Determination of Constant-Volume Combustion Energies for Zinc L-Threonate and Calcium L-Threonate

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Zinc L-threonate that was not reported in literature and calcium L-threonate were prepared. The constant-volume combustion energies of the compounds, $\Delta_c E$, were determined by a precision rotating bomb calorimeter at 298.15 K. Their values are (-2853.14 ± 1.49) kJ mol^{-1} and (-3133.13 ± 1.63) kJ mol^{-1}, respectively. The standard enthalpies of combustion, $\Delta_c H°$, and standard enthalpies of formation, $\Delta_f H°$, have been calculated for these compounds. They are (-2850.66 ± 1.49) kJ mol^{-1}, (-2648.69 ± 1.11) kJ mol^{-1} for zinc L-threonate and (-3130.65 ± 1.63) kJ mol^{-1}, (-2653.34 ± 1.08) kJ mol^{-1} for calcium L-threonate.

As one of metabolites in human body and the component of gastric juice, L-threonic acid is key to the life and cell activation. It has greatly improved absorption and utilization of L-ascorbic acid [1]. The study shows that L-threonic acid makes the combination of metal ion with amino acid and protein easy, which contributes to absorption and utilization by animal [2]. Zinc is one of trace elements essential for human body; it is connected with over 200 kinds of metal ferments, participates in ferment syntheses and plays an important role in metabolism of nucleic acid, protein, carbohydrate, and fat. The study on additive containing zinc has aroused general concern [3].

However, calcium L-threonate and zinc L-threonate have rarely been investigated by thermochemical methods. In this paper, calcium L-threonate and zinc L-threonate were prepared according to the literature [4]. The constant-volume combustion energies of these compounds, $\Delta_c E$, were determined by a precision rotating bomb calorimeter at 298.15 K. The standard enthalpies of combustion, $\Delta_c H°$, and standard enthalpies of formation, $\Delta_f H°$, have been calculated for these compounds. This work enriches the thermochemical database and provides a theoretical basis for further study on the title compounds and their application.

EXPERIMENTAL

L-Ascorbic acid, calcium carbonate, zinc carbonate, methanol, and hydrogen peroxide (30 mass %) were anal. grade chemicals made in China. Calcium L-threonate and zinc L-threonate were prepared and purified according to the literature [4], and the pu-

rity of them was greater than 99.9 % by HPLC. The chemical analytical results proved the formulas of the compounds to be $Ca(C_4H_7O_5)_2$, $Zn(C_4H_7O_5)_2$.

The constant-volume combustion energy of compound was determined by the precision rotating bomb (RBC-type II) [5]. The main experimental procedures have been described [6]. The initial temperature was regulated to (25.0000 ± 0.0005) °C by super constant temperature thermostat and the initial oxygen pressure was 2.5 MPa.

The correct value of the heat exchange was calculated according to the Linio—Pyfengdelel—Wsava formula [7]. The calorimeter was calibrated with benzoic acid of 99.999 % purity. Benzoic acid had an isothermal heat of combustion at 25 °C of (-26434 ± 3) J g^{-1}. The energy equivalent of calorimeter was (17936.23 ± 9.08) kJ K^{-1}. The analytical methods of final products (gas, liquid, solid) were the same as in the literature [4]. The analytical results of the final products showed that the combustion reactions were complete. Either carbon deposits or carbon monoxide formed during the combustion reactions and the amount of NO$_x$ in the final gas phase were neglected.

Purity determination of the samples: LC-6A type HPLC. PC 8 $\approx$ 10 s^{-1} 2504 column, mobile phase: solution A 10 % of methanol in water, solution B 90 % of methanol in water.

The constant-volume combustion energy determination of the samples: RBC-type II rotating bomb calorimeter.

RESULTS AND DISCUSSION

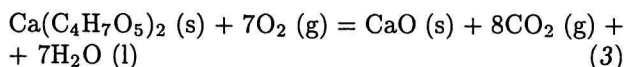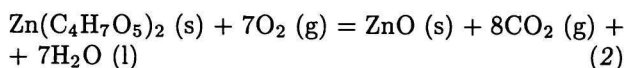The method of determination combustion energy

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for the samples was the same as for the calibration of the calorimeter with benzoic acid. The combustion energies of the samples were calculated by the formula

$$\Delta_c E = \frac{W \Delta T - Ga - 5.983b}{m} \qquad (1)$$

where $\Delta_c E$ denotes the constant-volume combustion energy of the samples, W is the energy equivalent of the RBC-type II calorimeter (J K^{-1}), ΔT the correct value of the temperature rise, G the combustion enthalpy of Ni-Cr wire for ignition (0.9 J cm^{-1}), a 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}), b the volume (cm^3) of consumed 0.1000 mol dm^{-3} solution of NaOH, and m is the mass (g) of the sample. The results of the calculations are given in Table 1.

