Low-Temperature Heat Capacities and Standard Molar Enthalpy of Formation of L-3-(3,4-Dihydroxyphenyl) Alanine ($C_9H_{11}NO_4$)

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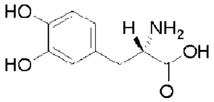
Low-temperature heat capacities of L-3-(3,4-dihydroxyphenyl) alanine ($C_9H_{11}NO_4$) were measured by a precision automated adiabatic calorimeter over the temperature range from (78 to 400) K. A polynomial equation of heat capacities as a function of temperature was fitted by the least-squares method. Based on the fitted polynomial, the smoothed heat capacities and thermodynamic functions of the compound relative to the standard reference temperature 298.15 K were calculated and tabulated at 5 K intervals. The constant-volume energy of combustion of the compound at $T = 298.15$ K was measured by a precision oxygen-bomb combustion calorimeter to be $\Delta_c U = -(21183.5 \pm 35.0)\ \mathrm{J \cdot g^{-1}}$. The standard molar enthalpy of combustion of the compound was determined to be $\Delta_c H^\circ_m = -(4177.8 \pm 6.9)\ \mathrm{kJ \cdot mol^{-1}}$, according to the definition of combustion enthalpy. Finally, the standard molar enthalpy of formation of the compound was calculated to be $\Delta_f H^\circ_m = -(935.9 \pm 7.0)\ \mathrm{kJ \cdot mol^{-1}}$ in accordance with Hess law.

Introduction

L-3-(3,4-Dihydroxyphenyl) alanine ($C_9H_{11}NO_4$) (CAS registry number, 59-92-7) is also called 3,4-dihydroxy-L-phenylalanine, levodoba, and L-doba. It is an important alkaloid. Not only can it be used to treat common senile diseases, such as senile dementia, Parkinson's disease, apoplexy, or stroke, but also it is an intermediate material in preparing the drugs for treating Parkinson's diseases, hepatic coma, CO poisoning, heart failure, and psychosis.[1] Its molecular structure is



Heat capacity and standard molar enthalpy of formation of a substance are some of the most fundamental thermodynamic properties and closely related to other physical, biological, physiological, and chemical properties. The standard molar enthalpy of formation of a substance is one of the important data that is used when calculating enthalpy changes, equilibrium constants, and theoretical yields of reactions for which the substance is involved in. However, up to now, no report about those thermodynamic properties of the title compound was found in the literature. In the present work, heat capacities, thermodynamic properties, and standard molar enthalpy of formation of the title compound were investigated by adiabatic calorimetry and combustion calorimetry.

Experimental Section

Sample. L-3-(3,4-Dihydroxyphenyl) alanine is a white crystal with a needlelike shape. The sample used in these calorimetric measurements was purchased from Alfa Aesar (Tianjin, China) Co., Ltd. The labeled purity was > 99.0 %. Its melting point is determined to be (276 to 278) °C by a micromelting point device, as reported in the literature.[1] The actual purity of the sample was determined to be more than 99.5 % by HPLC. FTIR and ^{1}H NMR were applied to verify the composition and structure of the compound. These results confirmed the reliability of the sample used in these calorimetric studies.

Adiabatic Calorimetry. A high-precision automatic adiabatic calorimeter that requires a small sample was used to measure the heat capacities in the temperature range from $T = (78$ to $400)$ K. The principle and design of the adiabatic calorimeter has been described in detail elsewhere.[2–4] Briefly, the calorimeter comprised a sample cell, a platinum resistance thermometer, an electric heater, inner and outer adiabatic shields, and a vacuum can. Two sets of six-junction chromel–constantan thermopiles are installed between the calorimetric cell and the inner shield and between the inner and outer shields, respectively. The miniature platinum resistance thermometer (IPRT No. 2, produced by Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter, and a nominal resistance of 100 Ω) was used to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Chinese Academy of Sciences. The thermometer was inserted into the copper sheath which was silver-soldered close to the bottom of the sample cell. The temperature differences between the sample cell and the inner shield and between the inner and outer shields were monitored by two sets of thermopiles and controlled by two sets of DWT-702 precision temperature controllers (manufactured by Shanghai No. 6 Automated Instrumentation Works). An auxiliary temperature-controlled sheath was placed in the outer side of the vacuum can. The temperature of the sheath was kept at (30 to 50) K lower than that of the sample cell for experiments above room temperature. After applying a known potential to the outer

