr>
<tr>
<td>VIII</td>
<td>C₁₀H₁₀O₆, 20</td>
<td>(2403.3 ±12.0)</td>
<td>(815.9 ±4.1)</td>
<td>2340.0</td>
<td>1057.8</td>
<td>(168.9 ±0.8)</td>
</tr>
</tbody>
</table>

S° = (6.9±25.4)+(8.1±0.8) (N-g); r 0.984, n5 (III,IV,IX,X)………10
Cp = (15.2±5.1)+(8.4±0.2) (N-g); r 0.998, So 5.7, n10 (I-VII, IX-XI)………11

The interdependence between entropy and heat capacity values is available too as shown in Eq. 12.

S° = (14.1±4.2) + (0.9±0.1) Cp; r 0.999, So 2.6, n 4 (I, II, IV, X)………12

The equations (10 and 11) allow to calculate entropy and heat capacity for sugars (III, VI, XI, XII) and not applicable for calculation for sugars including phosphorus atom.

The other way for definition of the same function is known as Gibbs’s equation (13). Last dependence can be used for phosphorus carbohydrates (XIII-XXVIII).

ΔG° = ΔH° - T S° ..................................................13
The analysis of entropic data for phosphor-containing carbohydrates allows to make some conclusion. A small positive magnitude of $S_0$ values (compounds XIII-XVII, XIX-XXVII) can characterize the fact that in these compounds there is a relatively big number of internal freedom degrees. The greater negative $S_0$ values for compounds (XVIII and XXVIII) correspond to the presence of strong hydrogen bonds, as shown by work of Kochetkov and co-

Table 1b. Thermodynamic Functions (kJ mol$^{-1}$, J mol$^{-1}$ K$^{-1}$) of Carbohydrates at 298.15 K; all Compounds are in The Condensed Phase

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>IX</td>
<td></td>
<td>2403.3 ±12.0</td>
<td>815.9 ±4.1</td>
<td>2345.3</td>
<td>1051.4</td>
<td>143.5</td>
<td>184.0</td>
</tr>
<tr>
<td>X</td>
<td></td>
<td>2889.5 ±14.4</td>
<td>918.3 ±4.6</td>
<td>2799.1</td>
<td>1276.9</td>
<td>220.9</td>
<td>228.6</td>
</tr>
<tr>
<td>XI</td>
<td></td>
<td>2889.5 ±14.4</td>
<td>918.3 ±4.6</td>
<td>2812.7</td>
<td>1263.4</td>
<td>201.3</td>
<td>214.2</td>
</tr>
<tr>
<td>XII</td>
<td></td>
<td>2888.9 ±14.4</td>
<td>918.3 ±4.6</td>
<td>2820.4</td>
<td>1255.7</td>
<td>201.3</td>
<td>-</td>
</tr>
<tr>
<td>XIII</td>
<td></td>
<td>1944.1</td>
<td>1439.1</td>
<td>1940.9 ±9.7</td>
<td>1769.6 ±8.8</td>
<td>10.7 ±0.05</td>
<td>-</td>
</tr>
</tbody>
</table>

Phosphor-Containing Sugars

| XIV |   | 2414.9 | 1599.9 | 2413.2 ±12.0 | 1976.7 ±9.9 | 5.7 ±0.03 | -      |
| XV  |   | 2888.1 | 1758.3 | 2885.5 ±14.4 | 2183.7 ±10.9 | 8.7 ±0.04 | -      |
| XVI |   | 2902.5 | 2600.8 | 2960.8 ±14.8 | 3530.4 ±17.6 | (-195.5 ±1.0) | -      |
| XVII|   | 3364.6 | 1913.3 | 3357.8 ±16.8 | 2390.8 ±11.9 | 22.8 ±0.1 | -      |
| XVIII|   | 3379.0 | 2755.8 | 3433.1 ±17.2 | 3308.7 ±16.5 | (-181.4 ±0.9) | -      |
| XIX |   | 2886.0 | 1760.3 | 2885.5 ±14.4 | 2183.7 ±14.4 | 1.7 ±0.01 | -      |
| XX  |   | 3617.3 ±18.1 | 1995.1 ±10.0 | 3594.0 ±18.0 | 1868.8 ±9.3 | 78.1 ±0.4 | -      |

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The obtained thermodynamic data can be possible use for the calculation of the heat of reaction ($\Delta H^o$) between the compressed glucose (II) and 1-adene-ribofuranoside-5-triphosphate (XXVII, ATP) (Eq. 14) for reception D-glucose-6-phosphate (XIX) and 1-adene-ribofuranoside-5-diphosphate (XXVII, ADP) in standard conditions (White et al, 1981).

$$\text{II} + \text{ATP(XXVIII)} \rightarrow \text{XIX} + \text{ADP(XXVII)} + \Delta H^o \ldots \ldots 14$$

