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Thermochimica Acta 265 (1995) 73–87

thermochimica
acta

Thermochemistry of lead 2,4- and 4,6-dinitroresorcinol

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Received 1 March 1995; accepted 27 May 1995

Abstract

Using an isoperibol twin Dewar solution calorimeter, the enthalpies of reaction of normal lead 2,4-dinitroresorcinol; monobasic lead 2,4-dinitroresorcinol; tribasic lead 2,4-dinitroresorcinol; quadrabasic lead 2,4-dinitroresorcinol; monobasic lead 4,6-dinitroresorcinol; dibasic lead 4,6-dinitroresorcinol and tribasic lead 4,6-dinitroresorcinol were determined as -29.36; -85.34; -179.12; -227.37; -96.62; -175.88 and $-162.47\,\mathrm{kJ\,mol^{-1}}$, respectively, which, with various ancillary data, gave the standard enthalpies of formation of -396.01; -628.46; -1397.37; -1637.55; -927.74; -1132.95 and $-1434.83\,\mathrm{kJ\,mol^{-1}}$, respectively.

Keywords: Calorimetry; Heat of formation; Isoperibol; Lead 2,4-dinitroresorcinol; Lead 4,6-dinitroresorcinol

1. Introduction

By far the most important of the polynitroresorcinols is styphnic acid (2,4,6-trinitroresorcinol or 2,4,6-trinitro-1,3-dihydroxybenzene). Another polyhydric phenol of important industrial use is dinitroresorcinol. Two isomers exist, 2,4- and 4,6-dinitroresorcinol (2,4- and 4,6-DNR). The 4,6-DNR isomer has always been the lesser important as it cannot be directly synthesised, though it may be prepared by nitration of diacetylresorcinol. The preparation of 2,4-dinitroresorcinol (2,4-DNR) has proved much easier, the best being found to be by dinitrosation of resorcinol by alkaline oxidation [1]. It is this synthesis that can be used in the preparation of styphnic acid by the addition of ice-cold dilute nitric acid to the 2,4-DNR. It is interesting to note that no 4,6-DNR is formed in the synthesis.

The first reported preparation of 4,6-DNR was in 1883 by Typke [2]. The method of synthesis consisted of treating diacetoxybenzene with cold nitric acid, followed by hydrolysis of the acetate group with hot hydrochloric acid.

SSDI 0040-6031(95)02548-0

As might be expected, lead-DNR is a less powerful explosive and less efficient initiator than lead styphnate. The metal salts of 2,4-DNR are far more commonly found amongst the 2,4- and 4,6-isomers because of the synthesis problems of 4,6-DNR. The preparation of the lead salt is generally via the sodium salt of the dinitroresorcinol, the sodium being introduced as sodium carbonate and the lead as lead nitrate. The metal dinitroresorcinols have only been used to any extent since 1940 and, like the styphnates, their uses are as primary composites.

2. Experimental

2.1. Materials and synthesis

Normal lead 2,4-dinitroresorcinol [3]

To an aqueous solution of sodium 2,4-dinitroresorcinol [250 cm^3; containing 2.5 g 2,4-DNR [4] and 1.33 g anhydrous sodium carbonate], a second boiling solution of lead nitrate [30 cm^3; containing 5 g lead nitrate (BDH, AR)] was slowly added with stirring. Upon completion of addition, the mixture was stirred for a further 20 min while cooling. The orange-coloured precipitate was then filtered under gravity and washed with water, alcohol and finally petroleum ether (30–40°C). The product was put in a warm oven (~ 40°C) for several hours, and finally stored in a vacuum desiccator over silica gel.

$$C_6H_2(NO_2)_2(ONa)_{2(aq)} + Pb(NO_3)_{2(aq)} \rightarrow C_6H_2(NO_2)_2O_2Pb\downarrow + 2NaNO_{3(aq)}$$

Monobasic lead 2,4-dinitroresorcinol [5]

To an aqueous solution of sodium 2,4-dinitroresorcinol, [40 cm^3; containing 1 g 2,4-DNR [4] and 20 cm^3 (N) sodium hydroxide] heated with stirring to 75°C, a solution of lead nitrate [33 cm^3; containing 3.3 g lead nitrate] also heated to 75°C was added. The temperature of the mixture was maintained at 75°C with constant stirring for 20 min. During this period the precipitate changed to a red tinge in colour from the initial orange colour. The product was filtered off under gravity and the precipitate was washed with water, alcohol and finally ether. The lead-DNR was placed in a warm oven (~ 40°C) for several hours and finally stored in a vacuum desiccator over silica gel.

