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Thermochemistry of Heteroatomic Compounds: Calculation of the heat of Combustion and the heat of Formation of some Bioorganic Molecules with Different Hydrophenanthrene Rows

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Abstract

On the basis of the known experimental heats of combustions of the seventeen alkanes in condensed state, the general equation $\Delta_{comb}H = i + f\left(N - g\right)$ has been deduced, in which *i* and *f* are correlation coefficients, *N* and *g* are a numbers of valence electrons and lone electron pairs of heteroatoms in molecule. The presented dependence has been used for the calculation of the heats of combustion of thirteen organic molecules with biochemical properties: holestan, cholesterol, methyl-cholesterol, ergosterol, vitamin-D$_2$, estradiol, androstenone, testosterone, androstanedione, morphine, morphinanone, codeine and pentasozine. It is noted that good convergence was obtained within the limits of errors of thermochemical experiments known in the literature and calculations of the heats of combustion for some of them were conducted. With the application of Hess law and the heats of vaporization $\left(\Delta_{vap}H\right)$, which has been calculated with the use of a topological solvation index of the first order $\left({}^{1}x^{s}\right)$, the heats of formation $\left(\Delta_{f}H^{\circ}\right)$ for condensed and gaseous phases were calculated for the listed bioorganic molecules.

Keywords: Alkanes, Biochemical Molecules, the Heat of Combustion, Heat of Formation, Heat of Vaporization, Topological Solvation Index

1. Introduction

In living organisms the organic molecules named as steroids are synthesized many. Extremely low reactivity of steroids complicates their metabolism, which can be compared to full oxidation (burning) in a live organism. In such cases, researchers use the theoretical calculation of the heat (enthalpy) of combustion for the biochemical substances.

The electronic conception of the interdependence of valence and the heat of combustion of organic compounds has been formulated in review of Kharasch and Sher [2] (Equation 1)

$$\Delta_{comb}H = -109.0_{*}\left(4a + b - c\right) + \Sigma\left(hc_{i}\right) * d_{i} \qquad (1)$$

The number -109.0 has been deduced from the combustion enthalpy of *n*-octane. It has dimension kJ·mol^{-1} electron^{-1} and characterizes the shift energy of the one electron. Such power is nearly equal to the sum of the heats of C-H and C-C breaking bonds in molecule at the combustion. The parameters *a* and *b* are a numbers of all carbon and hydrogen atoms and *c* is a number of the moving electrons from carbon to the more electronegative atoms in molecule. The sum of the heat corrections $\left(hc_{i}\right)$ has been introduced by authors of the above mentioned work for the identical $\left(d_{i}\right)$ types of bonds, spatial structures or groups in researching compounds.

2. Results and Discusion

In the complex organic and biochemical compounds with various heteroatoms, it is difficult to define a degree the group electronegativity and correspondingly a number of moving to them or inside of them, accordingly to Kharasch and Sher conception, electrons. In our opinion the majority of missing structural and energetic corrections can be in a complex considered within the limits of one-factorial regression analysis [3]. This consists in construction of a various correlations between the experimentally known values of the heats of combustion $\left(\Delta_{comb}H\right)$ of organic or heteroatomic compounds and a general number of the bond-forming electrons N in its Equation (2), in which

$$\Delta_{comb}H = i + f\left(N - g\right) \qquad (2)$$

i and f are the correlation coefficients, describing structurally-energetic contributions in the enthalpy of combustion and sensitivity of the last to a general number of electrons N, from which subtracted a number (g) of lone electron pairs of heteroatoms in the different functional groups. So, for IV group of Periodic Table (C, Si and below) g is equal 0, for V group (N, P and below) g is equal 1, for VI group (O, S and below) g is equal 2.

