Determination of Standard Molar Enthalpy of Formation for Crystalline endo-Tricyclo[5.2.1.0^{2,6}]decane by an Isoperibol Oxygen-Bomb Combustion Calorimeter

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The construction and principle of the new-established isoperibol oxygen-bomb combustion calorimeter are described. The energy equivalent (ε_{calor}) of the calorimeter has been determined from ten combustion experiments using about 0.7 g of NIST 39i benzoic acid with a certified mass energy of combustion, $\Delta_c U = -(26434 \pm 3)$ J g^{-1}, under experimental conditions: $\varepsilon_{calor} = (13572 \pm 2)$ J K^{-1}. The constant-volume energy of combustion of the compound, endo-tricyclo[5.2.1.0^{2,6}]decane ($C_{10}H_{16}$), has been determined to be $\Delta U_c(C_{10}H_{16}, s) = -(6070 \pm 3)$ kJ mol^{-1} by means of the oxygen-bomb combustion calorimeter at $T = (298.15 \pm 0.001)$ K. The standard molar enthalpy of combustion of the sample has been calculated, $\Delta_c H_m^o(C_{10}H_{16}, s) = -(6060 \pm 3)$ kJ mol^{-1}, from the constant-volume combustion energy. From the Hess thermochemical cycle, the standard molar enthalpy of formation of the compound has been determined, $\Delta_f H_m^o(C_{10}H_{16}, s) = -(161.83 \pm 3.55)$ kJ mol^{-1}.

The oxygen-bomb combustion calorimeter is one of the basic devices necessary for some thermochemical research. Although it is a classic method to determine the combustion energies of some elements, organic compounds, metallorganics, *etc.*, the combustion calorimetry is widely applied to obtain the standard molar enthalpies of formation of many important organic substances in industry and scientific research based on the data of enthalpies of combustion and some auxiliary thermodynamic quantities. These thermodynamic data play a very important role in production and utilization of fuels and propulsive agents, the calculation of the various properties difficult to be obtained through some experiments about some important organic substances by means of the theory of quantum chemistry, the computer-aided molecular designs for drugs and new materials, the destruction of the waste materials in incinerators, and so on. The standard molar enthalpies of formation, together with the standard or specified entropy, are equally important data in determining any chemical equilibrium. The equilibrium constants (K) and the yields of the chemical reactions, in which some given substances are involved, can be derived on the basis of the stan-

dard molar enthalpies of formation and the specified entropies of the reactants and products in some reactions applied to produce a required product in industry. For the purpose of the application in a laboratory, a precise and computer-controlled isoperibol oxygen-bomb combustion calorimeter suitable for investigating combustion enthalpies of many novel compounds is described in more detail based on some other commercial apparatuses [1—4] and our previous works [5, 6] as the first goal of the paper.

Diamantane has been widely used in medicine, dye and pesticide industries. An important route to synthesize the compound is the isomerization of endo-tricyclo[5.2.1.0^{2,6}]decane (molecular formula: $C_{10}H_{16}$, CAS 6004-38-2), which is produced through hydrogenation of tricyclopentadiene, the main component of C_5 distillates of oil plants [7—9]. Endo-tricyclo[5.2.1.0^{2,6}]decane, as one important intermediate compound of synthesizing diamantane, has been studied recently. In view of the importance of the endo-tricyclo[5.2.1.0^{2,6}]decane in many fields, in the present paper, the standard molar enthalpy of formation of the compound has been derived from the combination of the result of the standard molar en-

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thalpy of combustion with other auxiliary thermodynamic quantities as the second goal of the paper.

EXPERIMENTAL

The sample of endo-tricyclo[5.2.1.0^{2,6}]decane was prepared according to [9], dissolved in ethanol and analyzed to test the purity. The analysis was conducted on an Agilent 4890D gas chromatograph with FID. No impurity was found in the sample.

