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Thermochemistry of thallous styphnate

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Abstract

Using an isoperibol twin-dewar solution calorimeter, the enthalpies of reaction of thallous styphnate and the half-acid salt of thallous styphnate were determined as +64.56 and +26.80 kJ mol^{-1}, respectively, which with various ancillary data give the standard enthalpies of formation of −527.56 and −492.05 kJ mol^{-1}, respectively.

INTRODUCTION

It would be quite correct to say that the study of detonation reactions is a post-Second-World-War science; it has even acquired the title of 'detonics'. The traditional type-member of the class of primary explosives is mercury fulminate (mercuric isocyanate), 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. Two forms of thallium styphnate have been synthesised (see Formulae), namely the half-acid (a) and the full (b) thallous salt. Thallous styphnate typically explodes at 242°C with a moderate 'crack'.

Formulae: a, (half-acid) thallous styphnate $C_6H_2(NO_2)_3O_2Tl$; b, thallous styphnate $C_6H(NO_2)_3(OTl)_2$.

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EXPERIMENTAL

Materials and synthesis

(Half-acid) thallous styphnate (a)

Thallium nitrate (2.17 g, Aldrich Gold Label, 99.999%) was dissolved in distilled water (86.8 cm^3), and this aqueous solution was added to another consisting of styphnic acid (2.0 g) [1] dissolved in ice-cold acetone (260 cm^3). The mixture was stirred for 10 min and then allowed to settle. Upon evaporation of the acetone, golden-yellow crystals of the thallous styphnate were precipitated (yield, approx. 98%). The product was recrystallised from hot water (150 cm^3). The mixture was stirred, and allowed to settle. The product was filtered off and dried, first in air, then in a warm oven (~35°C) and finally in a vacuum desiccator over silica gel

$$C_6H(NO_2)_3(OH)_2(aq) + TlNO_3(aq) \rightarrow C_6H(NO_2)_3OHOTl\downarrow + HNO_3(aq)$$

Thallous styphnate (b)

To an aqueous solution of magnesium styphnate (50 cm^3, containing 0.625 g of styphnic acid [1], and 0.103 g of magnesium oxide), was added to a solution of thallium(I) acetate (50 cm^3, containing 6.57 g of thallium acetate (Aldrich Gold Label 99.99%)). Both solutions were pre-heated to 70°C and this temperature was maintained throughout the reaction. The yellow precipitate was filtered whilst hot under gravity, and the product was washed with distilled water and desiccated over silica gel

$$C_6H(NO_2)_3(OH)_2(aq) + 2CH_3CO_2Tl(aq) \rightarrow C_6H(NO_2)_3(OTl)_2\downarrow$$
$$+ 2CH_3CO_2H(aq)$$

Analysis

The analysis for thallium(I) was carried out according to the method described in the literature [2]

$$IO_3^- + 2Tl^+ + 6H^+ + Cl^- = ICl + 2Tl^{3+} + 3H_2O$$

$$KIO_3 \equiv 2Tl$$

A solution of potassium iodate (0.025 M) was prepared and used to titrate a solution containing hydrochloric acid (60 cm^3, conc.) and the thallium styphnate (0.30 g). Theoretical thallium(I) content of $C_6H(NO_2)_3OHOTl$ (a): 45.57%; found, 45.41% and 45.71% (mean 45.56%). Theoretical thallium(I) content of $C_6H(NO_2)_3(OTl)_2$ (b): 62.71%; found, 62.65% and 62.69% (mean 62.67%).

The results obtained by microanalysis for C, H and N are recorded in Table 1.

TABLE 1

Microanalysis results (%) for thallous styphnate (forms (a) and (b))

	(a) $C_6H(NO_2)_3OHOTl$		(b) $C_6H(NO_2)_3(OTl)_2$	
	Found	Expected	Found	Expected
Carbon	16.35	16.07	10.89	11.05
Hydrogen	0.42	0.45	0.24	0.15
Nitrogen	8.96	9.37	6.32	6.45

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, annealing for 3 h in an oven at 80°C, and cooling in a vacuum desiccator over silica gel.

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 [4].

Test reaction

The heat of reaction of tris(hydroxymethyl)methylamine (THAM or TRIS) $(HOCH_2)_3CNH_2$ was determined 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 [5], see Tables 2 and 3.

Enthalpy of reaction of (half-acid) thallous styphnate (a)

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 2

Enthalpy of solution of THAM in excess 0.1 M HCl

W/g	Dilution n [a]	$-\Delta_N H^\circ$/kJ mol^{-1}
0.23095	2884.8	29.88
0.24712	2696.1	29.88
0.23508	2834.2	29.87

$\Delta_N H^\circ_{(\text{mean})} = -29.88 \pm 0.01$ kJ mol^{-1} (lit. [5], $\Delta_N H^\circ = -29.790 \pm 0.031$ kJ mol^{-1}).

[a] n is the mole ratio of THAM to water.

TABLE 3

Enthalpy of solution of THAM in excess 0.05 M NaOH

W/g	Dilution n [a]	$+\Delta_N H^\circ$/kJ mol^{-1}
0.07737	8611.5	17.185
0.08195	8130.2	17.183
0.07863	8473.5	17.187

$\Delta_N H^\circ_{(\text{mean})} = +17.185 \pm 0.005$ kJ mol^{-1} (lit. [6], $\Delta_N H^\circ = +17.189 \pm 0.005$ kJ mol^{-1}).

[a] n is the mole ratio of THAM to water.