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adiabatic shield controlling the circuit through a temperature controller, the temperatures of the outer adiabatic shield can be maintained at (0.3 to 0.5) K lower than that of the inner adiabatic shield to avoid the temperature maladjustment of the inner shield when the temperature of the sample cell was above 300 K. On the basis of the above-mentioned steps, the temperature differences between the sample cell and the inner shield were kept at about 0.5 mK or smaller during the entire experimental process. The vacuum can was evacuated to 10^{-3} Pa during the heat capacity measurements so as to eliminate heat transfer by convection. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded by use of the Data Acquisition/Switch Unit (model 34970A, Agilent, USA) and processed online by a computer.

To verify the accuracy of the calorimeter, the heat-capacity measurements of the reference standard material, α-Al_2O_3, were made in the temperature range from $T = 78$ K to $T = 400$ K. The sample mass used was 1.6382 g, which was equivalent to 0.0161 mol based on its molar mass, M (Al_2O_3) = 101.9613 $g \cdot mol^{-1}$. The results indicated that deviations of the experimental data from those of the National Institute of Standards and Technology[5] in the same temperature range were within ± 0.3 %.

Heat-capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and the temperature increments were generally controlled at (0.1 to 0.4) $K \cdot min^{-1}$ and (1 to 3) K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within (10^{-3} to 10^{-4}) $K \cdot min^{-1}$ during the acquisition of all heat-capacity data. The sample mass used for the calorimetric measurements was 2.3972 g, which was equivalent to 0.01216 mol in terms of molar mass of the sample, L-3-(3,4-dihydroxyphenyl) alanine ($C_9H_{11}NO_4$), $M = 197.19$ $g \cdot mol^{-1}$.

Isoperibol Oxygen-Bomb Combustion Calorimetry. The constant-volume energy of combustion of the sample was measured by means of a homemade precision oxygen-bomb combustion calorimeter. It was an isoperibolic macrocalorimeter with a static oxygen bomb and was set up in our thermochemistry laboratory. The structure and principle of the calorimeter has been described in detail previously elsewhere.[6] It consisted of a static oxygen bomb, inner calorimetric vessel, outer thermostatic bath, platinum resistance thermometer, precision temperature controller, ignition system, and temperature measurement system. The system for controlling the temperature consisted of a thermostatic bath, an electric stirrer, an electric heater, a precision temperature controller, and a Cu 50 resistance thermometer. The precision of controlling the temperature for the thermostatic system can reach ± 0.001 K.

The temperature measurement system consisted of a precision platinum resistance thermometer (PTΦ5 × 40, 40 mm in length, 5 mm in diameter; $R_0 = 196.9865$ Ω, made by the Instrument Manufacture Co. of Yunnan, P.R. China) and a Data Acquisition/Switch Unit (model 34970A, Agilent, USA). The thermometer was calibrated on the basis of ITS-90 by the Chinese National Institute of Metrology (NIM).

The correction of the temperature rise (ς) was obtained from a formula described in refs 6 to 8.

Table 1. Energy Equivalent (ϵ) of the Calorimeter Determined from Combustion Experiments Using NIST 39i Benzoic Acid at 298.15 K and 0.1 MPa

no.	W/g	Q_{Ni}/J	Q_{HNO3}/J	ΔT/K	$\epsilon/(J \cdot K^{-1})$
1	0.68831	42.468	22.848	1.2424	14697.4
2	0.67416	41.589	21.290	1.2258	14589.4
3	0.68121	43.639	20.511	1.2277	14719.6
4	0.68036	41.003	16.617	1.2284	14687.6
5	0.67285	41.296	22.329	1.2135	14709.3
6	0.69058	43.867	22.989	1.2486	14673.8
7	0.67988	41.786	21.467	1.2257	14714.2
8	0.66896	41.106	21.908	1.2148	14608.4

