

Original Research

Science Vision 16 (1)
January-March
ISSN (print) 0975-6175
ISSN (online) 2229-6026

Thermochemical studies of thorium(IV) and zirconium(IV) tetrabenzoates

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Received 1 September 2015 | Revised 11 December 2015 | Accepted 15 January 2016

ABSTRACT

Thermochemical studies of metal compounds of 's' and 'f' block elements and those of organometallic compounds are of immense importance because not only they furnish invaluable information regarding analysis and characterization of the compound thermodynamically but also give vital information regarding 'specific enthalpy' and 'enthalpy density'. Thus viability and analysis of input and output of energy is of prime concern before any process or reaction or for that matter if any engine or industry is being set up because after all it is the process or reaction which takes place inside the engine. As the globe is gradually but certainly moving away from fossil fuel or carbon-based energy production as it immensely pollutes the environment due to evolution of greenhouse gases into the environment and contribute towards global warming, it is but necessary to evaluate the impact assessment of the pollutants on the environment before any engine or industry is being developed or installed. It is in this perspective that the thermochemical studies of metal compounds of 's' 'p' 'd' and 'f' block elements and those of organometallic compounds become extremely important as it clearly identifies and defines the products as well as absorption and evolution of energy involved therein.

Key words: Enthalpy density; thermochemical studies; specific enthalpy; thorium; zirconium tetrabenzoates.

INTRODUCTION

Thermochemical studies of alkali metals, alkaline earth metals, transition and inner transition metals and their compounds and also those

of organometallic compounds has been of long-standing interest for chemists to create a large reservoir of thermochemical data for host of purposes. These studies are not only important in analysis and characterization of the compound thermodynamically but also important from energetics and environmental points of views. The assignment of calorific values of fuels and food are of utmost importance in characterizing them

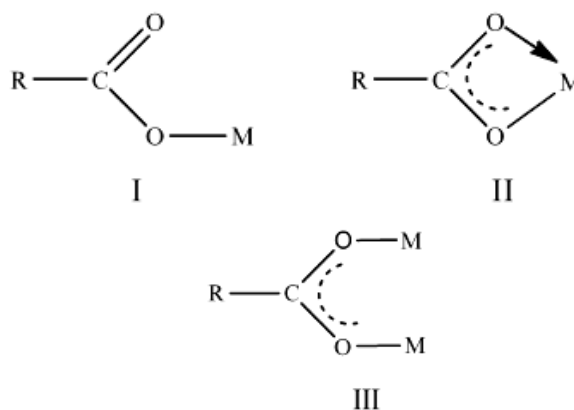
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as worthy and efficient and hence their thermochemical studies are so important. Thermochemical properties of fuels and foods are generally expressed in terms 'specific enthalpy' and 'enthalpy density' which is respectively defined as enthalpy of combustion per gram of material and enthalpy of combustion per litre of material. Thus, if the standard enthalpy of combustion is $\Delta_c H^\ominus$ and the molar mass of the compound is M , then the specific enthalpy is $\Delta_c H^\ominus/M$ and enthalpy density is $\Delta_c H^\ominus/V_m$, where V_m is the molar volume of the material.

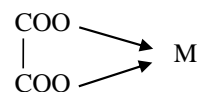
In fact major contributions to thermodynamic theory were made in 18th and 19th centuries but it was not until present century that thermodynamic methods were widely applied to chemistry. Willard Gibbs (1839-1903) developed the theory systematically but, with the exception of Haber's synthesis of ammonia (c.1905), little use of thermodynamic calculations was made by chemists until Lewis and Randall¹ published their book *Thermodynamics and the Free Energy of Chemical substances*.² The book which had introduced the science of thermodynamics to the chemists of the world, is considered to be one of the founding books on modern chemical thermodynamics and into the 1960s had been proclaimed as the 'thermodynamic bible' to the students of chemistry working in this field. Although the application of static oxygen-bomb calorimetric to organometallic compounds in the realization of enthalpy of combustion ($\Delta_c H$) and thereby enthalpy of formation ($\Delta_f H$) had been very successful, yet the experimental problems are severe and mainly concerned with the combustion part of the thermochemical investigation: a) in realizing complete combustion for both the organic part of the molecule and the metal, and b) in forming products which can be thermodynamically defined. 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 evaluation of enthalpy of combustion of thorium(IV)

and zirconium(IV) tetrabenzoates bomb calorimetrically and thereby to find the standard enthalpy of formation of these compounds.

