Thermochimica Acta, 170 (1990) 209–212
Elsevier Science Publishers B.V., Amsterdam

THERMOCHEMISTRY OF NITRORESORCINOLS. I. 2,4,6-TRINITRORESORCINOL (STYPHNIC ACID)

ARTHUR FINCH

The Bourne Laboratory, Royal Holloway and Bedford New College,
University of London, Egham, Surrey (Gt. Britain)

JOHN PAYNE

Royal Armament Research and Development Establishment, Fort Halstead,
Sevenoaks, Kent (Gt. Britain)

(Received 12 March 1990)

ABSTRACT

Using a static, oxygen-bomb calorimeter, the standard enthalpy of combustion of 2,4,6-trinitroresorcinol (styphnic acid) has been determined as -2322.31 ± 6.86 kJ mol^{-1}. This gives rise to a value for the standard enthalpy of formation of -467.50 ± 6.90 kJ mol^{-1}.

INTRODUCTION

Styphnic acid is one of several polyhydric phenols of industrial importance, especially to the explosives industry. Several methods of preparation have been used [1–6]; subsequent investigations [7–9] have found that boiling 2,4-dinitroresorcinol (2,4-DNR) with nitric acid under controlled conditions can give quantities of up to 400 kg of product. The metal salts of styphnic acid, particularly that of lead, have been extensively used as primary explosives for several years.

EXPERIMENTAL

Materials and synthesis

Styphnic acid

A commercial sample [7] was recrystallised five times from sodium-dried benzene (BDH, AnalaR). The dry compound was then added to fuming nitric acid and stirred vigorously for 30 min while a temperature of ca. 20 ° C

0040-6031/90/$03.50

TABLE 1

Styphnic acid (molecular weight, 245.106; $C_6H_3N_3O_8(s)$)

	Expected (%)	Found (%)
Carbon	29.39	28.61
Hydrogen	2.01	2.04
Nitrogen	14.00	14.06

was maintained in the mixture. The product was filtered and the nitric acid wash repeated prior to washing the product with distilled water. The pH of the final wash was checked for acidity before the compound was air dried and stored in a vacuum desiccator. The purified material had a very light yellow colour with no noticeable nitric acid odour.

Purity determination using differential scanning calorimetry (DSC; Perkin–Elmer, model 2) indicated 99.98% purity; indium metal (purity, 99.999%) was used as a calibrant. Microanalysis results of purified styphnic acid are collected in Table 1; a melting point of 176.5 ° C (literature 176–179 ° C [7]) was obtained.

Benzoic acid

Certified material (BCS Thermochemical Standard No. 190j, 99.97%) was used without further treatment.

Acetanilide

A commercial sample (BDH, OAS grade) was used as supplied after drying overnight at 110 ° C.

Combustion calorimeter

A commercial instrument (Gallenkamp Automatic Bomb Calorimeter, model CB-110) was used with the modifications given in detail elsewhere [10]. Calibration of the bomb and check experiments on the calorimetric system were as described [11]. The mean of two experiments using acetanilide as a test substance gave a value of $\Delta_c U^\ominus = -4223.27 \pm 3.65$ kJ mol^{-1}, in very good agreement with the recommended value of -4221.26 kJ mol^{-1} [12].

RESULTS AND DISCUSSION

Combustion

Relevant details of the combustion experiments are listed in Table 2. Collated values of the standard energies of combustion, $\Delta_c U^\ominus$, the standard

TABLE 2

Combustion calorimetry results for styphnic acid

m(sample) (g) [vacuo]	0.93951	0.98627	0.98325	0.89591	0.93021	1.01079
m(fuse) (g)	0.00279	0.00280	0.00291	0.00262	0.00326	0.002835
m(Pt wire) (g)	0.00898	0.00760	0.00845	0.00876	0.00923	0.00783
m(silica crucible) (g)	3.57988	3.18378	3.18390	3.57350	3.18376	3.57982
m(soot) (g)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$m(H_2O)$ (g)	10.8	10.8	10.8	10.8	10.8	10.8
q_i (kJ)	0.050627	0.050802	0.052726	0.047654	0.0588474	0.051414
q_n (kJ)	0.04658	0.05076	0.05016	0.4795	0.04927	0.05198
q_c (kJ)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
q_w (kJ)	0.022602	0.023744	0.023674	0.021477	0.022333	0.024356
$\Delta\theta$ (K)	1.0434	1.09315	1.0973	0.99225	1.0346	1.12465
ϵ_{cf} (kJ K^{-1})	0.058279	0.058028	0.058025	0.058229	0.057969	0.058355
$-\Delta_c U^\ominus$ (kJ g^{-1})	9.51996	9.50091	9.56549	9.49030	9.52117	9.53915

