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The Enthalpy of Combustion and Formation of Hydantoin

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In the present work, the author described the enthalpies of combustion and formation of hydantoin.

INTRODUCTION

Numerous investigators showed that the static bomb calorimeter is a satisfactory instrument for the application to compounds containing C, H, O, and N[1]. This calorimeter was used to determine the enthalpy of combustion (ΔH_c^0) in oxygen at 289.15 K of hydantoin for the first time as it is of great medicinal importance. The standard enthalpy of formation (ΔH_f^0) was calculated using the obtained data of (ΔH_c^0) and the accepted literature value for enthalpies of water and carbon dioxide[1].

The resulting values and their estimated 95% confidence limit are ;

For hydantoin :

$$\Delta H_c^0 = -1170.3 \pm 0.76 \text{ KJ. mol}^{-1}$$

$$\Delta H_f^0 = -581.89 \pm 1.14 \text{ KJ. mol}^{-1}$$

where (ΔH_c^0) corresponds to the reaction :

$$\underset{s}{C_3H_4O_2N_2} + 3\underset{g}{O_2} \rightarrow 3\underset{g}{CO_2} + 2\underset{l}{H_2O} + \underset{g}{N_2}$$

To check the precision of the calorimeter and the absence of any systematic errors, the enthalpy of combustion and formation of purified glutaric acid was determined and found to be :

For glutaric acid :

$$\Delta H_c^0 = -2150.35 \pm 0{\cdot}75 \text{ KJ. mol}^{-1}$$

$$\Delta H_f^0 = -960.53 \pm 1.1 \text{ KJ. mol}^{-1}$$

where ΔH_c^0 corresponds to the reaction :

$$\underset{s}{C_5H_8O_4} + 5\underset{g}{O_2} \rightarrow 5\underset{g}{CO_2} + 4\underset{l}{H_2O}$$

which is in good agreement with the literature value.

EXPERIMENTAL

(a) Hydantoin

This compound is of great medicinal importance, it has an effect in the treatment of grand mal epilepsy and psychomotor epilepsy. It has also a membrane stabilizing effect and is useful in treatment of cordial arrhythmia. So, it is of interest to study its physico-chemical and thermodynamic properties.

Hydantoin was purified by the familiar technique, namely, the fractional crystallization from solvents, the sample was extracted from pure ethanol to white odorless solid of m. pt. 493.15 K, dried in an oven till constant weight, then stored in vacuum desiccator.

(b) Glutaric Acid

Glutaric acid supplied from BDH with purity of 99% was purified by zone melting technique[2] to a colourless plate of melting point 371.15 K and purity of 99.995%. This purity was checked by D.T.A. and Gas Chromatography.

Units and Auxiliary Quantities

The heats of combustion and formation are given in joules, taking 1 cal = 4.184 abs. J. The relative atomic masses used were those recommended by the IUPAC commission[3]. The corrections for nitric acid formation were based on 597 kJ mol^{-1} for the energy of formation of 0.1 normal nitric acid from N_2, O_2 and water[4]. The energy of combustion of the wire was used as 2928.8 J g^{-1}. Weights in air were corrected to vacuum using the following density values (kg m^{-3}) at 289.15 K, hydantoin 1.38×10^{-3}, glutaric acid, 1.42×10^{-3} and 1.32×10^{-3} for benzoic acid.

To calculate ΔH_f^0 from ΔH_c^0 the following standard heats of formation were used :

$$\Delta H_f^0 (CO_2, g) = -393.509 \text{ KJ mol}^{-1} \text{ and}$$

$$\Delta H_f^0 (H_2O, l) = -285.830 \text{ KJ mol}^{-1}$$

Calorimeter

The bomb calorimeter, subsidiary apparatus and technique was described previously[5,6]. The calorimeter, figure 1, was used. The calorimetric jacket (7) was stirred by two propeller stirrers (9, 10) and its temperature was maintained constant by means of a precise contact thermometer (8) within ± 0.004 degree. The calorimeter vessel (1) of about 4.5 dm^3 capacity with highly polished surface, was stirred by a propeller stirrer (2) turned by asynchronous motor to ensure a constsnt stirring rate. The

