Thermochimica Acta 329 (1999) 109–115

thermochimica acta

Determination of combustion energies of thirteen amino acids

Xu Wu Yang[a], Jian Rui Liu[a], Sheng Li Gao[b,*], Yu Dong Hou[b], Qi Zhen Shi[b]

[a]*Thermochemical Laboratory, Northwest University, Xian Shaanxi 710069, China*
[b]*Department of Chemistry, Northwest University, Xian Shaanxi 710069, China*

Received 8 August 1998; received in revised form 12 October 1998; accepted 21 December 1998

Abstract

Combustion energies have been determined for 13 amino acids (Glycine, DL-Alanine, DL-Butyric acid, L-Aspurtic acid, L-Serine, L-Lysine, L-Glutamic acid, L-Arginine, L-Histidine, L-Tyrosine, DL-Phenylalanine, L-Cystine, L-Methioine) using a rotating-bomb calorimeter. The corresponding standard enthalpies of combustion, $\Delta_{c,Am(s)}\ H^\theta$, and the standard enthalpies of formation, $\Delta_{f,Am(s)}\ H^\theta$, have been calculated. The reliability of the results is illustrated through comparing with the values in references. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Rotating-bomb calorimeter; Amino acids; Combustion energy; Standard enthalpy of formation

1. Introduction

α-Amino acids are the basic units of protein. Studies on their thermodynamic properties have an important role in biology. The thermodynamic properties for most α-amino acids have been reported in the 1930s–1960s. However, their combustion energies have all been determined by using a static oxygen-bomb calorimeter, and the results are often different in different literatures. Zhu Yuanhai et al. [1,2] determined the combustion energies of some amino acids using a precision static oxygen-bomb calorimeter, calculated their standard enthalpies of formation in gaseous state, $\Delta_{f,Am(g)}\ H^\theta$. The standard enthalpies of sublimation, $\Delta_{sub,Am(S)}\ H^\theta$, were calculated using the Benson "group-addition" method [3] on the basis of their standard enthalpies of formation in solid which are reported in [4]. Because of the limitation of the static oxygen-bomb calorimeter itself, the results are often less accurate.

In this paper, the combustion energies were determined for 13 amino acids (Glycine, DL-Alanine, DL-Butyric acid, L-Aspartic acid, L-Serine, L-Lysine, L-Glutamic acid, L-Arginine, L-Histidine, L-Tyrosine, DL-Phenylalanine, L-Cystine, L-Methioine) by using a precision rotating-bomb calorimeter. The standard enthalpies of combustion, $\Delta_{c,Am(s)}\ H^\theta$, and the standard enthalpies of formation, $\Delta_{f,Am(s)}\ H^\theta$ were calculated. The reliability of the results is discussed through comparing with the values in the references.

2. Experimental

2.1. Materials

Amino acids were obtained as a chromatographically pure biochemical source from Shanghai Kangda and recrystallized three times from quadratic distilled