$$C_6H_2(NO_2)_2(ONa)_{2(aq)} + 2Pb(NO_3)_{2(aq)} \rightarrow$$

$$C_6H_2(NO_2)_2O_2Pb\cdot PbO\downarrow + 2HNO_{3(aq)} + 2NaNO_{3(aq)}$$

Tribasic lead 2,4-dinitroresorcinol [6]

The disodium 2,4-dinitroresorcinate was prepared [60 cm^3; containing 1 g 2,4-DNR [4] and 0.5 g sodium carbonate]. To this solution was added with stirring an aqueous lead nitrate solution [7.5 cm^3, 1.65 g lead nitrate (AR)]. Upon completion of addition, the mixture was stirred for several min before a second aqueous solution containing lead nitrate (AR) and sodium hydroxide [45 cm^3; 4.97 g lead nitrate and 1.2 g sodium hydroxide] was slowly added. The stirring was continued for 10 min before the product was allowed to settle and was isolated. The temperature of the reaction mixture was maintained at 90°C throughout the preparation (yield ca. 88%). The orange-coloured compound was stored under vacuum in a desiccator over silica gel.

$$C_6H_2(NO_2)_2(ONa)_{2(aq)} + 4Pb(NO_3)_{2(aq)} + 6NaOH_{(aq)} \rightarrow C_6H_2(NO_2)_2(OPbOH)_2 2PbO\downarrow + 8NaNO_{3(aq)}$$

Quadrabasic lead 2,4-dinitroresorcinol [6]

The disodium 2,4-dinitroresorcinate was prepared [60 cm^3; containing 1 g 2,4-DNR [4] and 0.5 g sodium carbonate]. To this solution was added with stirring an aqueous lead nitrate solution [7.5 cm^3; 1.66 g lead nitrate (AR)]. Upon completion of addition, the mixture was stirred for several min before a second aqueous solution containing lead nitrate (AR) and sodium hydroxide [60 cm^3; 6.626 g lead nitrate and 1.6 g sodium hydroxide] was slowly added. The stirring was continued for 10 min before the product was allowed to settle and was isolated. The crystals were a sand colour (yield ca. 91%).

$$C_6H_2(NO_2)_2(ONa)_{2(aq)} + 5Pb(NO_3)_{2(aq)} + 8NaOH_{(aq)} \rightarrow C_6H_2(NO_2)_2(OPbOH)_2 \cdot 3PbO\downarrow + 10NaNO_{3(aq)}$$

Monobasic lead 4,6-dinitroresorcinol [3]

To an aqueous solution of 4,6-dinitroresorcinol [4] [1.4 g of 4,6-DNR in 67.5 cm^3 of distilled water] heated to 90°C and vigorously stirred, was added a freshly made slurry of lead hydroxide, prepared as follows: 4.74 g of lead acetate trihydrate (AR), and 1.0 g of sodium hydroxide (AR), was added to 35 cm^3 of distilled water at room temperature. The mixture was stirred and gently warmed for ca. 5 min, then allowed to cool to room temperature and the white precipitate of lead hydroxide to settle. The precipitate was washed by decantation three times with 30 cm^3 of distilled water. The brick-red precipitate formed was agitated for 1 h while the temperature was maintained at 90°C. The resulting precipitate was then filtered off and washed with distilled water and alcohol. The basic lead-DNR was stored in a vacuum desiccator over silica gel for several days before analysis.

$$C_6H_2(NO_2)_2(OH)_{2(aq)} + 2Pb(OH)_{2(aq)} \rightarrow C_6H_2(NO_2)_2 \cdot (OPbOH)_2\downarrow + 2H_2O_{(l)}$$

Dibasic lead 4,6-dinitroresorcinol [6]

To an aqueous, basic solution of sodium 4,6-dinitroresorcinate [60 cm^3; containing 1 g 4,6-DNR [4] and 0.5 g sodium carbonate] was added with stirring a solution of lead nitrate [1.5 cm^3; containing 1.656 g lead nitrate (AR)]. A solution of sodium hydroxide and lead nitrate [30 cm^3; containing 3.313 g lead nitrate and 0.8 g sodium hydroxide] was then added slowly with stirring while the reaction mixture was maintained at 90°C. Stirring was continued for ca. 5 min before the mixture was allowed to cool and settle. The mother liquor was then decanted off, and the product washed with water before being first air-dried, then heated in a warm oven (~45°C) and finally stored in a vacuum desiccator over silica gel (yield ca. 92%). The crystals were dark red in colour.