It has been observed that in case of 'f' block elements, a variety of monobasic and dibasic carboxylates of aliphatic and aromatic acids are formed. The monobasic carboxylate ion COO^- acts as a donor in forming complexes with metal ions coordinating in one of the following modes (I-III).



In several metal carboxylates, a chelating bidentate structure (II) has been assigned^{3,4} though in some metal acetates, the acetate groups are monodentate.⁵ The general formulae⁶ of the dicarboxylic acids forming chelates in aqueous is



with the negatively charged oxygen of the carboxylate ion, COO^- , acting as a donor.

In yesteryears, enthalpies of precipitation of a number of oxinate complexes with divalent ions in aqueous phase have been studied and reported⁷ and also much later the standard heats of formation of uranyl (II) and thorium (IV) oxinates have been found out by Thakur *et al.*⁸ Although thermochemical studies of the compounds of inner transition metals have been scantily reported, some work has been done on uranium (VI) compounds earlier.^{9,10} Moreover the enthalpies of formation of the two oxalic

acid species and the first Th-oxalate complex have been measured at an ionic strength $I = 1.0M$ and temperature $t = 25^{\circ}C$ by Beiriger *et al.*¹⁷ and thereby corresponding entropy values were calculated from the van't Hoff equation.

MATERIALS AND METHODS

Preparation of thorium tetrabenzoate crystal [Th (C₆H₅COO)₄ (c)]

Thorium and zirconium tetrabenzoates were prepared by the known methods. Reagents of analytical grade were used for the preparation of the crystalline compounds. Thus, starting from analytical grade material, crystalline thorium tetrabenzoate Th(C₆H₅COO)₄(c) was prepared by boiling 2 g of thorium tetrahydroxide [Th(OH)₄] with 100 ml of benzoic acid [C₆H₅COOH] and the solution was evaporated to dryness on a waterbath. The crystalline precipitate (ppt) was washed with chloroform [CHCl₃] several times and finally with ether and then dried in a hot air oven at 110°C for six hours. It was analyzed for thorium. Found: Th 32.0%; Calculated for Th(C₆H₅COO)₄(c): Th 32.3%. Gravimetric estimation for thorium were completed by igniting the hydroxide ppt. to be converted into oxide and weighed directly.

Preparation of zirconium tetrabenzoate crystal [Zr (C₆H₅COO)₄ (c)]

1 g of zirconium chloride solution mixed with 200 ml of C₆H₅COOH solution was warmed gently and gradually until dissolution occurred. The solution was then evaporated to dryness on a waterbath. The crystallized product was dried in air in a hot- air oven at 110°C for 6 hours and stored in a desiccator. It was analyzed for zirconium. Found: Zr: 15.7%; calculated for Zr(C₆H₅COO)₄(c): Zr: 15.8%.

About 0.4-1 g of sample was pressed into pellets, loaded into the static bomb calorimeter and ignited under the oxygen gas [O₂ (g)] pressure of 30 atmosphere (atm). The completeness of com-

bustion process was examined in each case by analyzing the solid end products, viz., ThO₂(c) and ZrO₂(c). 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).¹¹ It was found to be 10574 ± 28 J°C⁻¹g⁻¹. Correctness due to the fuse wire (nichrome) and that for the cotton thread were already applied. Thorium tetrabenzoate and zirconium tetrabenzoate crystal pellets when ignited alone did not respond to complete combustion. Consequently, the sample pellets were sandwiched between two pellets of pure benzoic acid when combustion was found to be complete. Proper temperature corrections were applied for the benzoic acid as support pellets.

