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Thermochemistry of nitroresorcinols
Part 2. 2,4- and 4,6-Dinitroresorcinol

Arthur Finch[a] and John Payne[b]

[a] *The Bourne Laboratory, Royal Holloway College, University of London, Egham, Surrey (UK)*
[b] *Royal Armament Research and Development Establishment, Fort Halstead, Sevenoaks, Kent (UK)*

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Abstract

Using a static oxygen-bomb calorimeter, the standard enthalpies of combustion of 2,4-dinitroresorcinol (2,4-DNR) and 4,6-dinitroresorcinol (4,6-DNR) have been determined as -2509.95 ± 6.42 and -2489.31 ± 2.60 kJ mol^{-1}, respectively, which give values for the standard enthalpies of formation of -422.77 ± 6.47 and -443.41 ± 2.71 kJ mol^{-1}, respectively.

INTRODUCTION

Both isomers of dinitroresorcinol are of industrial importance, especially in the explosives industry. Several methods of preparation of the 2,4-DNR isomer have been investigated [1,2], the best being the dinitrosation of resorcinol by alkaline oxidation [3]. The 4,6-DNR isomer has always been less important as it cannot be synthesised directly, although it may be prepared by the nitration of diacetylresorcinol, its preparation being first reported in 1883 [4]. The method of synthesis consisted of treating diacetoxybenzene with cold nitric acid, followed by the hydrolysis of the acetate group with hot hydrochloric acid [5–8]. Three other methods for the preparation of 4,6-DNR have been recorded [9–11] but none is suitable for large-scale work. Metal salts, especially those of 2,4-DNR, have been used as primary composite explosives since 1940.

EXPERIMENTAL

Materials and Synthesis

4,6-Dinitroresorcinol

A commercial sample [12] was recrystallised four times by dissolving in aqueous sodium hydroxide (1.0 mol dm^{-3}), and was then precipitated by the

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TABLE 1

Microanalysis results for 2,4- and 4,6-dinitroresorcinol $C_6H_4N_2O_6$(s) [M.W., 200.112]

	Expected (%)	2,4-Dinitroresorcinol Found (%)	4,6-Dinitroresorcinol Found (%)
Carbon	36.00	36.10	35.86
Hydrogen	2.01	2.04	2.02
Nitrogen	14.00	14.06	14.14

addition of acetic acid (1.0 mol dm^{-3}) up to pH 4.4. The purified material was first dried in air, then in a low-temperature oven (40 ° C), and stored in a vacuum desiccator. The crystals obtained were a light sand colour.

Purity determination using differential scanning calorimetry (D.S.C., Perkin–Elmer, Model 2) indicated 99.98% purity; indium metal (purity 99.999%) was used as a calibrant. Micro-analysis results of the purified 4,6-DNR are collected in Table 1; a melting point of 217 ° C was obtained (literature values, 215–218 ° C [12]).

2,4-Dinitroresorcinol

A commercial sample [12] was recrystallised eight times from chloroform (B.D.H., AnalaR grade), dried in air, then in a low-temperature oven (40 ° C) and stored in a vacuum desiccator. The crystals obtained had a light golden-brown–orange colour.

Purity determination using differential scanning calorimetry (D.S.C., Perkin–Elmer, Model 2) indicated 99.98% purity; indium metal (purity 99.999%) was used as a calibrant. Microanalysis results of the purified 2,4-DNR are collected in Table 1; a melting point of 147 ° C was obtained (literature value, 146–149 ° C [12]).

Benzoic acid

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

Acetanilide

A commercial sample (B.D.H., OAS grade) was used as supplied as a test material 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 [13]. Calibration of the bomb, and verification experiments on the calorimetric system were as described [14]. The mean of two experiments using

TABLE 2

Combustion calorimetry results for 2,4-dinitroresorcinol, density = 1.81 g cm^{-3} at 25 ° C [16]

	1	2	3	4	5	6
M(sample) (g) [vacuo]	0.94173	0.96152	0.85829	0.98028	0.95016	0.93538
M(fuse) (g)	0.00257	0.00260	0.00324	0.00313	0.002785	0.00239
M(Pt wire) (g)	0.01044	0.00798	0.00812	0.00752	0.00740	0.00836
M(silica crucible) (g)	3.58047	3.18385	3.58695	3.18386	3.57968	3.18381
M(soot) (g)	0.00000	0.00033	0.00000	0.00000	0.00080	0.00033
$M(H_2O)$ (g)	10.8	10.8	10.8	10.8	10.8	10.8
q_i (kJ)	0.04678	0.04730	0.05849	0.05657	0.05054	0.04363
q_n (kJ)	0.05882	0.05464	0.05196	0.05554	0.05285	0.05327
q_c (kJ)	0.00000	0.01089	0.00000	0.00000	0.0264	0.01089
q_w (kJ)	2.46×10^{-2}	2.52154×10^{-2}	2.2379×10^{-2}	2.5728×10^{-2}	2.4920×10^{-2}	2.4504×10^{-2}
$\Delta\theta$ (K)	1.3737	1.4063	1.2615	1.42324	1.38905	1.36975
ε_{cf} (kJ K^{-1})	0.058512	0.058236	0.058408	0.0582604	0.0585219	0.058202
$-\Delta_c U^0$ (kJ g^{-1})	12.53362	12.584275	12.613256	12.55308	12.5925	12.60261

