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NOTE

Calorimetric Studies of the Acetates of Calcium(II), Strontium(II) and Barium(II)

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From experimentally measured enthalpies of combustion of Ca(II), Sr(II) and Ba(II) acetates, their standard enthalpies of formation were determined as -1488, -1496 and -1492 kJ. mol^{-1}, respectively. The metal-oxygen mean bond dissociation energy values were also estimated.

Key Words: Calorimetric studies, Acetates, Ca(II), Sr(II), Ba(II).

The thermochemical behaviour of acetates of Ca, Sr and Ba has already been studied[1-3]. The enthalpies of combustion, ΔH_c, of these compounds have been experimentally determined with a better accuracy by obtaining the plots using MATLAB pertaining to the temperature rise due to combustion as a function of time[2-5]. By substituting the auxiliary thermochemical data, the standard enthalpies of formation, ΔH_f^o, of the above compounds were determined[6]. These data have been used to estimate the mean bond dissociation enthalpies, $\underline{D}$(M-O).

The compounds were prepared by the reported procedure[7] by dissolving the respective carbonates in hot acetic acid and concentrating. The temperature rise per gram of the compound, Δt, was determined in a static oxygen bomb calorimeter by burning a weighed sample in an excess of oxygen and measuring the temperature-rise in known quantity of water. Before commencement of the experiment, the calorimeter was standardized making use of certified grade benzoic acid (crystalline) and the water equivalent W, was determined.

Water equivalent, W, of the calorimeter was determined by burning a weighed sample of benzoic acid and measuring the temperature rise/g of it, Δt, in known quantity of water. The time-temperature plot was obtained using MATLAB to determine Δt, as follows:

Time as function × (min) = [0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0]

Temperature as function y (ºC) = [1.000 1.001 1.002 1.003 1.004 3.490 3.501 3.490 3.480 3.470]

The plot is shown in Fig. 1 obtained by command plot (x,y).

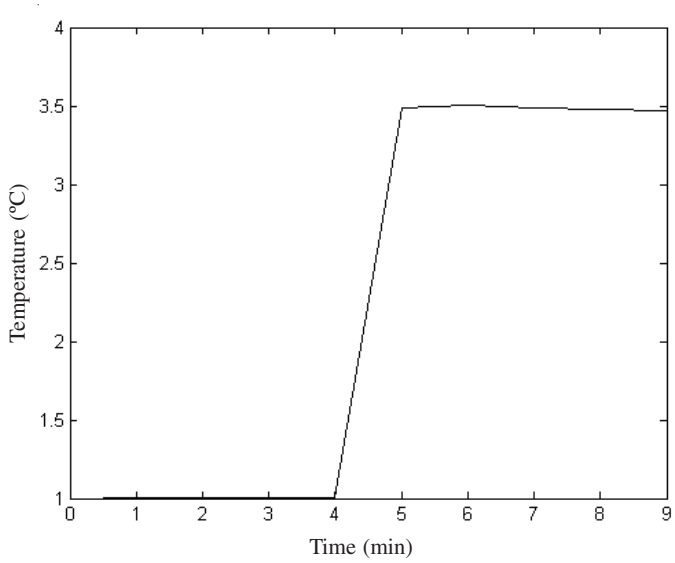

Fig. 1. Plot between time *vs.* temperature

Δt was calculated to be 2.501 °C g^{-1} from the relation,

$$W = \Delta H_c/\Delta t = 10569 \text{ joules } °C^{-1} \quad (1)$$

The enthalpies of combustion of acetates of Ca, Sr and Ba (Table-1) were determined from the relation:

$$\Delta H_c = M.W.\Delta t \text{ kJ mol}^{-1} \quad (2)$$

where M is the gram molecular weight of the compound; W, the water equivalent as found above and Δt, the temperature rise/g of the sample compound due to bomb calorimetric combustion determined by the time-temperature plots using MATLAB (Table-1) as stated above.

TABLE-1

Compound (cryst.)	Δt (°C g^{-1})	ΔH_c	$\Delta H_f°$	D(M–O)
		All values in kJ mol^{-1}		
$Ca(CH_3COO)_2$	0.944	-1578	-1488	244
$Sr(CH_3COO)_2$	0.684	-1527	-1496	241
$Ba(CH_3COO)_2$	0.551	-1487	-1492	247

The combustion products of the compounds under study were the respective oxides of the metals, CO_2 (gas) and H_2O (liq.) and $\Delta H = \Delta H_c$.

The standard enthalpies of formation of the compounds (Table-1) were calculated as follows:

$$\Delta H_f° \, Ca(CH_3COO)_2(c) = H_f° \, CaO(c) + 4\Delta H_f° \, CO_2(g) + 3\Delta H_f° \, H_2O(l) - \Delta H_c \quad (3)$$

$$\Delta H_f^\circ\ Sr(CH_3COO)_2(c) = \Delta H_f^\circ\ SrO(c) + 4\Delta H_f^\circ\ CO_2(g) + 3\Delta H_f^\circ\ H_2O(l) - \Delta H_c \quad (4)$$

$$\Delta H_f^\circ\ Ba(CH_3COO)_2(c) = \Delta H_f^\circ\ BaO(c) + 4\Delta H_f^\circ\ CO_2(g) + 3\Delta H_f^\circ\ H_2O(l) - \Delta H_c \quad (5)$$

The enthalpies of formation of the combustion products in their standard states have been compiled from standard sources[3,4]. The ΔH_f° values shown in Table-1 are compared with the reported values[4].

Estimation of metal-oxygen mean bond dissociation energy: The metal-oxygen mean bond dissociation energy is the enthalpy of gas phase reaction (ΔH_g) between the metal and the acetate as follows:

$$M(g) + 2CH_3COO(g) = M(CH_3COO)_2(g);\ \text{where } \Delta H = \Delta H_g \quad (6)$$

$$\Delta Hg = \Delta H_f^\circ\ M(CH_3COO)_2(g) - \Delta H_f^\circ\ M(g) - 2\Delta H_f^\circ CH_3COO(g)$$
$$= \Delta H_f^\circ\ M(CH_3COO)_2(c) + \Delta H_{sub} - \Delta H_f^\circ\ M(g) - 2\Delta H_f^\circ\ CH_3COO(g) \quad (7)$$

ΔH_{sub} is the enthalpy of sublimation and approximately assumed to be in the range of respective metallic chloride[3]. The estimated $\underline{D}$(M–O) values are shown in the Table-1.

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