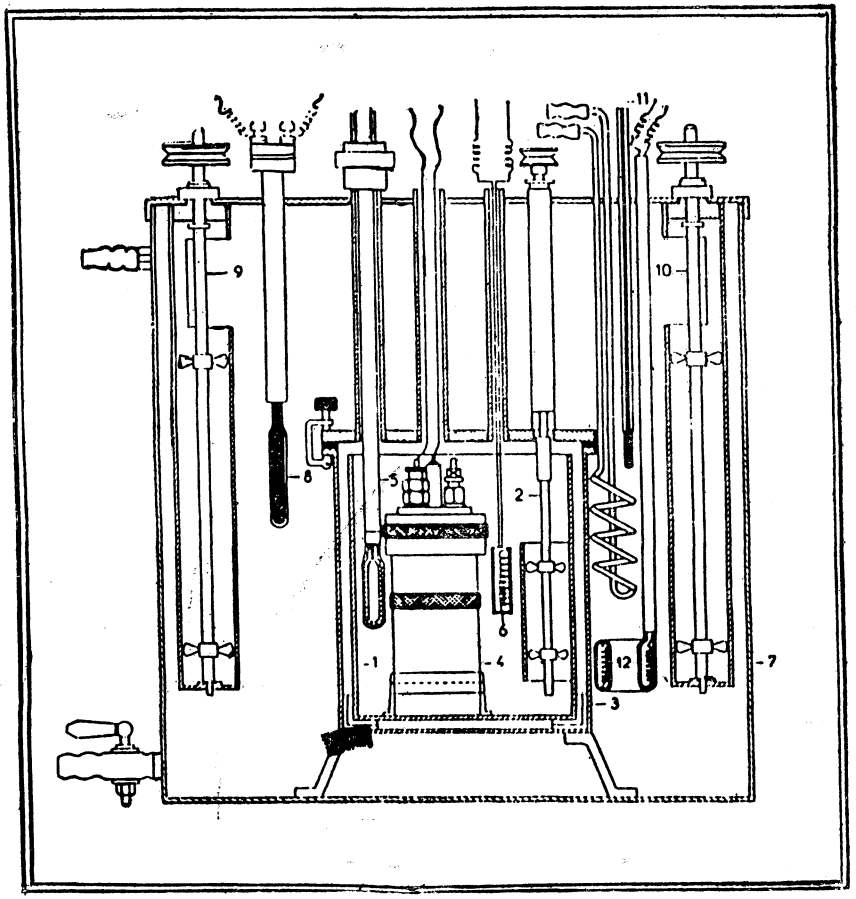

Fig. 1. Calorimetric System

crucible in which the sample was fired is made of platinum. The calorimeter is supplied by a manganin heater of low time lag (6). It was used to adjust the temperature of the calorimeter at the beginning of each experiment to 298.15 K. The calorimeter was calibrated using standard benzoic acid purified in our laboratory by zone melting technique[7]. The energy of combustion of the purified acid was determined in the same bomb calorimeter by using a sample of benzoic acid (SRM 39 i) supplied by the National Institute for Standards and Technology. The energy of combustion under standard bomb conditions for the purified acid is certified[7] to be 26433.3 ± 3.4 J g^{-1}. The solid samples were burned as pellets under an initial oxygen pressure of 30.39 10^5 Pa. The initial temperature was 298.15 K and an amount of substance sufficient to cause an increase of approximately 0.1Ω in the thermometric resistance (equivalent to 1K)

was burn in each experiment. All weights were reduced to weights in vacuum by correction for buoyancy of air.

Procedure

Following the same procedure previously described[6,7], the sample was pressed into pellets and weighed to ± 0.1 mg in a platinum crucible in which it was burnt. It was noticed that the sample of hydantoin did not completely burn in the bomb under 30.39×10^5 Pa of O_2. Benzoic acid was used as an auxiliary material to enhance burning[8]. For that purpose two pellets, one of benzoic acid and the other of the material under test, were prepared and then placed in the platinum crucible in which they were to be burned. The crucible was then placed in the bomb calorimeter such that the two samples were in contact with an iron wire of diameter 0.1 mm attached to the bomb electrodes and used for firing the two pellets. Two millilitres of distilled water in case of hydantoin and one millilitre in case of glutaric acid (the same millilitres were used in the case of calibration experiments) were placed in the bomb which was then tightly closed, flushed with oxygen and then filled to 30.39×10^5 Pa of oxygen. The experiments were then followed as previously described[6,7]. The temperature rise of the calorimeter vessel was measured using a four leads platinum resistance thermometer. For measurement of resistance an A.C. thermometer bridge was used.

The length of the main period was about 30 minutes. The temperature gradient in the initial and final periods of the calorimetric experiments with the sample under test were similar to those in calibration experiments with benzoic acid which is a criterion for the high precision of the calorimeter.

Combustion experiments were carried out using purified glutaric acid to be sure enough that the calorimeter and measuring equipments were free from any source of systematic errors.

