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Thermochemistry of lead styphnate

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Abstract

Using an isoperibol twin-Dewar solution calorimeter, the enthalpies of reaction of normal lead styphnate monohydrate, monobasic lead styphnate, tribasic lead styphnate dihydrate, and pentabasic lead styphnate dihydrate were determined as −17.29, −61.92, −196.37 and −261.12 kJ mol^{-1}, respectively, which, with various ancillary data, gave the standard enthalpies of formation of −738.27, −981.70, −1995.99 and −2487.84 kJ mol^{-1}, respectively.

Keywords: Calorimetry; Heat of formation; Isoperibol; Lead styphnate

1. Introduction

It would be quite correct to say that the study of detonation reactions is a post-Second-World-War science, and has even acquired the title of 'detonics'. The traditional type-member of the class of primary explosives is mercury fulminate, since its first use by Nobel.

In comparison, the metal salts of polynitroresorcinols are relatively recent compounds, and by far the most important is lead styphnate. Other metal salts of styphnic acid have been made, but as these are generally of little industrial interest, few literature reports exist. Three polymorphs of lead styphnate are known, and three monobasic lead salts with some higher basic salts.

The first preparation of a lead styphnate has never been substantiated but it is thought that it could have been by Griess [1] in 1874. The first preparation of

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anhydrous normal lead styphnate was by Herz [2] in 1919. Since then various preparations have been recorded [3]. Essentially the preparation method is the addition of a solution containing lead acetate to a solution of sodium or magnesium styphnate to precipitate the lead styphnate.

Lead styphnate is considered a relatively poor initiating agent, but because of its sensitivity to ignition, it is used to some extent as a cover charge for lead azide and as an ingredient of priming compositions [4]. The industrial purification of lead styphnate has long been a problem, as the compound readily decomposes in solution. One method for purification [5] employs glycerol and water. This method was not adopted in the present investigation owing to the danger of glycerol being occluded in the crystal structure of the final lead styphnate.

2. Experimental

2.1. Materials and synthesis

Normal lead styphnate monohydrate [2]

To a solution of styphnic acid [6] (1.23 g in 25 cm^3 ethanol) was added aqueous lead nitrate (25 cm^3, 0.20 M) and the mixture was heated to 70°C. Ethanolamine was then added dropwise with stirring, allowing the precipitate which formed after the addition of each drop to redissolve. The addition was continued until the pH, tested with Hydrion test paper was approx. 3.5. A further amount of ethanol (25 cm^3, Abs.) was then added and the reaction mixture brought back to temperture. A solution of ethanolamine (4.0 M) in ethanol was then prepared and added dropwise to the reaction mixture until a pH 4.8 was obtained. The orange precipitate formed was filtered off and washed with water and alcohol before drying.

Monobasic lead styphnate

A solution of lead nitrate (2.5 g in 62.5 cm^3 water) was prepared and added to an agitated solution of sodium styphnate (0.62 g styphnic acid [6], 0.4 g sodium hydroxide, 37.5 cm^3 water), pre-heated to 95°C. The precipitate was filtered hot, and the product was subsequently washed with water and then alcohol before being further dried under vacuum in a desiccator over silica gel for at least 25 h.

Tribasic lead styphnate [7]

To an aqueous, basic solution of disodium styphnate (25.0 cm^3, containing 0.96 g styphnic acid [6], and 0.40 g anhydrous sodium carbonate) was added with stirring a solution of lead nitrate (20.0 cm^3, containing 4.96 g lead nitrate (A.R.)), simultaneously with a solution of sodium hydroxide (20.0 cm^3, containing 0.9 g sodium hydroxide). The two solutions were added very slowly with stirring while the reaction mixture was maintained at 85°C. Stirring was continued for 5 min before the product was decanted hot. The orange precipitate was washed and filtered under gravity before washing with methylated spirits and dried in a 60°C oven. The product was finally stored in a vacuum desiccator over silica gel.

$$C_6H(NO_2)_3(ONa)_2(aq) + 4Pb(NO_3)_2(aq) + 6NaOH(aq) \rightarrow$$

$$C_6H(NO_2)_3(OPbOH)_2 2PbO(s)\downarrow + 8NaNO_3(aq) + 2H_2O(l)$$

Pentabasic lead styphnate [7]