Oxygen-Bomb Combustion Calorimetry

The constant-volume energy of combustion of the sample was measured by means of a home-made precision oxygen-bomb combustion calorimeter. It was an isoperibol macrocalorimeter with a static oxygen bomb and set up in our thermochemistry laboratory. The structure and principle of the calorimeter has been described previously in brief [5, 6]. The schematic diagram of the isoperibol oxygen-bomb combustion calorimeter is shown in Fig. 1. It consists of a static oxygen bomb, inner calorimetric vessel, outer thermostatic bath, platinum resistance thermometer, precision temperature controller, ignition system, and temperature measurement system. The oxygen bomb was made from a special stainless steel with good heat conduction. The efficient volume of the bomb was about 0.3 dm^3. Two stainless steel ignition electrodes of 0.8 cm in diameter were extended to the centre of the bomb downright from the lid of the bomb. The two ignition electrodes were installed in the lid of the bomb and linked with the ignition system. They had a good electrical insulation from the lid to eliminate the effect of the electric current of the ignition on the temperature measurements. Except for the two ignition electrodes, a filling-oxygen valve was also mounted in the lid. A small sample crucible of about 0.004 dm^3 was hanged in the bomb by means of a horizontal ring. The ring was vertically fixed on one of the two stainless steel electrodes and in a good electric contact with the sample crucible. The second electrode was not directly coupled with the ring, but it was in a good electrical contact with the first electrode through the ignition nickel fuse. The nickel fuse in the form of the coil in its middle was tightly pressed on the sample after a pellet of sample was horizontally put in the sample crucible. The oxygen bomb was immerged in 2.850 dm^3 of the deionized water contained in the inner calorimetric vessel during the whole combustion. The total mass of both inner calorimetric vessel and deionized water was 3900 g. The deionized water in the inner calorimetric vessel was stirred at a uniform rate of 150 rotations per min so that the heat released in the oxygen bomb was rapidly absorbed by the deionized water and the heat leakage from the inner calorimetric vessel to the surroundings was reduced to the minimum level during the combustion test.
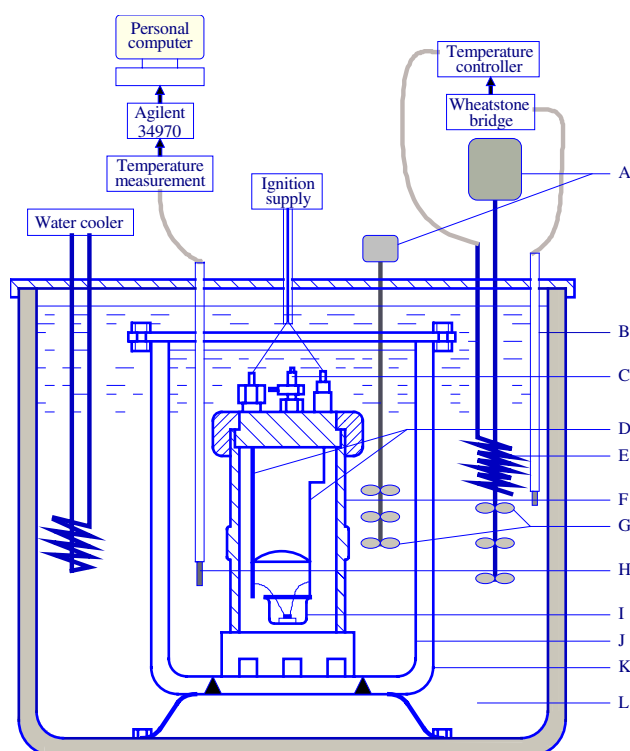

Fig. 1. The schematic diagram of an isoperibol oxygen-bomb combustion calorimeter. A – electric motor; B – Cu 50 resistance thermometer; C – oxygen-filling valve; D – ignition electrodes; E – heater; F – oxygen bomb; G – stirrers; H – Pt resistance thermometer; I – sample crucible; J – inner calorimetric vessel; K – thermal shield; L – water thermostat.

The system of controlling the temperature was composed of a thermostatic bath, an electric stirrer, an electric heater, a precision temperature controller, and a Cu 50 resistance thermometer. The thermostatic bath was made from the stainless steel plate of 5 mm in thickness, on the surface of which the thermal insulation paint was coated. The volume of the bath was about 60 dm^3. The thermostatic medium is the distilled water to protect the inner calorimetric vessel from the corrosion. The Cu 50 resistance thermometer was used to measure the temperature of the water in thermostatic bath. The inner calorimetric vessel was located at the centre of the outer thermostatic bath and completely immersed in the thermostatic water of the outer bath. The oxygen bomb was put in the centre of the inner calorimetric vessel containing the deionized water. There was an air jacket of 2.5 cm in thickness between the inner calorimetric vessel and the outer thermostatic bath so as to increase the thermal insulation of the calorimetric system. The temperature of the water in the outer thermostatic bath was controlled by means of a precision temperature controller with a liquid crystal display (model: AL-708, made in Yuguang Institute of Electronic Technology, Xiamen, P. R. China). The Cu 50 thermome-

Table 1. The Performance Comparison of the Home-Made Calorimeter with a Commercial Calorimeter, C 2000 Basic IKA Calorimeter (Ident. No. 8801900)

Performances	IKA Calorimeter	Home-Made calorimeter
Isoperibol temperature controlling precision	–	$\pm$ 0.001 K
Temperature measurement resolution	$\pm$ 0.0003 K	$\pm$ 0.0001 K
Working temperature range	25—30 ℃	20—33 ℃
Maximal oxygen filling pressure	40 bar	40 bar
Permissible ambient temperature	20—25 ℃	18—30 ℃
Isoperibol measurement time	22 min	25 min
Reproducibility with 1 g benzoic acid	0.05 % (RSD)	0.03 % (RSD)

ter and the electric heater were linked with the temperature controller through a precision Wheatstone electric bridge. The thermostatic water was stirred by an electric stirrer at a rate of 240 rotations per min. Measurements have shown that the precision of controlling the temperature for the thermostatic system can at least reach $\pm$ 0.001 K.

