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Thermochemistry of Heteroatomic Compounds: The Calculation of C-H and C-C Bonds Strength of Hydrocarbons in Gaseous and Condensed States.

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ABSTRACT

The calculation of thermodynamic functions ($\Delta\psi^0 \equiv \Delta G^0, \Delta H^0, S^0$) strength of C-H and C-C bonds, designated as S_b , 31 alkanes (from methane up to decane) with various on a configuration atoms of carbon (a normal structure, tertiary and quaternary) and their known experimental thermodynamic parameters are performed. The calculation was spent under program Microsoft-Excel-function "Search of the decision by a method of the interfaced gradients" with the use of minimization of atomization function ($\Delta_a\psi^0$) in the equation $R_i^2 = \sum\{|\Delta_a\psi_{\text{эксп}}^0 - \Delta_a\psi_{\text{теор}}^0| g_i\}^2$, in which R_i^2 it is the sums of the quadrates of the differences between the experimental and calculated values of functions atomization ($\Delta_a G^0, \Delta_a H^0, \Delta_a S^0$) alkanes and $g_i=1$ is their weight contributions. At the used way of calculation of value enthalpies C-H and C-C bonds for a gas phase well correspond with the same values in the literature. The calculation of strengths of the same bonds in the condensed phase is characterized by essential reduction of the values of all thermodynamic functions, that testifies to the significant contribution of the dispersive and structural intermolecular interactions in the condensed phase.

Keywords: Alkanes, strength of bond, free energy, heat, enthalpy, entropy.

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INTRODUCTION

The destruction of old and formation of new bonds in organic compounds is the caused and necessary phenomenon, proceeding in chemical and especially biochemical processes. It is well studied during long time and concerns to the processes, which are carried out as in gas and condensed phases and is characterized by such quantitative characteristic as energy of compounds E_b and as it is accepted, expressed in kJ mol^{-1} .

However, in spite of the fact that the overwhelming majority of really organic and vital bioorganic processes occur in the condensed phase, the researchers often judge their possible realization taking into account only fact of the energy of molecule in a gas phase. This thermochemical parameter Q as a first approximation represents a difference of the sums bond energies of formation ($n_i (E_b)_{\text{form}}$) in the products of reaction and broken off ($n_j (E_b)_{\text{break}}$) bonds in initial compounds (equation 1).

$$Q \approx \sum n_i (E_b)_{\text{form}} - \sum n_j (E_b)_{\text{break}} \quad (1).$$

Thus it is necessary to note, that the energy of process, defined on the equation (1), relates to a gas phase, because of the values of bond energies, which are summed in works, reviews and the monographies [1-3] known for a gas phase accordingly. In such cases probably not always the correct judgement of the researchers about the thermodynamic characteristic of the organic or biochemical process really, developing in the condensed phase or a solvents.

The energy of bonds of the organic molecule, which are being a gas phase, it is possible to define not only an experimental physical method [1-3], but also to calculate on the equation (2) with the application of one of the theoretical approaches, based on use atomization enthalpy ($\Delta_a H^\circ$), formations of a molecule ($\Delta_f H^\circ_{\text{gas}}$) and atoms making it ($\Delta_{\text{atom}} H^\circ_{\text{gas}}$) in a gas phase. It is necessary to note, that size $\Delta_a H^\circ$ it is possible (with the small amendment on $4RT \approx 2.7 \text{ kJ mol}^{-1}$, not exceeding an error of calculation; R is the universal gas constant $2.303 \text{ J mol}^{-1}\text{K}^{-1}$, T is 298.15) to consider to the equal sum energies (enthalpies) all compounds between atoms in a molecule [4-7].

$$\Delta_a H^\circ = \sum \Delta_{\text{atom}} H^\circ_{\text{gas/cond}} - \Delta_f H^\circ_{\text{gas/cond}} = \sum E_b \quad (2).$$

The similar equation will be for the calculation of the bond enthalpies of organic substances in the condensed phase if the all atom heat formations ($\Delta_{\text{atom}} H^\circ_{\text{cond}}$) of Periodic table and molecules ($\Delta_f H^\circ_{\text{cond}}$) to use for this condition.

