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Thermochemistry of barium styphnate

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Abstract

Using an isoperibol twin-Dewar solution calorimeter, the enthalpy of reaction of barium styphnate was determined as $+17.12\ \mathrm{kJ\,mol^{-1}}$, which with various ancillary data gave the standard enthalpy of formation of $-1308.88\ \mathrm{kJ\,mol^{-1}}$.

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

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 the 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. The first recognisable reference to barium styphnate was in 1967 by Taylor et al. [1]. The product formed was a yellow crystalline solid which had the formula $C_6H(NO_2)_3O_2Ba \cdot H_2O$, and had a density of $2.58\ \mathrm{g\,cm^{-3}}$ at 20°C. The temperature of ignition was 296°C being derived at a heating rate of $5°\mathrm{C\,min^{-1}}$. Its solubility in water at 25°C was 0.197 g per $100\ \mathrm{cm^3}$.

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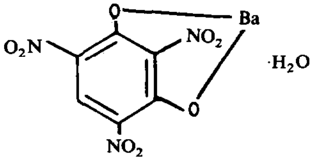


Barium styphnate.

2. Experimental

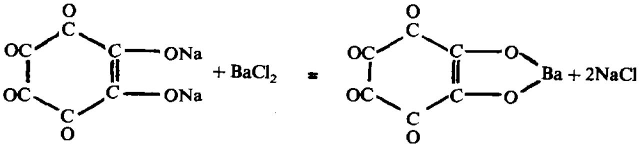
2.1. Materials and synthesis

Barium styphnate

To an aqueous solution (11.72 cm^3) of magnesium styphnate (18.75 cm^3, containing 5.0 g styphnic acid [2], and 1.83 g magnesium carbonate), 3.91 cm^3 of dilute nitric acid (2.3 cm^3 of ntric acid (S.G. 1.42) added to 7.7 cm^3 of water) was added with stirring at 55°C. This solution was added to a second solution of barium acetate (15.65 cm^3, containing 9.37 g of barium acetate (B.D.H., A.R., purity >99.5%)) with stirring at 75°C. After stirring for a further 10 min, and cooling, the mother liquor was removed by decantation and the product washed with water and dried in a warm oven ($\approx$40°C). The yellow precipitate was then placed in a vacuum desiccator over silica gel.

2.2. Analysis

The analysis of barium in barium styphnate was done titrimetrically [3]. To an aqueous solution of barium styphnate ($\approx$0.1 g barium styphnate in 10 cm^3 deionised distilled water and 5 cm^3 of 0.1 M hydrochloric acid), 10 drops of a freshly prepared solution of sodium rhodizonate indicator (15 mg sodium rhodizonate in 5 cm^3 of deioinised distilled water) were added with 2 cm^3 of absolute ethanol. With extremely vigorous shaking, the solution was titrated from red to a neutral colour with sulphuric acid (0.2 N). A blank was also analysed for comparison.



Sodium rhodizonate.

The results obtained are shown in Table 1, and those obtained from microanalysis for C, H and N are recorded in Table 2.

Table 1
Analysis for barium concentration

Theoretical barium(II) content of $C_6H(NO_2)_3O_2Ba \cdot H_2O = 34.47\%$
Found: Ba = 34.34% and 33.49% (mean 33.92%)

Table 2
Micro-analysis results for barium styphnate monohydrate (mol. wt. 398.448)

	C/%	H/%	N/%
Expected	18.08	0.76	10.55
Found	18.18	0.78	10.65

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 of a twin-Dewar isoperibol type [4]. 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 [5].

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 [6]. Some typical results obtained are shown elsewhere [4].

Enthalpy of solution of barium nitrate in a nitric acid/styphnic acid solution

The enthalpy of solution $\Delta_{sol}H^{\ominus}$ of barium nitrate (B.D.H., A.R., 99.5%) was measured using an LKB 8700-1 calorimeter. A solution of nitric acid (B.D.H.,

Table 3
Enthalpy of solution of barium nitrate in a nitric acid/styphnic acid solution

W/g	$+\Delta_{\mathrm{sol}}H^{\ominus}$/kJ mol^{-1} [a]	W/g	$+\Delta_{\mathrm{sol}}H^{\ominus}$/kJ mol^{-1} [a]
0.16197	39.757	0.26002	39.569
0.16827	39.702	0.19143	39.660
0.19671	39.736	0.18402	39.748

[a] $\Delta_{\mathrm{sol}}H^{\ominus}(\mathrm{mean}) = 39.69 \pm 0.18$ kJ mol^{-1}.