At the end of the calorimetric experiment, the bomb was opened and washed for nitric acid. In all experiments with hydantoin, benzoic and glutaric acids, no solid materials or traces of incomplete combustion were observed inside the bomb after combustion, which proved that the combustion was complete in all cases.

RESULTS AND DISCUSSION

Determination of Water Equivalent

The results of benzoic acid calibration experiments give the heat equivalent of the calorimetric system with the bomb containing the products of combustion of benzoic acid (W'). The heat equivalent of the

calorimetric system with the bomb containing the products of combustion of the material under test (W) is calculated from the formula:

$$W = W' - C$$

where C is a correction term calculated from the known values of mass and specific heat of the products of combustion in experiments with benzoic acid and the material under test.

The heat equivalent in case of hydantoin was found to be

$$W = 118403.2\ J^{-1}$$

and in case of glutaric acid is

$$W = 118406.8\ J^{-1}$$

Determination of Enthalpy of Combustion and Formation

The heat of combustion of compounds containing C, H, O, and N can be determined using bomb calorimeter, and the equation given below, though the stoichiometry of the combustion process is more complex.

$$C_aH_bO_cN_d + \left(\frac{4a + b - 2c + 5y}{4}\right)O_2(g)$$

$$\rightarrow aCO_2(g) + y\left(HNO_3\left\{\left(\frac{b - y}{2y}\right)H_2O\right\}\right)(l) + \frac{d - y}{2}N_2(g)$$

In practice the value of (y) is generally such that $y/d \simeq 1.5$, but the exact value of y for each experiment must be determined by analysis of nitric acid present in solution after combustion. Once y is known it is normal practice to calculate the energy of the reaction

$$\frac{y}{2}N_2(g) + \frac{5y}{4}O_2(g) + \frac{b}{2}H_2O(l) \rightarrow \left(HNO_3\left\{\left(\frac{b - y}{2y}\right)H_2O\right\}\right)(l)$$

and to subtract this energy from the measured energy of the bomb reaction. The energy of the follwing reaction is thereby obtained:

$$C_aH_bO_cN_d + \left(\frac{4a + b - 2c}{4}\right)O_2(g) \rightarrow aCO_2 + \frac{b}{2}H_2O(1) + \frac{d}{2}N_2(g)$$

The heat of combustion was calculated using the following equation:

$$\Delta U_c = \frac{W.\Delta\theta_{corr} - q_{wire} - q_{HNO_3}}{m_8}$$

The results of the combustion experiments are given in Tables 1 and 2,

TABLE 1

HEAT OF COMBUSTION, ΔU_c^0, OF HYDANTOIN

W = 118403.2 $J\Omega^{-1}$

ΔU = 26433.3 KJ mol^{-1}

Mol. wt. = 100.07753

mA g	mB g	$\Delta\theta_{corr}$ Ω	q_{HNO_3} J	q_{wire} J	q_w J	ΔU J g^{-1}	$-\Delta U_c^0$ kJ mol^{-2}
0.24250	0.26749	0.08419	10.3223	32.9373	10.48	11727.8	1173.7
0.29394	0.26137	0.08794	12.3577	35.4726	10.48	11220.7	1173.0
0.24541	0.29188	0.08987	10.3223	31.8929	10.48	11708.3	1171.7
0.29085	0.27690	0.09110	12.2123	36.2774	10.48	11718.0	1172.7
0.28860	0.28151	0.09195	12.0669	39.7576	10.48	11725.1	1173.4
0.25628	0.29262	0.09118	10.7585	37.3509	10.48	11714.3	1172.3

$\Delta U_c^0 = -1172.8 \pm 0.76$ kJ.mol^{-1}

$\Delta H_c^0 = -1170.3 \pm 0.76$ kJ.mol^{-1}

$\Delta H_f^0 = -581.89 \pm 1.14$ kJ.mol^{-1}

TABLE 2

HEAT OF COMBUSTION OF GLUTARIC ACID

W = 118406.8 J.Ω^{-1}

Mol. wt = 132.11711

mA g	$\Delta\theta_{corr}$ Ω	q_{HNO_3} J	q_{wire} J	q_w J	ΔU J.g^{-1}	$-\Delta U_c^0$ kJ.mol^{-1}
0.89809	0.12375	2.96886	24.8962	2.39	16282.14	2151.15
0.79009	0.10874	1.6996	16.4523	2.39	16270.95	2149.67
0.93560	0.12891	2.42356	25.33014	2.39	16282.42	2151.19
0.80073	0.11026	1.82061	17.2996	2.39	16276.00	2150.34
0.79665	0.10969	2.30238	23.82616	2.39	16268.13	2149.30
0.79815	0.10996	1.79362	18.3962	2.39	16285.05	2151.53
0.82094	0.11299	2.43356	19.95009	2.39	16267.25	2149.18
0.81205	0.11188	2.96886	24.6969	2.39	16277.01	2150.47