$$C_6H_2(NO_2)_2(ONa)_{2(aq)} + 3\,Pb(NO_3)_{2(aq)} + 4\,NaOH_{(aq)} \rightarrow C_6H_2(NO_2)_2(OPbOH)_2 \cdot PbO + 6\,NaNO_{3(aq)}$$

Tribasic lead 4,6-dinitroresorcinol [6]

Disodium 4,6-dinitroresorcinate was prepared [60 cm^3; containing 1 g 4,6-DNR [4] and 0.5 g sodium carbonate] and added with stirring to an aqueous lead nitrate solution [7.5 cm^3; 1.656 g lead nitrate (AR)]. Upon completion of addition, the mixture was stirred for several min before a second aqueous solution containing lead nitrate (AR) and sodium hydroxide [45 cm^3; 4.969 g lead nitrate and 1.2 g sodium hydroxide] was slowly added. The stirring was continued for 10 min before the product was allowed to settle and isolated by decantation of the mother liquor. The product was washed with water before being first air-dried, then heated in a warm oven (~ 45°C) and finally stored in a vacuum desiccator over silica gel. The crystals were deep orange colour.

$$C_6H_2(NO_2)_2(ONa)_{2(aq)} + 4\,Pb(NO_3)_{2(aq)} + 6\,NaOH_{(aq)} \rightarrow C_6H_2(NO_2)_2(OPbOH)_2 \cdot 2PbO\downarrow + 8\,NaNO_{3(aq)}$$

2.2. Analysis

The analysis of lead in the lead polynitroresorcinates was performed by a titrimetric method developed by Kurz and Kober [7]. The lead-DNR (~ 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 neutralize 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 nitroresorcinate mixture. The excess EDTA was then back-titrated with lead nitrate (0.02 M) solution 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 in Table 2.

2.3. Tris(hydroxymethyl)methylamine (THAM)

A commercial sample (BDH, 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 allowing to cool in a vacuum desiccator over silica gel.

2.4. Solution calorimeter

The calorimeter designed and constructed in this laboratory is of a twin-Dewar isoperibol type [8]. Temperature changes within the vessels were detected by thermi-

Table 1
Analysis for lead concentration

Normal lead 2,4-dinitroresorcinol

Theoretical lead content,/%, of 2,4-$C_6H_2(NO_2)_2O_2Pb$ = 51.12
Found,/%, 1. 52.41, 2. 50.19, (mean 51.3)

Monobasic lead 2,4-dinitroresorcinol

Theoretical lead content,/%, of 2,4-$C_6H_2(NO_2)_2O_2Pb \cdot PbO$ = 65.9
Found,/%, 1. 65.78, 2. 65.75, (mean 65.77)

Tribasic lead 2,4-dinitroresorcinol

Theoretical lead content,/%, of 2,4-$C_6H_2(NO_2)_2(OPbOH)_2 \cdot 2PbO$ = 75.83
Found,/%, 1. 75.98, 2. 75.09, (mean 75.5)

Quadrabasic lead 2,4-dinitroresorcinol

Theoretical lead content,/%, of 2,4-$C_6H_2(NO_2)_2(OPbOH)_2 \cdot 3PbO$ = 78.42
Found,/%, 1. 79.23, 2. 78.67, (mean 78.9)

Monobasic lead 4,6-dinitroresorcinol

Theoretical lead content,/%, of 4,6-$C_6H_2(NO_2)_2(OPbOH)_2$ = 64.1
Found,/%, 1. 64.15, 2. 64.05, (mean 64.1)

Dibasic lead 4,6-dinitroresorcinol

Theoretical lead content,/%, of 4,6-$C_6H_2(NO_2)_2(OPbOH)_2 \cdot PbO$ = 71.4
Found,/%, 1. 72.4, 2. 71.0, (mean 71.7)

Tribasic lead 4,6-dinitroresorcinol

Theoretical lead content,/%, of 4,6-$C_6H_2(NO_2)_2(OPbOH)_2 \cdot 2PbO$ = 75.84
Found,/%, 1. 75.63, 2. 75.38, (mean 75.5)

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stors, 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 stablised voltage supply, precision resistor and a very accurate digital voltmeter. Ther results were interpreted by Dickinson's method [9].

