STANDARD ENTHALPY OF FORMATION OF 3,4,5-TRIMETHOXYBENZOIC ACID

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Abstract

The energy of combustion of crystalline 3,4,5-trimethoxybenzoic acid in oxygen at T=298.15 K was determined to be –4795.9±1.3 kJ mol^{-1} using combustion calorimetry. The derived standard molar enthalpies of formation of 3,4,5-trimethoxybenzoic acid in crystalline and gaseous states at T=298.15 K, $\Delta_f H_m^{\ominus}$ (*cr*) and $\Delta_f H_m^{\ominus}$ (*g*), were –852.9±1.9 and –721.7±2.0 kJ mol^{-1}, respectively. The reliability of the results obtained was commented upon and compared with literature values.

Keywords: combustion calorimetry, standard enthalpy of formation, 3, 4,5-trimethoxybenzoic acid

Introduction

3,4,5-Trimethoxybenzoic acid (molecular structure: Fig. 1; formula: $C_{10}H_{12}O_5$; CAS registry number: 118-41-2; molecular mass: 212.20) is an important raw material and intermediate widely used in the synthesis of pharmaceuticals and agrochemicals. Several drugs in the family of 3,4,5-trimethoxybenzoic acid derivatives have considerable commercial importance. Russell have identified that it was one of the compo-
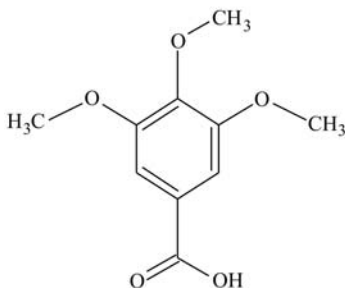

Fig. 1 Molecular structure of 3,4,5-trimethoxybenzoic acid

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nents responsible for the exceptionally high antibacterial activity of manuka (*Leptospermum scoparium*) honey [1].

Knowledge of the thermochemical properties of pharmaceuticals is useful if quantitative studies on the energetics of biochemical reactions are to be performed and for quantum chemistry, computer-aided molecular designs of drugs and new materials, working out technological processes of synthesis and purification [2, 3]. The thermochemistry of substituted benzoic acid has been of interest to many researchers for a long time, and many substituted benzoic acids have been investigated by theoretical estimation and experimental determination. The thermodynamic properties of methoxy-substituted benzoic acids, particularly monomethoxybenzoic acid [4], dimethoxybenzoic acid [5–7], and trimethoxybenzoic acid [8], have been studied, respectively. The effect of steric hindrance and intramolecular interaction (called the buttressing effect) of the groups COOH and OCH_3 in methoxy-substituted benzoic acid has been discussed [8, 9].

In the present work, the energy of combustion of 3,4,5-trimethoxybenzoic acid at T=298.15 K was determined by a rotating-bomb combustion calorimeter, and the standard molar enthalpies of formation of 3,4,5-trimethoxybenzoic acid in crystalline and gaseous states at T=298.15 K were derived. The values were in a good agreement with their quantities in literatue and their difference was discussed.

Experimental

Materials

3,4,5-Trimethoxybenzoic acid (white crystalline powder) was supplied by Tianxin Pharm. Chem. Co., Zhushan, Hubei Province, P. R. China and dried in a desiccator with P_4O_{10} at room temperature. The purity of 3,4,5-trimethoxybenzoic acid (mass fraction>0.999) was confirmed by HPLC measurement, as well as by the combustion carbon dioxide recovery ratios. The FT-IR and ^{1}H NMR spectrums of the sample showed no impurities in the sample. In the present calorimetric case, the mass of the sample was accurately weighed using a microbalance (Sartorius, ME215S) with a resolution of 0.01 mg.

Combustion calorimetry

The energy of combustion of 3,4,5-trimethoxybenzoic acid were determined with a RBC-II type rotating-bomb combustion calorimeter constructed in the Department of Chemistry, Northwest University, Xi'an 710069, P. R. China. The calorimeter mainly consisted of a water thermostat, a caloritube, a temperature gauge and an integrated circuit for temperature measurement and indication. More comprehensive descriptions about the calorimeter can be found in elsewhere [10–12].