$\epsilon/(J \cdot K^{-1}) = (14674.7 \pm 17.5)$

The sample was pressed into pellets of (0.5 to 0.6) g for each combustion and burned under an oxygen pressure of 3.01 MPa in the presence of 0.001 dm^3 of distilled water in the bomb to ensure equilibrium in the final state after the combustion. The purity of the oxygen used in the experiment was of research grade, mole fraction 0.99998. The mass of the sample has been calibrated from the air buoyancy on the basis of determination of the density for a pellet of the sample. At $T = (298.15 \pm 0.001)$ K, the differential quotient of the constant-volume energy of combustion with the oxygen pressure, $(\partial U/\partial P)_T$, for the solid was assumed to be -0.21 $J \cdot g^{-1} \cdot MPa^{-1}$, a typical value for organic solids.[6] The standard energy of combustion of the nickel fuse for ignition has been determined previously to be $\Delta_c U°/J \cdot cm^{-1} = 2.929$. The real energy of combustion of the nickel fuse (Q_{Ni}/J) was calculated from the formula, $Q_{Ni}/J = 2.929 \cdot \Delta L$, in which ΔL/cm was the length of the combusted nickel wire. The correction for the energy of formation of aqueous nitric acid, produced by oxidation of a trace of nitrogen contained in the oxygen bomb, was determined by the neutral titration with 0.1000 $mol \cdot dm^{-3}$ of sodium hydroxide solution using methyl orange as the indicator. The enthalpy of formation of the aqueous nitric acid in the oxygen bomb can be derived from the equation, $Q_{HNO3}/J = 59.8 \cdot C \cdot V$, in which $C/mol \cdot dm^{-3}$ is the concentration of the sodium hydroxide solution and V/dm^3 is the volume of the consumed sodium hydroxide solution, based on the molar energy of formation of HNO_3 (aq) from N_2(g), O_2(g), and H_2O(l), $\Delta_f H°_m = 59.8$ $kJ \cdot mol^{-1}$ for 0.1 $mol \cdot dm^{-3}$ of HNO_3(aq).[9]

After each combustion test, the combustion products were analyzed mainly for carbon dioxide by the Rossini method.[6,7] No soot was observed in the sample crucible after each of the combustion experiments. During the determination of the energy equivalent of the combustion calorimeter and measurements of constant-volume energies of combustion of L-3-(3, 4-dihydroxyphenyl) alanine, mole ratios of real amounts of carbon dioxide produced in the combustion to the theoretical amounts were determined to be higher than 0.9992. This demonstrated that the combustion of the sample in the oxygen bomb was complete. Qualitative tests for CO with indicator tubes were negative within the limits of their sensitivity {mole fraction x (CO) $< 1 \cdot 10^{-6}$}.

A new oxygen bomb was used to determine the combustion energy of the sample. The energy equivalent, $\epsilon_{calor}/J \cdot K^{-1}$, of the combustion calorimeter was determined from combustion of about 0.68 g of NIST 39i benzoic acid with a certified massic energy of combustion under experimental conditions of $\Delta_c U = -(26434 \pm 3)$ $J \cdot g^{-1}$ to be $\epsilon_{calor} = (14674.7 \pm 17.5)$ $J \cdot K^{-1}$, as indicated in Table 1. The uncertainty of the results was the standard deviation of the mean value from the respective measurements.