Let this reaction takes place in the absence of catalysis by hexokinase-enzyme as it is known for alive organisms. The free energy of this process it is possible to calculate by the

Table 1c. Thermodynamic Functions (kJ mol$^{-1}$, J mol$^{-1}$ K$^{-1}$) of Carbohydrates at 298.15 K; all Compounds are in The Condensed Phase

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^o$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^o$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta H^o$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^o$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XXI</td>
<td>(3617.3 ±18.1)</td>
<td>(1995.1± 10.0)</td>
<td>(3594.0 ±18.0)</td>
<td>(1868.8 ±9.3)</td>
</tr>
<tr>
<td>XXII</td>
<td>(3617.3 ±18.1)</td>
<td>(1995.1± 10.0)</td>
<td>(3594.0 ±18.0)</td>
<td>(1868.8 ±9.3)</td>
</tr>
<tr>
<td>XXIII</td>
<td>(4831.3 ±24.1)</td>
<td>(2391.3± 11.9)</td>
<td>(4774.7 ±23.9)</td>
<td>(1760.9 ±8.8)</td>
</tr>
<tr>
<td>XXIV</td>
<td>(6045.3 ±30.2)</td>
<td>(2787.3± 13.9)</td>
<td>(5955.4 ±29.8)</td>
<td>(544.9 ±2.7)</td>
</tr>
<tr>
<td>XXV</td>
<td>(6045.3 ±30.2)</td>
<td>(2787.3± 13.9)</td>
<td>(5930.3 ±29.6)</td>
<td>(570.0 ±2.8)</td>
</tr>
<tr>
<td>XXVI</td>
<td>(6045.3 ±30.2)</td>
<td>(2787.3± 13.9)</td>
<td>(5955.4 ±29.8)</td>
<td>(544.9 ±2.7)</td>
</tr>
<tr>
<td>XXVII</td>
<td>(6045.3 ±30.2)</td>
<td>(2787.3± 13.9)</td>
<td>(6030.7 ±30.1)</td>
<td>(1748.7 ±8.7)</td>
</tr>
<tr>
<td>XXVIII</td>
<td>(6045.3 ±30.2)</td>
<td>(2787.3± 13.9)</td>
<td>(6106.0 ±30.5)</td>
<td>(2666.6 ±13.3)</td>
</tr>
</tbody>
</table>

workers (Kochetkov et al, 1967).

2.4. The Application of P-Sugars for Energy Transmission

The obtained thermodynamic data can be possible use for the calculation of the heat of reaction ($\Delta H^o$) between the compressed glucose (II) and 1-adene-ribofuranoside-5-triphosphate (XXVII, ATP) (Eq. 14) for reception D-glucose-6-phosphate (XIX) and 1-adene-ribofuranoside-5-diphosphate (XXVII, ADP) in standard conditions (White et al, 1981).
Eq. 15. The heat of this reaction it is possible to calculate by the Eq. 16. The entropy of this interaction it is possible to calculate with the use of Eq. 17.

\[ \Delta G^\circ = \sum \Delta G^\circ_{\text{products}} - \sum \Delta G^\circ_{\text{reactants}} \] 15

\[ \Delta H^r = \sum \Delta H^r_{\text{products}} - \sum \Delta H^r_{\text{reactants}} \] 16

\[ \Delta S^o = \sum \Delta S^o_{\text{products}} - \sum \Delta S^o_{\text{reactants}} \] 17

The calculated values obtained are \( \Delta G^\circ = -843 \), \( \Delta H^r = +7 \), \( \Delta S^o = +45 \text{ kJ mol}^{-1} \text{ and J mol}^{-1} \text{ K}^{-1} \) correspondingly. Reaction can be carried out under the control of free energy. However it is necessary to remember, that the values used at calculation have been calculated approximately and have the significant uncertainty.

3. Conclusion

We have shown the application of the equation \( \Delta Y^o = i \pm f \) \((N - g)\) for the calculation of the free energy, of the heat of combustion and formation, of entropy and heat capacity for the big row of known sugars with a numbers valence electrons \( N \), from which the numbers of lone electron pair \( g \) are excluded. The calculated equations give a possibility to calculate the same thermodynamic parameters for phosphor-containing carbohydrates with the important biochemical function. The presented results can be used for an estimation of the energy transfer in living systems by the means of P-sugars like adenosine-triphosphate (ATP) too.

Acknowledgement

References


Putnam, R.L., and Boerio-Goates, J. (1993) Heat capacity measurements and thermodynamic functions of crystalline sucrose at temperatures from 5 to 342 K. Revised values for \(_{f}G^{m}\)(sucrose, cr, 298.15 K), \(_{f}G^{m}\)(sucrose, aq, 298.15 K), \(_{S}^{m}\)(sucrose, aq, 298.15 K); and \(_{r}G^{m}(298.15\) K) for the hydrolysis of aqueous sucrose. J. Chem. Thermodynam., 25(5), pp. 607-613.