TABLE 3

Combustion calorimetry results for 4,6-dinitroresorcinol, density = 1.85 g cm^{-3} at 25 °C [16]

	1	2	3	4	5	6
M(sample) (g) [vacuo]	0.81812	0.86435	1.00723	0.95854	0.93626	0.93789
M(fuse) (g)	0.00334	0.00258	0.002705	0.00222	0.00256	0.00246
M(Pt wire) (g)	0.010785	0.00781	0.009065	0.00784	0.00716	0.00698
M(silica crucible) (g)	3.18386	3.18384	3.18388	3.18379	3.18386	3.18389
M(soot) (g)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
$M(H_2)$ (g)	10.8	10.8	10.8	10.8	10.8	10.8
q_i (kJ)	0.06025	0.04695	0.04914	0.04066	0.04660	0.04486
q_n (kJ)	0.043297	0.048075	0.054644	0.051956	0.053151	0.052255
q_c (kJ)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
q_w (kJ)	2.1376×10^{-2}	2.2597×10^{-2}	2.64969×10^{-2}	2.51687×10^{-2}	2.45332×10^{-2}	2.4589×10^{-2}
$\Delta\theta$ (K)	1.19005	1.25435	1.4604	1.3907	1.3578	1.3633
ε_{cf} (kJ K^{-1})	0.058049	0.058109	0.0582957	0.0582321	0.058203	0.058205
$-\Delta_c U^0$ (kJ g^{-1})	12.48297	12.47016	12.46596	12.48038	12.46514	12.49717

TABLE 4

Energies of combustion, enthalpies of combustion and enthalpies of formation of 2,4- and 4,6-dinitroresorcinol

	2,4-Dinitroresorcinol		4,6-Dinitroresorcinol	
	This work	Lit. value [17]	This work	Lit. value [17]
$-\Delta_c U^0$ (kJ g^{-1})	2496.75 ± 2.60		2496.75 ± 2.60	
$-\Delta_c H^0$ (kJ mol^{-1})	2509.95 ± 6.42		2489.31 ± 2.60	
$-\Delta_f H^0$ (kJ mol^{-1})	422.77 ± 6.47	438.17	443.41 ± 2.71	463.17

acetanilide as a test substance gave a value of $\Delta_c U^0 = -4223.27 \pm 3.65$ kJ mol^{-1}, in very good agreement with the recommended value of -4221.26 kJ mol^{-1} [15].

RESULTS

Combustion

Relevant details of the combustion experiments are listed in Tables 2 and 3. Table 4 lists the collated values of the standard energies of combustion, $\Delta_c U^0$, the standard enthalpies of combustion, $\Delta_c H^0$, and the standard energies of formation, $\Delta_f H^0$, for both isomers, the latter calculated using the equation

$$C_6H_4N_2O_6(c) + 4O_2(g) = 6CO_2(g) + 2H_2O(l) + N_2(g) \qquad (1)$$

The internal energy changes of combustion were calculated from the equation

$$-\Delta_c U^0 = \left[(\varepsilon_{sf} + \varepsilon_{cf})\Delta\theta - q_i - q_n - q_w + q_c\right]/m_s \qquad (2)$$

where ε_{sf} is the energy equivalent of the final system, ε_{cf} the energy equivalent of the components (the crucible, platinium wire, etc.), q_n the correction for nitric acid formed during combustion, q_i the heat of ignition (fuse + firing wire), q_c the heat correction for soot, m_s the mass of sample, $\Delta\theta$ 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 [16]) and q_w the Washburn correction [18].

The sole literature [17] values given refer to combustions not at standard temperature, and rely on old ancillary data of $\Delta_f H^0[CO_2(g)]$ and $\Delta_f H^0[H_2O(g)]$. As a reliable value for the standard enthalpy of formation of 2,4- and 4,6-DNR was required for subsequent investigations of metallo-DNRs, a re-determination was made.

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