Thermochemistry of silver styphnate

J.R. Payne [1]

The Bourne Laboratory, Royal Holloway College, University of London, Egham, Surrey, UK

Abstract

Using an isoperibol twin-Dewar solution calorimeter, the enthalpy of reaction of silver styphnate was determined as $+14.17 \text{ kJ mol}^{-1}$, which with various ancillary data gave the standard enthalpy of formation of $-275.13 \text{ kJ mol}^{-1}$.

*Keywords:* Calorimetry; Heat of formation; Isoperibol; Silver styphnate

1. Introduction

It would be 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. Silver styphnate was first prepared in 1846 by Böttger and Will [1]. The product formed was described as a golden-yellow, palm-like crystal aggregate, for which the formula $Ag_2C_6HO_8N_3 \cdot H_2O$ was given.

---

[1] Present address: Combustion Dept. WH56, Rolls-Royce plc, Box 3, Filton, Bristol, United Kingdom.

$$O_2N \diagdown \underset{\underset{NO_2}{|}}{\overset{\overset{OAg}{|}}{\bigcirc}} \diagup \underset{OAg}{\diagdown} NO_2$$
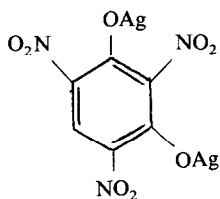
Silver styphnate: $C_6H(NO_2)_3(OAg)_2$.

Small golden-yellow plates were later obtained by treating a hot ammoniacal solution of styphnic acid with a solution of silver nitrate [2]. The use of more concentrated solutions gave brownish-red crystals. Further work was carried out by Taylor and Buxton in 1926 [3]. Silver styphnate explodes at 305°C, decomposes at lower temperature and darkens in sunlight. This compound has found extensive use in priming mixtures and in many respects is superior to normal lead styphnate [4].

2. Experimental

2.1. Materials and synthesis

Silver styphnate

Glacial acetic acid (2.5 cm³) was added to a boiling solution of styphnic acid [5] (6.12 g) and anhydrous sodium carbonate (2.65 g) in water (320 cm³). After effervescence had ceased a boiling solution of silver nitrate (17 g) in water (40 cm³) was added with stirring. A dense orange precipitate suddenly formed and was filtered off and washed successively with distilled water, methanol, and petroleum spirit before being air-dried. The precipitate obtained weighed approx. 10 g (yield ≈87%). The crystals were deep orange in colour with a metallic lustre and of a fibrous nature [3].

Physical properties

On heating, the crystals blackened at 325°C and exploded at 330°C. On addition to a stirred solution of hydrochloric acid (0.1 M), rapid precipitation of silver chloride occurred.

2.2. Analysis

The analysis of silver in silver styphnate was done gravimetrically. An aqueous solution (200 cm³) of silver styphnate (0.2 g) containing nitric acid (2 cm³) was heated to 70°C and hydrochloric acid (0.2 M) was slowly added with stirring until no further precipitation was noticed. The mixture was then cooled to 25°C and the precipitate allowed to settle for several hours in the dark. The silver chloride was then filtered on a sinter-glass crucible (No. 4) which had been dried to constant

Table 1
Analysis of silver in silver styphnate

Wt. of silver styphnate/g	Wt. of silver chloride/g	Silver expected/wt%	Silver found/wt%
0.0224	0.0141 0.0140 0.0141	47.02	47.04
0.0174	0.0108 0.0108 0.0108	47.02	46.72

Suggested formula $C_6H(NO_2)_3(OAg)_2$.

Table 2
Micro-analysis results for silver styphnate

	Expected/%	Found/%
Carbon	15.71	15.84, 15.88
Hydrogen	0.22	0.21, 0.20
Nitrogen	9.16	8.27, 8.94

weight. The solid was then washed with distilled water and air-dried. The crucible plus contents were then heated in an oven, set at 125°C for approx. 1 h and cooled in a desiccator to constant weight. Results are shown in Table 1. Micro-analysis results for C, H and N are recorded in Table 2.

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.

2.3. Solution calorimeter

The calorimeter designed and constructed in this labortory is of a twin-Dewar isoperibol type [6]. 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 [7].

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 enthalpies of solution in both were determined and the results obtained were compared with literature results [8]. Some typical results obtained are shown elsewhere [6].

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

The enthalpy of solution $\Delta_{sol}H^{\ominus}$, of silver nitrate (B.D.H., A.R.) was measured using an LKB 8700 calorimeter. A solution of nitric acid (B.D.H., 1.0 M A.V.S.) saturated with styphnic acid [5] was made, and the ampoule contained the silver nitrate

$$[HNO_3 + \text{styphnic acid(sat.)}](aq) + AgNO_3(s) \xrightarrow{\Delta_{sol}H^{\ominus}}$$

$$[HNO_3 + \text{styphnic acid(sat.)} + AgNO_3](aq)$$
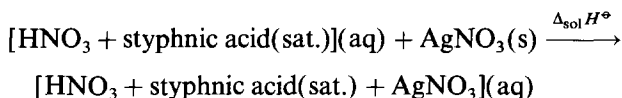
The calorimetric results obtained are shown in Table 3.