The basic experimental procedure was previously described in detail [10–12]. The temperature of the water thermostat was maintained at T=298.15±0.0005 K. The water temperature in the caloritube was subsequently adjusted to lower than that of

the water thermostat, and the temperature difference between the water in the caloritube and the water thermostat was equal to half of the temperature increment of the calorimeter during the combustion reaction. A known amount of double-distilled water was added into the caloritube. When the sample was placed in the crucible fixed on the support in the rotating-bomb, the Ni–Cr wire was fixed in the bomb and the initial bomb-solution was then injected into the rotating-bomb. After the bomb was filled with 2.5 MPa oxygen gas, it was sealed. Before the calorimetric test, the calorimeter was set up well. It was important to keep up a constant temperature change rate in the calorimeter at the beginning of the experiment. In the early period of the experiment, the magnitudes of the temperature were recorded *vs*. time typically with one entry every 30 s until the eleventh one. From the eleventh one, the sample was ignited and the magnitudes of the temperature were recorded every 60 s till the main period of the combustion reaction was finished. In the later period of the experiment, the magnitudes of the temperature were recorded as in the early period of the experiment. After the experiment was accomplished, the final products of the combustion reaction were analyzed.

Analysis of final products in the oxygen-bomb

The gases formed in the combustion reaction were collected in a gas collecting bag. The amounts of gas were measured by a gas meter, which was joined between the bag and the apparatus for gas analysis. The apparatus for gas analysis had four absorption pipes connected with each other. The first one was filled with P_4O_{10} and $CaCl_2$ (anhydrous) to sink up the water vapour in gases, the second one was filled with active MnO_2 in order to absorb the nitrogen oxides, the third one was filled with alkali asbestos to absorb the CO_2 which is for determination, and the fourth one was also filled with P_4O_{10} and $CaCl_2$ (anhydrous) to absorb the water formed in the process of determination.

The gaseous CO_2 formed in the combustion reaction was absorbed by the pipe with alkali asbestos. The amount of CO_2 was determined through the mass increment of the pipe after sinking up carbon dioxide. The amount of CO_2 dissolved in the final acidic solution was ignored.

Azo dyes were formed when NO_2 was absorbed by the absorption solution in the first flask. NO was oxided into NO_2 when it passed through an oxide pipe. The formed NO_2 was absorbed by the absorption solution in the second flask. The amount of NO and NO_2 were obtained by determination the absorbance at a wavelength between 540 and 545 nm (Saltzman calorimetric analysis method).

The fitting and internal wall of the bomb were washed with double-distilled water, and the final solution (including the washing solution) was transferred into a cone bottle, and then heated to boiling to remove CO_2. After neutralization, the solution was cooled to room temperature in a volumetric flask. The amount of NO_3^- in the final solution in the bomb was determined by using Devarda's alloy method.

The analytical results of the final solution showed that the combustion reactions were complete. Neither carbon deposits or carbon monoxide was formed during the combustion reactions. The amount of NO_x in the final gas was insignificant.

Energy equivalent

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

$$W = \frac{Qa + Gb + 5.983c}{\Delta T} \qquad (1)$$

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

The corrected value of the heat exchange is calculated by the following equation

$$\Delta(\Delta T) = nr_f + \frac{r_a - r_f}{T_a - T_f}\left(\frac{T_0 + T_a}{2} + \sum_{i=1}^{n-1} T_i - n\overline{T}_f\right) \qquad (2)$$

where $\Delta(\Delta T)$ denotes the corrected value of the heat exchange, n is the number of reading for the main (or reaction) period, r_f and r_a are the temperature change rate at the fore and after periods, respectively (r is positive when temperature decreased), $\overline{T}_f$ and $\overline{T}_a$ are the average temperature of the calorimeter at the fore and after periods, respectively, T_0 is the last value of the temperature of fore period, T_a is the first reading of the after period, $\sum_{i=1}^{n-1} T_i$ is the sum of all values of the temperature of main period, except for the last one of the main period, and $(r_a - r_f)/(T_a - T_f)$ must be constant.

The energy equivalent and the uncertainty of the rotating-bomb combustion calorimeter were calibrated by the combustion of benzoic acid (Standard Reference Material 39i, the National Institute of Standards and Technology) [13]. The energy equivalent was determined to be 18001 ± 8 J K^{-1}, where the uncertainty quoted is the standard deviation of the mean value. The uncertainty of the calorimeter was determined to be within $\pm 0.05\%$.