$\Delta U_c^0 = -2150.35 \pm 0.7$ kJ.mol^{-1}

$\Delta H_c^0 = -2150.35 \pm 0.75$ kJ.mol^{-1}

$\Delta H_f^0 = -960.53 \pm 1.1$ kJ.mol^{-1}

where,

m_A is the mass of the sample corrected for buoyancy

m_B is the mass of benzoic acid used as an auxiliary aid in the experiments with hydantoin

$\Delta\theta_{corr}$ is the corrected temperature rise in terms of ohms

q_{HNO_3} is the quantity of energy required to decompose any nitric acid formed in the combustion process into N_2, O_2 and water

q_{wire} is the heat of formation of iron oxide from the iron wire used for burning the sample

q_w is the washburn correction[1]

ΔU is the isothermal heat of combustion at 298.15 K of the material under test with all reactants and products in their respective thermodynamic standard states in terms of joule g^{-1}

ΔU_c^0 is the isothermal heat of combustion at 25°C with all reactants and products in their respective thermodynamic standard states in terms of $kJ \cdot mol^{-1}$ where

$$\Delta U_c^0 = \Delta U_c - q_w$$

From Table (1), we get

The isothermal heat of combustion of hydantoin,

$$(\Delta U_c^0) = -1172.8 \pm 0.76 \text{ kJ mol}^{-1}$$

Hence

The enthalpy of combustion $\Delta H_c^0 = -1172.8 \pm 0.76$ kJ mol^{-1}

The enthalpy of formation $\Delta H_f^0 = -597.4 \pm 1.14$ kJ mol^{-1}

Since the obtained data is determined for the first time and is not published in the litrature, and to be sure that the combustion experiments were complete, the ratios of the number of moles of HNO_3 acid formed after combustion to the number of N_2 moles of hydantoin (y) were calculated for each experiment and it was found to be 0.149 which is in good agreement with the literature value (0.15)[1].

To test the precision of the calorimeter and to indicate that the calorimeter and measuring equipments were free from any source of systematic errors, the ethalpy of combustion of purified glutaric acid was determined and is given in Table 2.

From the data given in Table 2, ΔU_c^0 ΔH_c^0, and ΔH_f^0 were found to be:

$$\Delta U_c^0 = -2150.35 \pm 0.75 \text{ kJ mol}^{-1}$$

$$\Delta H_c^0 = -2150.35 \pm 0.75 \text{ KJ mol}^{-1}$$

Hence

$$\Delta H_f^0 = -960.53 \pm 1.1 \text{ KJ mol}^{-1}$$

These values are in good agreement with the literature values given in Table (3).

From Table (3), the following conclusions can be deduced:

1. The value of enthalpy of combustion obtained from the present study is in good agreement with those previously obtained from the work of verkade *et. al.*[10], wilhoit *et. al.*[11] and the selected values of Cox and Pilcher[1].
2. The difference between the value obtained in this work and that of P. E. Verkade may be due to the difference in the degree of purity of the used samples, since in Verkade's work the degree of purity was not recorded.
3. The selected value for enthalpy of formation as given by Cox is 959.8 ± 1.2 kJ·mol^{-1}, for the sample of purity 99.8%, which is very close to the value determined in the present work 960.54 ± 1.1 KJ·mol^{-1}, for a sample of purity 99.995% as determined by gas liquid chromatography and differential thermal analysis.

TABLE 3

COMPARISON OF ENTHALPY OF COMBUSTION AND FORMATION OF GLUTARIC ACID WITH THE LITERATURE VALUES

$-\Delta U_c^0$ Heat of combustion kJ.mol^{-1}	$-\Delta_f H^0$ Heat of formation kJ.mol^{-1}	Degree of purity	Author
2151.58 ± 0.54	959.31 ± 0.54	—	Ref. No. 10
2150.91 ± 1.20	959.98 ± 1.2	99.8%	Ref No. 11
2150.91 ± 1.2	959.98 ± 1.2	99.8%	Ref. No. 1
2150.35 ± 0.75	960.54 ± 1.1	99.995%	Present work

From the above discussion, the enthalpies of combustion and formation, ΔH_c^0 and ΔH_f^0 of hydantoin which are -1170.3 ± 0.76 and -581.89 ± 1.14 kJ mol^{-1}, can be recommended as the precise values for this compound.

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