The temperature measurement system consisted of a precision platinum resistance thermometer and a Data Acquisition/Switch Unit (Model 34970A, Agilent, USA). The temperature of the water in the inner calorimetric vessel of the calorimeter was measured by the precision platinum resistance thermometer (40 mm in length, 5 mm in diameter; $R_0 = 196.9865\ \Omega$, made by the Instrument Manufacture Co. of Yunnan, P. R. China). The thermometer was calibrated on the basis of ITS-90 by the National Institute of Metrology (NIM). The thermometer was linked in four leads with two interfaces of the Agilent Data Acquisition/Switch Unit to measure the temperatures of the calorimetric system through a program on line by a personal computer.

The performance comparison of the home-made calorimeter with a commercial calorimeter, such as a C 2000 basic IKA calorimeter, is listed in Table 1. It can be seen that the performance of the home-made calorimeter was preferable to that of the instrument made by company IKA.

The correction of the temperature rise (ζ) was obtained from the following formula [10, 11]

$$\zeta = \left(\frac{V_n - V_0}{\theta_n - \theta_0} \right) \cdot \left(\frac{T_0 + T_f}{2} + \sum_{T_0}^{T_f} T_i - n\theta_n \right) + nV_n$$

(1)

in which $V_n/(\text{K min}^{-1})$ is the temperature drift rate in the final period, $V_0/(\text{K min}^{-1})$ the temperature drift rate in the initial period, θ_n/K the average temperature of the calorimeter during the final period, θ_0/K the average temperature of the calorimeter during the initial period, T_0/K the last reading of the temperatures in the initial period, T_f/K the first reading of the temperatures in the final period, n the number of readings for the reaction or main period. The corrected temperature rise of the combustion or reaction is: $\Delta T = (T_f - T_0) + \zeta$.

The ignition system was composed of a transformer and an electric switch. The voltage of the transformer used in the ignition was set at about 25 V. The length of the ignition nickel wire used in each of combustion tests was about 16 cm. The resistance of the ignition nickel fuse was about 6.5 Ω. The electric energy for the ignition was determined from the change in potential difference across a capacitor when discharged through the nickel wire, 0.89 J.

The sample was pressed into pellets of (0.6 to 1.0) 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 anal. grade, mole fraction 0.99998. The mass of the sample has been calibrated from the air buoyancy on the basis of the 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 these solids was assumed to be -0.21 J g^{-1} MPa^{-1}, a typical value for organic solids. The standard energy of combustion of the nickel fuse for ignition has been determined previously to be $\Delta_c U^\circ/(\text{J cm}^{-1}) = 2.929$. The real energy of combustion of the nickel fuse (Q_{Ni}) was calculated from the formula $Q_{\text{Ni}}/\text{J} = 2.929 \cdot \Delta L$ in which $\Delta L/\text{cm}$ 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 a 0.1000 mol dm^{-3} sodium hydroxide solution by using the methyl orange as the indicator. The heat of formation of the aqueous nitric acid in the oxygen bomb can be derived from the equation, $Q_{\text{HNO}_3}/\text{J} = 59.8 \cdot N \cdot V$ in which $N/(\text{mol dm}^{-3})$ is the concentration of the sodium hydroxide solution and V/cm^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$_2$O(l), $\Delta_f H_m^\circ = 59.8$ kJ mol^{-1} [1—4], for 0.1 mol dm^{-3} of HNO$_3$(aq).

The measurement was composed of initial (5 min), combustion (15 min), and final (5 min) periods. The data acquisition started automatically when the temperature of the calorimeter reached the equilibrium

Table 2. The Experimental Results of the Constant-Volume Energies of Combustion of the endo-Tricyclo[5.2.1.0^{2,6}]decane Obtained from the Oxygen-Bomb Combustion Calorimetry at $T = 298.15$ K

