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STUDY ON THE THERMODYNAMIC PROPERTIES OF CHOLESTEROL

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The standard molar enthalpy of combustion of cholesterol was measured at constant volume. According to value of $\Delta_r U_m^\theta$(–14358.4±20.65 kJ mol^{-1}), $\Delta_r H_m^\theta$(–14385.7 kJ mol^{-1}) of combustion reaction and $\Delta_f H_m^\theta$(2812.9 kJ mol^{-1}) of cholesterol were obtained from the reaction equation. The enthalpy of combustion reaction of cholesterol was also estimated by the average bond enthalpies. By design of a thermo-chemical recycle, the enthalpy of combustion of cholesterol were calculated between 283.15~373.15 K. Besides, molar enthalpy and entropy of fusion of cholesterol was obtained by DSC technique.

Keywords: *bond enthalpy, calorimetry, cholesterol, enthalpy, recycle*

Introduction

Cholesterol, or a closely related sterol, is an essential structural component of the plasma membrane of virtually all eukaryotic cells [1]. Cholesterol is a potent modulator of the bulk physical properties of biological membranes [2] and the presence of cholesterol or cholesterol-rich phospholipid domains in membranes can modify protein conformation and function. The concentration of cholesterol in plasma is maintained by biosynthesis through the endogenous pathway and absorption of dietary and biliary cholesterol through the exogenous pathway. In the endogenous pathway, cholesterol is synthesized by the liver and extrahepatic tissues and secreted into plasma, whereas the intestine is the primary site of the exogenous pathway of dietary cholesterol uptake [3]. Cholesterol is markedly enhanced in patients with obesity. It is quite clear that cholesterol synthesis in excessively enlarged adipose tissue covers insufficiently the markedly enhanced overall cholesterol formation in obesity.

Patients with obesity hope to control mass by consuming as much energy as possible in sports. Cholesterol and fattiness in body are rich in energy and heat. Thus, measurement of the thermo-chemical properties of cholesterol is very important. In the present study, we tried to measure the standard molar enthalpy of formation of cholesterol by combustion heat between 193.15 and 213.15 K. The molar enthalpy and entropy of fusion, heat stability of cholesterol were also evaluated with DSC technique.

Experimental

Materials

Anhydrous cholesterol (formula: $C_{27}H_{46}N_{46}O$; molecular mass: 386.66 g mol^{-1}) was bought from Bodi Chemical Corporation of Tianjin. Its molecular structure is shown in Fig. 1.

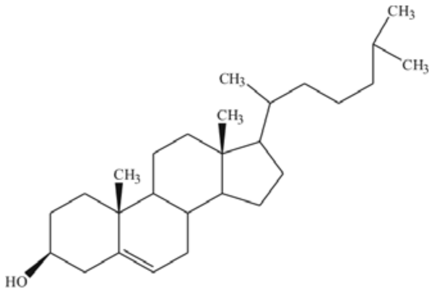

Fig. 1 The structure diagram of cholesterol

Methods

Measurement of enthalpy of combustion

The combustion heat of cholesterol was measured by bomb combustion calorimeter (Changsha Instrumental, SF-GR3500). The temperature of the water thermostat was maintained at T=298.15 K. The water temperature in the caloritube was subsequently adjusted to lower than that of the water thermostat. A known amount of double-distilled water was added into the calorimeter. When the sample was placed in the crucible fixed on the support in the rotating-bomb, the Ni wire was fixed in the bomb. After the bomb was filled with 2.4 MPa oxygen gas, it was sealed.

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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 5 s. Then the sample was ignited until 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. The change of temperature was recoded. The analysis methods have been discussed in the literature [4]. The analytical results of the final solution showed that the combustion reactions were complete. Neither carbon deposits nor carbon monoxide was formed during the combustion reactions. The amount of NO_x in the final gas was insignificant. The NIST Standard Reference Material, benzoic acid, was used to calibrate the combustion calorimeter [5].