RESULTS AND DISCUSSION

The enthalpies or heats of combustion ($\Delta_c H$) of the compounds have been measured bomb calorimetrically. By substituting the auxiliary thermochemical data from the standard reference sources,⁷⁻¹⁰ the standard enthalpies of formation of Th(C₆H₅COO)₄(c) and Zr(C₆H₅COO)₄(c) have been estimated using the following relationship

$$\Delta_c H = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$$

Also the auxiliary enthalpy of formation data for products like metal oxides, CO₂(g) and H₂O (l) have been taken from standard reference sources.¹²⁻¹⁴

The enthalpy of combustion of the compounds have been determined from the relation

$$\Delta_c H = M W \Delta t$$

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 pure benzoic acid (crystalline). The value of W was measured to be 10574 ± 28°C⁻¹g⁻¹ as shown in Table 1.

$$\text{Mean water equivalent } W = 10574 \pm 28 \text{ J}^\circ\text{C}^{-1}$$

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)	0.7899	0.6957	0.6794	0.9752
Temperature rise (°C)	1.9661	1.7442	1.7012	2.4371
Temp. rise per gm benzoic acid (°C g ⁻¹)	2.489	2.507	2.504	2.499
W (J °C ⁻¹)	10620.329	10544.076	10556.709	10577.831

Table 2. Molar enthalpy of combustion ($\Delta_c H$) of thorium tetrabenzoate crystal [Th (C₆H₅COO)₄ (c)] (Molar mass = 716.04)

Experiment No.	1	2	3
Wt. of the sample (g)	0.4942	0.5111	0.5220
Wt. of benzoic acid (g)	0.6821	0.7104	0.6945
Total temp. rise (°C)	2.522	2.628	2.603
Temp. rise due to benzoic acid (°C)	1.706	1.777	1.737
Temp. rise due to sample (°C)	0.816	0.851	0.866
Temp. rise per g of the sample Δt (°C g ⁻¹)	1.651	1.665	1.659
$\Delta_c H$ (kJmol ⁻¹)	12500.4	12606.4	12560.9
Average Δt (°C g ⁻¹)	1.6583 ± 0.006		

g⁻¹

The reported value of enthalpy of combustion of certified grade benzoic acid⁶ is 26434 ± 5 Jg⁻¹.

From Table 2,

Mean temp. rise per gm of the sample, $\Delta t = 1.6583 \pm 0.006$

$$\begin{aligned} \text{Now -- } \Delta_c H &= M W \Delta t \\ &= 716.04 \times 10574 \times 1.6583 \\ &= 12555.7 \end{aligned}$$

Therefore, mean $\Delta_c H = -12555.7 \pm 43 \text{ kJ mol}^{-1}$

where, M = gram (g) molar mass of the sample,

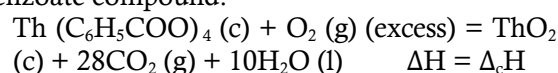
W = water equivalent of the bomb calorimeter = 10574 J °C⁻¹ g⁻¹,

and Δt = temp. rise per gm of combustion of the sample.

Standard enthalpy of formation ($\Delta_f H^\circ$) of Th (C₆H₅COO)₄ (c)

From the molar enthalpy of combustion, standard enthalpy of formation of thorium tetrabenzoate was evaluated. As a result of combustion of thorium tetrabenzoate, the following

products were characterized. The subsidiary key data have been substituted from the standard references.¹²⁻¹⁵ The percentage residue in the calorimeter as a result of combustion coincided with that of the respective metal oxide for each benzoate compound.⁴