---

*Corresponding author. Fax: +86-029-8303511; e-mail: hwws@nwu.edu.cn

PII: S0040-6031(99)00002-7

Table 1
Main content melting point (MP) and density for the samples

Sample	Content (%)		MP (°C)		
	Before recrystallization	After recrystallization	Before recrystallization	After recrystallization	Density (g cm^{-3})
Glycine (Gly) H_2NCH_2COOH	99.9	99.99	290d	292d	1.604
DL-Alanine (Ala) $CH_3CH(NH_2)COOH$	99.9	99.99	295d	297d	1.425
DL-Butyric acid (Buty) $CH_3CH_2CH(NH_2)COOH$	99.9	99.98	284d	285.5–286.0	1.229
L-Aspartic acid (Asp) $HOOCCH_2CH(NH_2)COOH$	99.9	99.98	269	270–271	1.660
L-Serine (Ser) $HOCH_2CH(NH_2)COOH$	99.9	99.99	226d	227–228d	1.537
L-Lysine (Lys) $NH_2(CH_2)_4CH(NH_2)COOH$	99.9	99.98	223d	224–225d	1.205
L-Glutamic acid (Glu) $HOOC(CH_2)_2CH(NH_2)COOH$	99.9	99.99	247d	248–249d	1.538
L-Arginine (Arg) H_2NC (:NH) NH $(CH_2)_3 \cdot CH$ (NH_2) COOH	99.9	99.99	242d	243–244d	1.103
L-Histidine (His) $C_3H_3N_2CH_2CH(NH_2)COOH$	99.9	99.99	275d	277d	1.136
L-Tyrosine (Tyr) *P*-$HOC_6H_4CH_2CH(NH_2)COOH$	99.9	99.98	342d	343–344d	1.450
DL-Phenylalanine (Phe) $C_6H_5CH_2CH(NH_2)COOH$	99.9	99.99	318d	319–320d	1.357
L-Cystine (Cyss) $[SCH_2CH(NH_2)COOH]_2$	99.9	99.98	258d	260–261d	1.671
L-Methionine (Met) $CH_3S(CH_2)_2CH(NH_2)COOH$	99.9	99.99	281d	282–283d	1.341

water. Recrystallized samples were sufficiently dried under vacuum prior to use. Main contents of the samples were determined using formalin method. Densities of the samples were determined by the bottle method using dimethyl benzene as solvent. The sample mass in vacuum was calculated from the density measured in air as usual. All manipulations involving dried samples were carried out in a dry-box. The results of determination are given in Table 1.

2.2. Apparatus and experimental procedures

The precision rotating-bomb calorimeter (RBC-type 1) and the basic experimental procedures used in this investigation have already been described [5]. The initial temperature was (25.0000±0.0005)°C, and the initial oxygen pressure was 2533.125 kPa. The calorimetric system was calibrated using benzoic acid prior to use.

The energy equivalent of the calorimeter was calculated according to the equation

$$W = \frac{Qa + Gb + 5.983c}{\Delta T}, \tag{1}$$

where W is the energy equivalent of the calorimeter (J K^{-1}), Q the combustion enthalpy of benzoic acid (J g^{-1}), a the mass of determined benzoic acid (g), G the combustion enthalpy of Ni–Cr wire for ignition (0.9 J cm^{-1}), b the length of actual Ni–Cr wire consumed (cm), 5.983 the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 cm^3 of 0.1000 mol dm^{-3} solution of NaOH (J cm^{-3}), c the volume (cm^{-3}) of consumed 0.1000 mol dm^{-3} solution of NaOH and ΔT the correct value of the temperature rise.

The correct value of the heat exchange was calculated by the following equation [6]:

$$\Delta(\Delta T) = nV_0 + \frac{V_n - V_0}{\bar{T}_n - \bar{T}_0} \times \left(\frac{T_0 + T_n}{2} + \sum_{i=1}^{n-1} T_i - n\bar{T}_0 \right), \tag{2}$$

where $\Delta(\Delta T)$ denotes the correct value of the heat exchange, n is the number of readings for the main (or reaction) period, V_0 and V_n are the rate of temperature change at the initial and final stages, respectively (V is positive when temperature decreases), $\bar{T}_0$, $\bar{T}_n$ the average temperatures of the calorimeter at the initial and final stages, respectively (average temperature for first and last reading), T_0 the last reading of the initial stage, T_n the first reading of the final stage, $\sum_{i=1}^{n-1} T_i$ the sum of all the readings except the last one of the main period, $(V_n - V_0)/(\bar{T}_n - \bar{T}_0)$ must be constant.