It is necessary take into account also not only on enthalpy formations of simple atoms in the gas and condensed phases, but also other thermodynamic functions: change of free energy ($\Delta_f G^\circ_{\text{cond}}$), entropy ($f S^\circ_{\text{cond}}$) and a heat capacity (C_p), which are known for atoms in the literature [8]. Then the equation (2) can be presented as the generalized expression (3) displaying display of all thermodynamic functions ($\Delta_{G,H,S} \psi^\circ$), and «energy of bonds E_b » to replace expression and a designation expression and a designation «strength of bond, S_b » as the last will display not only one function «enthalpy».

$$\Delta_a \psi^\circ = \sum \Delta_{\text{atom}} \psi^\circ_{\text{gas/cond}} - \Delta_f \psi^\circ_{\text{gas/cond}} \approx \sum S_b \quad (3).$$

RESULTS AND DISCUSSION

The calculation of all thermodynamic functions C-H and C-C bonds of different alkanes (Table 1, compounds **1-31**) with various structural fragments: linear structures $\text{CH}_3\text{-(CH}_2)_n\text{CH}_3$, branched alkanes with a tertiary $>\text{C-H}$ and quaternary $>\text{C}<$ carbon atoms, the experimental thermodynamic functions of which are summed in the work [9], was conducted with the use of function "Search of the decision by a method of the interfaced gradients" by the Microsoft-Excel-program (equation 4), in which R_i^2 is the sums of quadrates of the differences between the experimental and calculated values of atomization functions ($\Delta_a G^\circ$, $\Delta_a H^\circ$, ${}_a S^\circ$) of gaseous and condensed alkanes and g_i is equal to 1, showing their weight contributions.

$$R_i^2 = \sum \{ | \Delta_a \psi^\circ_{\text{exp}} - \Delta_a \psi^\circ_{\text{calc}} | g_i \}^2 \quad (4)$$

The atomization values of the simple hydrogen and carbon atoms in the gaseous and condensed phases ($\Delta_{\text{atom}}\psi^{\circ}_{\text{gas/cond}}$) are taken from the work [8] and present by self the next magnitudes:

- for gaseous hydrogen atom: $\Delta_f G^{\circ}$ 103.0, $\Delta_f H^{\circ}$ 218.0, rS° 144.1,
- for condensed hydrogen atom: $\Delta_f G^{\circ}$ 1.0, $\Delta_f H^{\circ}$ 2.4, rS° 37.9,
- for gaseous carbon atom: $\Delta_f G^{\circ}$ 669.5, $\Delta_f H^{\circ}$ 716.0, rS° 157.9
- for condensed carbon atom: $\Delta_f G^{\circ}$ 2.9, $\Delta_f H^{\circ}$ 16.5, rS° 5.8.

The calculated via Eq. (3) and via an experimental $\Delta_a \psi^{\circ}_{\text{exp}}$ thermodynamic functions of values C-H and C-C bonds of alkanes are presented in Table 1 and are expressed in Table 2 as the strengths of bonds with the uncertainties for the gaseous and condensed phases.

Table 1: The experimental and calculated on equation (4) atomization thermodynamic functions of alkanes in gaseous and condensed phases (kJ mol⁻¹ and J mol⁻¹·K⁻¹) according to work [9].