The standard enthalpy of formation of the crystalline compounds were calculated from the relationship

$$\begin{aligned} \Delta_c H &= \sum \Delta_f H^\circ \text{ (products) -- } \sum \Delta_f H^\circ \text{ (reactants)} \\ \Delta_c H &= \Delta_f H^\circ \text{ ThO}_2 \text{ (c) + } \Delta_f H^\circ \text{ 28CO}_2 \text{ (g) + } \\ &\Delta_f H^\circ \text{ 10H}_2\text{O (l) -- } \Delta_f H^\circ \text{ Th (C}_6\text{H}_5\text{COO)}_4 \text{ (c)} \end{aligned}$$

Therefore,

$$\begin{aligned} \Delta_f H^\circ \text{ Th (C}_6\text{H}_5\text{COO)}_4 \text{ (c)} &= \Delta_f H^\circ \text{ ThO}_2 \text{ (c) + } \Delta_f H^\circ \text{ 28CO}_2 \text{ (g) + } \\ &\Delta_f H^\circ \text{ 10H}_2\text{O (l) -- } \Delta_c H \\ &= -1226.4 + 28(-393.5) + 10(-288.5) - (-12555.7) \\ &= -1226.4 - 11018 - 2885 + 12555.7 \\ &= -2573.7 \text{ kJmol}^{-1}. \end{aligned}$$

From Table 3,

Mean temp. rise per gm of the sample, $\Delta t =$

Table 3. Molar enthalpy of combustion ($\Delta_c H$) of zirconium tetrabenzoate crystal [$Zr(C_6H_5COO)_4(c)$] (Molar mass = 575.22)

Experiment No.	1	2	3
Wt. of the sample (g)	0.4831	0.4917	0.5014
Wt. of benzoic acid (g)	0.7978	0.8145	0.8323
Total temp. rise ($^{\circ}C$)	2.354	2.332	2.414
Temp. rise due to benzoic acid ($^{\circ}C$)	2.414	1.226	1.285
Temp. rise due to sample ($^{\circ}C$)	1.086	1.106	1.129
Temp. rise per g of the sample Δt ($^{\circ}C g^{-1}$)	2.248	2.249	2.251
$\Delta_c H$ ($kJ mol^{-1}$)	13673.2	13679.2	13691.4
Average Δt ($^{\circ}C g^{-1}$)	2.2493 \pm 0.005		

2.2493 \pm 0.005

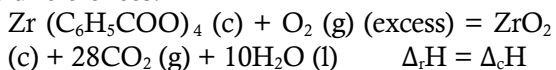
$$\begin{aligned} \text{Now, } -\Delta_c H &= M W \Delta t \\ &= 575.22 \times 10574 \times 2.2493 \\ &= 13681.1 \text{ kJ mol}^{-1} \end{aligned}$$

Therefore, mean $\Delta_c H = -13681.1 \pm 21 \text{ kJ mol}^{-1}$

where, M, W Δt have their usual meanings and the value of W = 10574 $J ^{\circ}C^{-1} g^{-1}$.

Standard enthalpy of formation ($\Delta_f H^{\circ}$) of $Zr(C_6H_5COO)_4(c)$

From the molar enthalpy of combustion, standard enthalpy of formation of zirconium tetrabenzoate was evaluated. As a result of combustion of zirconium tetrabenzoate, the following products were characterized. The subsidiary key data have been substituted from the standard references.⁸⁻¹¹



Since, $\Delta_c H = \Sigma \Delta_f H^{\circ} \text{ (products)} - \Sigma \Delta_f H^{\circ} \text{ (reactants)}$

$$\Delta_c H = \Delta_f H^{\circ} ZrO_2(c) + \Delta_f H^{\circ} 28CO_2(g) + \Delta_f H^{\circ} 10H_2O(l) - \Delta_f H^{\circ} Zr(C_6H_5COO)_4(c)$$