Results and Discussion

Low-Temperature Heat Capacity. All experimental heat-capacity values tabulated in Table 2 show that the structure

Table 2. Experimental Molar Heat Capacities of L-3-(3,4-Dihydroxyphenyl) Alanine ($C_9H_{11}NO_4$) (M = 197.19 g·mol^{-1})

T/K	$C_{p,m}$ (J·K^{-1}·mol^{-1})	T/K	$C_{p,m}$ (J·K^{-1}·mol^{-1})	T/K	$C_{p,m}$ (J·K^{-1}·mol^{-1})
78.466	71.34	166.921	146.40	274.764	239.03
79.827	72.35	168.928	148.17	277.823	242.01
81.490	73.75	170.889	150.21	280.880	244.64
83.001	75.18	172.803	151.86	283.915	247.23
84.816	76.68	174.764	153.40	286.950	249.50
86.630	78.19	176.679	155.02	289.938	252.13
88.442	79.60	178.590	156.36	292.921	255.42
89.942	80.73	180.489	157.89	295.758	258.06
91.354	82.27	182.374	159.54	298.791	261.00
93.065	83.62	184.402	161.10	301.774	263.53
94.811	84.79	186.394	162.67	304.660	266.35
97.139	86.20	188.350	164.31	307.790	269.29
98.885	87.89	190.449	165.92	310.969	272.35
100.715	89.28	192.512	167.41	313.953	275.23
102.644	90.78	194.575	169.47	317.083	278.06
104.709	92.24	196.603	171.19	320.262	281.06
106.740	93.97	198.737	173.02	323.197	284.12
108.740	95.89	200.729	174.55	325.789	286.40
110.711	97.80	202.721	176.35	328.382	288.56
112.655	99.36	204.749	178.18	331.072	291.45
114.575	101.07	206.741	179.90	333.759	293.85
116.471	103.00	208.733	181.70	336.367	296.31
118.496	104.72	210.725	183.49	338.975	299.04
120.648	106.43	212.574	185.10	341.736	301.82
122.772	108.44	214.566	186.74	344.651	304.77
124.855	110.39	216.487	188.38	347.412	307.50
126.956	112.16	218.408	190.07	350.173	309.96
129.011	113.95	220.365	191.82	352.935	312.58
131.018	115.50	222.250	193.70	355.849	315.20
133.026	117.12	224.064	195.34	358.457	317.71
135.033	118.60	226.732	197.52	361.218	320.33
136.994	120.14	229.578	199.77	363.980	323.17
138.955	121.84	232.559	202.63	366.587	325.79
140.869	123.73	235.594	205.29	369.349	328.08
142.783	125.45	238.768	207.95	372.110	330.75
144.698	127.02	241.756	210.58	374.871	333.10
146.705	128.82	244.744	212.99	377.490	335.94
148.666	130.53	247.732	215.37	380.087	338.83
150.674	132.25	250.767	218.10	382.848	341.72
152.728	133.85	253.755	220.62	385.609	344.62
154.829	135.87	256.743	223.00	388.831	347.29
156.876	137.96	259.760	225.81	391.438	350.03
158.937	139.53	262.766	228.18	394.353	352.91
160.945	141.56	265.754	230.91	396.807	355.28
162.952	143.50	268.602	233.50	399.262	357.83
164.955	144.99	271.683	236.23		

of the compound was stable over the temperature range between T = 78 K and T = 400 K; that is, no phase change, association, nor thermal decomposition occurred. The 137 experimental points in the temperature region between T = 78 K and T = 400 K were fitted by means of the least-squares method, and a polynomial equation of the experimental molar heat capacities ($C_{p,m}$) vs reduced temperature (X), $X = f(T) = [T/\mathrm{K} - 1/2(T_1 + T_2)]/[1/2(T_1 - T_2)]$ (where T_1 = 400 K and T_2 = 78 K) has been obtained. The experimental molar heat capacities in the temperature range of (78 to 400) K were fitted to

$$C_{p,m}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 207.960 + 140.701X + 5.922X^2 + 3.253X^3 + 1.338X^4 \quad (1)$$

in which $X = (T/\mathrm{K} - 239)/161$. The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation were within ± 0.3 % except for several points around the lower and upper temperature limits. The coefficient of determination for the fitting R^2 equals 0.99995. The uncertainties of the coefficients of the equation have been determined to be 0.07 %, 0.5 %, 0.45 %, 0.66 %, and 1.3 %, respectively.