Density, 1.84 g cm^{-3} at 20 °C [7].

enthalpies of combustion, $\Delta_c H^\ominus$, and of standard energies of formation, $\Delta_f H^\ominus$, the latter calculated using the equation

$$C_6H_3N_3O_8(c) + 2\tfrac{3}{4}O_2(g) = 6CO_2(g) + 1\tfrac{1}{2}H_2O(l) + 1\tfrac{1}{2}N_2(g)$$

are displayed in Table 3. The internal energy changes of combustion were calculated from equation

$$-\Delta_c U^\ominus = \left[(\epsilon_{sf} + \epsilon_{cf})\ \Delta\theta, - q_i - q_n - q_w + q_c\right]/m_s$$

where ϵ_{sf} is the energy equivalent of the final system, ϵ_{cf} is the energy equivalent of the components, i.e. crucible, platinium wire, etc., q_n is the correction for nitric acid formed during combustion, q_i is the heat of ignition (fuse + firing wire), q_c is the heat correction for soot, m_s is the mass of sample, $\Delta\theta$ is the corrected temperature rise (as the system is not perfectly adiabatic, back-extrapolations from fore and after periods to a corresponding 0.63 of the observed temperature change [14]) and q_w is the Washburn correction [15].

TABLE 3

Energies of combustion, enthalpies of combustion and of formation of styphnic acid

	This work	Literature value [13]
$-\Delta_c U^\ominus$ (kJ g^{-1})	2334.10 ± 6.86	
$-\Delta_c H^\ominus$ (kJ mol^{-1})	2322.31 ± 6.86	
$-\Delta_f H^\ominus$ (kJ mol^{-1})	467.50 ± 6.90	444.34

The sole literature [13] value was referenced to combustions not at the standard temperature, and relied on old ancillary data for $\Delta_f H^\ominus[CO_2(g)]$ and $\Delta_f H^\ominus[H_2O(g)]$. A reliable value for the standard enthalpy of formation of styphnic acid was required for subsequent investigations of metallostyphnates, and a re-determination was made.

ACKNOWLEDGEMENTS

This work has been carried out with the support of Procurement Executive, Ministry of Defence.

REFERENCES

1 M.H. Vermeulew, Recl. Trav. Chim. Pays-Bas, 38 (1919) 107.
2 T. Kametani and K. Ogasawara, Chem. Pharm. Bull., 15 (1967) 893.
3 M. Fieser and L.F. Fieser, Reagents for Organic Synthesis, Vol. 3, Wiley–Interscience, New York, 1972, p. 212.
4 J.W. Wilkinson, U.S. Patent 2,246,936, July 1941.
5 P. Aubertein and J.M. Emeury, Mém. Poudres, 39 (1957) 7.
6 P.P.T. Sah, Sci. Rept. Natl. Tsing Hua Univ., Ser. A, 1 (1932) 197.
7 P.H. Collins, personal communication.
8 R. Benedikt and A.F.V. Hubl, Monatsh. Chem., 2 (1881) 323.
9 D.R. Jones and C.L. Roberts, U.S. Patent 2,301,912, November 1942.
10 A. Finch, P.J. Gardner and A.E. Smith, Thermochim. Acta, 49 (1981) 281.
11 A. Finch and A.E. Smith, Thermochim. Acta, 53 (1982) 349.
12 W.H. Johnson, J. Res. Natl. Bur. Stand., Sect. A, 79 (3) (1975) 487.
13 L. Médard and M. Thomas, Mém. Poudres, 31 (1949) 173.
14 J.R. Payne, Ph.D. Thesis, University of London, February 1986.
15 G.J. Prosen, in F.D. Rossini (Ed.), Experimental Thermochemistry, Interscience, London, 1956, p. 149.