Proceeding from the listed above and also scheme of the process combustion of saturated, unsaturated and aromatic hydrocarbons (Equation 3)

$$p\mathrm{C_nH_{2n(+2)}} + q\mathrm{O_2} \rightarrow r\mathrm{CO_2}\left(gas\right) + s\mathrm{H_2O}\left(liq\right) + \Delta_{\mathrm{comb}}H \qquad (3)$$

in which p, q, r, s are stoichiometric coefficients (values of $\Delta_f H^o$ for CO_2 = –393.5 and H_2O = –285.8 kJ·mol^{-1} are taken from monography [4]), we have calculated dependence (4), which included itself the heat of combustion of saturated of alkanes (**Table 1**, compounds **1-17**) of a various *normal*-and *cyclic* structure and a number valence electrons in its (g = 0)

$$\begin{aligned}&\Delta_{\mathrm{comb}}H / \mathrm{kJ\cdot mol^{-1}}\\&= \left(-25.63 \pm 27.37\right) - \left(108.54 \pm 0.49\right) * N\end{aligned} \qquad (4)$$

r 0.999, s_o 32.9, n 17.

From the deduced Equation (4) it is possible to see, pletely corresponds to the suggested earlier by Kharasch and Sher, that testifies to qualitative and their quantitative conformity. Besides, using last dependence, we calculated the combustion enthalpy of *cis*-decalin (**18**) and compared it with known in the literature. It is equal –6320.4 ± 31.6 and within the error, estimated by us in ± 0.5 %, coincides with experimental –6287.7 ± 0.9 kJ·mol^{-1} [4]. The specified circumstances gives the possibility to apply the last equation for calculations of the **heat** of combustions for the variously substituted alkanes: cholestane, (**19**), cholesterol (**20**), O-methyl- cholesterol (2**1**), ergosterol (**22**), vitamin D_2, received by the isomerization of ergosterol [5], (**23**), estradiole (**24**), androstenone (**25**), testosterone (**26**), androstanedione (**27**), having the important biochemical properties. It is necessary to note also a good correspondence (within the limits of ± 2%) of the thermochemical parameters calculated by us with the known in the literature (**Table 2**, Equation (5))

$$\begin{aligned}&\Delta_{\mathrm{comb}}H_{\mathrm{exp}} / \mathrm{kJ\cdot mol^{-1}} = \left(-476.4 \pm 308.2\right)\\&+\left(96.6 \pm 216.7\right) * \Delta_{\mathrm{comb}}H_{calc} / \mathrm{kJ\cdot mol^{-1}}\end{aligned} \qquad (5)$$

r 0.999, s_o 158.7, n 6 (20-22, 25-27).

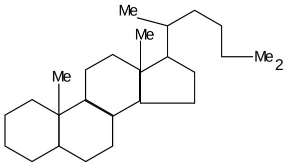
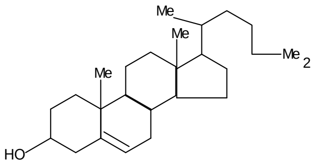
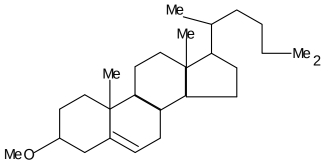
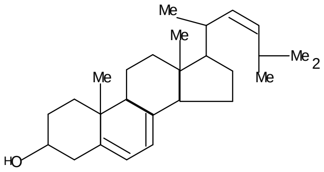
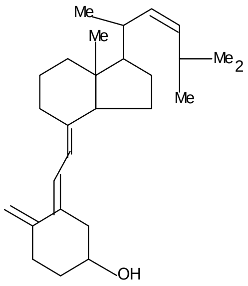
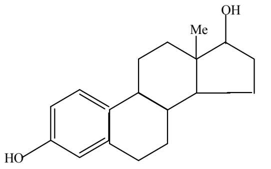
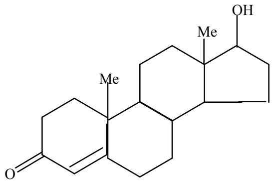
Moreover, necessary to note, that the experimental results for cholesterol (20), androstenone (25), testosterone (26) and androstanedione (27) (**Table 2**, column 5, 8) are very different each to other in the essential values, but they are rather near to calculated by us values (**Table 2**, column 4).