Table 3. Thermodynamic Functions of L-3-(3,4-Dihydroxyphenyl) Alanine ($C_9H_{11}NO_4$) (M = 197.19 g·mol^{-1})

T/K	$C_{p,m}$ (J·K^{-1}·mol^{-1})	$(H_T - H_{298.15K})$ (kJ·mol^{-1})	$(S_T - S_{298.15K})$ (J·K^{-1}·mol^{-1})	$(G_T - G_{298.15K})$ (kJ·mol^{-1})
80	72.92	−36.1	−192	−20.8
85	77.07	−35.7	−187	−19.8
90	81.22	−35.3	−182	−18.9
95	85.38	−34.9	−178	−18.0
100	89.55	−34.5	−173	−17.1
105	93.72	−34.0	−169	−16.3
110	97.91	−33.5	−165	−15.4
115	102.1	−33.0	−160	−14.6
120	106.3	−32.5	−156	−13.8
125	110.5	−32.0	−151	−13.1
130	114.7	−31.4	−147	−12.3
135	118.9	−30.8	−142	−11.6
140	123.1	−30.2	−138	−10.9
145	127.3	−29.6	−134	−10.2
150	131.6	−28.9	−129	−9.57
155	135.8	−28.3	−125	−8.93
160	140.0	−27.6	−120	−8.32
165	144.3	−26.9	−116	−7.73
170	148.5	−26.1	−112	−7.16
175	152.8	−25.4	−107	−6.61
180	157.0	−24.6	−103	−6.08
185	161.3	−23.8	−98.6	−5.58
190	165.6	−23.0	−94.2	−5.10
195	169.9	−22.2	−89.9	−4.63
200	174.2	−21.3	−85.5	−4.20
205	178.5	−20.4	−81.2	−3.78
210	182.8	−19.5	−76.8	−3.38
215	187.1	−18.6	−72.5	−3.01
220	191.4	−17.6	−68.1	−2.66
225	195.8	−16.7	−63.8	−2.33
230	200.1	−15.7	−59.4	−2.02
235	204.5	−14.7	−55.1	−1.73
240	208.8	−13.6	−50.7	−1.47
245	213.2	−12.6	−46.4	−1.23
250	217.6	−11.5	−42.0	−1.01
255	222.0	−10.4	−37.7	−0.808
260	226.4	−9.29	−33.3	−0.631
265	230.9	−8.14	−28.9	−0.476
270	235.3	−6.98	−24.6	−0.343
275	239.8	−5.79	−20.2	−0.232
280	244.2	−4.58	−15.9	−0.142
285	248.7	−3.35	−11.5	−0.074
290	253.2	−2.09	−7.12	−0.028
295	257.8	−0.82	−2.75	−0.004
298.15	260.6	0	0	0
300	262.3	0.48	1.62	−0.002
305	266.9	1.81	5.99	−0.021
310	271.5	3.15	10.4	−0.062
315	276.1	4.52	14.8	−0.125
320	280.8	5.91	19.1	−0.210
325	285.4	7.33	23.5	−0.317
330	290.1	8.77	27.9	−0.445
335	294.8	10.2	32.3	−0.595
340	299.6	11.7	36.7	−0.767
345	304.3	13.2	41.1	−0.961
350	309.2	14.8	45.5	−1.18
355	314.0	16.3	50.0	−1.42
360	318.9	17.9	54.4	−1.68
365	323.8	19.5	58.8	−1.96
370	328.7	21.1	63.2	−2.26
375	333.7	22.8	67.7	−2.59
380	338.7	24.5	72.1	−2.94
385	343.8	26.2	76.6	−3.31
390	348.9	27.9	81.1	−3.70
395	354.0	29.7	85.5	−4.12
400	359.1	31.5	90.0	−4.56

Thermodynamic Functions of the Compound. The smoothed molar heat capacities and thermodynamic functions were calculated based on the fitted polynomial of the heat capacities as a function of the reduced temperature (X) according to the following thermodynamic equations

$$(H_T - H_{298.15}) = \int_{298.15}^{T} C_p \mathrm{d}T \qquad (2)$$

$$(S_T - S_{298.15}) = \int_{298.15}^{T} C_p \cdot T^{-1} \mathrm{d}T \qquad (3)$$

$$(G_T - G_{298.15}) = \int_{298.15}^{T} C_p \mathrm{d}T - T \cdot \int_{298.15}^{T} C_p \cdot T^{-1} \mathrm{d}T \qquad (4)$$

