

Standard Enthalpies of Formation of Rare Earth Stearate

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The constant volume combustion energies of four rare earth metal stearates (RE(St)₃, RE = Ce, Pr, Nd, Sm), $\Delta_c E$, are determined by a precision rotating bomb calorimeter. The standard enthalpies of combustion, $\Delta_c H_m^\circ$, and the standard enthalpies of formation, $\Delta_f H_m^\circ$, are calculated for these salts. $\Delta_{f,RE(St)_3(s)} H_m^\circ / (\text{kJ mol}^{-1})$ of the stearates are (-1274.32 ± 22.40) (Ce), (-5312.81 ± 17.37) (Pr), (-4811.30 ± 19.12) (Nd), and (-4202.18 ± 16.04) (Sm), respectively.

Rare earth stearate is a kind of novel, low-poisonous thermostabilizer of PVC industry [1]. Cerium stearate as a useful photosensitizer is colourless, tasteless, and low-poisonous [2]. It is used for controllable photodegradable polyvinyl, polypropylene food-stuff bag, wrapper, agricultural film, and so on [3, 4]. However, rare earth stearate thermochemical properties have not yet been reported in literature.

In this paper, the constant volume combustion energies of the four rare earth stearates are determined by using a precision rotating bomb calorimeter. The standard enthalpies of combustion, $\Delta_c H_m^\circ$, and the standard enthalpies of formation, $\Delta_f H_m^\circ$, are calculated. $\Delta_{f,RE(St)_3(s)} H_m^\circ / (\text{kJ mol}^{-1})$ of the stearates are (-1274.32 ± 22.40) (Ce), (-5312.81 ± 7.37) (Pr), (-4811.30 ± 19.12) (Nd), and (-4202.18 ± 16.04) (Sm), respectively. This work enriches thermodynamical data base and provides a theoretical basis for further study on the title compounds and their applications.

EXPERIMENTAL

The title compounds were prepared according to the Refs. [5, 6]. Chemical analyses show that the compositions of the compounds are RE(St)₃ (RE = Ce, Pr, Nd, Sm). The purity of the compounds is greater than 99.9 % as determined by LC.

The constant volume combustion energies of the stearates are determined by using the precision rotating bomb calorimeter (RBC-type II) [7]. The main experimental procedures are as follows: the room temperature is regulated to $(25 \pm 1)^\circ\text{C}$, the temperature of outer casing water bath of the rotating bomb is

controlled, $(25.0000 \pm 0.0005)^\circ\text{C}$, the water temperature in the caloritube is adjusted lower than that of the outer casing. Certain amount of distilled water is added to the caloritube. The sample is put into the crucible fixed onto the support (double-rings of normal axis on the same plane) in the rotating bomb but not fallen into the solution. The combustion wire is fixed in the bomb. The initial bomb solution is injected into the rotating bomb. Oxygen (2.5 MPa) is filled after sealing the bomb and a constant rate of temperature change of the calorimeter is kept. The temperature is read every 30 s after the experiment has begun and recorded 11 times as the initial stage. At the eleventh time, the stearate is fired and the temperature read once every 30 s till the temperature changes at a constant rate as the main stage. Then, the temperature is read once every 30 s and recorded 10 times as the final stage. The final products of the combustion reaction are analyzed after the experiment.

The procedures for analyzing the final products of the bomb are the same as in the literature [8]. Analytical results of the final products indicate that the combustion reaction is complete and carbon deposits and carbon monoxide are not formed during the combustion reaction. It is proved that the final product is CeO₂ or RE₂O₃ by IR spectroscopy and chemical analysis.

The energy equivalent of the calorimeter is calculated according to the following equation

$$W = \frac{Qa + Gb + 5.983c}{\Delta T} \quad (1)$$

where W is the energy equivalent of the calorimeter (in J K^{-1}), Q the combustion enthalpy of benzoic acid

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Table 1. Calibrated Results for the Energy Equivalent of the Calorimeter Using Benzoic Acid

| No. | Mass of benzoic acid, <i>a</i> /g | Changed temperature ΔT /K | Correction for nitric acid formation, q_n /J | Correction for the combustion of wire, q_c /J | Energy equivalent of calorimeter, W /(J K ⁻¹) |
|-----|-----------------------------------|-----------------------------------|--|---|---|
| 1 | 1.00323 | 1.4813 | 7.72 | 12.60 | 17916.49 |
| 2 | 1.04187 | 1.5339 | 7.47 | 11.78 | 17967.30 |
| 3 | 0.96425 | 1.4207 | 8.80 | 12.60 | 17956.21 |
| 4 | 1.00014 | 1.4753 | 14.95 | 11.94 | 17938.45 |
| 5 | 1.07238 | 1.5839 | 9.64 | 12.60 | 17910.73 |
| 6 | 0.98764 | 1.4574 | 8.92 | 12.32 | 17928.17 |