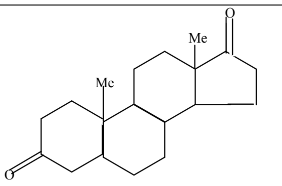
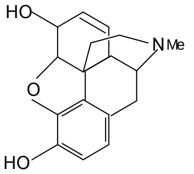
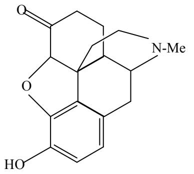
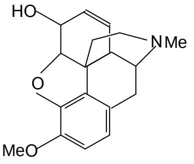
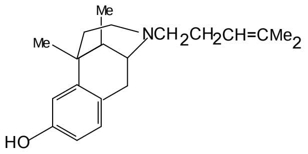
In structure of other well-known bioorganic molecules [5], such as morphine (28), morphinanone (29), codeine (30) and pentasozine (31) the aromatic rings are included. Nevertheless, accordingly to Kharasch-Sher-conception there is a mention about the application of the Equation (1) to the saturated and aromatic compounds. For this reason expediently to calculate the combustion enthalpy of these substances with the use dependence (4) of for saturated hydrocarbons.

Table 1. The number of valence electrons (*N*) and the heats of combustion (kJ·mol^{-1} of the different structural *n*-and *cyclo*-lkanes [4]. P 101kPa; T 298.15; all compounds are in condensed state.

No	Compound, formula	N	-$\Delta_{\mathrm{comb}}H$	No	Compound, formula	N	-$\Delta_{\mathrm{comb}}H$
1	Methylcyclopentane (C_6H_{12})	36	3938.6	**10**	2-Methylheptane, (C_8H_{18})	50	5456.5
2	Cyclohexane, (C_6H_{12})	36	3920.0	**11**	2,5- Dimethylhexane, (C_8H_{18})	50	5460.2
3	*n*-Hexane, (C_6H_{14})	38	4163.3	**12**	3,4- Dimethylhexane, (C_8H_{18})	50	5468.7
4	Cycloheptane, (C_7H_{14})	42	4597.0	**13**	Ethylhexane, (C_8H_{18})	50	5470.2
5	Methylcyclohexane, (C_7H_{14})	42	4565.3	**14**	n-Decane, ($C_{10}H_{22}$)	62	6778.6
6	1,1-Diethylcyclohexane, (C_8H_{16})	48	5216.0	**15**	n-Dodecane, ($C_{12}H_{26}$)	74	8090.6
7	*trans*-1,3- Dimethyl-cyclohexane, (C_8H_{16})	48	5219.0	**16**	*trans-syn-trans*-Pentahydroanthracene,($C_{14}H_{24}$)	80	8608.5
8	*trans*-1,4- Dimethyl-cyclohexane, (C_8H_{16})	48	5212.3	**17**	*n*-Hexadecane, ($C_{16}H_{34}$)	98	10700.1
9	*n*-Octane, (C_8H_{18})	50	5471.8				

Table 2. The structural ($^{1}x^{s}$) and thermochemical parameters (kJ·mol^{-1}) of some types of biochemical molecules. P 101 kPa; T 298.15; all compounds are in condensed state.

No	Compound, formula	(N-g) electrons	-$\Delta_{\text{comb}}H$		$^{1}x^{s}$	$\Delta_{\text{vap}}H$	-$\Delta_{\text{f}}H^{o}$	
		Eq.2	Eq.4	Experiment			Condens	Gas
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
19	 $C_{27}H_{48}$	156	16958.1 ± 84.8		12.860	126.4 ± 6.3	526.6 ± 2.6	400.2 ± 2.0
20	 $C_{27}H_{46}O$	152	16578.3 ± 82.9	16524.0[12] ± 3.9 16590.0[13] ± 67.0	13.254	157.2 ± 7.9 114.6[14] (sub)	620.5 ± 3.1 674.9[12] 607.0[13]	463.3 ± 2.3
21	 $C_{28}H_{48}O$	158	17202.4 ± 86.0	17226.4[4] ± 5.0	13.503	132.3 ± 6.6	675.8 ± 3.4	543.5 ± 2.7
22	 $C_{28}H_{44}O$	154	16877.0 ± 84.4	16516.7[4] ± 5.7	13.664	161.0 ± 8.0	429.5 ± 2.1	268.5 ± 1.3
23	 $C_{28}H_{44}O$	154	16985.8 ± 84.9		13.719	161.5 ± 8.1	320.8 ± 1.6	159.2 ± 0.8
24	 $C_{18}H_{24}O_{2}$	92	10093.0 ±50.4		9.593	177.7 ±8.9	420.1 ±2.1	242.4 ±1.2
26	 $C_{19}H_{28}O_{2}$	100	10934.2 ± 54.7	11080.0[13] ± 30.0	9.949	126.6 ± 6.3	544.1 ± 2.7 390.0[13]	417.5 ± 2.1