Enthalpy of reaction of silver styphnate

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.

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

W/g	$+\Delta_{sol}H^{\ominus}/kJ\ mol^{-1}$ [a]	W/g	$+\Delta_{sol}H^{\ominus}/kJ\ mol^{-1}$ [a]
0.20493	20.78	0.21686	20.74
0.26946	20.812	0.30798	20.85
0.16055	21.06	0.16714	20.60

[a] $\Delta_{sol}H^{\ominus}$(mean) = +20.81 ± 0.16 kJ mol^{-1}. Literature value of silver nitrate in (5000) water: $\Delta_{sol}H^{\ominus}$(mean) = +22.68 ± 0.01 kJ mol^{-1} [9].

$$C_6H(NO_2)_3(OAg)_2(s) + 2HNO_3(aq) \xrightarrow{\Delta_rH^{\ominus}} C_6H(NO_2)_3(OH)_2(s) + 2AgNO_3(aq)$$
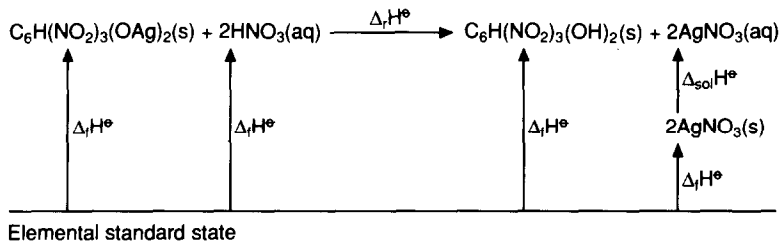
Elemental standard state

Fig. 1. Thermochemistry of silver styphnate.

Table 4
Enthalpy of reaction of silver styphnate

W/g	$+\Delta_r H^\circ$/kJ mol^{-1} [a]	W/g	$+\Delta_r H^\circ$/kJ mol^{-1} [a]
0.12093	14.193	0.16518	14.347
0.11474	14.491	0.10800	14.847
0.09245	13.663	0.15354	13.490

[a] $\Delta_r H^\circ$(mean) = $+14.17 \pm 0.54$ kJ mol^{-1}.

Reaction test analysis

The silver styphnate reaction consisted of using a pre-saturated solution of styphnic acid [5] 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 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 following results were obtained: calculated, 45.24%; found, 45.20% and 45.28%.

Enthalpy of formation of silver styphnate

From the enthalpy of reaction of silver styphnate and various ancillary data, the enthalpy of formation of the silver styphnate was calculated from the thermochemical equation

$$\Delta_f H^\circ[C_6H(NO_2)_3(OAg)_2(s)]$$
$$= \Delta_f H^\circ[C_6H(NO_2)_3(OH)_2(s)] + 2\Delta_{sol} H^\circ[AgNO_3(aq)]$$
$$+ 2\Delta_f H^\circ[AgNO_3(s)] - 2\Delta_f H^\circ[HNO_3(aq)] - \Delta_r H^\circ$$
$$\Delta_f H^\circ[C_6H(NO_2)_3(OAg)_2(s)]$$
$$= [-467.50] + 2[-124.39]$$
$$+ 2[20.81] - 2[-206.85] - [14.17]$$
$$-275.13 \pm 7.04 \text{ kJ mol}^{-1}$$

Ancillary data

The following data were used: $\Delta_f H^\circ[C_6H(NO_2)_3(OH)_2(s)] = -467.50 \pm 6.90$ kJ mol^{-1} [5]; $\Delta_f H^\circ[AgNO_3(s)] = -124.39 \pm 0.9$ kJ mol^{-1} [9]; $\Delta_f H^\circ[(1.0 \text{ N})HNO_3$-(aq)] = -206.85 ± 0.03 kJ mol^{-1} [9].

References

[1] R. Böttger and H. Will, Annalen, 58 (1846) 298.
[2] F. Hemmelmayr, Monatsh., 25 (1904) 573; 26 (1905) 185.
[3] C.A. Taylor and E.P. Buxton, Army Ordnance, 7 (1926) 68.
[4] W. Brun, U.S. Pat. 2,097,510, Nov. 1937.
[5] A. Finch and J.R. Payne, Thermochim. Acta, 170 (1990) 209–212.
[6] J.R. Payne, Ph.D. Thesis, University of London, February 1986.
[7] H.C. Dickinson, Bull. Natl. Bur. Stand. (U.S.), 11 (1914) 189.
[8] E.J. Prosen and M.V. Kilday, J. Res. Nat. Bur. Stand. Sect. A, 77 (1973) 581.
[9] D.D. Wagman, W.H. Evans, V.B. Parker, R.M. Schumm, I. Malow, S.M. Bakey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data Natl. Bur. Stand., 11 (1982) 2.