Journal of Thermal Analysis and Calorimetry, Vol. 57 (1999) 867-874

MICRO-COMBUSTION CALORIMETRY AIMING AT 1 mg SAMPLES[*]

Yatsuhisa Nagano[**] *and Takehiko Sugimoto*

Microcalorimetry Research Center, Faculty of Science, Osaka University, Toyonaka
560-0043, Japan

Abstract

A micro-combustion calorimeter was developed. The small energy equivalent (ca. 68 J K^{-1}) of this calorimeter makes it possible to measure combustion energies of very small samples. The energy equivalent was determined by burning 2 mg of benzoic acid. The standard deviation of the mean energy equivalent was reduced to 0.014% in 5 experiments. The standard massic energy of combustion of salicylic acid and the standard deviation of the mean were determined to be -21871 ± 5 J g^{-1}, which agrees well with the literature values. The standard molar enthalpy of formation of salicylic acid was derived as -591.2 ± 1.7 kJ mol^{-1}.

Keywords: micro-combustion calorimetry, standard enthalpy of formation of salicylic acid

Introduction

The standard enthalpies of formation of many organic compounds have been determined by oxygen combustion calorimetry. These thermodynamic quantities have contributed to the progress in quantum chemistry and have provided the numerical basis of the recent computer-aided molecular designs of drugs and new materials. However, conventional combustion calorimeters consume huge amounts of samples. For example, typically, 1 g of an organic compound is burned in one experiment. The experiment is repeated 5–6 times at least, to reduce the statistical error in the combustion energy. Moreover, combustion calorimetry requires highly purified samples in order to obtain reliable thermodynamic quantities. In modern chemistry, new compounds are rarely synthesized on a macroscale for research work. It has therefore become urgent to miniaturize the combustion calorimeter.

The energy equivalent of the isoperibol calorimeter has to be reduced in proportion to the mass of the samples, in order to miniaturize the calorimeter with maintenance of the precision of the calorimeter. So far, several groups have reduced the energy equivalent to ca. 1/10 of that of the conventional calorimeter [1–3]. Another type of microcalorimeter was developed in Marseille [4, 5]. However, as compared

---

[*] Contribution No. 157 from the Microcalorimetry Research Center.

[**] Author to whom correspondence should be addressed.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

with other modern analytical techniques, such miniaturization is not yet good enough: 10–20 mg of sample is burned in each experiment. In the present study, we have developed an isoperibol micro-combustion calorimeter with a very small energy equivalent, which allows measurement of the combustion energy of even 1 mg of organic compounds.

Equipment and operation

Figure 1 shows a cross-sectional view of micro-combustion bomb. The main part of the bomb is made of stainless steel. A pellet of 1–2 mg of a sample is loaded into a platinum boat measuring 2 mm×6 mm. A small amount of vaseline is pasted onto the pellet to guarantee ignition. The pellet is tied to the boat by a platinum wire 0.05 mm in diameter. The boat is loaded into a platinum cylinder 8 mm in length, 4 mm in diameter and 0.03 mm in thickness. The platinum wire is wound to two platinum electrodes in a bomb for ignition. In this arrangement, the combustion flame is caged in the cylinder. This promotes complete combustion of the small sample and avoids direct heating of the ceiling of the bomb by the flame. The upper part of the bomb is composed of 3-fold caps of stainless steel and copper. The interior is platinum-lined in order to prevent corrosion. The bomb is filled with 3.0 MPa oxygen gas. Water is dropped into the bomb in a quantity of 0.01 ml to provide humidity saturation.

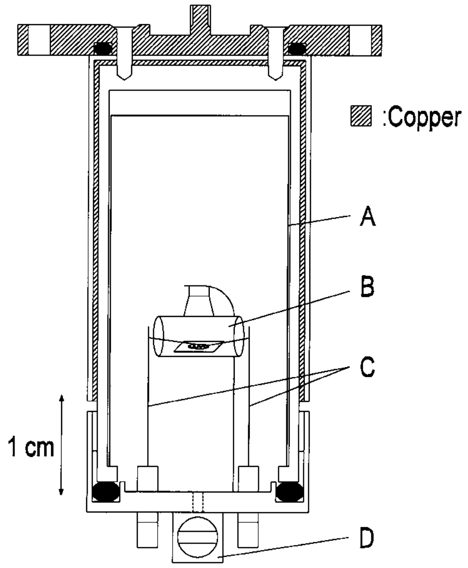

Fig. 1 A cross-sectional view of the micro-combustion bomb; A – platinum liner; B – platinum cylinder; C – electrodes; D – valve