2.5. Test reaction

The heat of solution of tris(hydroxymethyl)methylamine (THAM or TRIS) $(HOCH_2)_3CNH_2$ was measured in an excesss of either aqueous hydrochloric acid (0.100 M, BDH, AVS) for an exothermic change, or aqueous sodium hydorxide (0.05 M,

Table 2
Microanalysis results

	Expected/%	Found/%
Normal lead 2,4-dinitroresorcinol (MW 405.296)		
Carbon	17.78	17.70
Hydrogen	0.50	0.53
Nitrogen	6.91	6.94
Monobasic lead 2,4-dinitroresorcinol (MW 628.476)		
Carbon	11.47	11.52
Hydrogen	0.32	0.25
Nitrogen	4.46	4.38
Tribasic lead 2,4-dinitroresorcinol (MW 1092.872)		
Carbon	6.59	6.64
Hydrogen	0.37	0.35
Nitrogen	2.56	2.49
Quadrabasic lead 2,4-dinitroresorcinol (MW 1316.109)		
Carbon	5.47	5.25
Hydrogen	0.31	0.32
Nitrogen	2.13	2.15
Monobasic lead 4,6-dinitroresorcinol (MW 646.512)		
Carbon	11.15	11.07
Hydrogen	0.62	0.67
Nitrogen	4.33	4.58
Dibasic lead 4,6-dinitroresorcinol (MW 869.682)		
Carbon	8.28	8.25
Hydrogen	0.46	0.39
Nitrogen	3.22	3.27
Tribasic lead 4,6-dinitroresorcinol (MW 1092.872)		
Carbon	6.59	6.61
Hydrogen	0.37	0.39
Nitrogen	2.56	2.63

BDH. AVS) 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 [8].

2.6. Direct measurement of the enthalpy of solution of lead nitrate in nitric acid/2,4-DNR mixture

The enthalpy of solution, $\Delta_{sol}H^{\ominus}$, of lead nitrate [BDH, AR, recrystallised from water] was measured using an LKB 8700-1 calorimeter. A solution of nitric acid [BDH, 1.0 M AVS] saturated with 2,4-DNR [4] was made, and the ampoule contained the lead nitrate.

$$[HNO_3 + 2,4\text{-DNR(sat)}]_{(aq)} + Pb(NO_3)_{2(s)} \xrightarrow{\Delta_{sol}H^{\ominus}} [HNO_3 + 2,4\text{-DNR}_{(sat)} + Pb(NO_3)_2]_{(aq)}$$

The calorimetric results obtained are shown in Table 3.

2.7. Direct measurement of the enthalpy of solution of lead nitrate in nitric acid/4,6-DNR mixture

The enthalpy of solution, $\Delta_{sol}H^{\ominus}$, of lead nitrate [BDH, AR, recrystallised from water] was measured using an LKB 8700-1 calorimeter. A solution of nitric acid [BDH, 1.0 M AVS] saturated with 4,6-DNR [4] was made, and the ampoule contained the lead nitrate.

$$[HNO_3 + 4,6\text{-DNR(sat)}]_{(aq)} + Pb(NO_3)_{2(s)} \xrightarrow{\Delta_{sol}H^{\ominus}} [HNO_3 + 4,6\text{-DNR}_{(sat)} + Pb(NO_3)_2]_{(aq)}$$

The calorimetric results obtained are shown in Table 4.

2.8. Enthalpy of reaction of normal lead 2,4-dinitroresorcinol

The reaction shown in Fig. 1 was carried out and an exothermic enthalpy change was measured, the results of which are shown in Table 5.

Table 3

Enthalpy of solution of lead nitrate in a nitric acid/2,4-DNR solution

W/g	$+\Delta_{sol}H^0$/kJ mol^{-1}
0.50842	24.34
0.26581	24.34
0.40006	24.37
0.14732	24.39
0.24219	24.38
0.31689	24.33
$\Delta_{sol}H^{\ominus}$(mean) =	24.36 ± 0.06

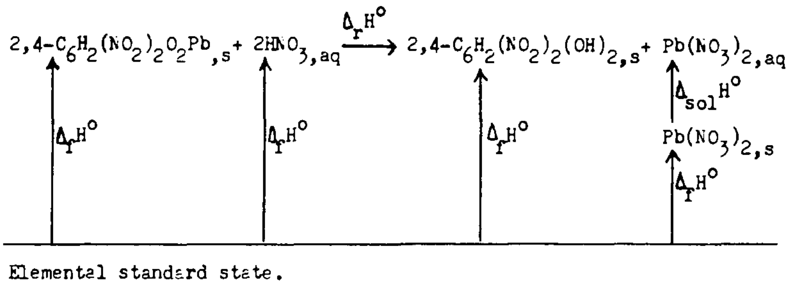

Fig. 1. Thermochemistry of lead 2,4-dinitroresorcinols.