Sample mass m/g	Heat value of nickel wire Q_{Ni}/J	Heat value of nitric acid Q_{HNO_3}/J	Corrected temperature rise ΔT/K	Combustion energies $-\Delta U_c$/(kJ mol^{-1})
0.7733	40.710	169.409	2.5542	6061.57
0.8789	46.275	187.560	2.9130	6080.78
0.8828	43.932	211.761	2.9992	6074.37
0.8233	42.468	199.660	2.8018	6067.29
0.7868	41.003	181.510	2.6016	6064.02
0.7181	39.538	157.308	2.3766	6070.83
Avg. $\Delta U_c(C_{10}H_{16}, s) = -(6070 \pm 3)$ kJ mol^{-1}				

point of controlling the temperature at $T = (298.15 \pm 0.001)$ K. In each period, all the values (current and voltage) across the platinum resistance thermometer were collected at the same time at the interval of 30 s by using the Agilent Data Acquisition/Switch Unit, and the corresponding temperatures were calculated on line according to the calibrated parameters of the thermometer by a personal computer. The sample was ignited at 600 s from the start of data acquisition. After each run, the combustion products were analyzed mainly for carbon dioxide by the Rossini method [12]. No soot was observed in the sample crucible after each of combustion experiments for the endo-tricyclo[5.2.1.0^{2,6}]decane ($C_{10}H_{16}$). Qualitative tests for CO with indicator tubes were negative within the limits of their sensitivity (mole fraction $x(CO) < 1 \times 10^{-6}$).

The energy equivalent, ε_{calor}, of the calorimeter has been determined from ten combustion experiments using about 0.7 g of NIST 39i benzoic acid with a certified mass energy of combustion under experimental conditions of $\Delta_c U = -(26434 \pm 3)$ J g^{-1}: $\varepsilon_{calor} = (13572 \pm 2)$ J K^{-1}. The uncertainty of the results was the standard deviation of the mean value from the respective measurements.

RESULTS AND DISCUSSION

The method for determining the constant-volume combustion energy of the sample was the same as that used in the calibration of the calorimeter with benzoic acid. The constant-volume combustion energy of the substance can be calculated from the equation

$$\Delta_c U^\circ/(J\ mol^{-1}) = (\varepsilon_{calor} \cdot \Delta T - Q_{Ni} - Q_{HNO_3}) \cdot M/W \quad (2)$$

in which $\varepsilon_{calor}/(J\ K^{-1})$ is the energy equivalent of the oxygen-bomb calorimeter, $\varepsilon_{calor} = (13572 \pm 2)$ J K^{-1}, ΔT/K the corrected temperature rise; M/(g mol^{-1}) the molar mass of the sample, W/g the mass of the sample.

The calculated results of the constant-volume combustion energies of the endo-tricyclo[5.2.1.0^{2,6}]decane obtained from the six combustion tests are indicated in Table 2.

The standard molar enthalpy of combustion of the endo-tricyclo[5.2.1.0^{2,6}]decane, $\Delta_f H_m^\circ$ ($C_{10}H_{16}$, s), was the combustion enthalpy change of the following reaction at $T = 298.15$ K and $p = 100$ kPa

$$C_{10}H_{16}(s) + 14O_2(g) = 10CO_2(g) + 8H_2O(l) \quad (A)$$
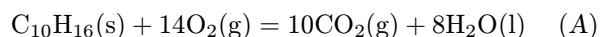
The standard molar enthalpy of combustion of the compound can be derived from the constant-volume combustion energy by the following formula

$$\Delta_c H_m^\circ = \Delta_c U_m^\circ + \Delta n \cdot RT$$

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

where Σn_i is the total amount (in mol) of gases present in the reaction (A) as products or as reactants. The calculated standard molar enthalpy of combustion of the endo-tricyclo[5.2.1.0^{2,6}]decane is: $\Delta_c H_m^\circ(C_{10}H_{16},$ s$) = -(6060 \pm 3)$ kJ mol^{-1}.

The standard molar enthalpy of formation of the compound, $\Delta_f H_m^\circ$, was calculated by the designed Hess thermochemical cycle according to the reaction (A) as follows

$$\Delta_f H_m^\circ(C_{10}H_{16}, s) = (10\Delta_f H_m^\circ(CO_2, g) + \\ + 8\Delta_f H_m^\circ(H_2O, l)) - \Delta_c H_m^\circ(C_{10}H_{16}, s) \quad (3)$$

In the above formula (3), the standard molar enthalpies of formation of $CO_2(g)$ and $H_2O(l)$, recommended by CODATA [13, 14], $\Delta_f H_m^\circ(CO_2,$ g$) = -(393.51 \pm 0.13)$ kJ mol^{-1} and $\Delta_f H_m^\circ(H_2O,$ l$) = -(285.83 \pm 0.04)$ kJ mol^{-1}, were employed in the calculation of $\Delta_f H_m^\circ(C_{10}H_{16},$ s). Finally, the standard molar enthalpy of formation of the compound can be derived based on these values and standard molar enthalpy of combustion of the substance: $\Delta_f H_m^\circ(C_{10}H_{16},$ s$) = -(161.83 \pm 3.55)$ kJ mol^{-1}.

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