The calorimeter was calibrated with benzoic acid of purity 99.999%. Benzoic acid has an isothermal heat

Table 2
Calibrated experimental results for the energy equivalent of the calorimeter using benzoic acid

No.	Mass of benzoic acid a (g)	Calibrated ΔT (K)	Calibrated heat of acid containing nitrogen q_N (J)	Calibrated heat of combustion wire q_c (J)	Energy equivalent of calorimeter W (kJ K^{-1})
1	1.02220	1.5010	17.38	8.55	18.0459
2	1.14830	1.7023	16.83	5.31	17.8708
3	1.06805	1.5870	19.82	7.65	17.8208
4	1.10430	1.6226	33.67	10.80	18.0227
5	0.90470	1.3278	21.72	9.50	18.0513
6	1.04065	1.5352	20.09	7.70	17.9507
7	0.93050	1.3791	25.52	8.10	17.9831
8	0.98310	1.4571	19.82	5.00	17.8665
9	1.08140	1.5978	22.53	9.45	17.9213

$W=17.9359\pm0.288$ kJ K^{-1}.

of combustion at 25°C of (-26476.0 ± 5.8) J g^{-1}. The calibrated experimental results with an uncertainty 0.16% are summarized in Table 2.

2.3. Analysis of final products in oxygen-bomb

2.3.1. Analysis of final gas products

The gases formed in the combustion reaction are collected in a gas-collecting bag. The amount of gas was measured by a gas meter which was joined between the bag and the instrument of gas determination.

2.3.1.1. The analytical principle and technique of carbon dioxide. The gaseous CO_2 formed in the combustion reaction is absorbed by a weighed absorption pipe with alkali asbestos. The amount of CO_2 can be determined through the weight increment of the pipe after sinking up carbon dioxide. The amount of CO_2 dissolved in the final acidic solution was ignored.

Each measurement must have four absorption pipes connected with each other. The first one is filled with P_4O_{10} and $CaCl_2$ (anhydrous) to sink up the water-vapour in gases; the second one is filled with active MnO_2 in order to absorb the nitrogen oxides; the third one is filled with alkali asbestos to absorb the CO_2 which is for determination; the fourth one is also filled with P_4O_{10} and $CaCl_2$ to absorb the water formed in the process of determination.

2.3.1.2. The analytical principle and technique of sulfur dioxide. A steady complex dichloride sulphurous acid salt forms when sulfur dioxide is absorbed by tetrachloromercurate (TCM). This complex reacts with formalin and pararosaniline producing a purplish-red complex. The amount of sulfur dioxide can be determined through TCM-pararosaniline colorimetric analysis method.

2.3.1.3. The analytical principle and technique of nitrogen oxides (NO_x). Azo dyes form when the NO_2 is sunk up by the absorption solution in the first flask. The NO does not react with the absorption solution but becomes NO_2 when it passes through an oxide pipe. The formed NO_2 is absorbed by the absorption solution in the second flask. The amount of NO_2 and NO can be got by determination of the absorbance at wavelength between 540 and 545 nm (Saltzman colorimetric analysis method).

2.3.2. Analysis of the final solution

Wash the fittings and the inside wall of the bomb using quadratic distilled water, then transfer the bomb solution (including the washing solution) to a cone bottle completely, heat to boiling to remove CO_2, titrate the solution to the final point of phenolphthalein using the standard solution of NaOH to get the total amount of acid. The solution after neutralization cooled to room temperature is transferred to a volumetric flask. The amount of NO_3^- can be determined by using Devarda's alloy method. The amount of H_2SO_4 in the solution is corrected through the difference in values of the total amount of acid and the amount of HNO_3 in solution. Then, the corrected heat of acid is obtained based on the results.

The analytical results of the final products show that the combustion reaction is complete, neither carbon deposits or carbon monoxide formed during the combustion reaction, and the amount of NO_x in the final gas phase is insignificant.

3. Results and discussion

3.1. Combustion energy of the samples

The determination method of combustion energy for the samples is the same as for the calibration of the calorimeter with benzoic acid. The sample mass in vacuum was calculated as described above. The combustion energies of the samples were calculated by the formula

$$\Delta_{\mathrm{c,Am(s)}}E = \frac{W\Delta T - Gb - 5.983c}{m}, \qquad (3)$$

where $\Delta_{\mathrm{c,Am(s)}}E$ denotes the constant volume combustion energy of the sample, and m is the mass (g) of the sample. The other symbols are as in Eq. (1). The results of the calculations are given in Table 3.