27	 $C_{19}H_{28}O_2$	100	10879.8 ± 54.4	10930.0[13] ± 46.0	9.949	99.4 ± 5.0	598.5 ± 2.7 544.0[13]	449.1 ± 2.5
28	 $C_{17}H_{19}NO_3$	82	9034.8 ± 45.1		9.892	180.5 ± 9.0	370.2 ± 1.8	189.8 ± 0.9
29	 $C_{17}H_{19}NO_3$	82	8980.4 ± 44.9		9.504	149.7 ± 7.5	424.6 ± 2.1	274.9 ± 1.4
30	 $C_{18}H_{21}NO_3$	88	9631.7 ± 48.1		10.330	130.1 ± 6.5	452.7 ± 2.3	322.6 ± 1.6
31	 $C_{20}H_{29}NO$	108	11856.9 ± 59.3		10.414	158.1 ± 7.9	157.8 ± 8.0	0.300 ± 0.1

With a view of the correct of the Equation (4) application, it has been lead the calculation of the combustion enthalpy of tetraline (**32**) (–5620.2 ± 28.1 kJ·mol^{-1}) and then it compared to the literary value ΔH_{comb} (–5621.54 ± 0.88 kJ·mol^{-1}) [6]. Except for listed above it is necessary to note, that with a view of the efficiency of the calculation of the combustion enthalpy by us, as soon as by Kharasch and Sher, the corrections on the presence in bioorganic molecules primary and secondary HO-groups, C = C-bond, a five-membered cycle with oxygen –54.4, –27.2, –54.4 and 27.2 kJ·mol^{-1} correspondingly were introduced.

The formation enthalpies ($\Delta_f H^o_{\text{cond}}$) of all bioorganic molecules (19-31) in the condensed state have been calculated according to the resulted above equations (3,4) and Hess law (Equation 6)

$$\Delta_{\text{comb}} H = \sum\left(\Delta_f H^{\circ}_{cond}\right)_{prod} - \sum\left(\Delta_f H^{\circ}_{cond}\right)_{reag} \qquad (6)$$

Good correspondence between the calculated and the experimental literary data [4,13] for the combustion of some biochemical molecules (**Table 2**) is observed.

The heat of vaporization $\left(\Delta_{\text{vap}} H\right)$ for compounds (**19 -31**) are calculated on the Equation (7), in which the topological solvation index of the first order is included. Such way of the $\Delta_{\text{vap}}H$ estimation for neutral trivalent compounds of P, As, Sb and Bi [1,3,8,9], phosphorus acids [10] and 2-methoxy-2-oxo-1,3,2-dioxaphoapholane [11] has been successfully used by us earlier

$$\Delta_{vap} H = 7.29 + 9.26\,{}^1x^s \qquad (7).$$

Such circumstance gives a possibility for the calculation the formation enthalpies of researching biocompounds in gaseous phase $\left(\Delta_{\text{f}} H^{\circ}_{\text{gas}}\right)$ as a sum of the same values in condensed state $\left(\Delta_{\text{f}} H^{\circ}_{\text{cond}}\right)$ and their heat of vaporization $\left(\Delta_{\text{vap}} H\right)$.

3. Conclusions

Thus, as it has been shown during this work the simple linear Equation (4), worked up for the correlations between the heats of combustion of saturated alkanes of the different spatial structure and the general number of the valence electrons, excluding of the lone electron pare of heteroatoms in its, could be useful applicable to the calculation of the same thermochemical parameters of the bioorganic molecules of hydrophenanthrene rows.

The calculated the heats of formation in a gaseous phase are necessary for an estimation of the bond energies in biochemical substances.

4. References

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