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K were tabulated in Table 3 at 5 K intervals. The uncertainties of $(H_T - H_{298.15})$, $(S_T - S_{298.15})$, and $(G_T - G_{298.15})$ were evaluated to be ± 0.45 %, ± 0.48 %, and ± 0.53 %, respectively, mainly accounting uncertainties of the temperature, experimental heat capacities, and relative deviations of the experimental heat capacities from the smoothed values.

Constant-Volume Energy of Combustion and Standard Molar Enthalpy of Combustion of the Compound. The method for determining the constant-volume energy of combustion of the sample was the same as that used in the calibration of the combustion calorimeter with benzoic acid. The constant-volume energy of combustion of the sample can be calculated according to the formula in refs 6 to 8.

$$\Delta_c U = \left(\frac{\epsilon_{\mathrm{calor}} \cdot \Delta T - Q_{\mathrm{Ni}} - Q_{\mathrm{HNO_3}}}{W} \right) \qquad (5)$$

The measured result of the constant-volume energy, $\Delta_c U/(\mathrm{J \cdot g^{-1}})$, of combustion of the sample was indicated in Table 4. At T = 298.15 K, the differential quotient of the constant-volume energy of combustion with the oxygen pressure, $(\partial U/\partial P)_T$, is $-0.21\ \mathrm{J \cdot g^{-1} \cdot MPa^{-1}}$.[6] Considering that the pressure in the oxygen bomb in the combustion of the sample was corrected from (3.01 to 0.1) MPa (standard pressure), $\Delta P \approx -2.91$ MPa, the change of the constant-volume energy of combustion of the sample $\Delta(\Delta_C U)$ was calculated to $0.61\ \mathrm{J \cdot g^{-1}}$. Therefore, the real constant-volume energy of combustion of the compound was corrected to $\Delta_c U = -(21184.1 \pm 35.0)\ \mathrm{J \cdot g^{-1}} + 0.61\ \mathrm{J \cdot g^{-1}} = -(21183.5 \pm 35.0)\ \mathrm{J \cdot g^{-1}}$.

The total uncertainty of the mean value of $\Delta_c U/\mathrm{J \cdot g^{-1}}$ has been estimated to be within ± 0.3 %, mainly accounting the uncertainties of the energy equivalent, temperature rise, Q_{HNO3}, Q_{Ni}, and correction of the standard-state value during the combustion of the sample, and so on.

The standard molar enthalpy of combustion of the sample $(\Delta_c H^\circ_m)$ referred to the enthalpy change of the following reaction at 298.15 K and 100 kPa

$$C_9H_{11}NO_4(s) + \frac{39}{4}O_2(g) = 9CO_2(g) + \frac{11}{2}H_2O(l) + \frac{1}{2}N_2(g) \qquad (6)$$

The standard molar enthalpy of combustion of the sample can be derived from the constant-volume energy of combustion by eqs 7 and 8

$$\Delta_c H^o_m = \Delta_c U^o_m + \Delta n \cdot RT \qquad (7)$$

$$\Delta n = \sum n_i(\text{products, g}) - \sum n_i(\text{reactants, g}) \qquad (8)$$

where Σn_i was the total amount (in moles) of the gases present as products or as reactants. The calculated standard molar enthalpy of combustion of the sample was calculated to be as follows

$$\Delta_c U = -(21183.5 \pm 35.0)\ \mathrm{J \cdot g^{-1}} \cdot 197.19\ \mathrm{g \cdot mol^{-1}} \cdot 0.001 = -(4177.2 \pm 6.9)\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_c H^o_m = \Delta_c U + \Delta n \cdot RT = -(4177.2 \pm 6.9) + (-0.25) \cdot 8.314 \cdot 298.15 \cdot 10^{-3} = -(4177.8 \pm 6.9)\ \mathrm{kJ \cdot mol^{-1}}$$