Measurement of molar heat capacity of cholesterol

Heat capacity of cholesterol was measured by Isothermal Calorimeter (Thermometric AB, TAM Air 3114/3236). TAM Air is an isothermal heat conduction calorimeter operating in the milliwatt range. All eight calorimetric channels are mounted together to form a single heat-sink block housed in a temperature controlled air thermostat. Each calorimetric channel is constructed in twin configuration with one side for the sample and the other side for a static reference. The twin configuration of sample and reference within a channel allows the heat flow from the active sample to be compared directly with the heat flow from the inert reference. The voltage difference is a quantitative expression of the overall rate of heat production in the sample. Heat capacity can be determined from a stepwise change of temperature [6, 7]. Upon a stepwise change of temperature, the upward response of the instrument indicates the exothermal process. α-Al_2O_3 (He Lian Chem. Ltd, 50 μm particle size) was used as a reference material to test the accuracy of measurement of heat capacity by the Calorimeter. Before measurement, α-Al_2O_3 was heated at 1273.15 K for 2 h. The final data from 298 to 300 K is 78.95±0.26 J K^{-1} mol^{-1}, which is in accordance with the reported results [8, 9].

Enthalpy of phase transition and heat stability of cholesterol

DSC experiments were carried out in a differential scanning calorimeter, TA DSC Q10 from TA Instrument. The instrument was calibrated using the indium before the measurement. About 6.4 mg cholesterol was used and it was encapsulated in the sealed pans in each experimental run. The heating rate was 10 K min^{-1}, and the temperature range was from 300 to 440 K.

Results and discussion

The constant-volume energy of combustion of cholesterol, $\Delta_r U_m^\theta$, was –14358.4±20.6 kJ mol^{-1}, which was determined by a rotating-bomb oxygen combustion calorimeter. The detailed values were summarized in Table 1. The standard molar enthalpy of combustion of cholesterol, $\Delta_r H_m^\theta$, refers to the combustion enthalpy change of the following ideal combustion reaction at T=298.15 K and P=101.325 kPa.

$$C_{27}H_{46}O(s)+38O_2(g)\Rightarrow 27CO_2(g)+23H_2O(l)$$

The standard molar enthalpy of combustion of cholesterol at T=298.15 K was calculated from the constant-volume energy of combustion at T=298.15 K by the following equation.

$$\Delta_r H_m^\theta=\Delta_r U_m^\theta+\Delta(pV)=\Delta_r U_m^\theta+\Delta nRT$$

where n was the total amount (in mol) of gas present as products or reactants, $n=n_{\mathrm{productor}}-n_{\mathrm{reactant}}=-11$ mol, R=8.314 J mol^{-1} K^{-1}, T=298.15 K. We can obtain the standard molar enthalpy of reaction, $\Delta_r H_m^\theta=-14385.7$ kJ mol^{-1}. With the standard enthalpy of formation of $CO_2(g)$ and $H_2O(l)$ at 298.15 K, the standard molar enthalpy of formation of cholesterol can be obtained, $\Delta_f H_m^\theta=2812.9$ kJ mol^{-1}.

The enthalpy of combustion reaction of cholesterol can also be estimated by the average bond enthalpies without considering the intermolecular forces [10]. $\Delta_r H_m^\theta=\Sigma$ (bond enthalpies of bonds broken)-Σ (bond enthalpies of bonds formed). The molar enthalpy of combustion of cholesterol can be calculated from the average bond enthalpies in [11], $\Delta_r H_m^\theta=-15522$ kJ mol^{-1}. The process of calculation was shown in Table 2. This value is higher than obtained from combustion experiment because the average bond enthalpy is smaller than the bond enthalpy of C–C of cholesterol with polycyclic structure.