To an aqueous, basic solution of disodium styphnate (25 cm^3, containing 0.96 g styphnic acid [6], and 0.40 g anhydrous sodium carbonate) was added with stirring a solution of lead nitrate (20.0 cm^3, containing 7.45 g lead nitrate (A.R.)), simultaneously with a solution of sodium hydroxide (20.0 cm^3, containing 1.5 g sodium hydroxide). The two solutions were added very slowly with stirring while the reaction mixture was maintained at 85°C. Stirring was continued for 5 min before the product was decanted hot. The orange precipitate was washed and filtered under gravity before washing with methylated spirits and dried in a 60°C oven. The product was finally stored in a vacuum desiccator over silica gel.

$$C_6H(NO_2)_3(ONa)_2(aq) + 6Pb(NO_3)_2(aq) + 10NaOH(aq) \rightarrow$$

$$C_6H(NO_2)_3(OPbOH)_2 4PbO(s)\downarrow + 12NaNO_3(aq) + 4H_2O(l)$$

2.2. Analysis

For the analysis of lead in the lead polynitroresorcinates, a titrimetric method developed by Kurz and Kober [8] was used. The lead styphnate (200 mg, 0.5×10^{-3} mol) was added to ethanol (20 cm^3) containing nitric acid (5 cm^3, 0.1 mol). The mixture was swirled to dissolve all the lead compound. To this mixture, EDTA (25.0 cm^3, 0.02 mol), water (250 cm^3) and xylenol orange solution (10–15 drops, 0.2%) were added, and then sodium hydroxide (1 N) was carefully added to neutralise to the first reddish tinge. A further amount of nitric acid (1–2 drops, 0.1 N) was then added until the colour changed to bright yellow. Acetic acid (100 cm^3, 1 M) was added to sodium acetate (1 dm^3, 1 M) and 5 cm^3 of this buffer solution was added to the styphnate mixture. The excess EDTA was then back-titrated with lead nitrate solution (0.02 M) to the first reddish tinge. The analysis was performed in duplicate and also with a blank. Results for lead are shown in Table 1, and those obtained for C, H and N microanalysis are in Table 2.

Table 1
Analysis for lead concentration

Normal lead styphnate monohydrate
Theoretical lead content of $C_6H(NO_2)_3O_2Pb \cdot H_2O = 44.24\%$; found, 44.34% and 44.28%
Monobasic lead styphnate
Theoretical lead content of $C_6H(NO_2)_3O_2Pb \cdot Pb(OH)_2 = 59.93\%$; found, 58.82% and 59.94%
Tribasic lead styphnate dihydrate
Theoretical lead content of $C_6H(NO_2)_3(OPbOH)_2 2PbO \cdot 2H_2O = 74.81\%$; found, 72.34% and 72.18%
Pentabasic lead styphnate dihydrate
Theoretical lead content of $C_6H(NO_2)_3(OPbOH)_2 4PbO \cdot 2H_2O = 76.72\%$; found, 76.95% and 76.83%

Table 2
Micro-analysis results

	Expected/%	Found/%
Normal lead styphnate monohydrate (mol. wt. 468.29)		
Carbon	15.39	15.63
Hydrogen	0.65	0.60
Nitrogen	8.97	8.76
Monobasic lead styphnate (mol. wt. 691.48)	Expected/%	Found/%
Carbon	10.42	10.40
Hydrogen	0.44	0.42
Nitrogen	6.08	5.97
Tribasic lead styphnate dihydrate (mol. wt. 1146.969)	Expected/%	Found/%
Carbon	6.28	6.15
Hydrogen	0.62	0.55
Nitrogen	3.66	3.59
Pentabasic lead styphnate dihydrate (mol. wt. 1620.27)	Expected/%	Found/%
Carbon	4.45	4.42
Hydrogen	0.44	0.46
Nitrogen	2.59	2.29

Tris(hydroxymethyl)methylamine (THAM)

A commercial sample (B.D.H., Aristar grade, min. 99.9%) was used as supplied after being ground to a very fine powder using an agate mortar, and annealed for 3 h in an oven at 80°C before being allowed to cool in a vacuum desiccator over silica gel.