Table 4
Enthalpy of solution of lead nitrate in a nitric acid/4,6-DNR solution

W/g	$+\Delta_{sol}H^0$/kJ mol^{-1}
0.53373	24.20
0.51657	24.18
0.35832	24.35
0.41816	24.31
0.44935	24.44
0.35724	24.42
$\Delta_{sol}H^\ominus$(mean) =	24.32 ± 0.09

Table 5
Enthalpy of reaction of normal lead 2,4-dintroresorcinol

W/g	$-\Delta_r H^\ominus$/kJ mol^{-1}
0.14122	161.88
0.09929	162.31
0.10645	162.93
0.15174	162.94
0.13862	162.91
0.23212	162.83
$\Delta_r H^\ominus$(mean) =	− 162.47 ± 0.53

2.9. Enthalpy of reaction of monobasic lead 2,4-dinitroresorcinol

The reaction used was the same as that for normal lead 2,4-dinitroresorcinol. This reaction gave rise to an exothermic enthalpy change, the results of which are shown in Table 6.

Table 6
Enthalpy of reaction of monobasic lead 2,4-dintroresorcinol

W/g	$-\Delta_r H^\ominus$/kJ mol^{-1}
0.04256	86.069
0.06159	85.478
0.07222	85.257
0.05200	84.649
0.06471	85.613
0.06178	84.960
$\Delta_r H^\ominus$(mean) =	-85.35 ± 0.53

2.10. Enthalpy of reaction of tribasic lead 2,4-dinitroresorcinol

The reaction used was the same as that for normal lead 2,4-dinitroresorcinol. This reaction gave rise to an exothermic enthalpy change, the results of which are shown in Table 7.

2.11. Enthalpy of reaction of quadrabasic lead 2,4-dinitroresorcinol

The reaction used was the same as that for normal lead 2,4-dinitroresorcinol. This reaction gave rise to an exothermic enthalpy change, the results of which are shown in Table 8.

2.12. Enthalpy of reaction of monobasic lead 4,6-dinitroresorcinol

The reaction shown in Fig. 2 was carried out and an exothermic enthalpy change was measured, the results of which are shown in Table 9.

Table 7
Enthalpy of reaction of tribasic lead 2,4-dintroresorcinol

W/g	$-\Delta_r H^\ominus$/kJ mol^{-1}
0.10260	178.40
0.14644	179.34
0.15036	179.24
0.14211	179.57
0.13159	179.15
0.12978	179.03
$\Delta_r H^\ominus$(mean) =	-179.12 ± 0.42

Table 8
Enthalpy of reaction of quadrabasic lead 2,4-dintroresorcinol

W/g	$-\Delta_r H^\ominus$/kJ mol^{-1}
0.12534	227.01
0.07677	226.78
0.11020	226.51
0.11740	228.68
0.10070	226.97
0.12095	228.25
$\Delta_r H^\ominus$(mean) =	-227.37 ± 0.92

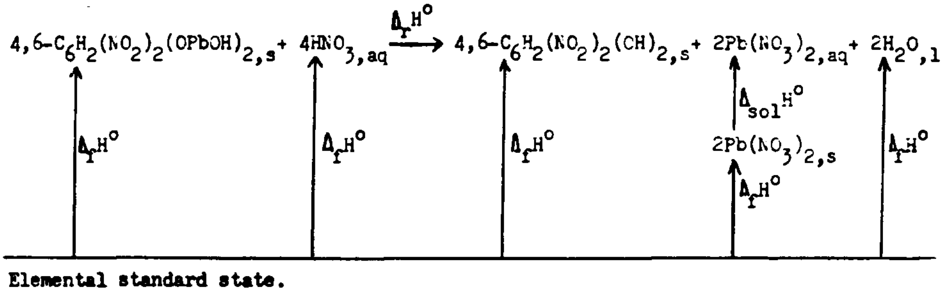

Fig. 2. Thermochemistry of lead 4,6-dinitroresorcinols.

