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Thermochemical studies of crystalline tris (acetylacetonato) manganese (III) $[Mn(C_5H_7O_2)_3(c)]$ compound through calorimetry

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Abstract
The present work gives an account of the thermochemical studies of crystalline *tris* (acetylacetonato) manganese (III) compound. The heat of combustion (Δ_cH) and thereby standard heat of formation (Δ_fH°) of crystalline *tris* (acetylacetonato) manganese (III) $[Mn(C_5H_7O_2)_3(c)]$ has been measured experimentally with the help of static oxygen bomb calorimeter at 298 K and the values so obtained for Δ_cH and the Δ_fH° have been compared with those available in literature to judge the efficacy of the present process. The values for Δ_cH and Δ_fH° in the solid phase have been experimentally found to be - 8047·371 k J mol^{-1} and - 1341·46 ± 15 kJ mol^{-1} respectively.

Keywords: thermochemical studies, heat of combustion, standard heat of formation, organometallic compounds, tris (acetylacetonato) manganese (III) compound

1. Introduction
Divalent and trivalent transition metal acetylacetonates $[M(acac)_2$ or $M(acac)_3$, where M = Cu (II), Cr (III), Mn (III), Fe (III), Co (III) and Ni (III)] have been extensively investigated by the researchers since long due to their interesting thermochemical properties. Several workers have calculated standard molar enthalpies of formation of these metal acetylacetonato - compounds using different calorimeters [1, 7]. However, standard molar heats of formation of *tris*(acetylacetonato) Cr (III) and Ga (III) were determined by Hill and Irving & Irving and Walter respectively using solution reaction calorimetry [8, 9]. In this paper the bomb- calorimetric evaluation of enthalpy of combustion and thereby calculation of enthalpy of formation of *tris*(acetylacetonato) manganese (III) $[Mn(C_5H_7O_2)_3(c)]$ have been done through the use of static oxygen bomb calorimeter under standard conditions.

2. Materials and Methods
2.1. Preparation of *tris* (acetylacetonato) manganese (III) $[Mn(C_5H_7O_2)_3(c)]$
Tris (acetylacetonato) manganese (III) $[Mn(C_5H_7O_2)_3(c)]$ was prepared by dissolving 5g of $KMnO_4$ in a minimum volume of water (about 50 -75 ml) and heating the resultant solution over water bath for 5 minutes. The solution mixture was then filtered. To the hot filtrate about 25 ml of distilled acetylacetone $[(C_5H_8O_2)$ or Hacac] was added slowly with vigorous stirring and the resultant solution mixture was again heated on water bath for another 30 minutes which upon cooling furnished black – brown shiny crystalline mass. It was filtered off, washed with water and then redissolved in hot C_6H_6 followed by slow addition of light petroleum (b.p. 40-60°C) until solution turned turbid or cloudy. Upon cooling, dark violet shiny crystals of $Mn(acac)_3$ separated out. The compound decomposed at 155-160°C and did not possess a sharp melting point. Dried in vacuum over fused $CaCl_2$ over 15 minutes [10, 11]. Analysed for manganese (Found: Mn = 15·7%; calculated for Mn $(C_5H_7O_2)_3$: Mn = 15·6%).

$KMnO_4$ + 4 Hacac → Mn $(acac)_3$ + Kacac + $2H_2O$ + O_2

It can also be prepared via several other routes [12, 13].

$4MnCl_2 .4H_2O + KMnO_4 + 15(Hacac) \rightarrow 5[Mn(acac)_3] + 20H_2O + 7HCl + KCl$

2.2 The average water equivalent of the bomb calorimeter was experimentally found to be (by burning a certified grade benzoic acid) 10550 ± 10 $J°C^{-1}g^{-1}$.

3. Results and Discussion
3.1 The molar heat of combustion (Δ_cH) of the compound was determined using the relation

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

where, M is the formula 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 calorimetric combustion. The molar enthalpy of combustion of the sample was given in table 1.

By substituting the auxiliary thermochemical data from the standard reference sources [14, 15], the standard enthalpy of formation of $[Mn(C_5H_7O_2)_3(c)]$ was calculated using the relation $\Delta_cH = \Sigma\ \Delta_fH^e$ (products) - $\Sigma\ \Delta_fH^e$ (reactants). The auxiliary data of allied products like metal oxides, CO_2 (g) and H_2O (l) have also been taken from standard reference sources [16, 18].

Table 1: Molar enthalpy of combustion (Δ_cH) of $[Mn(C_5H_7O_2)_3(c)]$

(Molar mass = 352·097 g mol^{-1})			
Experiment No.	1	2	3
Wt. of the sample (g)	0·3462	0·3493	0·3739
Temperature rise (°C)	0·746	0·765	0·805
Temp. rise per g of the sample Δt (°C)	2·157	2·190	2·155

3.2 Reckoning of standard enthalpy of formation (Δ_fH^o) of [$Mn(C_5H_7O_2)_3(c)$]

By substituting auxiliary data from standard sources [14, 18], standard enthalpy of formation of tris (acetylacetonato) manganese (III) [$Mn(C_5H_7O_2)_3(c)$] was computed.

$Mn(C_5H_7O_2)_3(c) + O_2$ (g) (excess) = ½ Mn_2O_3 (c) + 15 CO_2 (g) + 10·5 H_2O (l)

$\Delta_cH = \Sigma \Delta_fH^o$ (products) - $\Sigma \Delta_fH^o$ (reactants)

or, Δ_cH = ½ Δ_fH^o Mn_2O_3 (c) + 15 Δ_fH^o CO_2 (g) + 10·5 $\Delta_fH^o10H_2O$ (l) – Δ_fH^o $Mn(C_5H_7O_2)_3(c)$

Therefore,

Δ_fH^o $Mn(C_5H_7O_2)_3(c)$ = ½ Δ_fH^o Mn_2O_3 (c) + 15 Δ_fH^o CO_2 (g) + 10·5 $\Delta_fH^o10H_2O$ (l) - Δ_cH

= ½ × (- 970·87) + 15 × (- 393·5) + 10·5 × (- 285·8) - (- 8049·588)

= - 485·435 - 5902·5 - 3000·9 + 8049·588

= - 9388·835 + 8049·588

= - 1339·247 ± 15 kJmol^{-1}.

The present Δ_fH^o value of $Mn(C_5H_7O_2)_3(c)$ compares well with that of = – 332·1 ± 0·7 kcal. /mole obtained by Hill and Irving at 25° by reaction calorimetry [19]. If conversion factor of 1 cal = 4·184 J is used then the value comes out to be 1389·5064 ± 2·92 kJmol^{-1}.

4. Conclusion

The negative value of Δ_fH^o of $Mn(C_5H_7O_2)_3(c)$ indicates stability of the compound. The heat of formation of $Mn(C_5H_7O_2)_3(c)$ was calculated by regarding all the six Mn-O bonds as equivalent [20], which was further supported by the known X-ray crystal structure of tris (2,4-pentanedionato) manganese (III), where the manganese-oxygen bond lengths are equal (198.5 ± 1.7 pm) [21]. Inductive or steric hindrance due to $–C_7H_5$ group seems to have no or little effect on the donor properties of the coordinated oxygen atoms.

5. References

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