2.3. Solution calorimeter

The calorimeter designed and constructed in this laboratory is a twin-Dewar isoperibol type [3]. Temperature changes within the vessels were detected by thermistors, which were connected to a differential a.c. thermistor bridge. A reaction was initiated by breaking an ampoule within one (reaction) of the calorimeter vessels. Using amplifiers and voltage back-off, the reaction was monitored on a chart recorder. On completion, the vessel was cooled to the initial starting temperature and left until thermal stability was re-established. The reaction was then simulated using a precision heater for the same thermal change. The time of heating was accurately recorded, and the current and voltage were measured using a stabilised voltage supply, precision resistor and a very accurate digital voltmeter. The results were interpreted using Dickinson's method [9].

Test reaction

To check for satisfactory operation of the calorimeter, the heat of solution of tris(hydroxymethyl)methylamine (THAM or TRIS) $(HOCH_2)_3CNH_2$ was measured in an excess of either aqueous hydrochloric acid (0.100 M, B.D.H., A.V.S.) for an exothermic change, or aqueous sodium hydroxide (0.050 M, B.D.H., A.V.S.) for an endothermic change. The enthalpy of solution in both were determined and the results obtained were compared with literature results [10]. Some typical results obtained are shown elsewhere [3].

Direct measurement of the enthalpy of solution of lead nitrate in nitric acid/styphnic acid mixture

The enthalpy of solution of lead nitrate (B.D.H., A.R., re-crystallized from water) was measured using an LKB 8700-1 calorimeter. A solution of nitric acid (B.D.H., 0.1 M, A.V.S.) saturated with styphnic acid [6] was made, and the ampoule contained lead nitrate

$$[HNO_3 + \text{styphnic acid(sat.)}](aq) + Pb(NO_3)_2(s) \rightarrow$$

$$[HNO_3 + \text{styphnic acid(sat.)} + Pb(NO_3)_2](aq)$$

The calorimetric results obtained are shown in Table 3.

Enthalpy of reaction of normal lead styphnate monohydrate

The reaction shown in Fig. 1 was carried out and a small exothermic enthalpy change was measured, the results of which are shown in Table 4.

Enthalpy of reaction of monobasic lead styphnate

The reaction used was the same as that for normal lead styphnate. This reaction gave rise to an exothermic change, the results of which are shown in Table 5.

Enthalpy of reaction of tribasic lead styphnate dihydrate

The reaction used was the same as that for normal lead styphnate. This reaction gave rise to an exothermic change, the results of which are shown in Table 6.

Table 3
Enthalpy of solution of lead nitrate in aqueous nitric acid/styphnic acid

W/g	Dilution/n [a]	$\Delta_{sol}H^{\ominus}$/kJ mol^{-1} [b]
0.16259	11204.0	24.46
0.12595	14463.9	24.49
0.31646	5756.2	24.71
0.19693	9250.2	24.45
0.20648	8822.4	24.42
0.19856	9174.3	24.43
0.15923	11440.4	24.47

[a] n = molar ratio of lead to water. [b] $\Delta_{sol}H^{\ominus}(\text{mean}) = 24.49 \pm 0.09$ kJ mol^{-1}.

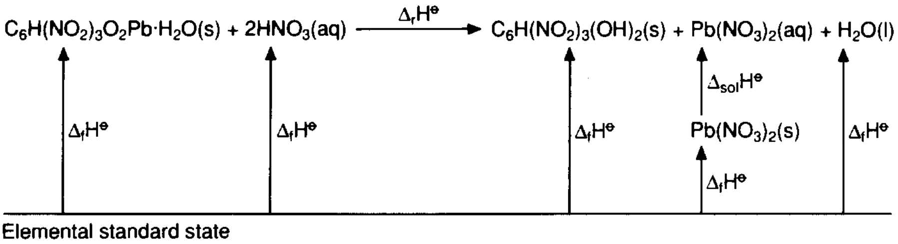

Fig. 1. Thermochemistry of lead styphnates.

Enthalpy of reaction of pentabasic lead styphnate dihydrate

The reaction used was the same as that for normal lead styphnate. This reaction gave rise to an exothermic change, the results of which are shown in Table 7.

Reaction test analysis

All lead styphnate reactions consisted of using a pre-saturated solution of styphnic acid [6] in nitric acid, the styphnate being placed in an ampoule which was

Table 4
Enthalpy of reaction of normal lead styphnate monohydrate

W/g	$-\Delta_rH^\ominus$/kJ mol^{-1} [a]	W/g	$-\Delta_rH^\ominus$/kJ mol^{-1} [a]
0.13224	17.08	0.14352	17.18
0.18164	17.38	0.06766	17.30
0.08151	17.21	0.24786	17.56

[a] $\Delta_rH^\ominus$(mean) = −17.29 ± 0.18 kJ mol^{-1}.