Results

The standard atomic masses recommended by the IUPAC Commission in 2001 [14] were used in the calculation of all molar quantities.

The energy of combustion of crystalline 3,4,5-trimethoxybenzoic acid at $T = 298.15$ K, $\Delta_c U_m^{\ominus}$ (cr), determined by the rotating-bomb combustion calorimeter was -4795.9 ± 1.3 kJ mol^{-1}. The detailed results of combustion calorimetric experiment were summarized in Table 1.

The standard molar enthalpy of combustion of crystalline 3,4,5-trimethoxy-benzoic acid at T=298.15 K, $\Delta_c H_m^\ominus$ (cr), refers to the enthalpy of combustion reaction of the following ideal combustion reaction at T=298.15 K and P=101.325 kPa.

$$C_{10}H_{12}O_5 \ (cr) + 21/2 O_2 \ (g) = 10 CO_2 \ (g) + 6 H_2O \ (l) \tag{3}$$

The standard molar enthalpy of combustion of crystalline 3,4,5-trimethoxy-benzoic acid at T=298.15 K was calculated from the experimental energy of combustion at T=298.15 K by Eq. (4):

$$\Delta_c H_m^\ominus \ (cr) = \Delta_c U_m^\ominus \ (cr) + \Delta nRT \tag{4}$$

where n is the total amount (in mol) of gas present as products or reactants, R=8.314510 J mol^{-1} K^{-1} [15], T=298.15 K.

Table 1 Heat of combustion of 3,4,5-trimethoxybenzoic acid in oxygen at T=298.15 K[a]

No.	m/g	Q_c/J	Q_N/J	ΔT/K	$\Delta_c U_m^\ominus(cr)$/ kJ mol^{-1}
1	1.01292	11.70	34.62	1.2757	−4801.00
2	1.00325	12.60	34.29	1.2622	−4795.75
3	1.00153	12.60	34.23	1.2597	−4794.47
4	1.02360	10.80	35.07	1.2870	−4793.17
5	1.05257	12.60	36.06	1.3250	−4798.58
6	1.01280	12.60	34.70	1.2734	−4792.69
Mean					−4795.9±1.3

[a] m: mass of sample; Q_c– heat of combustion of igniting wire; Q_N– heat of formation and solution of nitric acid; T– temperature increment; $\Delta_c U_m^\ominus$ (cr)– energy of combustion of crystalline 3,4,5-trimethoxybenzoic acid; the uncertainty quoted for $\Delta_c U_m^\ominus$ (cr) corresponds to the standard deviation of six independent experiments

The standard molar enthalpy of formation of crystalline 3,4,5-trimethoxybenzoic acid at T=298.15 K, $\Delta_f H_m^\ominus$ (cr), was derived by Hess's law according to the following thermochemical equation:

$$\Delta_f H_m^\ominus \ (cr) = [10\Delta_f H_m^\ominus(CO_2, g) + 6\Delta_f H_m^\ominus(H_2O, l)] - \Delta_c H_m^\ominus \ (cr) \tag{5}$$

where $\Delta_f H_m^\ominus$ $(CO_2, \ g) = -393.51 \pm 0.13$, $\Delta_f H_m^\ominus$ $(H_2O, \ l) = -285.83 \pm 0.042$ kJ mol^{-1} [16, 17]. The standard molar enthalpy of combustion and formation of crystalline 3,4,5-trimethoxybenzoic acid at T=298.15 K were derived: $\Delta_c H_m^\ominus$ $(cr) = -4797.2 \pm 1.3$ kJ mol^{-1} and $\Delta_f H_m^\ominus$ $(cr) = -852.9 \pm 1.9$ kJ mol^{-1}, respectively.

The uncertainty for $\Delta_f H_m^\ominus$ (cr) of 3,4,5-trimethoxybenzoic acid was calculated as follows:

$$
\begin{aligned}
s[\Delta_f H_m^\ominus \ (cr)] &= \\
&= \{[10s\Delta_f H_m^\ominus(CO_2, g)]^2 + [6s\Delta_f H_m^\ominus(H_2O, l)]^2 + [s\Delta_c H_m^\ominus(cr)]^2\}^{1/2}
\end{aligned} \tag{6}
$$

where $s\Delta_f H_m^{\ominus}$ (CO_2, g) represents the uncertainty of the enthalpy of formation of gaseous CO_2, $s\Delta_f H_m^{\ominus}$ (H_2O, l) represents the uncertainty of the enthalpy of formation of liquid H_2O, and $s\Delta_c H_m^{\ominus}$ (cr) represents the uncertainty of the enthalpy of combustion of crystalline 3,4,5-trimethoxybenzoic acid.