Table 3
The experimental results for the combustion energies of the samples

Samples	No.	Mass of sample a (g)	Calibrated ΔT (K)	Calibrated heat of acid q_N (J)	Calibrated heat of combustion wire q_c (J)	Combustion energy of sample $-\Delta_c E$ (J g^{-1})
Gly	1	1.01080	0.7385	31.25	11.70	13062.46
	2	1.02585	0.7477	31.27	12.60	13030.24
	3	0.98275	0.7146	30.46	12.60	12997.57
	4	1.00430	0.7329	31.33	12.60	13045.63
	5	0.89945	0.6546	27.88	11.70	13010.20
	6	0.99765	0.7276	30.93	10.80	13038.77
	Mean					13030.81±9.69
DL-Ala	1	1.30241	1.3195	66.25	12.60	18110.24
	2	1.20346	1.2135	61.22	12.60	18020.96
	3	1.00538	1.0127	51.27	11.70	18003.83
	4	1.07450	1.0852	54.80	12.60	18051.20
	5	1.22355	1.2377	62.40	11.70	18087.43
	6	1.00394	1.0114	51.19	12.60	18009.32
	Mean					18046.33±17.54
DL-Buty[a]	1	1.33390	1.6489	91.78	7.20	22097.24
	2	1.26671	1.5620	84.72	7.20	22044.64
	3	1.21942	1.5034	77.66	7.20	22043.59
	4	1.20820	1.4914	70.60	7.20	22075.00
	5	1.17610	1.4527	77.66	7.20	22081.97
	6	1.38821	1.7269	105.90	5.40	22190.15
	Mean					22088.77±49.29
L-Asp	1	0.70270	0.4747	34.32	7.20	12057.28
	2	0.76002	0.5109	37.44	12.60	11990.89
	3	0.73575	0.4960	36.05	11.70	12026.30
	4	0.82380	0.5570	40.37	12.60	12063.53
	5	0.80465	0.5406	39.43	12.60	11984.57
	6	0.86796	0.5840	42.53	12.60	12023.95
	Mean					12024.42±13.32
L-Ser	1	1.13400	0.8757	37.44	12.60	13806.10
	2	1.10601	0.8549	36.19	12.60	13820.06
	3	1.00245	0.7704	33.05	11.70	13740.14

Table 3 (*Continued*)

Samples	No.	Mass of sample a (g)	Calibrated ΔT (K)	Calibrated heat of acid q_N (J)	Calibrated heat of combustion wire q_c (J)	Combustion energy of sample $-\Delta_c E$ (J g^{-1})
	4	0.99865	0.7686	32.96	12.60	13758.23
	5	1.03720	0.7996	34.23	12.60	13747.47
	6	1.00475	0.7720	33.16	11.70	13736.64
	Mean					13768.11±14.65
L-Lys	1	0.87380	1.0949	62.40	11.70	22389.45
	2	0.90132	1.1314	65.52	12.60	22428.21
	3	0.95475	1.1998	69.41	12.60	22454.03
	4	1.00360	1.2557	72.90	12.60	22356.76
	5	1.12045	1.4052	81.42	11.70	22410.20
	6	0.96841	1.2148	70.40	12.60	22414.08
	Mean					22408.79±13.58
L-Glu	1	0.67201	0.5698	36.19	10.80	15138.52
	2	0.76840	0.6522	37.40	12.60	15159.58
	3	0.78575	0.6646	42.43	12.60	15101.34
	4	0.80060	0.6814	43.20	12.60	15196.00
	5	0.83452	0.7084	45.06	11.70	15158.27
	6	0.96235	0.8159	51.97	12.60	15140.03
	Mean					15148.96±12.74
L-Arg	1	0.94360	1.1311	81.12	12.60	21400.06
	2	0.84050	1.0071	72.21	12.60	21390.75
	3	0.96555	1.1534	83.04	12.60	21325.43
	4	1.00321	1.2003	86.27	11.70	21362.68
	5	1.03435	1.2415	88.95	12.60	21430.10
	6	1.00061	1.1949	86.00	12.60	21320.24
	Mean					21371.54±17.75
L-His	1	0.57100	0.6634	49.92	11.70	20731.07
	2	0.98251	1.1391	85.90	11.70	20695.84
	3	0.83545	0.9700	73.04	10.80	20724.65
	4	0.69730	0.8092	61.05	12.60	20709.30
	5	0.72041	0.8351	63.08	12.60	20686.43
	6	0.68535	0.7941	60.01	9.90	20680.00
	Mean					20704.55±8.44
L-Tyr	1	0.87205	1.1912	64.27	12.60	24411.22
	2	0.76622	1.0442	56.16	12.60	24353.82
	3	0.90350	1.2298	66.86	12.60	24325.97
	4	0.95475	1.3033	70.65	11.70	24397.65
	5	0.87651	1.1977	64.86	12.60	24420.43
	6	0.99670	1.3600	73.76	11.70	24388.25
	Mean					24382.89±14.77
DL-Phe	1	0.57320	0.8987	21.00	9.00	28068.74
	2	0.63325	0.9973	22.23	10.80	28106.53
	3	0.67367	1.0538	23.58	9.90	28007.94
	4	0.64250	1.0045	22.49	11.70	27987.67
	5	0.60320	0.9471	21.11	12.60	28103.69
	6	0.61436	0.9628	21.50	12.60	28053.42
	Mean					28054.66±19.97