No	Akane, formula	Free energy		Enthalpy		Entropy	
		$\Delta_a G^{\circ}$, gas calc	$\Delta_a G^{\circ}$, condens calc	$\Delta_a H^{\circ}$, gas calc	$\Delta_a H^{\circ}$, condens calc	aS° , gas calc	aS° , condens calc
1	2	3	4	5	6	7	8
1	Methane, CH ₄	<u>1132.1</u> 1132.1	<u>37.9</u> 37.9	<u>1661.9</u> 1661.9	<u>96.9</u> 96.9	<u>545.6</u> 545.6	<u>51.2</u> 51.2
2	Ethane, C ₂ H ₆	<u>1990.0</u> 1990.0	<u>37.4</u> 37.4	<u>2822.5</u> 2822.5	<u>144.0</u> 144.0	<u>950.4</u> 950.4	<u>112.3</u> 112.3
3	Propane, C ₃ H ₈	<u>2855.5</u> 2855.5	<u>39.7</u> 36.9	<u>3993.7</u> 3997.7	<u>188.5</u> 190.4	<u>1356.5</u> 1356.5	<u>149.6</u> 150.5
4	<i>n</i> -Butane, C ₄ H ₁₀			<u>5173.6</u> 5173.3	<u>238.5</u> 238.2		
5	<i>n</i> -Pentane, C ₅ H ₁₂	<u>4591.9</u> 4606.6	<u>36.0</u> 36.1	<u>6337.8</u> 6346.9	<u>284.8</u> 284.5	<u>2170.9</u> 2170.3	<u>220.3</u> 236.6
6	<i>n</i> -Hexane, C ₆ H ₁₄	<u>5493.4</u> 5471.3	<u>35.6</u> 35.6	<u>7521.1</u> 7520.8	<u>331.3</u> 331.5		<u>296.3</u> 281.5
7	<i>n</i> -Heptane, C ₇ H ₁₆		<u>35.0</u> 35.1	<u>8694.8</u> 8694.7	<u>378.3</u> 378.6		<u>318.4</u> 326.4
8	<i>n</i> -Oktane, C ₈ H ₁₈	<u>7193.3</u> 7200.7	<u>34.8</u> 34.6	<u>9868.4</u> 9868.7	<u>425.2</u> 425.6	3389.9 3390.5	<u>367.4</u> 371.3
9	<i>n</i> -Nonane, C ₉ H ₂₀		<u>34.2</u> 34.1	<u>11041.3</u> 11042.6	<u>471.2</u> 472.6	<u>3796.6</u> 3797.2	<u>416.5</u> 416.2
10	<i>n</i> -Decane, C ₁₀ H ₂₂		<u>33.6</u> 33.6	<u>12215.7</u> 12216.5	<u>518.8</u> 519.7	<u>4203.4</u> 4203.9	<u>465.9</u> 461.1
11	<i>n</i> -Undecane, C ₁₁ H ₂₄ , 68		<u>33.1</u> 33.1	<u>13389.3</u> 13390.4	<u>566.3</u> 566.7	<u>4611.7</u> 4610.6	<u>515.3</u> 506.0
12	<i>n</i> -Dodecane, C ₁₂ H ₂₆		<u>32.4</u> 32.6	<u>14562.9</u> 14564.3	<u>612.5</u> 613.8		<u>564.3</u> 550.9
13	2-Methylbutane, C ₅ H ₁₂			<u>6354.7</u> 6353.3	<u>289.5</u> 289.1		<u>260.4</u> 242.0
14	2-Methylpentane, C ₆ H ₁₄			<u>7528.3</u> 7526.9	<u>336.9</u> 335.4		<u>290.6</u> 275.9
15	3-Methylpentane, C ₆ H ₁₄			<u>7525.6</u> 7528.4	<u>334.7</u> 336.2		<u>292.5</u> 286.4
16	2-Methylhexane, C ₇ H ₁₆			<u>8702.0</u> 8700.8	<u>383.7</u> 382.4		<u>323.3</u> 320.8
17	2-Methylheptane, C ₈ H ₁₈			<u>9875.5</u> 9874.8	<u>430.4</u> 429.5		<u>356.4</u> 365.7
18	3-Methylheptane, C ₈ H ₁₈			<u>9872.6</u> 9875.9	<u>427.7</u> 429.5		<u>362.6</u> 365.3
19	3-Methylhexane, C ₇ H ₁₆			<u>8699.3</u> 8700.0	<u>381.3</u> 381.1		<u>309.6</u> 302.1

20	2,4-Dimethylhexane, C ₈ H ₁₈			<u>9879.4</u> 9880.5	<u>432.4</u> 433.1		
21	2-Methylnonane, C ₁₀ H ₂₂			<u>12226.2</u> 12222.6	<u>527.6</u> 523.5		<u>420.1</u> 455.6
22	2,2-Dimethylpropane, C ₅ H ₁₂			<u>6368.9</u> 6368.9	<u>301.6</u> 301.6		<u>216.8</u> 216.8
23	2,2-Dimethylbutane, C ₆ H ₁₄			7539.6 7533.1	<u>346.0</u> 341.9		<u>272.5</u> 253.4
24	2,2-Dimethylpentane, C ₇ H ₁₆			<u>8713.2</u> 8708.7	<u>392.6</u> 389.7		<u>300.3</u> 305.6
25	2,2,3-Trimethylbutane, C ₇ H ₁₆			<u>8711.8</u> 8713.7	<u>390.8</u> 393.5		<u>292.2</u> 300.5
26	3,3-Dimethylpentane, C ₇ H ₁₆			<u>8708.5</u> 8709.6	<u>388.5</u> 389.3		<u>305.6</u> 316.0
27	2,2,4-Trimethylpentane, C ₈ H ₁₈			<u>9884.1</u> 9886.7	<u>434.5</u> 439.1		<u>328.0</u> 326.7
29	2,2,3,3-Tetramethylbutane, C ₈ H ₁₈			<u>9886.2</u> 9893.4	<u>444.3</u> 446.3		
30	2,2,5-Trimethylhexane, C ₉ H ₂₀			<u>11066.1</u> 11060.6	<u>489.8</u> 486.1		
31	3,3-Diethylpentane, C ₉ H ₂₀				<u>471.9</u> 471.9		<u>333.4</u> 338.4