Standard Molar Enthalpy of Formation of the Compound. A reaction scheme used to determine the standard molar enthalpy of formation of L-3-(3,4-dihydroxyphenyl) alanine ($C_9H_{11}NO_4$) was shown in Table 5. It was calculated by a designed Hess thermochemical cycle according to the reaction (6) as follows

$$\begin{aligned} \Delta H_4 = {} & \Delta_f H^o_m(C_9H_{11}NO_4,\ s) \\ & = 9\Delta_f H^o_m(CO_2,\ g) + \frac{11}{2}\Delta_f H^o_m(H_2O,\ l) - \Delta_c H^o_m (C_9H_{11}NO_4,\ s) \\ & = 9\Delta H_2 + \frac{11}{2}\Delta H_3 - \Delta H_1 \end{aligned} \qquad (9)$$

In eq 9, the standard molar enthalpies of formation of $CO_2(g)$ and $H_2O(l)$, recommended by *CODATA*,[10,11] $\Delta_f H^\circ_m(CO_2,\ g) =$

Table 4. Experimental Results of the Constant-Volume Energy of Combustion for L-3-(3,4-Dihydroxyphenyl) Alanine ($C_9H_{11}NO_4$) at 298.15 K and 0.1 MPa

no.	mass of sample W/g	corrected heat of ignition wire Q_{Ni}/J	corrected heat of nitric acid Q_{HNO3}/J	corrected temperature rise $\Delta_c T$/K	combustion energy of sample $-\Delta_c U/(\mathrm{J \cdot g^{-1}})$
1	0.51690	44.225	25.964	0.7565	21341.1
2	0.53425	41.435	30.637	0.7749	21149.9
3	0.53251	43.932	28.56	0.7718	21132.8
4	0.50969	44.811	28.041	0.7436	21266.4
5	0.55463	44.518	31.156	0.7991	21006.6
6	0.52364	43.637	29.124	0.7601	21162.4
7	0.51469	42.768	28.755	0.7491	21219.2
8	0.54773	44.246	30.908	0.7962	21194.4
mean: $\Delta_c U = -(21184.1 \pm 35.0)\ \mathrm{J \cdot g^{-1}}$					

Table 5. Reaction Scheme Used to Determine the Standard Molar Enthalpy of Formation of L-3-(3,4-Dihydroxyphenyl) Alanine ($C_9H_{11}NO_4$)

no.	reactions	$\Delta_f H^\circ_m$ or $(\Delta_c H^\circ_m = \pm \sigma_a)^a/(\mathrm{kJ \cdot mol^{-1}})$
1	$C_9H_{11}NO_4(s) + 39/4O_2(g) = 9CO_2(g) + 11/2H_2O(1) + 1/2N_2(g)$	$-(4177.8 \pm 6.9)$, ΔH_1
2	$O_2(g) + C(s) = CO_2(g)$	$-(393.51 \pm 0.13)$, ΔH_2
3	$H_2(g) + 1/2O_2(g) = H_2O(l)$	$-(285.83 \pm 0.04)$, ΔH_3
4	$9C(s) + 11/2H_2(g) + 2O_2(g) + 1/2\ N_2(g) = C_9H_{11}NO_4(s)$	$-(935.9 \pm 7.0)$, ΔH_4

[a] $\sigma_a = \sigma / \sqrt{n} = \sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2/(n-1)} \Big/ \sqrt{n} = \sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2/n(n-1)}$, in which n is the experimental number; x_i is a single value obtained from a series of measurements; and $\bar{x}$ is the mean value of the results.

$-(393.51 \pm 0.13)$ kJ·mol^{-1} and $\Delta_f H°_m(H_2O, l) = -(285.83 \pm 0.04)$ kJ·mol^{-1}, were employed in the calculation of $\Delta_f H°_m[C_9H_{11}NO_4, s]$. At last, the standard molar enthalpy of formation of the compound can be derived to be $\Delta_f H°_m(C_9H_{11}NO_4, s) = -(935.9 \pm 7.0)$ kJ·mol^{-1}.

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