Figure 2 shows a cross-sectional view of the calorimeter. The bomb is inserted in the bomb holder of the calorimeter. The bomb holder is made of gold-plated copper and is fixed to the bottom of the calorimeter with 4 thin stainless-steel tubes 0.88 mm in diameter and 10 mm in length. The air in the holder is sealed by the flange attached to the top of the bomb to promote thermal contact between the bomb and the holder, while the calorimeter vessel is evacuated to high vacuum to reduce the cooling constant. The cooling constant therefore depends on the heat flow through the stainless-steel tubes and radiation. A thermistor of 10 kΩ at 25°C is . The resistance of the thermistor is measured by a Wheatstone bridge (Yokokawa Electric Works 2768) fixed at an appropriate dial setting and a nanovoltmeter (Hewlett Packard 34420A). The digital data of the off-balance voltage are fed into a computer every 2 s. The energy equivalent of the calorimeter is composed of the heat capacities of the bomb and the holder. The calorimeter is set in a water bath. The temperature of the bath is controlled at (25.262±0.001)°C by a precision temperature controller (Tronac, PTC-41).

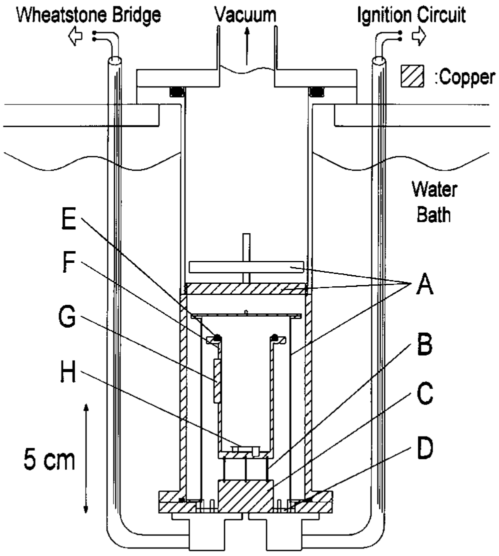

Fig. 2 A cross-sectional view of the calorimeter. The micro-bomb is fixed in the bomb holder (F). A – radiation shields; B – stainless steel tubes; C – thermal anchor; D – hermetic seals; E – O-ring; G – thermistor housing; H – terminals

A typical temperature variation in a combustion experiment is shown in Fig. 3. The measurement is started at 24°C. The temperature curve is divided into the initial, reaction and final periods. The curves in the initial and final periods, 0–1800 and 4000–6600 s, respectively, are perfectly fitted by the equation

$$T = T_c - \frac{1}{\left(\frac{1}{T_c - T_o} + \frac{k_r}{k_c}\right)\exp(k_c t) - \frac{k_r}{k_c}}$$

which is derived from an approximate equation,

$$\frac{\mathrm{d}T}{\mathrm{d}t} = k_c(T_c - T) + k_r(T_c - T)^2$$

where k_c is an apparent cooling constant due to conduction, k_r is an approximate cooling constant due to radiation and T_0 is the temperature at t=0. The heat flow in the reaction period is exactly evaluated by this equation. Typically, k_c and k_r are 0.054 ks^{-1} and 0.002 ks^{-1} K^{-1}, respectively.

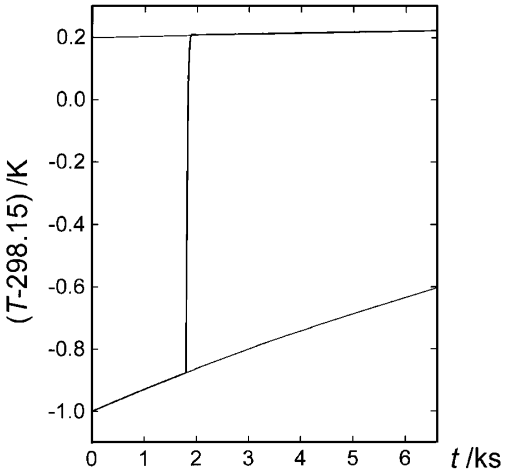

Fig. 3 A typical temperature variation in an experiment. 2.2 mg of benzoic acid and 0.3 mg of vaseline were burned. The initial and final periods are fitted by the curves of the function given in the text

Calibration experiments

The energy equivalent was determined by burning the thermochemical standard benzoic acid (NIST SRM 39i). The details of 5 calibration experiments are shown in Table 1. The mean and the standard deviation of the mean (*sdm*) are determined to be (67.895±0.010) J K^{-1}. The energy equivalent is 1/200 of that of the conventional calorimeter. The small energy equivalent provides a large temperature jump on the burning of a small sample.

Figure 4 shows the *sdm*s of the energy equivalents of several calorimeters as a function of the amount of benzoic acid burned in a calibration experiment. In the present case, the sample mass was weighed on an ultra-microbalance (Sartorius S4). The mass is read down to the digit of 0.1 μg. The present *sdm* is the best so far attained in micro-combustion calorimeters and is very close to the limiting line due to the uncertainty in the weighing.