Table 1 The constant-volume energy of combustion of cholesterol at 298.15 K

1	2	3	4	5	Average/kJ mol^{-1}
14361	14335	14388	14365	14343	14358.4±20.7

Table 2 The estimation of molar enthalpy of combustion of cholesterol by bond enthalpies

Bond of reactants	Number	Average bond enthalpies/kJ mol^{-1}	Bond of products	Number	Average bond enthalpies/kJ mol^{-1}
C–H	45	413	C=O (CO_2)	27·2=54	799
C–C	29	348	O–H (H_2O)	23·2=46	463
C=C	1	614			
C–O	1	358			
O–H	1	463			
O=O (O_2)	38	495			
Amount to		48922	Amount to		64444

$\Delta_r H_m^\theta = \Sigma$ (bond enthalpies of bonds broken)-Σ (bond enthalpies of bonds formed) = –15522 kJ mol^{-1}

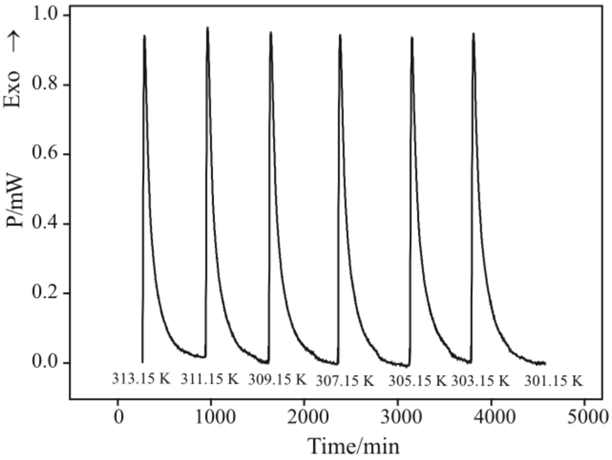

Fig. 2 The thermogenic curve in the process of measuring the heat capacity of cholesterol.

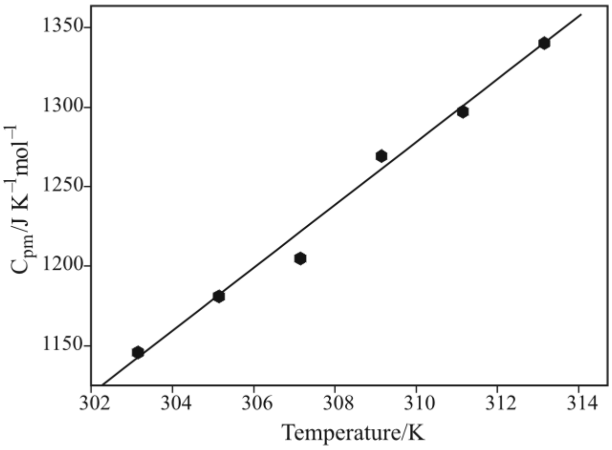

Fig. 3 The relationship of molar heat capacity and temperature of cholesterol

The heat capacities of cholesterol were measured by the calorimeter over the temperature range from 313.15 to 301.15 K. The result was shown in Figs 2 and 3. The temperature increment for each experimental point was about 2 K in the whole temperature range. No phase transition was observed in this temperature region. The data of the molar heat capacities of cholesterol between 301.15 and 313.15 K are very close to a straight line and can be represented to within a few percent by the following equation with a correlation coefficient of 0.9936.

$$C_{p,m} = -4857+19.785T$$

To estimate the enthalpy of combustion of cholesterol with a wide range of temperature, the following recycle of thermo-chemistry was designed.

$$\begin{array}{c} C_{27}H_{46}O(s)+38O_2(g) \Rightarrow 27CO_2(g)+23H_2O(l) \\ \downarrow \Delta H_1 \qquad\qquad\qquad\qquad \Delta H_2 \uparrow \\ C_{27}H_{46}O(s)+38O_2(g) \Rightarrow 27CO_2(g)+23H_2O(l) \end{array}$$

According to data in [12], it can be known that
$C_{p,m(CO_2)}=44.22+8.79\cdot10^{-3}T–8.62\cdot10^5T^{-2}$,
$C_{p,m(O_2)}=29.96+4.18\cdot10^{-3}T–1.67\cdot10^5T^{-2}$,
$C_{p,m(H_2O)}=75.48$.