Table 9
Enthalpy of reaction of monobasic lead 4,6-dintroresorcinol

W/g	$-\Delta_r H^\ominus$/kJ mol^{-1}
0.14543	92.701
0.08829	92.692
0.08176	92.767
0.07089	92.572
0.07714	92.542
0.05440	92.413
$\Delta_r H^\ominus$(mean) =	-96.62 ± 0.14

2.13. Enthalpy of reaction of dibasic lead 4,6-dinitroresorcinol

The reaction used was the same as that for monobasic lead 4,6-DNR. This reaction gave rise to an exothermic enthalpy change, the results of which are shown in Table 10.

2.14. Enthalpy of reaction of tribasic lead 4,6-dinitroresorcinol

The reaction used was the same as that for monobasic lead 4,6-DNR. This reaction gave rise to an exothermic enthalpy change, the results of which are shown in Table 11.

Table 10
Enthalpy of reaction of dibasic lead 4,6-dintroresorcinol

W/g	$-\Delta_r H^\ominus$/kJ mol^{-1}
0.16898	175.609
0.09795	175.286
0.17040	176.125
0.09920	176.489
0.14927	176.035
0.16552	175.711
$\Delta_r H^\ominus$(mean) =	-175.88 ± 0.45

Table 11
Enthalpy of reaction of tribasic lead 4,6-dintroresorcinol

W/g	$-\Delta_r H^\ominus$/kJ mol^{-1}
0.14122	161.88
0.09929	162.31
0.10645	162.93
0.15174	162.94
0.13862	161.91
0.23212	162.83
$\Delta_r H^\ominus$(mean) =	-162.47 ± 0.53

2.15. *Reaction test analysis*

All lead 2,4-DNR reactions consisted of using a pre-saturated solution of 2,4-DNR [4] in nitric acid. The lead 2,4-DNR was placed in an ampoule which was broken at the relevant time. A quantitative analysis was performed on the product to confirm complete reaction. This was done by extracting the product mixtue twice with chloroform [AR, 100 cm^3] . The resulting nitric acid solution was then tested for the metal ion [7]. The results are shown in Table 12.

All lead 4,6-DNR reactions consisted of using a pre-saturated solution of 4,6-DNR [4] in nitric acid. The lead 4,6-DNR was placed in an ampoule which was broken at the relevant time. A quantitative analysis was performed on the product to confirm complete reaction. This was done by extracting the product mixture twice with chloroform [AR, 100 cm^3]. The resulting nitric acid solution was then tested for the metal ion [7]. The results are shown in Table 12.

Table 12
Analysis results for lead(II) cation in various calorimetric reactions

	Calc./%	Found/%
Normal lead 2,4-dinitroresorcinol	51.12	(a) 51.10 (b) 51.11
Monobasic lead 2,4-dinitroresorcinol	65.94	(a) 65.85 (b) 66.01
Tribasic lead 2,4-dinitroresorcinol	75.83	(a) 75.95 (b) 75.90
Quadrabasic lead 2,4-dinitroresorcinol	78.42	(a) 78.53 (b) 78.40
Monobasic lead 4,6-dinitroresorcinol	64.10	(a) 64.13 (b) 64.17
Dibasic lead 4,6-dinitroresorcinol	71.47	(a) 72.07 (b) 71.56
Tribasic lead 4,6-dinitroresorcinol	75.84	(a) 75.65 (b) 75.82

2.16. *Enthalpy of formation of normal lead 2,4-dinitroresorcinol*

From the enthalpy of reaction obtained for normal lead 2,4-DNR and using various ancillary data, the enthalpy of formation was calculated.

$$\begin{aligned}&\Delta_f H^{\ominus}[2,4\text{-}C_6H_2(NO_2)_2O_2Pb_{(s)}]\\&= \Delta_f H^{\ominus}[2,4\text{-}C_6H_2(NO_2)_2(OH)_{2(s)}] + \Delta_f H^{\ominus}[Pb(NO_3)_{2(s)}]\\&\quad + \Delta_{sol} H^{\ominus}[Pb(NO_3)_{2(aq)}] - \Delta_r H^{\ominus} - 2\Delta_f H^{\ominus}[HNO_{3(aq)}]\end{aligned}$$

Calculation of $\Delta_f H^{\ominus}[2,4\text{-}C_6H_2(NO_2)_2O_2Pb_{(s)}]$

$$\begin{aligned}&= [-422.77] + [-440.66] + [+24.36] - [-29.36] - 2[-206.85]\\&= -396.01 \pm 6.53\,\text{kJ}\,\text{mol}^{-1}.\end{aligned}$$

2.17. *Enthalpy of formation of monobasic lead 2,4-dinitroresorcinol*

From the enthalpy of reaction obtained for monobasic lead 2,4-DNR and using various ancillary data, the enthalpy of formation was calculated.