Table 3 (*Continued*)

Samples	No.	Mass of sample a (g)	Calibrated ΔT (K)	Calibrated heat of acid q_N (J)	Calibrated heat of combustion wire q_c (J)	Combustion energy of sample $-\Delta_c E$ (J g^{-1})
L-Cyss[b]	1	1.33800	1.2702	3267.95	12.60	14575.20
	2	1.39150	1.3200	3398.61	12.60	14562.82
	3	1.00355	0.9491	2451.08	12.60	14506.94
	4	1.02631	0.9757	2506.65	11.70	14598.35
	5	1.10352	1.0480	2695.20	12.60	14579.78
	6	1.12485	1.0695	2747.34	10.80	14601.00
	Mean					14570.68±14.04
L-Met[b]	1	0.66100	0.8748	1343.64	12.60	21685.44
	2	0.59541	0.7919	1210.28	12.60	21804.42
	3	0.67558	0.8965	1373.24	11.70	21750.37
	4	0.70035	0.9274	1423.59	12.60	21700.89
	5	0.68427	0.9093	1390.90	11.70	21783.51
	6	0.80533	1.0693	1636.98	12.60	21776.03
	Mean					21750.11±19.44

[a] This work in our thermochemical laboratory has been reported in [9].

[b] Since Cyss and Met are the compounds containing sulfur, H_2SO_4 forms when the SO_2 formed from the combustion of sulfur are absorbed by the solution in oxygen-bomb.The formation enthalpy and the solution enthalpy of H_2SO_4 are so great that the calibrated heat of acid is greater.

3.2. Standard enthalpies of combustion and standard enthalpies of formation of the samples

The standard combustion enthalpy of the sample, $\Delta_{c,Am(s)}\ H^{\theta}$, refers to the combustion enthalpy change of the ideal combustion reaction of samples at 298.15 K and 101.325 kPa. The standard combustion enthalpies of the samples were calculated from the combustion energy using the following equation:

$$\Delta_{c,Am(s)}H^{\theta} = \Delta_{c,Am(s)}E + \Delta nRT \tag{4}$$

$$\Delta n = n_{gas}\ (\text{products}) - n_{gas}\ (\text{reactants})$$

where n_{gas} is the total amount (mol) of gas present as products or as reactants. R=8.314 J mol^{-1} K^{-1}, T=298.15 K. The results of the calculations are given in Table 4, where $\Delta_{f,CO_2(g)}\ H^{\Theta}$=(−393.51±0.13) kJ

