Journal of Thermal Analysis and Calorimetry, Vol. 85 (2006) 3, 585–587

THERMOCHEMICAL STUDIES ON THE THIOPROLINE

L. Qiang-Guo[1*], *L. Xu*[1], *D. Bin*[1] *and Y. Xu-Wu*[2]

[1]College of Chemistry and Life Science, Xiangnan University, Chenzhou, Hunan 423000, China
[2]Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Department of Chemistry, Northwest University, Xi'an 710069, Shaanxi, China

The combustion energy of thioproline was determined by the precision rotating-bomb calorimeter at 298.15 K to be $\Delta_c U$= –2469.30±1.44 kJ mol^{-1}. From the results and other auxiliary quantities, the standard molar enthalpy of combustion and the standard molar enthalpy of formation of thioproline were calculated to be $\Delta_c H^{\theta}_m C_4H_7NO_2S$, (s), 298.15 K= –2469.92±1.44 kJ mol^{-1} and $\Delta_f H^{\theta}_m C_4H_7NO_2S$, (s), 298.15K= –401.33±1.54 kJ mol^{-1}.

Keywords: *combustion energy, rotating-bomb calorimeter, standard enthalpy of formation, thioproline*

Introduction

Thioproline ($C_4H_7NO_2S$) is an analog of the proline which is an amino acid necessary to body. The experimentation indicated it possesses some special functions as prolonging body life, controlling medicament toxicity and catalyzing plant growth, and in particular, function as anticancer drugs which can make cancer cell reverse to normal cell [1–3]. Moreover, it has indicated low-toxicity and the property of tranquilizing the patient after his treatment in the clinic test. On the other hand, the complexes of thioproline with rare earth salts possess have the functions of strengthening its fat deliquescence, reinforcing osmosis for membrane and improving pharmacologic effect etc. [4–7]. So it is very interesting to make research on and exploiture of the thioproline, which has become a hotspot [8] in the cross field of chemistry and biology since the eighties of the twentieth century when it was first reported. But those researches were just about the synthesis, properties and pharmacologic effect of thioproline and its complexes. The combustion energy and the standard molar enthalpy of combustion and the standard molar enthalpy of the formation of thioproline have not yet been reported. Obviously, it is necessary to obtain their basic thermodynamic data as the gist and basis for theoretical researches and industrial designing when they are synthesized and developed industrially. In the paper, combustion energy of thioproline has been determined by using a rotating-bomb calorimeter. The standard molar enthalpy of combustion and the standard molar enthalpy of the formation of thioproline have been calculated.

Experimental

Chemicals and instruments

L-Cysteine (s) (obtained from Shanghai Reagent Company) used was of analytical reagent grade, a purity >99.5%. Benzoic acid (obtained from Shanghai Reagent Company), calorimetric primary standard of purity >99.999%, was dried in a vacuum oven for 6 h prior to the use.

Elemental analyzer (Perkin-Elmer 2400 CHN, USA), FT-IR spectrometer (Avatar 360, with KBr pellet, USA), differential thermal analyzer (CDR-type 1, China), precision rotating-bomb calorimeter [9] (RBC-type 2, Northwest University, China, a calorimetric system that is calibrated by benzoic acid with standard calorific value prior to use and the basic experimental procedures used in this investigation have already been described [10]. The initial temperature was 25.0000±0.0005°C, and the initial oxygen pressure was 2533.125 kPa).

Preparation of sample

Thioproline ($C_4H_7NO_2S$) was prepared with *L*-cysteine according to the method given [11]. The sample was obtained by thrice repeated crystallizations in distilled water. Elementary analysis, melting point (capillary tube method), specific rotation and IR spectra of the product were studied. The results are shown in Table 1. The differential thermal analysis (DTA) curve of the compound was determined with CDR-1. The results indicating that thioproline is melted and decomposed and showed one framework rupture endothermic strong peak at 203°C. These results are identical with [11, 12]. The product

* Author for correspondence: liqiangguo@163.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Melting point, specific rotation, elementary analysis and major IR spectra date of thioproline

	M.P./°C	$[.]_D^{20}$/°	C/%	H/%	N/%	υ_{N-H}/ cm^{-1}	δ_{N-H}/ cm^{-1}	υ_{asCOO^-}/ cm^{-1}	υ_{sCOO^-}/ cm^{-1}
Literature [11, 12]	196–197	–100	36.06	5.26	10.52	3058	16.32	1556	1434
Test	196–197	–100	36.04	5.28	10.49	3053.27	1627.30	1554.94	1431.80

was proved to be pure thioproline. The consistency of thioproline was determined to be 1.425 g cm^{-3} by using a pycnometer in contrast with ethanol. The mass of the sample in air is corrected as the mass of the sample in vacuum by the consistency value.