$$\begin{aligned}&\Delta_f H^{\ominus}[2,4\text{-}C_6H_2(NO_2)_2O_2Pb\cdot PbO_{(s)}]\\&= \Delta_f H^{\ominus}[2,4\text{-}C_6H_2(NO_2)_2(OH)_{2(s)}] + 2\Delta_f H^{\ominus}[Pb(NO_3)_{2(s)}]\\&\quad + 2\Delta_{sol} H^{\ominus}[Pb(NO_3)_{2(aq)}] + \Delta_f H^{\ominus}[H_2O_{(l)}] - \Delta_r H^{\ominus} - 4\Delta_f H^{\ominus}[HNO_{3(aq)}]\end{aligned}$$

Calculation of $\Delta_f H^\ominus[2{,}4\text{-}C_6H_2(NO_2)_2O_2Pb\cdot PbO_{(s)}]$

$$= [-422.77] + 2[-440.66] + 2[+24.36] - [-85.34] - 4[-206.85] + [-285.83]$$

$$= -628.46 \pm 6.74\,\mathrm{kJ\,mol^{-1}}.$$

2.18. *Enthalpy of formation of tribasic lead 2,4-dinitroresorcinol*

From the enthalpy of reaction obtained for tribasic lead 2,4-DNR and using various ancillary data, the entalpy of formation was calculated.

$$\begin{aligned}&\Delta_f H^\ominus[2{,}4\text{-}C_6H_2(NO_2)_2(OPbOH)_2 2PbO_{(s)}]\\ &= \Delta_f H^\ominus[2{,}4\text{-}C_6H_2(NO_2)_2(OH)_{2(s)}] + 4\Delta_f H^\ominus[H_2O_{(l)}]\\ &\quad + 4\Delta_f H^\ominus[Pb(NO_3)_{2(s)}] + 4\Delta_{sol} H^\ominus[Pb(NO_3)_{2(aq)}] - \Delta_r H^\ominus\\ &\quad - 8\Delta_f H^\ominus[HNO_{3(aq)}]\end{aligned}$$

Calculation of $\Delta_f H^\ominus[2{,}4\text{-}C_6H_2(NO_2)_2(OPbOH)_2 2PbO_{(s)}]$

$$= [-422.77] + 4[-440.66] + 4[24.36] - 8[-206.85] + 4[-285.83] - [-179.12]$$

$$= -1397.37 \pm 7.31\,\mathrm{kJ\,mol^{-1}}.$$

2.19. *Enthalpy of formation of quadrabasic lead 2,4-dinitroresorcinol*

From the enthalpy of reaction obtained for quadrabasic lead 2,4-DNR and using various ancillary data, the enthalpy of formation was calcualted.

$$\begin{aligned}&\Delta_f H^\ominus[2{,}4\text{-}C_6H_2(NO_2)_2(OPbOH)_2 3PbO_{(s)}]\\ &= \Delta_f H^\ominus[2{,}4\text{-}C_6H_2(NO_2)_2(OH)_{2(s)}] + 5\Delta_f H^\ominus[H_2O_{(l)}]\\ &\quad + 5\Delta_f H^\ominus[Pb(NO_3)_{2(s)}] + 5\Delta_{sol} H^\ominus[Pb(NO_3)_{2(aq)}] - \Delta_r H^\ominus\\ &\quad - 10\Delta_f H^\ominus[HNO_{3(aq)}]\end{aligned}$$

Calculation of $\Delta_f H^\ominus[2{,}4\text{-}C_6H_2(NO_2)_2(OPbOH)_2 3PbO_{(s)}]$

$$= [-422.77] + 5[-285.83] + 5[-440.66] + 5[24.36] - 10[-206.85] - [-227.37]$$

$$= -1637.55 \pm 7.78\,\mathrm{kJ\,mol^{-1}}.$$

2.20. *Enthalpy of formation of monobasic lead 4,6-dinitroresorcinol*

From the enthalpy of reaction obtained for monobasic lead 4,6-DNR and using various ancillary data, the enthalpy of formation was calculated.

$$\begin{aligned}&\Delta_f H^\ominus[4{,}6\text{-}C_6H_2(NO_2)_2(OPbOH)_{2(s)}]\\ &= 2\Delta_{sol} H^\ominus[Pb(NO_3)_{2(aq)}] + 2\Delta_f H^\ominus[Pb(NO_3)_{2(s)}]\end{aligned}$$

$$+2\Delta_f H^\ominus[H_2O_{(l)}]+\Delta_f H^\ominus[4,6\text{-}C_6H_2(NO_2)_2(OH)_{2(s)}]-\Delta_r H^\ominus$$
$$-4\Delta_f H^\ominus[HNO_{3(aq)}]$$