Table 1 Results of calibrations with benzoic acid

Property	Unit	Experiment number				
		1	2	3	4	5
$m_{\text{benzoic acid}}$	mg	2.0701	1.9674	2.1661	2.2171	1.9104
m_{vaseline}	mg	0.3715	0.3766	0.3357	0.3233	0.4035
$n(\text{HNO}_3)$	μmol	0.0084	0.0092	0.0155	0.073	0.0047
ε^{i}	J K^{-1}	0.336	0.336	0.336	0.336	0.336
ε^{f}	J K^{-1}	0.340	0.340	0.340	0.340	0.340
T_{i}–273.15	K	24.124317	24.123558	24.124959	24.123404	24.123016
T_{f}–273.15	K	25.193405	25.160002	25.205744	25.213949	25.155645
ΔT_{c}	K	0.012850	0.016919	0.010219	0.009054	0.016884
ΔT_{ad}	K	1.056238	1.019525	1.070566	1.081491	1.015746
U_{ign}	J	0.185	0.191	0.258	0.261	0.191
$-\Delta_{\text{IBP}}U$	J	71.868	69.389	75.752	73.527	69.124
$\Delta U(\text{HNO}_3)$	J	0.000	0.001	0.001	0.000	0.000
ΔU_{Σ}	J	0.039	0.036	0.039	0.040	0.036
$-\Delta U$	J	71.829	69.352	72.712	73.487	69.088
ε^{o}	J K^{-1}	67.918	67.901	67.860	67.891	67.904

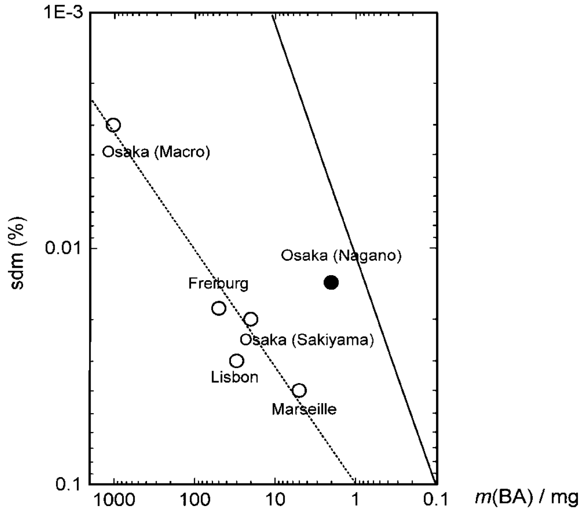

Fig. 4 Standard deviations of the mean (*sdm*) of the energy equivalents of several calorimeters as a function of the mass of benzoic acid (BA) burned in calibration experiments. The solid line is the uncertainty due to the weighing limit of the ultra-microbalance. The dashed line is drawn as an eye-guide indicating the past trend of the development

Combustion experiments

The combustion calorimetry of salicylic acid was carried out. Salicylic acid (Wako Pure Chemical) was recrystallized from distilled water. Vaseline was used as a combustion aid. The combustion energy of vaseline was also determined in this study. After the combustion experiments, nitric acid in the bomb solution was determined by UV spectrometry. Standard energies were derived by taking Washburn's correction into account.

Results and discussion

Tables 2 and 3 summarize the results of the combustion experiments on salicylic acid and vaseline, respectively. It is noteworthy that the *sdm* of the combustion energy of vaseline is as small as that of salicylic acid. Conventional combustion calorimetry has often suffered from the large scattering of the combustion energy data on vaseline. The present result suggests that the caging fire in the platinum cylinder works well to depress the scattering. The massic combustion energy of salicylic acid is compared with the literature values in Table 4. The present value agrees very well with the literature values. It is emphasized that only 5 experiments was sufficient to