The analysis of the strength of C-H and C-C bonds should be begun with the gaseous enthalpy characteristics, as the previous experimental and theoretical determinations have been made for these thermodynamic functions [2, 3]. The calculated average sizes enthalpies of these bonds (415.9 ± 9.0 and 333.1 ± 28.6 kJ mol⁻¹ accordingly) well correspond, within the limits of the specified errors, to average literary values [1-3, 8] in spite of the fact, that in both cases were investigated the various spatial structure of alkanes.

At the condensed phase the values of strengths of the same bonds are essentially less and present only 21.6 ± 1.8 and 1.6 ± 0.7 kJ mol⁻¹ accordingly. Surprisingly, the values for some types alkanes are practically near to zero, that it is difficult to explain through the "an incorrectness of calculations" of computer program, since the reliability of her work was confirmed at the calculations of a gaseous alkanes (Table 2). In the values of strengths of both bonds of not polar alkanes apparently it is necessary to explain as essential distinctions in dispersive and structural interaction between molecules in the condensed phase.

The similar conclusions can be made for calculations of the strengths of the same bonds for the values of free energy and entropy in the condensed phase (Tables 1, 2). Necessary to add to it, that the comparisons with the similar published thermodynamic data to do it was not possible, because they absent in the literature at this time.

Table 2: The calculated strength of bonds C-H and C-C (S_b , kJ mol^{-1} and $\text{J mol}^{-1} \text{K}^{-1}$) for the various structural positions groups of alkanes on the basis of values their gaseous and condensed functions ($\Delta_a G^\circ$, $\Delta_a H^\circ$, $a S^\circ$).

The position of the calculated bond in alkane	S_b through $\Delta_a G^\circ$				S_b through $\Delta_a H^\circ$				S_b through $a S^\circ$			
	C-H		C-C		C-H		C-C		C-H		C-C	
	gas	cond	gas	cond	gas	cond	gas	cond	gas	cond	gas	cond
1	2	3	4	5	6	7	8	9	10	11	12	13
Bond C-H												
H-CH ₃	283.0				415.5				136.4			
H-CH ₂ CH ₂ -H	275.4				419.9				143.3			
H-CH ₂ -Alk, Trailer CH ₃ -group	271.3	0.0			427.5	24.9			144.1	6.5		
H ₃ CC-H(H)(Alk), At trailer CH ₃ -group	290.1	6.9			408.2	21.3			164.5	15.2		
Alk-(H-C-H)-Alk, In the middle of chain	269.1	0.0			407.2	20.9			159.3	10.3		
H-C-(CHAlk ₂), At tertiary carbon					406.4	19.3						

Table 2: (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
Bond C-C												
H ₃ C-CH ₃			337.6				303.3				90.5	
H ₃ C-CH ₂ -Alk, At trailer CH ₃ -group			323.8	0.0			308.2	0.0			81.4	33.4
Alk-H ₂ C-CH ₂ -, Near to trailer Alk-group			316.3	3.4			359.2	3.9			83.1	0.0
Alk-H ₂ C-CH ₂ -Alk, In the middle of chain			326.4	0.0			359.5	3.7			88.1	2.6
Alk-H ₂ C-C(CH ₃) ₃ , Near to tertiary carbon							358.6	0.5				12.7
Alk-H ₂ C-(H ₃ C)-(CH ₃) ₂ , In tertiary group							309.8	0.0				
Middle values												
	277.8 ±8.7	2.3 ±2.2	326.0± 8.8	1.1 ± 0.5	415.9± 9.0	21.6 ± 1.8	333.1± 28.6	1.6 ± 0.7	149.5 ±11.8	10.2 ± 7.2	85.8 ± 4.2	15.3 ± 6.8



CONCLUSIONS

1. The correspondence of the calculated enthalpy values C-H and C-C bonds with the use of function "Search of the decision by a method gradient descent" of gaseous alkanes of various spatial structure (31 compounds) with similar literary data it has been shown.
2. The values of free energy, enthalpy and entropy of C-H and C-C bonds in condensed alkanes for the first time are calculated.
3. In values of force of both bonds designated as force of strength of bond S_b non polar alkanes apparently it is necessary to explain by the distinctions significant dispersive and structural interaction between molecules in the condensed phase.

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