Therefore,

$$\begin{aligned} \Delta_f H^{\circ} Zr(C_6H_5COO)_4(c) &= \Delta_f H^{\circ} ZrO_2(c) + \Delta_f H^{\circ} 28CO_2(g) + \Delta_f H^{\circ} 10H_2O(l) - \Delta_c H \\ &= -1100.03 + 28(-393.5) + 10(-403.9) - (-13681.1) \end{aligned}$$

$$= -1100.03 - 11018 - 4039 + 13681.1$$

$$= -2475.93 \text{ kJ mol}^{-1}$$

The $\Delta_f H^{\circ}$ values of $ThO_2(c)$, $ZrO_2(c)$, $CO_2(g)$ and $H_2O(l)$ have been taken from the literature.^{8,16}

CONCLUSION

Complexes of acetates, propionates, formates, oxalates and benzoates occur in living system and many of them are of biological importance in controlling body metabolism such as synthesis of proteins, enzymes, hormones, etc. A perception of their enthalpies of formation and metal-nitrogen (M-N) and metal-oxygen (M-O) bond energies in such complexes may be useful in predicting the life processes. The values of $\Delta_c H$ and $\Delta_f H^{\circ}$ so obtained are in close agreement with those of latest values reported in the literature.

REFERENCES

- Lewis GN & Randall M (1923). *Thermodynamics and the Free Energy of Chemical Substances*. McGraw-Hill Book Company, New York, p. 653.
- Herington EFG (1964). The measurement of thermodynamic properties at the National Chemical Laboratory. Proc Chem Soc, 161, 161-200.
- Trotman-Dickensen AF & Bailar JC (1975). *Comprehensive Inorganic Chemistry* 1st edition. Oxford: Pergamon Press, 4,

- pp.1–1010.
- Oldham C (1968). Complexes of Simple Carboxylic Acids. In: *Progress in Inorganic Chemistry*. (FA Cotton, ed.), Interscience Publishers, a division of John Wiley & Sons, Inc., Hoboken, NJ, USA, 10, pp. 223–258.
 - Ashcroft SJ & Mortimer CT (1970). *Thermochemistry of Transition Metal Complexes*. Academic Press, New York, pp. 1–488.
 - Weast RC (1985). *Handbook of Chemistry and Physics*, 66th Edition. CRC Press, Florida, pp. 1–2363.
 - Jonassen HB & Oliver JR (1958). Metallated dye complexes. IV. The stereochemistry of copper(II)-dye complexes. *J Am Chem Soc*, 80, 2347.
 - Thaku S, Kumar A & Pathak R (1995). Standard heats of formation of uranyl (II) and thorium (IV) oxinates. *J Indian Chem Soc*, 72, 823–824.
 - Chernyaev II (1966). *Complex Compounds of Uranium*. Jerusalem Israel: Programme for Scientific Translation, pp. 1–520.
 - Thakur L, Thakur S, Pathak M & Jha RN (1992). Thermochemical studies of diaquodipropionatodioxouranium (VI). *J Indian Council Chem*, 8, 25–26.
 - Cox JD & Pilcher G (1970). *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London; New York, 74 (7), 70.
 - The International Council of Scientific Union (ICSU) Committee on Data for Science and Technology (CODATA), (1978). 10, 903.
 - Weast RC (1978). *Handbook of Chemistry and Physics*, 59th Edition. CRC Press, Florida, pp.1–2488.
 - Dean JA (1973). *Lange's Handbook of Chemistry* 11th Edition. McGraw Hill Book Company, New York, 9, 53–54.
 - Cox JD & Pilcher G (1970). *Thermochemistry of Organic and Organometallic Compounds*. Academic Press, London, 74 (7), 222.
 - Lange NA & Dean JA (1985). *Lange's Handbook of Chemistry* 13th Edition. McGraw Hill Book Company, New York, pp. 1–1792.
 - Beiriger JM & Grant PM (1991). Enthalpy of reaction of thorium (IV) with oxalate. *J Radioanal Nucl Chem*, 154, 89–94.