Calculation of the energy equivalent of the RBC-type 2 calorimeter

The energy equivalent of the RBC-type 2 calorimeter was calculated according to the equation:

$$W=\frac{Qa+Gb+5.97c}{\Delta T} \quad (1)$$

where W (J K^{-1}) is the energy equivalent of the RBC-type 2 calorimeter, Q (J g^{-1}) is the combustion energy of benzoic acid, a (g) is the mass of determined benzoic acid, G (0.9 J cm^{-1}) is the combustion energy of Ni–Cr wire for ignition, b (cm) is the length of actual Ni–Cr wire consumed, 5.97 (J mL^{-1}) is the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 mL of 0.1000 mol dm^{-3} solution of NaOH, c (mL) is the volume of consumed 0.1000 mol dm^{-3} solution of NaOH and ΔT (K) is the correct value of the temperature rise $\Delta T=\Delta T_{test}+\Delta(\Delta T)$, where $\Delta(\Delta T)$ denotes the correct value of the heat exchange.

Correction of the heat exchange

The correction of the heat exchange was calculated by the Eq. [12]

$$\Delta(\Delta T)=nV_0+\frac{V_n-V_0}{Q_n-Q_0}\left(\frac{T_0+T_n}{2}+\sum_{i=1}^{n-1}T_i-nQ_0\right) \quad (2)$$

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 changes at the initial and the final stages respectively (V is positive when temperature decreases), Q_0 and Q_n are the average temperatures of the calorimeter at the initial and the final stages respectively (average temperature for first and last readings), T_0 is the last reading of the initial stage, T_n is the first reading of the final stage, $\sum_{i=1}^{n-1}T_i$ is the sum of all the readings except the last one of the main period.

Results and discussion

Calculation of the energy equivalent for the calorimeter

The calorimeter RBC—type 2 was calibrated by benzoic acid of purity 99.999%. Benzoic acid has an isothermal heat of combustion at 298.15 K of –26434.0±5.8 J g^{-1}. The calibrated experimental results are summarized in Table 2. The uncertainty is 0.16%.

Combustion energy of the thioproline

The method of combustion energy determination for the thioproline is the same as for the calibration of the calorimeter with benzoic acid. The thioproline masses were determined in vacuum. The combustion energies of the thioproline were calculated according to the formula

$$-\Delta_c U=\frac{(W\Delta T-Gb-q_N)M}{m\cdot 1000} \quad (3)$$

Table 2 The experimental results of the energy equivalent of the calorimeter

No.	Mass of benzoic acid a/g	Heat of combustion wire q_c/J	Heat of acid containing nitrogen q_N/J	Calibrated ΔT/K	Energy equivalent of calorimeter W/J K^{-1}
1	0.76823	10.80	23.96	1.1281	18032.22
2	0.80052	12.60	25.22	1.1783	17990.98
3	0.86965	12.60	22.70	1.2808	17975.97
4	0.81237	11.70	23.06	1.1959	17985.58
5	0.80250	12.60	24.28	1.1802	18005.55
6	0.79825	12.60	24.03	1.1734	18013.95
avg.					18000.71±8.42

Table 3 The experimental results of combustion energy of thioproline

No.	Mass of thioproline m/g	Heat of combustion wire q/J	Heat of total acid q_N/J	Calibrated ΔT/K	Combustion energy of thioproline $-\Delta_c U$/kJ mol^{-1}
1	1.00326	12.60	2090.38	1.1502	2469.10
2	0.97360	11.70	2028.58	1.1140	2463.77
3	0.98262	12.60	2047.37	1.1288	2474.59
4	0.98437	10.80	2051.02	1.1291	2470.67
5	1.00169	12.60	2087.11	1.1480	2468.14
6	1.00031	12.60	2084.23	1.1470	2469.54
avg.					2469.30±1.44

where $-\Delta_c U$ kJ mol^{-1} denotes the constant-volume combustion energy of the thioproline, M is the molar mass of the thioproline and m (g) is the mass of the thioproline. The other symbols are as in Eq. (1). The results of the calculations are given in Table 3.

