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Empirical and ab initio Computation of Thermochemical Parameters of Amino Acids: V.[1] Non-Canonical L-Amino Acids

E. V. Sagadeev[a], A. A. Gimadeev[a], D. V. Chachkov[b], and V. P. Barabanov[a]

[a] *Kazan State Technological University, ul. K. Marksa 68, Kazan, Tatarstan, 420015 Russia*
e-mail: sagadeev@list.ru

[b] *Interdepartment Supercomputer Center of Russian Academy of Sciences, Kazan Branch, Kazan, Tatarstan, Russia*

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Abstract—Using a set of computational methods, we have evaluated the basic thermochemical characteristics of the ten non-canonical L-amino acids, other than α-acids.

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Many natural amino acids are not expressed by standard genetic code. They are so called non-canonical amino acids; among them there are non-canonical L-α-amino acids as well as L-amino acids with different location of NH_2 groups with respect to the carboxyl [2]. These compounds are biologically active. For example, proteins carnosine and anserine contain β-alanine **I** (Table 1); the same amino is a fragment of pantothenic acid (vitamin B5), which in turn is a part of coenzyme A [2]. Furthermore, β-alanine is an important component of bodybuilding supplement. γ-Aminobutyric acid **II** is an inhibitor of neurotransmitters in the central nervous system [2] and is used in medicine (Aminolon drug) [5].

The analysis of published thermochemical data has shown that the information on thermochemistry of L-amino acids other than α-acids is fairly scarce. This worked aimed to fill the gap.

The calculations were performed using the Enthalpy [6] software via the additive scheme of enthalpies of amino acids formation. The thermochemical parameters related to crystalline state as well as to gas phase were evaluated on the basis of the previously published group contributions [7–11]. The results are listed in Table 1. For all the studied compounds, the computed enthalpy of formation was in good agreement with the experimental data.

Following [1, 10–12], the sublimation enthalpy of the amino acids was determined as the difference of the formation enthalpies related to the gas phase and to the crystalline state. In some cases (Table 1) there was only partial agreement between the experimental and calculated values of the sublimation enthalpy. For example, in the case of δ-aminovaleric (**III**), ε-aminocaproic (**IV**), and ω-aminocaprylic (**VI**) acids, the experimental values (143.9, 154.8, and 169.9 kJ mol^{-1}, respectively) were underestimated by the computed values (156.0, 164.8, and 182.1 kJ mol^{-1}, respectively). The observed discrepancy was apparently due to the fact that the experimental values were measured at elevated temperature rather than under standard conditions (298 K) [10–12]. In particular, the enthalpy of sublimation of **III**, **IV**, and **VI** was determined at 394 K, 407 K, and 402 K, respectively [3]. Therefore, in the cases of discrepancy, the calculated sublimation enthalpy listed in Table 1 should be regarded as the reliable.

We further performed ab initio calculations of gas-phase formation enthalpy of the amino acids. Based on the results of previous studies [1, 10–12], the B3LYP/6-31G(d) was chosen as a first approximation for rapid seeking for the optimal conformations of molecules. For the energetically most favorable conformation, we calculated ΔH^0_{form} via the B3PW91/cc-pVQZ method. The results of the calculations are listed in Table 2.

Thus, the approach used in this paper gave reliable computed thermochemical parameters of non-canonical amino acids, for many of them the corresponding experimental data was missing.

[1] For communication IV, see [1].

Table 1. Experimental and computed enthalpies of formation and sublimation non-canonical L-amino acids

Compound	Formula	ΔH^0_{subl}, kJ mol^{-1}		ΔH^0_{form}, kJ mol^{-1}			
		experiment	calculation	gas phase		Crystal phase	
				experiment	calculation	experiment	calculation
β-Alanine (**I**)	$C_3H_7O_2N$	133.9[a]	138.6	–422.6[a]	–420.5	–558.0[a]	–559.1
γ-Aminobutyric acid (**II**)	$C_4H_9O_2N$	140.2[a]	147.3	–439.3[a]	–441.2	–581.0[a]	–588.5
δ-Aminovaleric acid (**III**)	$C_5H_{11}O_2N$	143.9[a]	156.0	–460.2[a]	–461.9	–604.2[a]	–617.9
ε-Aminocaproic acid (**IV**)	$C_6H_{13}O_2N$	154.8[a]	164.8	–482.3[a]	–482.6	–637.3[a]	–647.4
ω-Aminoenanthic acid (**V**)	$C_7H_{15}O_2N$	–	173.5	–	–503.3	–667.4[b]	–676.8
ω-Aminocaprylic acid (**VI**)	$C_8H_{17}O_2N$	169.9[a]	182.1	–523.0[a]	–524.1	–694.5[a]	–706.2
ω-Aminopelargonic acid (**VII**)	$C_9H_{19}O_2N$	–	190.8	–	–544.8	–727.8[b]	–735.6
ω-Aminodecanoic acid (**VIII**)	$C_{10}H_{21}O_2N$	–	199.5	–	–565.5	–	–765.0
β-Aminoisobutyric acid (**IX**)	$C_4H_9O_2N$	–	138.5	–	–449.3	–	–587.8
β-Lysine (**X**)	$C_6H_{14}O_2N_2$	–	174.5	–	–463.6	–	–638.1

[a] [3]. [b] [4].

Table 2. Ab initio computation of formation enthalpy of non-canonical L-amino acids

Comp. no.	$-\Delta H^0_{form}$ (gas), kJ mol^{-1}	
	B3LYP/6-31G(d)	B3PW91/cc-pVQZ
I	350.6	411.2
II	363.0	429.9
III	376.9	449.3
IV	389.7	467.7
V	403.0	486.6
VI	416.0	505.1
VII	427.5	522.0
VIII	442.2	542.5
IX	362.8	427.2
X	343.5	441.3

All quantum-chemical calculations were performed with GAUSSIAN 98 software [13] in the Kazan branch of the Interdepartment Supercomputer Center of Russian Academy of Sciences (Kazan Branch) (http://wt.knc.ru).

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