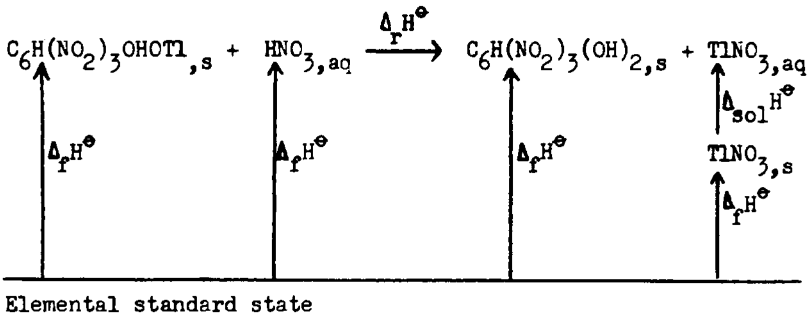

Fig. 1. Thermochemistry of (half-acid) thallous styphnate (a).

TABLE 4

Enthalpy of reaction of (half-acid) thallous styphnate (a)

W/g	$+\Delta_r H^\circ$/kJ mol^{-1}	W/g	$+\Delta_r H^\circ$/kJ mol^{-1}
0.06314	26.909	0.07878	26.812
0.06563	26.815	0.08198	26.495
0.07984	26.957	0.07934	26.803

$\Delta_r H^\circ_{(\text{mean})} = +26.80 \pm 0.17$ kJ mol^{-1}.

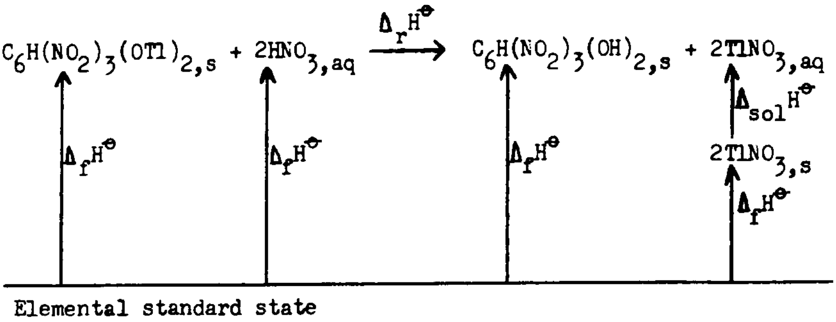

Fig. 2. Thermochemistry of thallous styphnate (b).

Enthalpy of reaction of thallous styphnate (b)

The reaction shown in Fig. 2 was carried out and an endothermic enthalpy change was measured, the results of which are shown in Table 5.

Enthalpy of formation of (half-acid) thallous styphnate (a)

From the enthalpy of reaction of thallous styphnate (a) and various ancillary data, the enthalpy of formation of the styphnate was calculated

$$\begin{aligned}&\Delta_fH^\ominus[C_6H(NO_2)_3OHOTl(s)]\\&\quad=\Delta_fH^\ominus[C_6H(NO_2)_3(OH)_2(s)]+\Delta_fH^\ominus[TlNO_3(s)]-\Delta_fH^\ominus[HNO_3(aq)]\\&\qquad+\Delta_{sol}H^\ominus[TlNO_3(aq)]-\Delta_rH^\ominus\end{aligned}$$

Calculation of $\Delta_fH^\ominus[C_6H(NO_2)_3OHOTl(s)]$ yields

$$\begin{aligned}&(-467.50)+(-243.93)+(+39.21)-(-206.97)-(+26.80)\\&\quad=-492.05\pm6.91\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Enthalpy of formation of thallous styphnate (b)

From the enthalpy of reaction of thallous styphnate (b) and various ancillary data, the enthalpy of formation of the styphnate was calculated

$$\begin{aligned}&\Delta_fH^\ominus[C_6H(NO_2)_3(OTl)_2(s)]\\&\quad=\Delta_fH^\ominus[C_6H(NO_2)_3(OH)_2(s)]+2\Delta_{sol}H^\ominus[TlNO_3(aq)]\\&\qquad+2\Delta_fH^\ominus[TlNO_3(s)]-2\Delta_fH^\ominus[HNO_3(aq)]-\Delta_rH^\ominus\end{aligned}$$

TABLE 5

Enthalpy of reaction of thallous styphnate (b)

W/g	$+\Delta_rH^\ominus$/kJ mol^{-1}	W/g	$+\Delta_rH^\ominus$/kJ mol^{-1}
0.03118	64.516	0.02791	64.511
0.03553	64.421	0.05314	64.626
0.03109	64.956	0.04121	64.300

$\Delta_rH^\ominus_{(mean)}=+64.56\pm0.24\ \mathrm{kJ\ mol^{-1}}$.

Calculation of $\Delta_f H[C_6H(NO_2)_3(OTl)_2(s)]$ yields

$$(-467.50)+2(-243.93)+2(+39.21)-2(-206.97)-(+64.56)$$
$$=-527.56\pm 6.93\ \mathrm{kJ\ mol^{-1}}$$

Ancillary data

The following data were used

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

$\Delta_f H^{\ominus}[TlNO_3(s)] = -243.90 \pm 0.3\ \mathrm{kJ\ mol^{-1}}$ [7]

$\Delta_{sol} H^{\ominus}[TlNO_3(aq)] = +39.21 \pm 0.1\ \mathrm{kJ\ mol^{-1}}$ [7]

$\Delta_f H^{\ominus}[(0.1\ N)HNO_3(aq)] = -206.97 \pm 0.04\ \mathrm{kJ\ mol^{-1}}$ [7]

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