

THE ENTHALPIES OF COMBUSTION AND FORMATION OF CRYSTALLINE L-CITRULLINE

Iulia Contineanu*

The standard ($p^0 = 0,1$ MPa) molar enthalpy of combustion in oxygen at $T=298,15$ K for crystalline L-citrulline (δ -ureidovalerianic acid) was measured by static bomb adiabatic calorimeter in presence of an auxiliary (cotton) of combustion to improve the complete oxidation reaction. These value was used to derive the standard molar enthalpy of formation of crystalline compound at $T=298,15$ K as $-821,45 \pm 4,3$ kJ mol⁻¹.

Introduction

Amino acids are basic units of proteins and so their thermochemical properties an of great biological importance in quantitative studies on energetic of biochemical reactions. Although for a large number of amino acids the properties were reported a few values are either lacking or, in other cases the literature values for the same compound do not agree. The knowledge of the values of enthalpies of combustion and formation are an intrinsic importance for the characterization of these classes of compounds and for a better understanding of the properties of the proteins

The experimental enthalpies of combustion for a large number of α -amino acids have been reported by different researchers, such those obtained by Tsuzuki et al. [1,2], Hutchens et al. [3], Kamaguchi et al. [4], Sabbah et al.[5,6] and very recently by Yang et al. [7].

As a continuation of our interest on the study of thermochemical properties [8÷10] we realized that the value for the enthalpy of formation of crystalline L-citrulline was not available in the literature.

The studied compound L-citrulline (δ -ureidovalerianic acid) is not just a protein amino acid; it is contained in the water melon (*citrullus vulgaris*) and appears as an intermediary compound in the metabolic cycle of ammonia.

Experimental

The sample for combustion was prepared from commercially available compound. The L-citrulline was purchased from Fluka AG puriss. The sample was dried over silica gel in a desiccator under reduced pressure, at room temperature. Use has been made of an adiabatic calorimeter with an oxygen static bomb; the jacket of the calorimeter traces the rising temperature of the core owing the two temperature sensors (platinum resistance

* Institute of Physical Chemistry, "I.G.Murgulescu", Splaiul Independentei 202 Bucharest,77208, e-mail:icontineanu@rol.ro

thermometers) connected in a Wheatstone bridge. The temperature rise was measured by means of a differential Beckmann thermometer graduated in hundredths degree. The 0,3 L bomb, made of stainless steel, allowed the burning of about 1 g of substance. Most of experimental procedure is that described is that previously described [10].

The substance studied was pelletized and weighed with an accuracy of 0,1 mg. The bomb was purged with purified oxygen then filled up with oxygen at $p = 0,3$ MPa and sealed. After the experiment the gas mixture was evacuated from the bomb whose walls and accessories were washed with bi-distilled water and the solutions resulted were saved. The amount of HNO_3 formed was determined by titration with 0,1 N NaOH solution in presence of methyl orange.

The constant of the calorimeter was determined by benzoic acid combustion (standard reference material 39i from NIST). The certified value for energy of combustion of benzoic acid was $26458 \pm 3,7 \text{ J.g}^{-1}$ under standard conditions in the bomb. The calorimeter constant was calculated from the results of at least 8 combustion runs. The constant of calorimeter so obtained was $8993,56 \pm 2,8 \text{ J.K}^{-1}$ at 0,1 MPa oxygen pressure.

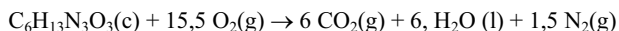
The correction for nitric acid formed of $0,1 \text{ mol.L}^{-1} \text{ HNO}_3$ (aq.) from N_2 , O_2 and $\text{H}_2\text{O(l)}$ was based on $-59,7 \text{ kJ.mol}^{-1}$ [11]. For the cotton thread fuse of empirical formula $\text{CH}_{1,686}\text{O}_{0,843}$ the value $-\Delta_c u^0 = 16250 \text{ J.g}^{-1}$ [12] was used.

The substance studied was pelletized and weighed with an accuracy of 0,1 mg. The bomb was purged with purified oxygen then filled up with oxygen at $p = 0,3$ MPa and sealed. After the experiment the gas mixture was evacuated from the bomb whose walls and accessories were washed with bidistilled water and the solutions resulted were saved. The amount of HNO_3 formed was determined by titration with 0,1 N NaOH solution in presence of methyl orange.

