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Empirical and ab initio Calculations of Thermochemical Parameters of Aminoacids: II.[1] Diaminomonocarboxylic Acids, Hydroxyamino Acids, Thioamino Acids, and Heterocyclic Amino(imino) Acids

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Abstract—With the use of a complex of calculation methods the basic thermochemical characteristics of ten standard L-α-amino acids of diaminomonocarboxylic, hydroxyaminomonocarboxylic, and thioaminomonocarboxylic series as well as of a series of heterocyclic amino(imino)carboxylic acids were calculated.

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In continuation of preceding investigations on the calculation of thermochemical parameters of amino acids [1], in this work we calculated thermochemical characteristics of ten standard (coded by genetic code [2]) L-α-amino acids. For this purpose we used the calculation procedure described in [1].

For the calculation of the enthalpy of formation of the amino acids both in the gas phase and in the crystalline state we applied additive method of group contributions [3–5].

On the basis of analysis of experimental results (Table 1) with accounting for the data of [5] and using Enthalpy program [15] we calculated a set of group contributions (increments) of the sulfur-containing fragments of molecules into the enthalpy of formation in the crystalline state (Table 2). The increments are designated in accordance with the symbolism of group contributions proposed by Benson and Buss [16]. For example, the designation S–(C)(H) denotes HS group in cysteine (**VI**); S–$(C)_2$ designates sulfur atom connected with two carbon atoms in methionine (**VII**). The record C–(C)(S)$(H)_2$ corresponds to the carbon atom connected with sulfur and two hydrogen atoms in cysteine (**VI**) and methionine (**VII**).

Calculations of amino acid enthalpies of formation were carried out with Enthalpy program [15] on the basis of published [3-5] and calculated by us ([1] and Table 2) group increments. The results of calculations are listed in Table 1. Consideration of the data in Table 1 shows that there is a good agreement between the experimental data and the values of enthalpy of formation obtained by calculation for all compounds.

There are not enough experimental data now for calculating enthalpy of formation of arginine (**II**) (both in the gas phase and in the condensed state) and of histidine (**IX**) and triptophan (**X**) in the crystalline state.

The enthalpies of sublimation of amino acids were calculated as differences between the enthalpies of formation in the gas phase and in the crystalline state [1]. Analysis of the data in Table 1 shows that in two cases the agreement between experimental and calculated values of enthalpy of formation is not satisfactory. For methionine (**VII**) and proline (**VIII**) the experimental values (164.0 and 127.2 kJ mol^{-1}) are below the calculated ones (181.4 and 140.2 kJ mol^{-1}, respectively). The inconsistence is probably caused by the fact that experimental values of ΔH_{subl} in both cases were measured at elevated temperature rather than under ambient conditions (298 K). Enthalpy of methionine (**VII**) sublimation has been determined

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

Table 1. Experimental and calculated enthalpies of formation and sublimation of L-α-amino acids

Comp. no.	Compound	Formula	ΔH^0_{subl}, kJ mol^{-1}		ΔH^0_{form}, kJ mol^{-1}			
			experiment	calculation	Gas phase		Crystalline state	
					experiment	calculation	experiment	calculation
			Diaminomonocarboxylic acids					
I	Lysine	$C_6H_{14}O_2N_2$	–	233.6	–	–443.4	–678.6 [6]	–677.0
II	Arginine	$C_6H_{14}O_2N_4$	–	–	–	–	–637.7 [7]	–
			Hydroxyamino acids					
III	Serine	$C_3H_7O_3N$	–	173.7	–	–567.8	–732.7 [8]	–741.5
IV	Threonine	$C_4H_9O_3N$	–	180.6	–	–603.7	–776.3 [9]	–784.3
V	Tyrosine	$C_9H_{11}O_3N$	–	184.1	–	–481.9	–685.6 [10]	–666.0
			Thioamino acids					
VI	Cysteine	$C_3H_7O_2SN$	–	160.6	–	–378.1	–534.1 [11]	–538.7
VII	Methionine	$C_5H_{11}O_2SN$	164.0 [11]	181.4	–413.5 [11]	–412.1	–588.4 [7]	–593.5
			Heterocyclic amino(imino) acids					
VIII	Proline	$C_5H_9O_2N$	127.2 [12]	140.2	–366.2 [13]	–373.3	–515.2 [13]	–513.5
IX	Histidine	$C_6H_9O_2N_3$	–	–	–	–221.8	–466.5 [14]	–
X	Tryptophan	$C_{11}H_{12}O_2N_2$	–	–	–	–215.0	–	–

[11] at 400 K, and ΔH_{subl} of proline (**VIII**), at 416 K [12]. As has been noted earlier [1, 17], the higher temperature of measuring the ΔH_{subl} of a compound leads to a lower value. Therefore for methionine (**VII**) and proline (**VIII**) it is calculated data listed in Table 1 that should be suggested as the more reliable ones.

