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Estimation of enthalpy of combustion and thereby enthalpy of formation of trisacetylacetonatoiron (III)[Fe $(C_5H_7O_2)_3$ (c)]

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ABSTRACT

Thermochemical studies of organometallic compounds have been an interesting area of research since long as they provide a host of thermodynamic data for researchers of various fields to work upon/play with. In this paper, enthalpy of combustion of crystalline tris acetyl acetonatoiron (III) [Fe $(C_5H_7O_2)_3$ (c)] has been estimated bomb-calorimetrically and thereby enthalpy of formation of the said compound has been evaluated.

KEYWORDS: Thermo chemical studies, organ metallic compounds, trisacetyl acetonatoiron (III)

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INTRODUCTION

Thermochemical studies of organometallic compounds of transition metals has been a subject of fascinating area of research since long as they provide invaluable thermodynamic data for researchers of various fields to play with [1-6]. Quantitative measurements of heat changes involved during physical, chemical and biological processes are usually done through by the use of different types of calorimeters [7]. In recent years, values obtained as a result of thermochemical investigations of several organometallic compounds have been reported by many investigators, yet their importance in energetics and in other areas of research cannot be overemphasized. The present paper deals with the bomb calorimetric evaluation of enthalpy of combustion and thereby estimation of enthalpy of formation of tris acetyl acetonatoiron (III) [Fe $(C_5H_7O_2)_3$ (c)].

EXPERIMENTAL

1. Preparation of tris acetyl acetonatoiron (III) [Fe $(C_5H_7O_2)_3$ (c)]: Tris acetyl acetonatoiron (III) was prepared by the known methods. 10 g of $FeCl_3$ was dissolved in 20 ml of water. Into the solution 20 ml of acetylacetone is added slowly with constant stirring. The reaction being exothermic. Thereafter dilute NH_4OH was added dropwise until pH of the solution becomes about 5. The said compound was recrystallised with CCl_4 and dried. (Found Fe = 16·29%; calculated for Fe $(C_5H_7O_2)_3$; Fe = 15·8%.
2. The water equivalent or the mean heat capacity of the bomb calorimeter was determined by burning a certified grade pure benzoic acid (a primary standard substance having enthalpy of combustion = 26434 ± 5 Jg^{-1}) [8]. It was found to be 10550 ± 10 $J°C^{-1}g^{-1}$.

RESULTS AND DISCUSSION

The enthalpy of combustion (Δ_cH) of the compound was measured bomb calorimetrically by burning a weighed sample of the compound in known quantity of water in excess of O_2 gas under pressure and temperature rise was recorded through temperature sensor fitted in the bomb calorimeter. By substituting the auxiliary thermochemical data from the standard reference sources [9, 10], the standard enthalpies of formation of [Fe $(C_5H_7O_2)_3$(c)] have been estimated using the following relationship

$$\Delta_cH = \Sigma\ \Delta_fH^{\theta}\ (\text{products}) -- \Sigma\ \Delta_fH^{\theta}\ (\text{reactants})$$

Also the auxiliary enthalpy of formation data for products like metal oxides, CO_2 (g) and H_2O (l) have also been taken from standard reference sources [11-13]. The enthalpy of combustion of the compounds have been determined using the relation

$\Delta_cH = M\ W\ \Delta t$

where M is the gram molecular weight of the crystalline compound, W the water equivalent of the bomb calorimeter and Δt, the temperature rise per gram of the sample due to bomb calorimetric combustion. The water equivalent W of the bomb calorimeter was determined by burning certified grade benzoic acid. The value of W was measured to be 10550 ± 10 $°C^{-1}g^{-1}$ given in the table 1.

Table 1. Enthalpy of combustion of certified grade benzoic acid and water equivalent W of the bomb calorimeter.

Experiment No.	1	2	3	4
Wt. of benzoic acid (g)	0.9181	0.9737	1.0056	1.0595
Temperature rise (°C)	2.302	2.435	2.528	2.5136
Temp. rise per gm benzoic acid ($°C\ g^{-1}$)	2.507	2.492	2.522	2.485
W ($J\ °C^{-1}$)	10534	10549	10558	10567

Mean water equivalent W = 10550 ± 10 J $°C^{-1}g^{-1}$

The reported value of enthalpy of combustion of certified grade benzoic acid is 26434 ± 5 J g^{-1}.

Table 2. Molar enthalpy of combustion (Δ_cH) of trisacety lacetonatoiron (III) [$Fe(C_5H_7O_2)_3(c)$]

(Molar mass = 353.006)

Experiment No.	1	2	3
Wt. of the sample (g)	0.3125	0.5824	0.6428
Temperature rise (°C)	0.666	1.250	1.378
Temp. rise per g of the sample Δt ($°C\ g^{-1}$)	2.131	2.146	2.143
Average Δt ($°C\ g^{-1}$)		2.140	

Mean temperature rise per gm of the sample, Δt (°C) = 2.140

Now, -- Δ_cH = M × W × Δt

= 353.006 × 10550 × 2.140

= 7969816.5

Therefore, mean Δ_cH = -- 7969.816 ± 10 k J mol^{-1}

where, M = molar mass of the sample,

W = water equivalent of the bomb calorimeter = 10550 J $°C^{-1}$ g^{-1}, and

Δt = temperature rise per gm of combustion of the sample = 2.140

Standard enthalpy of formation (Δ_fH^0) of [$Fe(C_5H_7O_2)_3(c)$]:

From the molar enthalpy of combustion, standard enthalpy of formation of tris acetyl acetonatoiron (III) was evaluated by substituting auxiliary data from the standard references [9,10].

$Fe(C_5H_7O_2)_3(c) + O_2$ (g) (excess) = ½ Fe_2O_3 (c) + 15CO_2 (g) + 10·5 H_2O (l) $\Delta H = \Delta_c H$

$\Delta_c H = \Sigma \Delta_f H^o$ (products) -- $\Sigma \Delta_f H^o$ (reactants)

$\Delta_c H$ = ½ $\Delta_f H^o$ Fe_2O_3 (c) + 15 $\Delta_f H^o$ CO_2 (g) + 10·5 $\Delta_f H^o 10H_2O$ (l)

– $\Delta_f H^o$ $Fe(C_5H_7O_2)_3$(c)

Therefore,

$\Delta_f H^o Th (C_6H_5COO)_4$ (c) = ½ $\Delta_f H^o$ Fe_2O_3 (c) + 15 $\Delta_f H^o$ CO_2 (g)

+ 10·5 $\Delta_f H^o 10H_2O$ (l) – $\Delta_c H$

= ½ × (– 821.95 + 15 × (–393.5) + 10.5 × (– 285.8)

– (– 7969.816)

= – 410.975 – 5902.5 – 3000.9 + 7969.816

= – 9314.375 + 7969.816

= -- 1344.559 ± 10 $kJmol^{-1}$.

This value of -1344.559 ± 10 $kJmol^{-1}$ is supposed to be more consistent and coherent than those given by Wood and Jones [14] (- 1486 ± 10 $kJmol^{-1}$) $kJmol^{-1}$ through combustion calorimeter, Hill *et al* [15] (- 1310 ± 5 $kJmol^{-1}$) through solution calorimeter and Farrar *et al* [16] (- 1455.10 ± 10 $kJmol^{-1}$), which are very much inconsistent and incoherent.

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