Standard combustion enthalpy of the combustion energy of thioproline

The standard combustion enthalpy of the combustion energy of thioproline $\Delta_c H_m^\theta$ refers to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 101.325 kPa.

$$C_4H_7NO_2S(s)+\frac{23}{4}O_2(g)=$$
$$4CO_2(g)+\frac{7}{2}H_2O(l)+SO_2(g)+\frac{1}{2}N_2(g)$$

The standard combustion enthalpy of the above thioproline was calculated on the bases of the combustion energy according to the equation

$$\Delta_c H_m^\theta = \Delta_c U + RT\Delta n \quad (4)$$

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

where n_{gas} is the total amount (in moles) of gas present as products or as reactants, R 8.314 J mol^{-1} K^{-1} T 298.15 K. The result of the calculation is to be $\Delta_c H_m^\theta$ [$C_4H_7NO_2S$, s, 298.15 K]= –(2469.92± 1.44) kJ mol^{-1}

Standard molar enthalpy of the formation of thioproline

The Standard molar enthalpy of formation of thioproline was calculated according to Hess's law to the thermochemical equation:

$$\Delta_f H_m^\theta = \sum (n\Delta_f H_m^\theta)_{Prod.} - \Delta_c H_m^\theta =$$
$$= 4\Delta_f H_m^\theta [CO_2(g)] + \frac{7}{2}\Delta_f H_m^\theta [H_2O(l)] + \quad (5)$$
$$+\Delta_f H_m^\theta [SO_2(g) - \Delta_c H_m^\theta$$

According to Ref. [10],

$\Delta_f H_m^\theta$ [CO_2, (g), 298.15 K] = –(393.51±0.13) kJ mol^{-1}

$\Delta_f H_m^\theta$ [H_2O, (l), 298.15 K] = –(285.83±0.042) kJ mol^{-}

$\Delta_f H_m^\theta$ [SO_2, (g), 298.15 K] = –(296.81±0.02) kJ mol^{-1}

The Standard molar enthalpy of formation of thioproline is obtained:

$\Delta_f H_m^\theta$ [$C_4H_7NO_2S$, (s), 298.15 K] = –(401.33±1.54) kJ mol^{-1}.

References

1 G. Z. Yuan, J. J. Huang and G. M. Zhang, Chem. J. Chinese Univ., 9 (1989) 5.
2 H. P. Zhao and G. H. Feng, Acta Pharmacologica Sinnica, 5 (1984) 30.
3 X. M. Yang, D. H. Zhao and B. H. Sheng, Acta Pharmacologica Sinnica, 7 (1986) 134.
4 L. B. Yuan, B. Q. Wu and Q. W. Wang, Pharm. Bull., 20 (1985) 748.
5 S. Zhong, Y. X. Sun, J. J. Liu and Y. H. Li, J. Chemical World, 9 (1998) 463.
6 R. H. Li and S. Zhong, J. East China Normal Univ. (Natural Science), 1 (2000) 63.
7 R. H. Li and S. Zhong, J. Chemical World, 10 (1997) 515.
8 W. D. Yang and B. H. Chen, Chinese J. Inorg. Chem., 2 (1986) 5.
9 X. W. Yang, S. P. Chen, S. Li Gao and Q. Z. Shi, Instrum. Sci. Technol., 30 (2002) 311.
10 J. D. Cox, D. D. Wagman and V. A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere Publishing Corp., New York, 1984, 1.
11 S. Ranter and H. T. Clarke, J. Am. Chem. Soc., 59 (1937) 200.
12 M. D. Xia, W. F. Tang, P. Z. Ni and Z. S. Hu, J. Jiangsu Chem. Industry, 20 (1994) 8.

DOI: 10.1007/s10973-006-7630-2