The standard combustion enthalpy of the compounds, $\Delta_c H^\circ$, referred to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 0.1 MPa.

$$Zn(C_4H_7O_5)_2 \text{ (s)} + 7O_2 \text{ (g)} = ZnO \text{ (s)} + 8CO_2 \text{ (g)} + 7H_2O \text{ (l)} \qquad (2)$$

$$Ca(C_4H_7O_5)_2 \text{ (s)} + 7O_2 \text{ (g)} = CaO \text{ (s)} + 8CO_2 \text{ (g)} + 7H_2O \text{ (l)} \qquad (3)$$

The standard combustion enthalpies of the compounds were calculated from the combustion energy by the equations

$$\Delta_c H^\circ = \Delta_c E + \Delta n R T \qquad (4)$$

$$\Delta n = n_{gas}(\text{products}) - n_{gas}(\text{reactants}) \qquad (5)$$

where n_{gas} is the total amount of substances (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 2.

The standard enthalpies of formation of the compounds, $\Delta_f H^\circ$, were calculated by Hess' law according to the thermochemical equations.

a) The standard enthalpy of formation of L-Ca(C$_4$H$_7$O$_5$)$_2$

$$\Delta_f H^\circ = \Delta_{f,CaO(s)} H^\circ + \\ + 8\Delta_{f,CO_2} H^\circ + 7\Delta_{f,H_2O} H^\circ - \Delta_c H^\circ \qquad (6)$$

b) The standard enthalpy of formation of L-Zn(C$_4$H$_7$O$_5$)$_2$

$$\Delta_f H^\circ = \Delta_{f,ZnO(s)} H^\circ + \\ + 8\Delta_{f,CO_2} H^\circ + 7\Delta_{f,H_2O} H^\circ - \Delta_c H^\circ \qquad (7)$$

where $\Delta_{f,ZnO(s)} H^\circ = (-350.46 \pm 0.27)$ kJ mol^{-1}, $\Delta_{f,CaO(s)} H^\circ = -635.1$ kJ mol^{-1}, $\Delta_{f,CO_2} H^\circ =$

Table 1. Experimental Results for the Combustion Energies of the Samples

Sample	No.	Mass of sample	Calibrated heat of combustion wire	Calibrated heat of acid	Calibrated	Combustion energy of sample
		m/g	q_c/J	q_N/J	ΔT/K	$\Delta_c E$/(J g^{-1})
L-Ca(C$_4$H$_7$O$_5$)$_2$	1	1.20342	12.60	6.54	0.6780	−10089.27
	2	1.17936	12.60	6.42	0.6659	−10111.18
	3	1.21205	12.60	6.46	0.6838	−10103.32
	4	1.10970	12.60	5.90	0.6246	−10078.82
	5	1.22320	12.60	6.48	0.6905	−10109.46
	6	1.23438	12.60	6.53	0.6955	−10090.50
	Mean					−10097.09 ± 5.26
L-Zn(C$_4$H$_7$O$_5$)$_2$	1	0.84783	8.10	11.72	0.4037	−8517.08
	2	0.78768	8.10	10.88	0.3748	−8510.46
	3	0.74350	8.10	10.28	0.3535	−8503.13
	4	0.79300	11.70	10.96	0.3769	−8496.22
	5	0.85682	12.60	11.84	0.4070	−8491.40
	6	0.80425	12.60	11.11	0.3820	−8489.81
	Mean					−8501.35 ± 4.44

Table 2. Combustion Energy, Standard Combustion Enthalpy, and Standard Enthalpy of Formation of the Compounds (in kJ mol^{-1})

Complex	M_r	$\Delta_c E$	$\Delta_c H^\circ$	$\Delta_f H^\circ$
L-Ca(C$_4$H$_7$O$_5$)$_2$	310.30	−3133.13 ± 1.63	−3130.65 ± 1.63	−2653.34 ± 1.08
L-Zn(C$_4$H$_7$O$_5$)$_2$	335.61	−2853.14 ± 1.49	−2850.66 ± 1.49	−2648.69 ± 1.11

(-393.51 ± 0.13) kJ mol^{-1}, $\Delta_{f,H_2O} H^\circ = (-285.83 \pm 0.042)$ kJ mol^{-1} [8]. The results of the calculation are also shown in Table 2.

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