$$\Delta_r H_m^\theta(T)=\Delta_c H_m^\theta(298.15\text{ K})+\Delta H_1+\Delta H_2$$

$$=\Delta_r H_m^\theta(298.15\text{ K})+\int_{298.15}^{T}\Delta C_{p,m}\,dT$$

$$=\Delta_r H_m^\theta(298.15\text{ K})+\int_{298.15}^{T}(6649.68-19.71T-1.7\cdot10^7T^{-2})\,dT$$

$$\Delta_r H_m^\theta = -15548.88+\frac{6649.68T-9.86T^2+1.7\cdot10^7T^{-1}}{1000}(\text{kJ mol}^{-1})$$

DSC curve (Fig. 4.) showed that the onset temperature of the fusion of cholesterol was 421.15 K and the peak temperature was 423.05 K. Before this temperature, no phase transition was observed with increasing temperature. The molar enthalpy and entropy of fusion were determined as 25.10 kJ mol^{-1} and 59.60 J K^{-1} mol^{-1}, respectively. Another paper has studied the phase transition of cholesterol by adiabatic calorimetry and suggests that there is a solid–solid phase transition between 306 and 314 K

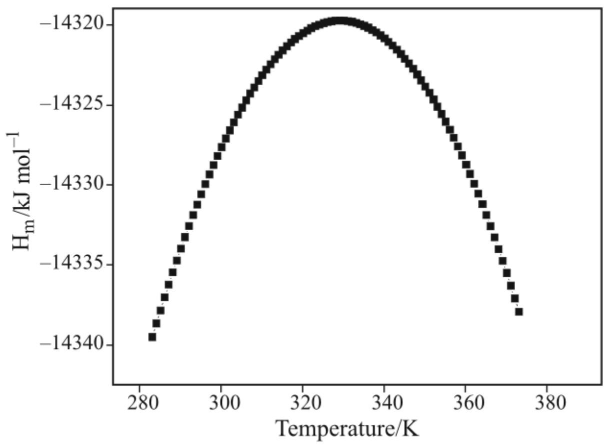

Fig. 4 The relationship between molar enthalpy of combustion and temperature

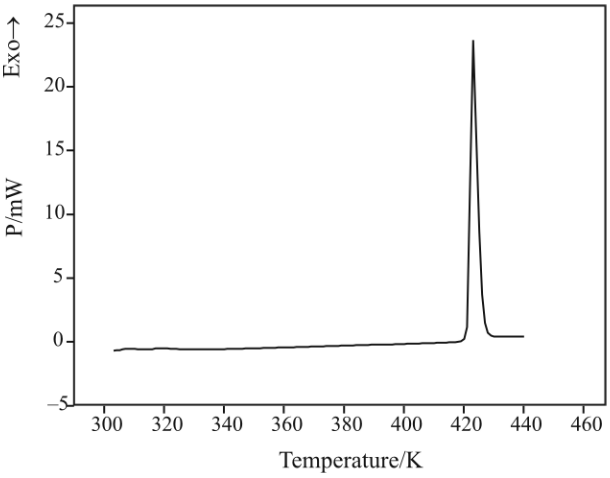

Fig. 5 DSC curve of cholesterol

[13, 14]. But by DSC technique no change was observed on thermogenic curve with temperature increasing. Further work should be done to compare these differences obtained from a variety of technique and methods.

Conclusions

In recent year, researchers have pay attention to reaction properties of biological material. As to the reaction which biological material takes part in, one important question lie at the heart of understanding the biological change: How far toward completion does the reaction proceed? As is same to common chemical changes, the properties for biological reaction must obey the laws of thermodynamics, which involved the changes of thermodynamic parameters. To understand the biological reaction better, laws of thermodynamics should be applied in this kind of study [15, 16]. Therefore, the measurement of thermodynamics of materials is important for studying their properties in many aspects, such as interaction between protein-nucleic acid, protein-enzyme and protein-bilayer.

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