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THERMOCHEMISTRY OF 2,6-DINITROTOLUENE

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ABSTRACT

Using a static, oxygen-bomb calorimeter, the standard enthalpy of combustion of 2,6-dinitrotoluene has been determined as -3556.834 ± 1.018 kJ mol^{-1}. This gives rise to a value for the standard enthalpy of formation of -55.23 ± 2.25 kJ mol^{-1}.

INTRODUCTION

This study is part of a systematic investigation of nitroaromatic compounds related to the explosives industry [1]. Although 2,6-dinitrotoluene has been long known, the literature value for the standard enthalpy of formation ΔH_f^0 is derived from measurements made in 1939 under non-standard conditions [2]. Further, there is apparent ambiguity about the melting point, which has been variously quoted as 59–59.5°C [2] but also as 66°C [3]. Preliminary differential scanning calorimetric experiments (DSC) in this laboratory [4] suggest that there are two crystal modifications of the pure compound, with melting points of 60°C and 66°C, respectively; these are designated here as A and B, respectively.

EXPERIMENTAL

Materials and synthesis

2,6-Dinitrotoluene

A commercial sample (B.D.H.) was recrystallised five times from sodium-dried benzene (B.D.H., AnalaR grade), dried in air, and stored in a vacuum

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TABLE 1

Combustion calorimetry results for 2,6-dinitrotoluene

	1	2	3	4	5	6	7	8	9	10	11	12
M(sample) (g)	1.075269	0.9924756	0.9903342	0.9533105	1.002842	1.050023	1.013057	1.014838	1.136117	1.007264	1.02243	0.9404102
M(fuse)(g)	0.00486	0.00384	0.00468	0.00454	0.00458	0.00516	0.00428	0.00260	0.00476	0.00527	0.00450	0.00444
M(Pt wire)(g)	0.00718	0.00908	0.00777	0.00776	0.00668	0.008859	0.0078	0.00652	0.00574	0.00781	0.00702	0.00824
M(silica crucible)(g)	7.31934	2.79518	3.42786	2.79520	3.42792	3.42794	7.31920	3.42786	3.42782	7.31912	3.42784	7.3191
M(soot)(g)	0.00084	0.00060	0.00120	0.00044	0.0005	0.00060	0.00040	0.00050	0.00036	0.0006	0.000879	0.00080
M(H_2)(g)	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8
q_i (kJ)	0.08683139	0.0689916	0.0836832	0.0812346	0.08193419	0.09207839	0.0766872	0.047304	0.08508239	0.09400229	0.080535	0.0794856
q_n (kJ)	0.0734556	0.0668864	0.062706	0.0609144	0.0677822	0.0722612	0.0680808	0.0677822	0.07465	0.0674836	0.0680808	0.05972
q_c (kJ)	0.00084	0.00060	0.00120	0.00044	0.00050	0.00060	0.00040	0.00050	0.00036	0.0006	0.000879	0.00080
q_w (kJ)	0.03193429	0.0937221	0.02935474	0.02820128	0.02969111	0.03114125	0.03001031	0.03007065	0.0387079	0.02983306	0.03030299	0.02780495
$\Delta\theta$ (K)	2.4407	2.2547	2.2503	2.1626	2.2795	2.3873	2.2970	2.3000	2.5803	2.2887	2.3155	2.1342
ϵ_f (kJ K^{-1})	8.62853	8.62853	8.62853	8.62853	8.62853	8.62853	8.62864	8.62864	8.62864	8.62864	8.62864	8.62864
ϵ_{cf} (kJ K^{-1})	0.0619705	0.05839056	0.05886751	0.0583232	0.05888884	0.05897004	0.06186388	0.05890934	0.05911714	0.06185388	0.05892209	0.06173931
$-\Delta U_c^0$ (298.15 K)(kJ g^{-1})	19.54816	19.5659	19.5638	19.52803	19.56844	19.56605	19.53267	19.54666	19.56116	19.55716	19.50417	19.54551

desiccator in the dark. Purity determinations using D.S.C. (Perkin–Elmer, Model 1B) indicated 99.93% purity; indium metal (purity 99.999%) was used as calibrant. The compound melted sharply near 60°C; after cooling and re-heating the melting point rose to nearly 66°C. This latter value was reproducible. Samples for subsequent combustion were taken from the original compound (A), melting at 60°C, and from a sample which had been melted (B), and then ground in an agate mortar and melted at 66°C. Density measurements, using a standard pyknometric method, were made, giving the following values: crystal A, 1.51 g cm^{-3}; crystal B, 1.49 g cm^{-3}. These values were subsequently used for buoyancy correction purposes.

Benzoic acid and acetanilide

Calibration of the bomb, and check experiments on the calorimetric system were as described previously [1].

Combustion calorimeter

A commercial instrument (Gallenkamp Automatic Bomb Calorimeter, Model CB-110) was used with the modifications given in detail elsewhere [5]. The mean of two experiments using acetanilide as a test substance gave a value of $\Delta U_c^0 = -31.2380$ kJ g^{-1}, in very good agreement with the recommended value of -31.2300 ± 0.0069 kJ g^{-1} [6].

RESULTS AND DISCUSSION

Combustion

Relevant details of the combustion experiments are listed in Table 1; runs 1–6 refer to crystal A, and runs 7–12 to crystal B. Collated values of the standard energies of combustion, ΔU_c^0, the standard enthalpies of combustion, ΔH_c^0, and of standard energies of formation, ΔH_f^0, the latter calculated using the equation

$$C_7H_6N_2O_{4(c)} + 13/2\ O_{2(g)} = 7\ CO_{2(g)} + 3\ H_2O_{(l)} + N_{2(g)}$$

are displayed in Table 2.

The value of ΔH_f^0 for crystal A appears to be ca. 2.83 kJ mol^{-1} less

TABLE 2

Energies of combustion, and enthalpies of combustion and of formation of 2,6-dinitrotoluene

	A	B	Combined values	Lit. value [7]
ΔU_c^0(kJ g^{-1})	19.557 ± 0.017	19.541 ± 0.022	19.549 ± 0.012	
$-\Delta H_c^0$(kJ mol^{-1})	3558.247 ± 3.063	3555.422 ± 4.005	3556.834 ± 1.018	3560.92 ± 3.56
$-\Delta H_f^0$(kJ mol^{-1})	53.813 ± 3.063	56.638 ± 4.005	55.226 ± 2.246	51.13 ± 3.6

exothermic than that of crystal B, but this difference is not significant at the 99.5 confidence level, using a t-test. Hence the results have been pooled, and mean values from all twelve experiments are given in column 3. These are seen to be significantly different from the (re-calculated) literature values listed in column 4.

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