Table 2 Results of combustion experiments on salicylic acid

Property	Unit	Experiment number				
		1	2	3	4	5
$m_{\mathrm{salicylic\ acid}}$	mg	2.2048	2.0452	1.7997	2.3747	2.4357
m_{vaseline}	mg	0.5069	0.5440	0.6528	0.4342	0.4048
$n(\mathrm{HNO_3})$	μmol	0.0264	0.0250	0.0076	0.0166	0.0192
ε^{i}	$\mathrm{J\,K^{-1}}$	0.337	0.337	0.337	0.337	0.337
ε^{f}	$\mathrm{J\,K^{-1}}$	0.340	0.340	0.340	0.340	0.340
T_{i}–273.15	K	24.124772	24.124731	24.123590	24.123839	24.122906
T_{f}–273.15	K	25.190787	25.167618	25.161409	25.193416	25.193047
ΔT_{c}	K	0.012801	0.015703	0.015868	0.011949	0.012491
ΔT_{ad}	K	1.053214	1.027184	1.021951	1.057628	1.057692
U_{ign}	J	0.196	0.191	0.187	0.163	0.174
$-\Delta_{\mathrm{IBN}}U$	J	71.677	69.906	69.552	72.002	71.993
$\Delta U(\mathrm{HNO_3})$	J	0.002	0.001	0.000	0.001	0.001
ΔU_{Σ}	J	0.039	0.038	0.034	0.041	0.042
$-\Delta U$	J	71.636	69.867	69.518	71.960	71.950
$-\Delta_{\mathrm{c}}u^{\mathrm{o}}(c)$	$\mathrm{J\,g^{-1}}$	21871	21877	21876	21861	21867
$-\Delta_{\mathrm{c}}U^{\mathrm{o}}(c)$	$\mathrm{kJ\,mol^{-1}}$	3020.9	3021.7	3021.6	3019.6	3020.3

Table 3 Results of combustion experiments on vaseline

Property	Unit	Experiment number			
		1	2	3	4
m_{vaseline}	mg	1.5726	1.5803	1.5081	1.5395
$n(\mathrm{HNO_3})$	μmol	0.0082	0.0048	0.0048	0.0068
ε^{i}	$\mathrm{J\ K^{-1}}$	0.336	0.336	0.336	0.336
ε^{f}	$\mathrm{J\ K^{-1}}$	0.341	0.341	0.341	0.341
T_{i}–273.15	K	24.122600	24.124786	24.121664	24.123839
T_{f}–273.15	K	25.200169	25.203975	25.159524	25.193416
ΔT_{c}	K	0.010481	0.009660	0.014762	0.011949
ΔT_{ad}	K	1.067087	1.072529	1.023098	1.045084
U_{ign}	J	0.225	0.192	0.190	0.193
$-\Delta_{\mathrm{IBP}}U$	J	72.585	72.989	69.618	71.115
$\Delta U(\mathrm{HNO_3})$	J	0.000	0.000	0.000	0.000
ΔU_{Σ}	J	0.014	0.014	0.014	0.014
$-\Delta U$	J	72.571	72.975	69.605	71.101
$-\Delta_{\mathrm{c}}u^{\mathrm{o}}(c)$	$\mathrm{J\ g^{-1}}$	46147	46178	46154	46185

Table 4 Standard energies of combustion of salicylic acid

$-\Delta_{\mathrm{c}}u^{\mathrm{o}}(c)$ and *sdm**/J $\mathrm{g^{-1}}$	Reference	Comment
21846±10	[6]	
21865±4	[7]	micro
21871±5	this work	micro
21880±4	[8]	
21881±4	[9]	
21882±4	[10]	
21886±10	[11]	
21887±5	[12]	
21892±4	[2]	micro
21895±4	[3]	micro

* standard deviation of mean

attain a *sdm* comparable to those in the literature. Finally, the molar standard enthalpy of formation of salicylic acid is derived as –591.2±1.7 kJ $\mathrm{mol^{-1}}$, where the uncertainty is twice the total *sdm*.

Conclusions

A micro-combustion calorimeter has been developed. The platinum cylinder in the microbomb promotes complete combustion of very small samples. The energy equivalent was successfully reduced to ca. 68. J K^{-1} (1/20–1/30 of those of earlier micro-calorimeters). The present calorimeter permits the determination of combustion energies with good accuracy, even with a total of less than 10 mg of sample.

References

1 M. Månsson, in Combustion Calorimetry, Pergamon Press, Oxford 1979, p. 388.
2 T. Kiyobayashi, Doctoral Thesis, Osaka University, 1995.
3 H. P. Diogo and M. E. Minas da Piedade, J. Chem. Thermodynamics, 27 (1995) 197.
4 E. Calvet, P. Chovin, H. Moureu and H. Tachoire, J. Chim. Phys., 57 (1960) 593.
5 R. Sabbah and M. Coten, Thermochim. Acta, 49 (1980) 307.
6 M. Milone and P. Rossignoli, Gazz. Chim. Ital., 62 (1932) 644.
7 R. Sabbah and T. H. D. Le, Can. J. Chem., 71 (1993) 1378.
8 R. D. Stieler and H. M. Huffman, J. Am. Chem. Soc., 57 (1935) 1734.
9 L. J. P. Keffler, J. C90 him. Phys., 28 (1931) 457.
10 M. Colomina, P. Jimenez, M. V. Roux and C. Turrion, J. Calorim. Anal. Therm., 11 (1980) 1.
11 M. Badoche, Bull. Soc. Chim. Fr., 4 (1937) 549.
12 M. Beckers, Bull. Soc. Chim. Belg., 40 (1931) 518.