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

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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 caloric values of fuels and food are of utmost importance in characterizing them...
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 $\Delta_cH^\circ$ and the molar mass of the compound is $M$, then the specific enthalpy is $\Delta_cH^\circ/M$ and enthalpy density is $\Delta_cH^\circ/V_m$, 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 Randall$^1$ 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 ($\Delta_cH$) and thereby enthalpy of formation ($\Delta_fH$) 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 $\text{COO}^-$ acts as a donor in forming complexes with metal ions coordinating in one of the following modes (I–III).

![Diagram of molecular structures](image)

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 formulae$^6$ of the dicarboxylic acids forming chelates in aqueous is

\[
\begin{align*}
\text{COO} & \quad \text{M} \\
\text{COO} & \quad \text{M}
\end{align*}
\]

with the negatively charged oxygen of the carboxylate ion, $\text{COO}^-$, 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 reported$^7$ 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°C by Beiriger et al.\textsuperscript{17} and thereby corresponding entropy values were calculated from the van’t Hoff equation.

**MATERIALS AND METHODS**

**Preparation of thorium tetrabenzoate crystal [Th(C$_6$H$_5$COO)$_4$ (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(C$_6$H$_5$COO)$_4$ (c) was prepared by boiling 2 g of thorium tetrahydroxide [Th(OH)$_4$] with 100 ml of benzoic acid [C$_6$H$_5$COOH] and the solution was evaporated to dryness on a waterbath. The crystalline precipitate (ppt) was washed with chloroform [CHCl$_3$] 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(C$_6$H$_5$COO)$_4$ (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(C$_6$H$_5$COO)$_4$ (c)]**

1 g of zirconium chloride solution mixed with 200 ml of C$_6$H$_5$COOH 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(C$_6$H$_5$COO)$_4$ (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 [O$_2$ (g)] pressure of 30 atmosphere (atm). The completeness of combustion process was examined in each case by analyzing the solid end products, viz., ThO$_2$ (c) and ZrO$_2$ (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$^{-1}$).\textsuperscript{11} It was found to be 10574 ± 28 J°C$^{-1}$g$^{-1}$. 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 (\(\Delta H\)) of the compounds have been measured bomb calorimetrically. By substituting the auxiliary thermochemical data from the standard reference sources,\textsuperscript{7-10} the standard enthalpies of formation of Th(C$_6$H$_5$COO)$_4$ (c) and Zr(C$_6$H$_5$COO)$_4$ (c) have been estimated using the following relationship

\[
\Delta H = \Sigma \Delta H^\circ (\text{products}) - \Sigma \Delta H^\circ (\text{reactants})
\]

Also the auxiliary enthalpy of formation data for products like metal oxides, CO$_2$ (g) and H$_2$O (l) have been taken from standard reference sources.\textsuperscript{12-14} The enthalpy of combustion of the compounds have been determined from the relation

\[
\Delta H = M W \Delta t
\]

where M is the gram molecular weight of the crystalline compound, W the water equivalent of the bomb calorimeter and \(\Delta t\), 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$^{-1}$g$^{-1}$ as shown in Table 1.

Mean water equivalent W = 10574 ± 28 J°C$^{-1}$.
The reported value of enthalpy of combustion of certified grade benzoic acid is 26434 ± 5 Jg⁻¹.

From Table 2,

Mean temp. rise per gm of the sample, Δt = 1.6583 ± 0.006

Now -- ΔH = M W Δt
= 716.04 × 10574 × 1.6583
= 12555.7

Therefore, mean ΔH = -- 12555.7 ± 43 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 (ΔfH°) 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.¹²¹³ The percentage residue in the calorimeter as a result of combustion coincided with that of the respective metal oxide for each benzoate compound.³

Th (C₆H₅COO)₄(c) + O₂ (g) (excess) = ThO₂ (c) + 28CO₂ (g) + 10H₂O (l)

Therefore, ΔfH° = ΔH = 12555.7 ± 43 kJ mol⁻¹

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

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of benzoic acid (g)</td>
<td>0.7899</td>
<td>0.6957</td>
<td>0.6794</td>
<td>0.9752</td>
</tr>
<tr>
<td>Temperature rise (°C)</td>
<td>1.9661</td>
<td>1.7442</td>
<td>1.7012</td>
<td>2.4371</td>
</tr>
<tr>
<td>Temp. rise per gm benzoic acid (°C g⁻¹)</td>
<td>2.489</td>
<td>2.507</td>
<td>2.504</td>
<td>2.499</td>
</tr>
<tr>
<td>W (J °C⁻¹)</td>
<td>10620.329</td>
<td>10544.076</td>
<td>10556.709</td>
<td>10577.831</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of the sample (g)</td>
<td>0.4942</td>
<td>0.5111</td>
<td>0.5220</td>
</tr>
<tr>
<td>Wt. of benzoic acid (g)</td>
<td>0.6821</td>
<td>0.7104</td>
<td>0.6945</td>
</tr>
<tr>
<td>Total temp. rise (°C)</td>
<td>2.522</td>
<td>2.628</td>
<td>2.603</td>
</tr>
<tr>
<td>Temp. rise due to benzoic acid (°C)</td>
<td>1.706</td>
<td>1.777</td>
<td>1.737</td>
</tr>
<tr>
<td>Temp. rise due to sample (°C)</td>
<td>0.816</td>
<td>0.854</td>
<td>0.866</td>
</tr>
<tr>
<td>Temp. rise per g of the sample Δt (°C g⁻¹)</td>
<td>1.651</td>
<td>1.665</td>
<td>1.659</td>
</tr>
<tr>
<td>ΔcH (kJmol⁻¹)</td>
<td>12500.4</td>
<td>12606.4</td>
<td>12560.9</td>
</tr>
<tr>
<td>Average Δt (°C g⁻¹)</td>
<td>1.6583 ± 0.006</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Now, \[\Delta c_H = M W \Delta t = 575.22 \times 10574 \times 2.2493 = 13681.1 \text{ kJ mol}^{-1}\]

Therefore, mean \[\Delta c_H = 13681.1 \pm 21 \text{ kJ mol}^{-1}\]

where, \(M, W \Delta t\) have their usual meanings and the value of \(W = 10574 \text{ J} \cdot ^\circ\text{C}^{-1} \text{ g}^{-1}\).

\textbf{Standard enthalpy of formation (}\Delta H^\circ\text{) of Zr (C}_6\text{H}_5\text{COO)}_4(c)\text{ (i)}}

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.\(^8\)\(^11\)

\[\text{Zr (C}_6\text{H}_5\text{COO)}_4(c) + O_2(g) (excess) = ZrO}_2(c) + 28\text{CO}_2(g) + 10\text{H}_2\text{O(l)} \quad \Delta H = \Delta H^\circ\]

Since, \[\Delta H = \Sigma \Delta H^\circ \text{ (products)} - \Sigma \Delta H^\circ \text{ (reactants)}\]

\[\Delta H = -1100.03 + 28(\text{-393.5}) + 10(-403.9) - (-13681.1)\]

\[= -2475.93 \text{ kJ mol}^{-1}\]

The \(\Delta H^\circ\) values of \(\text{ThO}_2(c), \text{ZrO}_2(c), \text{CO}_2(g)\) and \(\text{H}_2\text{O(l)}\) have been taken from the literature.\(^8\)\(^16\)

\textbf{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 \(\Delta H\) and \(\Delta H^\circ\) so obtained are in close agreement with those of latest values reported in the literature.

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