Calculation of $\Delta_f H^\ominus[4,6\text{-}C_6H_2(NO_2)_2(OPbOH)_{2(s)}]$

$$=2[-440.66]+2(24.32]+[-443.41]+2[-285.83]-[-92.62]$$
$$-4[-206.85]$$
$$=-927.74\pm 3.20\,\mathrm{kJ\,mol^{-1}}.$$

2.21. *Enthalpy of formation of dibasic lead 4,6-dinitroresorcinol*

From the enthalpy of reaction obtained for dibasic lead 4,6-DNR and using various ancillary data, the enthalpy of formation was calculated.

$$\Delta_f H^\ominus[4,6\text{-}C_6H_2(NO_2)_2(OPbOH)_2\,PbO_{(s)}]$$
$$=\Delta_f H^\ominus[4,6\text{-}C_6H_2(NO_2)_2(OH)_{2(s)}]+3\Delta_f H^\ominus[H_2O_{(l)}]$$
$$+3\Delta_f H^\ominus[Pb(NO_3)_{2(s)}]+3\Delta_{sol} H^\ominus[Pb(NO_3)_{2(aq)}]-\Delta_r H^\ominus$$
$$-6\Delta_f H^\ominus[HNO_{3(aq)}]$$

Calculation of $\Delta_f H^\ominus[4,6\text{-}C_6H_2(NO_2)_2(OPbOH)_2\,PbO_{(s)}]$

$$=[-443.41]+3[-440.66]+3[-285.83]+3[24.32]-[-175.88]$$
$$-6[-206.85]$$
$$=-1132.95\pm 3.74\,\mathrm{kJ\,mol^{-1}}.$$

2.22. *Enthalpy of formation of tribasic lead 4,6-dinitroresorcinol*

From the enthalpy of reaction obtained for tribasic lead 4,6-DNR and using various ancillary data, the enthalpy of formation was calculated.

$$\Delta_f H^\ominus[4,6\text{-}C_6H_2(NO_2)_2(OPbOH)_2 2PbO_{(s)}]$$
$$=\Delta_f H^\ominus[4,6\text{-}C_6H_2(NO_2)_2(OH)_{2(s)}]+4\Delta_f H^\ominus[H_2O_{(l)}]$$
$$+4\Delta_f H^\ominus[Pb(NO_3)_{2(s)}]+4\Delta_{sol} H^\ominus[Pb(NO_3)_{2(aq)}]-\Delta_r H^\ominus$$
$$-8\Delta_f H^\ominus[HNO_{3(aq)}]$$

Calculation of $\Delta_f H^\ominus[4,6\text{-}C_6H_2(NO_2)_2(OPbOH)_2 2PbO_{(s)}]$

$$=[-443.41]+4[-440.66]+4[-285.83]+4[24.32]-[-162.47]$$
$$-8[-206.85]$$
$$=-1434.83\pm 4.37\,\mathrm{kJ\,mol^{-1}}.$$

2.23. *Ancillary data*

The following data were used:

$\Delta_f H^{\ominus}[H_2O_{(l)}] = -285.83 \pm 0.04\,\mathrm{kJ\,mol^{-1}}$ [11].

$\Delta_f H^{\ominus}[Pb(NO_3)_{2(s)}] = -440.66 \pm 0.84\,\mathrm{kJ\,mol^{-1}}$ [12].

$\Delta_f H^{\ominus}[(1.0\,N)HNO_{3(aq)}] = -206.85 \pm 0.03\,\mathrm{kJ\,mol^{-1}}$ [13].

$\Delta_f H^{\ominus}[4,6\text{-}C_6H_2(NO_2)_2(OH)_{2(s)}] = -443.41 \pm 2.71\,\mathrm{kJ\,mol^{-1}}$ [4].

$\Delta_f H^{\ominus}[2,4\text{-}C_6H_2(NO_2)_2(OH)_{2(s)}] = -422.77 \pm 6.47\,\mathrm{kJ\,mol^{-1}}$ [4].

Acknowledgements

This work was carried out with the support of the Procurement Executive, Ministry of Defence. I would also like to thank Prof. A. Finch of Royal Holloway College for his help with this work.

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