$$W = (17936.23 \pm 9.08) \text{ J K}^{-1}.$$

(in J g⁻¹), *a* the mass of the determined benzoic acid (in g), *G* the combustion enthalpy of Ni—Cr wire for ignition (in 0.9 J cm⁻¹), *b* the length of actual Ni—Cr wire consumed (in cm), 5.983 the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 cm³ of 0.1000 mol dm⁻³ solution of NaOH (in J cm⁻³), *c* the volume (in cm³) of consumed 0.1000 mol dm⁻³ solution of NaOH, and ΔT the value of the temperature changed (in K) ($\Delta T = T_t - T_0 + \Delta(\Delta T)$).

The corrected value of the heat exchange is calculated by the equation [9]

$$\Delta(\Delta T) = tV_0 + \frac{V_t - V_0}{\bar{T}_t - \bar{T}_0} \left(\frac{T_0 + T_t}{2} + \sum_{i=1}^{t-1} T_i - t\bar{T}_0 \right) \quad (2)$$

where $\Delta(\Delta T)$ denotes the corrected value of the heat exchange (in K), *t* is the time of readings for the main reaction period. V_0 and V_t are the rates of temperature change at the initial and final stages (in K), respectively (e.g. $V_0 = \frac{T_1 - T_0}{10}$ (in K), *V* is positive when temperature decreases). \bar{T}_0 and \bar{T}_t are the average temperatures of the calorimeter at the initial and final stages, respectively (average temperature for the first and last reading). T_0 is the last reading of the initial stage, T_t the first reading of the final stage. $\sum_{i=1}^{t-1} T_i$ is the sum of all the readings except the last one of the main period. $(V_t - V_0)/(\bar{T}_t - \bar{T}_0)$ is constant.

The calorimeter is calibrated with benzoic acid of purity 99.999%. The energy of combustion of benzoic acid is -26434 J g⁻¹ at 25 °C. The calibrated experimental results are given in Table 1.

The method of determining the combustion energy for the samples is the same as for the calibration of the calorimeter with benzoic acid.

RESULTS AND DISCUSSION

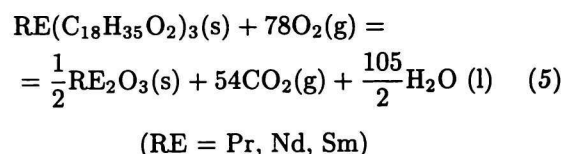
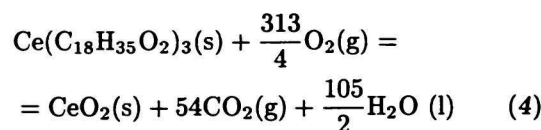
The combustion energies of the samples are calculated according to the formula

$$\Delta_c E = \frac{W\Delta T - Gb - 5.983c}{m} \quad (3)$$

where $\Delta_c E$ denotes the constant volume combustion energy of the sample (in J g⁻¹), *m* is the mass of the

determined sample (in g). The other symbols are the same as in eqn (1). The results of the calculations are given in Table 2.

The standard combustion enthalpy of the stearates, $\Delta_c H_m^\circ$, refers to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 101.325 kPa



The standard combustion enthalpies of the stearates are calculated from the combustion energy by the equations

$$\Delta_c H_m^\circ = \Delta_c E + \Delta nRT \quad (6)$$

$$\Delta n = n_{\text{gas}}(\text{products}) - n_{\text{gas}}(\text{reactants})$$

where n_{gas} is the total amount (in mol) of gas present as products or as reactants, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 298.15 \text{ K}$. The results of the calculations are shown in Table 3.

The standard enthalpies of formation of the stearates were calculated by Hess' law according to the following equation

$$\begin{aligned} \Delta_{f,\text{RE}(\text{St})_3(\text{s})} H_m^\circ &= \sum (\Delta_f H_m^\circ(\text{products})) - \\ &\quad - \Delta_{c,\text{RE}(\text{St})_3(\text{s})} H_m^\circ \quad (7) \end{aligned}$$

(RE = Pr, Nd, Sm)

In eqn (7), $\Delta_{f,\text{RE}_2\text{O}_3} H^\circ$ /(kJ mol⁻¹): (-1827.6 ± 1.52) (Pr), (-1808.12 ± 1.00) (Nd), (-1815.40 ± 2.01) (Sm) [10]; $\Delta_{f,\text{CeO}_2(\text{s})} H^\circ = (-1088.59 \pm 1.38) \text{ kJ mol}^{-1}$ [10]; $\Delta_{f,\text{CO}_2(\text{g})} H^\circ = (-393.51 \pm 0.13) \text{ kJ mol}^{-1}$ [11], and $\Delta_{f,\text{HO}_2(\text{g})} H^\circ = (-285.83 \pm 0.042) \text{ kJ mol}^{-1}$ [11].