0.1 M A.V.S.) saturated with styphnic acid [2] was made, and the ampoule contained the barium nitrate

$$[\mathrm{HNO_3} + \text{styphnic acid(sat.)}](\mathrm{aq}) + \mathrm{Ba(NO_3)_2(s)} \xrightarrow{\Delta_{\mathrm{sol}}H^{\ominus}}$$
$$[\mathrm{HNO_3} + \text{styphnic acid(sat.)} + \mathrm{Ba(NO_3)_2}](\mathrm{aq})$$

The calorimetric results obtained are shown in Table 3.

Enthalpy of reaction of barium styphnate monohydrate

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

Reaction test analysis

The barium styphnate reaction consisted of using a pre-saturated solution of styphnic acid [2] in nitric acid. The styphnate was placed in an ampoule which was broken at the relevant time. A quantitative analysis was performed on the product

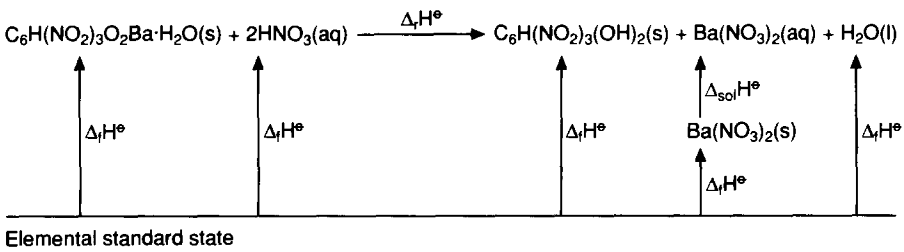


Fig. 1. Thermochemistry of barium styphnate.

Table 4
Enthalpy of reaction of barium styphnate monohydrate

W/g	$+\Delta_{\mathrm{r}}H^{\ominus}$/kJ mol^{-1}	W/g	$+\Delta_{\mathrm{r}}H^{\ominus}$/kJ mol^{-1} [a]
0.08514	16.851	0.10225	17.492
0.09724	17.06	0.09290	17.108
0.10416	17.306	0.10690	16.906

[a] $\Delta_{\mathrm{r}}H^{\ominus}(\mathrm{mean}) = +17.12 \pm 0.62$ kJ mol^{-1}.

Table 5
Analysis results for barium ion produced in calorimetric reaction

	Calc./%	Found/%
Barium styphnate monohydrate	34.47	(a) 34.40 (b) 34.45

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 (as above). The results are shown in Table 5.

Enthalpy of formation of barium styphnate monohydrate

From the enthalpy of reaction of barium styphnate monohydrate and with various ancillary data, the enthalpy of formation was calculated. The thermochemical equation is

$$\Delta_f H^\ominus[C_6H(NO_2)_3O_2Ba \cdot H_2O(s)]$$

$$= \Delta_f H^\ominus[C_6H(NO_2)_3(OH)_2(s)] + \Delta_{sol} H^\ominus[Ba(NO_3)_2(aq)]$$

$$+ \Delta_f H^\ominus[Ba(NO_3)_2(s)] - 2\Delta_f H^\ominus[HNO_3(aq)] + \Delta_f H^\ominus[H_2O(l)] - \Delta_r H^\ominus$$

$$\Delta_f H^\ominus[C_6H(NO_2)_3O_2Ba \cdot H_2O(s)]$$

$$= [-467.50] + [-992.01] + [39.69] + [-285.83] - [+17.12] - 2[-206.97]$$

$$= -1308.88 \pm 6.97 \text{ kJ mol}^{-1}$$

Ancillary data

The following data were used:

$\Delta_f H^\ominus[C_6H(NO_2)_3(OH)_2(s)] = -467.50 \pm 6.90 \text{ kJ mol}^{-1}$ [2]

$\Delta_f H^\ominus[H_2O(l)] = -285.83 \pm 0.04 \text{ kJ mol}^{-1}$ [7]

$\Delta_f H^\ominus[Ba(NO_3)_2(s)] = -992.07 \pm 0.7 \text{ kJ mol}^{-1}$ [8]

$\Delta_f H^\ominus[(0.1\ N)HNO_3(aq)] = -206.97 \pm 0.04 \text{ kJ mol}^{-1}$ [8]

Acknowledgements

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