Table 4
Combustion energy, standard enthalpy of combustion and standard enthalpy of formation of samples (in kJ mol^{-1})

Sample		$-\Delta_c E$	$-\Delta_c H^{\theta}$	$-\Delta_f H^{\theta}$	
Name	Molecular weight			Experimental	Ref. value
Gly	75.07	978.22±0.73	977.60±0.73	524.00±0.78	528.5±0.5 [8]
DL-Ala	89.09	1607.75±1.56	1608.37±1.56	572.57±1.61	563.58±0.6 [8]
DL-Buty	103.12	2277.79±5.08	2279.65±5.08	580.63±5.11	–
L-Asp	133.10	1600.45±1.77	1598.59±1.77	975.86±1.85	973.3±0.8 [8]
L-Ser	105.09	1446.89±1.54	1446.27±1.54	734.67±1.60	732.7 [8]
L-Lys	146.19	3275.94±1.99	3279.66±1.99	1082.21±2.16	–
L-Glu	147.13	2228.87±1.87	2228.25±1.87	1025.53±1.99	1009.7±0.8 [8]
L-Arg	174.20	3722.92±3.09	3724.16±3.09	637.71±3.20	–
L-His	155.16	3212.52±1.31	3211.98±1.31	435.39±1.54	466.7±2.3 [8]
L-Tyr	181.19	4417.94±2.68	4419.80±2.68	693.86±2.93	685.1±1.67 [8]
DL-Phe	165.19	4634.35±3.30	4637.45±3.30	476.21±3.51	460.6±2.6 [8]
L-Cyss	248.37	3618.92±3.49	3618.92±3.49	1050.74±3.58	1032.7±3.8 [8]
L-Met	149.21	3245.33±2.90	3248.43±2.90	588.43±2.98	–

mol^{-1}, $\Delta_{f,H_2O(l)}$ H^{θ}=($-$285.83±0.042) kJ mol^{-1} and $\Delta_{f,SO_2(g)}$ H^{θ}=($-$296.81±0.02) kJ mol^{-1} [7].

It can be seen from Table 4 that the heat values obtained by a rotating-bomb calorimeter are often greater than those obtained by a static-bomb calorimeter. The reason is that the processes of combustion and reactions in a rotating-bomb are complete with distributed stirring. For straight chain amino acids, the longer the carbon chain, the greater the heat values. For example,the constant-volume combustion energies of Gly, DL-Ala and DL-Buty increase in turn. The standard enthalpies of formation of L-Lys, L-Arg and L-Met are reported first.

Acknowledgements

We thank the National Natural Science Foundation of China and the Special Foundation of the Educational Commission of Shaanxi Province for financial support.

References

[1] Y.H. Zhu, Y.J. Li, C.J. Li, S. Gao, J. Daqing Petroleum Institute (China) 19(2) (1995) 55.
[2] D.Q. Wu, Y.H. Zhu, Z.M. Gao, S.S. Qu, J. Wuhan University (China) 3 (1993) 78.
[3] S.W. Benson, J.H. Buss, J. Chem. Phys. 29 (1958) 546.
[4] J.P. Cox, G. Pilcher, Thermochemistry of Organic Organometallic Compounds, Academic Press, London, 1970, pp. 500–510.
[5] X.F. Yang, X.W. Yang, L.Z. Sun, Chem. J. Chinese Univ. (China) 7(4) (1986) 363.
[6] M.M. Popov, Thermometry and Calorimetry, Moscow University Publishing House, Moscow, 1954, p. 382.
[7] J.D. Cox, D.D. Wagman, V.A. Medvedev (Eds.), CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.
[8] J.B. Pedley, R.D. Muylor, S.P. Kirby, Thermochemical Data of Organic Compounds, 2nd ed., Chapman and Hall, London, 1992, p. 174.
[9] S.L. Gao, X.W. Yang, D.C. Wen, D.H. Ren, J. Inorg. Chem. (China) 10(3) (1994) 234.