Table 5
Enthalpy of reaction of monobasic lead styphnate

W/g	$-\Delta_rH^\ominus$/kJ mol^{-1} [a]	W/g	$-\Delta_rH^\ominus$/kJ mol^{-1} [a]
0.13895	61.901	0.08281	61.858
0.11012	62.150	0.06749	61.920
0.10006	62.072	0.03179	61.611

[a] $\Delta_rH^\ominus$(mean) = −61.91 ± 0.20 kJ mol^{-1}.

Table 6
Enthalpy of reaction of tribasic lead styphnate dihydrate

W/g	$-\Delta_rH^\ominus$/kJ mol^{-1} [a]	W/g	$-\Delta_rH^\ominus$/kJ mol^{-1} [a]
0.08140	196.591	0.17427	196.320
0.23295	196.398	0.17479	196.334
0.20671	196.058	0.12541	196.519

[a] $\Delta_rH^\ominus$(mean) = −196.37 ± 0.19 kJ mol^{-1}.

Table 7
Enthalpy of reaction of pentabasic lead styphnate dihydrate

W/g	$-\Delta_r H^\circ/\mathrm{kJ\ mol^{-1}}$ [a]	W/g	$-\Delta_r H^\circ/\mathrm{kJ\ mol^{-1}}$ [a]
0.30192	282.057	0.17605	280.815
0.19705	281.998	0.20512	280.877
0.13374	280.143	0.17968	280.837

[a] $\Delta_r H^\circ(\mathrm{mean}) = -281.12 \pm 0.79\ \mathrm{kJ\ mol^{-1}}$.

Table 8
Analysis results for lead ion produced in various calorimetric reactions

Compound	Calc./%	Found/%
Normal lead styphnate monohydrate	44.24	(a) 44.22 (b) 44.24
Monobasic lead styphnate	59.93	(a) 59.85 (b) 59.90
Tribasic lead styphnate dihydrate	74.81	(a) 74.79 (b) 74.89
Pentabasic lead styphnate dihydrate	76.72	(a) 76.77 (b) 76.70

broken at the relevant time. A quantitative analysis was performed on the products to confirm complete reaction. This was done by twice extracting the product mixture with chloroform (A.R., 100 cm^3). The resulting nitric acid solution was then tested for the metal ion [8]. The results are shown in Table 8.

Enthalpy of formation of normal lead styphnate monohydrate

From the enthalpy of reaction obtained for normal lead styphnate monohydrate and using various ancillary data, the enthalpy of formation of the styphnate was calculated

$$\begin{aligned}&\Delta_f H^\circ[\mathrm{C_6H(NO_2)_3O_2Pb \cdot H_2O(s)}]\\&\quad = \Delta_f H^\circ[\mathrm{C_6H(NO_2)_3(OH)_2(s)}] + \Delta_{sol} H^\circ[\mathrm{Pb(NO_3)_2(aq)}]\\&\qquad + \Delta_f H^\circ[\mathrm{Pb(NO_3)_2(s)}] - 2\Delta_f H^\circ[\mathrm{HNO_3(aq)}] + \Delta_f H^\circ[\mathrm{H_2O(l)}] - \Delta_r H^\circ\end{aligned}$$

$$\begin{aligned}&\Delta_f H^\circ[\mathrm{C_6H(NO_2)_3O_2Pb \cdot H_2O(s)}]\\&\quad = [-467.50] + [24.49]\\&\qquad + [-440.66] + [-285.83] - 2[-206.97] - [-17.29]\\&\quad = -738.27 \pm 6.95\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Enthalpy of formation of monobasic lead styphnate