The molar enthalpy of sublimation of 3,4,5-trimethoxybenzoic acid at $\langle T_m \rangle$=363.17 K, $\Delta_{sub} H_m^{\ominus}$(363.17 K), was determined to be 127.9±0.8 kJ mol^{-1} by Roux using Knudsen-effusion method, where $\langle T_m \rangle$ was the mean temperature of its experimental range. The molar enthalpy of sublimation of 3,4,5-trimethoxybenzoic acid at T=298.15 K, $\Delta_{sub} H_m^{\ominus}$(298.15 K), was calculated to be 131.2±0.8 kJ mol^{-1} [8].

Table 2 Heat of combustion, standard molar enthalpies of combustion and formation of 3,4,5-trimethoxybenzoic acid at T=298.15 K [b]

Property	Unit	Reference [6]	This work
$\Delta_c U_m^{\ominus}$ (cr)	kJ mol^{-1}	−4793.8±2.9	−4795.9±1.3
$\Delta_c H_m^{\ominus}$ (cr)	kJ mol^{-1}	−4795.1±2.9	−4797.2±1.3
$\Delta_f H_m^{\ominus}$ (cr)	kJ mol^{-1}	−855.0±3.2	−852.9±1.9
$\Delta_f H_m^{\ominus}$ (g)	kJ mol^{-1}	−723.8±3.3	−721.7±2.0

[b]$\Delta_c U_m^{\ominus}$(cr) is the energy of combustion of crystalline 3,4,5-trimethoxybenzoic acid, $\Delta_c H_m^{\theta}$(cr) is the standard molar enthalpy of combustion of crystalline 3,4,5-trimethoxybenzoic acid, $\Delta_f H_m^{q}$(cr) and $\Delta_f H_m^{\ominus}$ (g) are the standard molar enthalpies of formation of 3,4,5-trimethoxybenzoic acid in crystalline and gaseous states, respectively. The uncertainties assigned to the values of $\Delta_c U_m^{\ominus}$(cr), $\Delta_c H_m^{\ominus}$(cr), $\Delta_f H_m^{\ominus}$ (cr) and $\Delta_f H_m^{\ominus}$ (g) correspond to the standard deviations, respectively

From the above experimental and estimated results, the standard molar enthalpy of formation of 3,4,5-trimethoxybenzoic acid in gaseous state at T=298.15 K was derived to be −721.7±2.0 kJ mol^{-1}. The results of our experiment and the values in [8], including the energy of combustion, the enthalpy of combustion, and the standard enthalpies of formation in crystalline and gaseous states of 3,4,5-trimethoxybenzoic acid at T=298.15 K, were tabulated in Table 2 for comparison.

Discussion

The standard molar enthalpy of formation of 3,4,5-trimethoxybenzoic acid at T=298.15 K was recently determined by Roux [8]. The small difference of 2 kJ mol^{-1} between the only available literature value, $\Delta_f H_m^{\ominus}$ (cr)=−855.0±3.2 kJ mol^{-1}, and our experimental result, $\Delta_f H_m^{\ominus}$ (cr)=−852.9±1.9 kJ mol^{-1}, suggests that the values determined by us are in good agreement with those obtained by Roux. The experimental conditions used by Roux for the combustion of 3,4,5-trimethoxybenzoic acid were: a static mode of combustion, and using vaseline as auxiliary material of combustion, which seems to be efficient for the combustion of 3,4,5-trimethoxybenzoic acid. But in our experiment, we used a rotating-bomb calorimeter without any auxiliary to promote complete combustion. The energy of combustion obtained by the rotating-bomb combustion calorimeter was greater than that obtained by a static-bomb combustion calorimeter.

Conclusions

The energy of combustion of 3,4,5-trimethoxybenzoic acid at T=298.15 K was determined by a rotating-bomb combustion calorimeter. The derived standard molar enthalpies of formation of 3,4,5-trimethoxybenzoic acid in crystalline and gaseous states at T=298.15 K were in good agreement with literature values.

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