The absence of respective data for arginine (**II**), histidine (**IX**) and tryptophan (**X**) prevent nowadays the calculation of their sublimation enthalpy.

Further, we performed *ab initio* calculation of the gas phase enthalpy of formation for each amino acid listed in Table 1. The results of calculations are shown in Table 3. Like in [1], the best agreement between the experiment and the results of additive-group method is obtained with the calculation scheme G3 that requires significant computer resources. Therefore in this work we continued search of optimal (from a viewpoint of the ratio of calculation time and accuracy of results) quantum-chemical method for the calculation of thermochemical characteristics of L-α-amino acids.

We extended the scope of used quantum-chemical methods. In particular, we obtained the values of

Table 2. Group contributions X_i for calculation of enthalpy of formation of compounds in crystalline state, and standard deviations

Run. no.	Group contribution	X_i, kJ mol^{-1}	s
1	C–S)(H)$_3$	–46.7 [5]	–
2	C–(C)(S)(H)$_2$	–24.1	0.04
3	C–(C)$_2$(S)(H)	–7.0	0.14
4	S–(C)(H)	–5.8	–
5	S–(C)$_2$	15.6	0.02

Table 3. Results of ab initio calculation of enthalpy of formation of L-α-amino acids

Comp. no.	$-\Delta H^0_{form}$ (gas), kJ mol^{-1}									
	B3LYP/ 6-31G(d)	B3LYP/ 6-311++ G(df,p)	B3LYP/ cc-pVTZ	B3LYP/ 6-311++ G(3df,3pd)	B3PW91/ cc-pVTZ	B3PW91/ 6-311++ G(3df,3pd)	B3PW91/ cc-pVQZ	PBELYP/ 6-311++ G(df,p)	PBEPBE/ 6-311++ G(df,p)	G3
I	340.4	341.2	373.5	398.6	417.0	448.1	436.0	565.0	660.8	–
II	252.2	280.8	315.7	349.7	356.9	398.0	382.1	584.4	687.3	–
III	491.9	510.0	530.5	552.6	555.7	582.4	568.3	689.1	750.2	582.1
IV	519.4	526.7	551.7	573.9	585.2	612.8	598.6	722.3	798.5	–
V	348.4	341.0	377.0	403.9	481.2	515.5	–	642.7	829.1	–
VI	292.5	303.2	326.9	349.1	360.4	386.8	373.0	464.3	534.7	386.1
VII	314.7	303.1	335.9	360.2	386.5	416.1	402.4	493.3	592.2	420.0
VIII	305.7	287.0	312.1	330.2	368.5	391.9	381.4	464.0	569.3	380.9
IX	181.0	184.8	213.6	239.5	281.1	313.9	–	470.1	604.1	272.7
X	98.0	78.7	115.7	143.4	253.6	289.6	–	426.5	665.9	–

enthalpy of formation of amino acids using two additional non-hybride DFT methods, PBELYP and PBEPBE [18, 19], with a large enough basis set 6-311++G(df,p). Analysis of the obtained data shows that both these methods like the method of PW91PW91 [1] leads to significant discrepancies in the calculation of enthalpy of formation of these compounds.

We also extended the scope of used basic sets and applied cc-pVTZ and cc-pVQZ [20, 21] sets. Note that the best accuracy at the calculation of ΔH^0_{form} of amino acids with DFT methods we obtained with the method B3PW91/cc-pVQZ: the relative error for a series of compounds (as compared with the results of the additive calculation) was 0.1–2.4% only. However, the calculation of enthalpy by this method is time-consuming enough (although less demanding toward computer resources compared to G3 scheme). Therefore we failed to obtain values of enthalpy of formation for tyrosine (**V**), histidine (**IX**) and tryptophan (**X**) within acceptable time.

On the basis of the obtained quantum-chemical results with accounting for the data of [1] we can note that deviations in the values of enthalpy of formation of the amino acids containing aromatic ring in their structures is somewhat larger than for other compounds. Therewith, with the B3LYP method the increase in the basis (number of basic functions) leads to significant increase in errors at the calculation of enthalpy of formation of compounds containing aromatic ring. On the other hand, with B3PW91 method and basic sets cc-pVTZ and cc-pVQZ the errors at the calculations of enthalpy of formation of amino acids are considerably fewer compared to those obtained with 6-311++G(3df,3pd) basis and with B3LYP with all basises (Table 3).

All quantum-chemical calculations were carried out with Gaussian 98 program [22] in the Supercomputer Center of Kazan Scientific Center, Russian Academy of Sciences (http://wt.knc.ru).

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