From the enthalpy of reaction obtained for monobasic lead styphnate and using various ancillary data, the enthalpy of formation of the styphnate was calculated

$$\begin{aligned}
&\Delta_f H^\ominus[\mathrm{C_6H(NO_2)_3(OPbOH)_2(s)}]\\
&\quad = \Delta_f H^\ominus[\mathrm{C_6H(NO_2)_3(OH)_2(s)}] + 2\Delta_f H^\ominus[\mathrm{Pb(NO_3)_2(s)}]\\
&\qquad + 2\Delta_{sol} H^\ominus[\mathrm{Pb(NO_3)_2(aq)}] + 2\Delta_f H^\ominus[\mathrm{H_1O(l)}] - \Delta_r H^\ominus\\
&\qquad - 4\Delta_f H^\ominus[\mathrm{HNO_3(aq)}]
\end{aligned}$$

$$\begin{aligned}
&\Delta_f H^\ominus[\mathrm{C_6H(NO_2)_3(OPbOH)_2(s)}]\\
&\quad = [-467.50] + 2[24.49]\\
&\qquad + 2[-285.83] - [-61.92] - 4[-206.97]\\
&\qquad + 2[-440.66]\\
&\quad = -981.70 \pm 7.11\ \mathrm{kJ\ mol^{-1}}
\end{aligned}$$

Enthalpy of formation of tribasic lead styphnate dihydrate

From the enthalpy of reaction obtained for tribasic lead styphnate dihydrate and using various ancillary data, the enthalpy of formation of the styphnate was calculated

$$\begin{aligned}
&\Delta_f H^\ominus[\mathrm{C_6H(NO_2)_3(OPbOH)_2 2PbO \cdot 2H_2O(s)}]\\
&\quad = \Delta_f H^\ominus[\mathrm{C_6H(NO_2)_3(OH)_2(s)}] + 6\Delta_f H^\ominus[\mathrm{H_2O(l)}] + 4\Delta_f H^\ominus[\mathrm{Pb(NO_3)_2(s)}]\\
&\qquad + 4\Delta_{sol} H^\ominus[\mathrm{Pb(NO_3)_2(aq)}] - \Delta_r H^\ominus - 8\Delta_f H^\ominus[\mathrm{HNO_3(aq)}]
\end{aligned}$$

$$\begin{aligned}
&\Delta_f H^\ominus[\mathrm{C_6H(NO_2)_3(OPbOH)_2 2PbO \cdot 2H_2O(s)}]\\
&\quad = [-467.50] + 6[-285.83] + 4[24.49]\\
&\qquad + 4[-440.66] - 8[206.85] - [-196.37]\\
&\quad = -1995.99 \pm 7.69\ \mathrm{kJ\ mol^{-1}}
\end{aligned}$$

Enthalpy of formation of pentabasic lead styphnate dihydrate

From the enthalpy of reaction obtained for pentabasic lead styphnate dihydrate and using various ancillary data, the enthalpy of formation of the styphnate was calculated

$$\begin{aligned}
&\Delta_f H^\ominus[\mathrm{C_6H(NO_2)_3(OPbOH)_2 4PbO \cdot 2H_2O(s)}]\\
&\quad = \Delta_f H^\ominus[\mathrm{C_6H(NO_2)_3(OH)_2(s)}] + 8\Delta_f H^\ominus[\mathrm{H_2O(l)}] + 6\Delta_f H^\ominus[\mathrm{Pb(NO_3)_2(s)}]\\
&\qquad + 6\Delta_{sol} H^\ominus[\mathrm{Pb(NO_3)_2(aq)}] - \Delta_r H^\ominus - 12\Delta_f H^\ominus[\mathrm{HNO_3(aq)}]
\end{aligned}$$

$$\begin{aligned}
&\Delta_f H^\ominus[\mathrm{C_6H(NO_2)_3(OPbOH)_2 4PbO \cdot 2H_2O(s)}]\\
&\quad = [-467.50] + 8[-285.83] - 12[-206.85]\\
&\qquad + 6[-440.66] + 6[-24.49] - [-281.12]\\
&\quad = -2487.84 \pm 8.61\ \mathrm{kJ\ mol^{-1}}
\end{aligned}$$

Ancillary data

The following data were used: $\Delta_f H^\ominus[H_2O(l)] = -285.83 \pm 0.04$ kJ mol^{-1} [11]; $\Delta_f H^\ominus[Pb(NO_3)_2(s)] = -440.66 \pm 0.84$ kJ mol^{-1} [12]; $\Delta_f H^\ominus[(1.0\ N)HNO_3(aq)] = -206.85 \pm 0.03$ kJ mol^{-1} [13]; $\Delta_f H^\ominus[(0.1\ N)HNO_3(aq)] = -206.97 \pm 0.04$ kJ mol^{-1} [13]; $\Delta_f H^\ominus[C_6H(NO_2)_3(OH)_2(s)] = -467.50 \pm 6.90$ kJ mol^{-1} [6].

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