The results of calculations are also given in Table 3.

Table 2. The Combustion Energies of the Four RE(St)₃

| Stearate | No. | Mass of complex, m/g | Correction for the combustion of wire, q_c/J | Correction for nitric acid, q_n/J | Changed temperature $\Delta T/K$ | Combustion energy, $\Delta E/(J g^{-1})$ |
|---------------------|------|------------------------|--|-------------------------------------|----------------------------------|--|
| Ce(St) ₃ | 1 | 0.52758 | 12.60 | 23.16 | 1.0728 | -36403.70 |
| | 2 | 0.44400 | 12.60 | 19.49 | 0.9008 | -36316.58 |
| | 3 | 0.49124 | 12.60 | 21.55 | 0.9957 | -36284.94 |
| | 4 | 0.50635 | 12.60 | 22.21 | 1.0277 | -36334.36 |
| | 5 | 0.51238 | 12.60 | 22.47 | 1.0407 | -36361.32 |
| | 6 | 0.52816 | 12.60 | 23.17 | 1.0745 | -36421.43 |
| | mean | | | | | -36353.72 ± 21.31 |
| Pr(St) ₃ | 1 | 0.70052 | 12.60 | 24.55 | 1.2521 | -32005.33 |
| | 2 | 0.62419 | 12.60 | 21.87 | 1.1191 | -32102.35 |
| | 3 | 0.60753 | 11.70 | 21.26 | 1.0884 | -32078.19 |
| | 4 | 0.61620 | 12.60 | 21.56 | 1.1049 | -32105.78 |
| | 5 | 0.66478 | 12.60 | 23.27 | 1.1902 | -32057.86 |
| | 6 | 0.63536 | 12.60 | 22.23 | 1.1391 | -32101.40 |
| | mean | | | | | -32075.15 ± 15.86 |
| Nd(St) ₃ | 1 | 0.54010 | 9.00 | 18.42 | 0.9789 | -32456.99 |
| | 2 | 0.55560 | 12.60 | 18.95 | 1.0088 | -32509.32 |
| | 3 | 0.51650 | 11.70 | 17.61 | 0.9377 | -32505.66 |
| | 4 | 0.56052 | 12.60 | 19.10 | 1.0171 | -32489.28 |
| | 5 | 0.54027 | 12.60 | 18.42 | 0.9779 | -32406.92 |
| | 6 | 0.52328 | 12.60 | 17.84 | 0.9506 | -32524.49 |
| | mean | | | | | -32462.11 ± 17.73 |
| Sm(St) ₃ | 1 | 0.70214 | 12.60 | 17.55 | 1.2893 | -32891.72 |
| | 2 | 0.71063 | 11.70 | 17.75 | 1.3016 | -32810.19 |
| | 3 | 0.67435 | 12.60 | 16.86 | 1.2389 | -32907.71 |
| | 4 | 0.73538 | 12.60 | 18.50 | 1.3493 | -32867.08 |
| | 5 | 0.68420 | 12.60 | 17.12 | 1.2561 | -32894.46 |
| | 6 | 0.75369 | 12.60 | 18.75 | 1.3840 | -32894.06 |
| | mean | | | | | -32875.87 ± 14.21 |

Table 3. Combustion Energy, Standard Enthalpy of Combustion, and Standard Enthalpy of Formation of the Four RE(St)₃

| Stearate | $\Delta_c E/(kJ mol^{-1})$ | $\Delta_c H_m^0/(kJ mol^{-1})$ | $\Delta_f H_m^0/(kJ mol^{-1})$ |
|---------------------|----------------------------|--------------------------------|--------------------------------|
| Ce(St) ₃ | -36009.78 ± 21.11 | -36069.09 ± 21.11 | -1274.32 ± 22.40 |
| Pr(St) ₃ | -31797.12 ± 15.72 | -31856.61 ± 15.72 | -5312.81 ± 17.37 |
| Nd(St) ₃ | -32288.89 ± 17.64 | -32348.38 ± 17.64 | -4811.30 ± 19.12 |
| Sm(St) ₃ | -32901.65 ± 14.22 | -32961.14 ± 14.22 | -4202.18 ± 16.04 |

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