To bring the values obtained to standard state, calculations were the more intricate, the more complex the structure of substance. In the case of compounds with carbon, hydrogen and oxygen of $\text{C}_m\text{H}_n\text{O}_q$ general formula the procedure of reduction to standard state is summed by Washburn's equation [13]: The equation applies fairly well in the case of nitrogen compounds as well.

Results

The calculation of standard enthalpy of combustion was effected after application of Washburn's corrections by equation $\Delta_c H^0 = \Delta_c U^0 + \Delta n(g)RT$ where Δn (g) stand the variation of number of the moles of gaseous products following the standard combustion reaction and product $RT = 2,479 \text{ kJ mol}^{-1}$. In the case of combustion studied, $\Delta n = -0,25$. The average values and standard deviation were calculated. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion and formation are twice the overall standard deviation of the mean. The results of combustion experiments are listed in Table 1.



To derive the standard enthalpy of formation at $T = 298,15 \text{ K}$ the standard molar enthalpies

of formation for H₂O (l): $-(285,83 \pm 0,04)$ kJ mol⁻¹ and for CO₂ (g): $-(393,51 \pm 0,13)$ kJ mol⁻¹ [14] were used.

The enthalpy of formation of crystalline L-citrulline so obtained is $-825,41 \pm 4,3$ kJ mol⁻¹.

It is worth mentioning that all evaluations based on the experimental values are only qualitative, the enthalpies of formation in solid states being the results of contributions of intermolecular as well as intramolecular bonds which are eventually present in the studied compounds. To be able to establish quantitative correlations between the values of the enthalpies of formation of the compound in question on their molecular structure requires knowledge of enthalpies of formation in gas state, which implies the enthalpies of sublimation.

Table 1. The combustion of crystalline L - citrulline

Δm (g)	ΔT (K)	Q (J)	q_i (J)	q_n (J)	q_b (J)	$\Delta_c U^{\text{exp}}$ (J g ⁻¹)	$\Delta_c U^{\theta}$ (kJ mol ⁻¹)
0,67826	1,463	13402,14	53,50	9,15	169,95	19378,85	3395,03
0,9791	2,092	19127,63	53,50	10,49	167,82	19322,63	3385,21
0,91397	1,967	17984,74	51,95	13,66	186,67	19401,55	3398,92
0,80300	1,733	15845,20	53,50	11,41	237,38	19356,03	3391,06
0,95452	2,048	18725,35	53,50	10,45	167,70	19374,84	3394,32
0,94475	2,029	18551,63	52,25	11,62	184,54	19373,63	3390,35
0,93282	2,000	18286,49	53,50	12,24	180,53	19339,39	3388,14
0,98865	2,119	19374,50	50,24	11,05	172,71	19360,25	3391,77
Average Value							3392,36
Standard Deviation							± 4,30

REFERENCES

1. Tsuzuki, T. and Hunt, H. (1957) *J. Phys. Chem.* 61, 1668-1674.
2. Tsuzuki, T., Harper, D. O. and Hunt, H. (1958) *J. Phys. Chem.* 62, 1594- 1602
3. Hutchens, J. O., Cole, A. G. and Stout, J. W. (1963) *J. Phys. Chem.* 67, 1128-1130.
4. Kamaguchi, A., Sato, T., Sakiyama, M. and Seki, S. (1975) *Bull. Chem. Soc. Japan* 48. 3749-3750.
5. Ngauv, S. N., Sabbah, R. and Laffite, . (1977) *Thermochim. Acta* 20, 371-380.
6. Sabbah, R and Skoulika, S. (1980) *Thermochim. Acta* 36, 179-187.
7. Yang, X. W., Liu, J. R., Gao, S. L. Hou, Y. D. and Shi, Q. Z. (1999) *Thermochim. Acta* 329, 109-115.
8. Contineanu, I and Marchidan, D. I. (1984) *Rev. Roum. Chim.* 29, 43-48.
9. Contineanu, I. and Marchidan, D. I. (1994) *Rev. Roum. Chim.* 12, 1391-1395.
10. Contineanu, I and Marchidan, D. I. (1997) *Rev. Roum. Chim.* 42, 605-608.
11. The NBS Tables of Chemical Thermodynamic Properties (1982) *J. Phys. Chem. Ref. Data* 2.
12. Coops, J., Jessup, R. S. and (1956) *Experimental Thermochemistry*, vol. I, Interscience, New York, 256-258.
13. Washburn, E. W. (1933) *J. Res. Nat. Bureau Standards* 10, 525.
14. Cox, J. Wagman, D. D. and Medvedev, V. A. (1989) *CODATA Key Values for Thermodynamics*, Hemisphere, New York.