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# THERMOCHEMISTRY OF NITROPHENOLS. V. ENTHALPIES OF FORMATION OF 2,4- AND 2,6-DINITROPHENOLS

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## ABSTRACT

Using static oxygen-bomb calorimetry, the standard enthalpies of combustion of the 2,4- and 2,6-isomers of dinitrophenol have been determined as $-2697.22$ and $-2723.08 \pm 3.18$ kJ mole$^{-1}$, respectively. Standard enthalpies of formation have been calculated as $-235.50$ and $-209.64 \pm 3.27$ kJ mole$^{-1}$, respectively.

## INTRODUCTION

The 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dinitrophenols (DNP) are well known, and some few thermochemical studies are available for the 2,4- and 2,6-isomers [1,2]. However, there is only one value extant for $\Delta H_f^{\ominus}$ 2,6 DNP and two for $\Delta H_f^{\ominus}$ 2,4 DNP, the latter differing by ca. 6 kJ mole$^{-1}$. This study was made to check the published values, and as part of a systematic investigation of nitro-aromatic compounds.

## EXPERIMENTAL

### *Materials*

#### *2,4-Dinitrophenol*

A commercial sample (B.D.H. Ltd., Analar grade) was recrystallised three times from ethanol to give a m.p. of 112°C. Literature values [3–7] for this datum vary between 112.8 and 114°C. The purity of the sample was found to be $\geqslant 99.9\%$ using differential scanning calorimetry [8] (DSC).

#### *2,6-Dinitrophenol*

A sample prepared at Woolwich Arsenal (by F. Stansfield, ca. 1942) was used. It was recrystallised twice from ethanol and dried in vacuo over $P_2O_5$,

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to give a m.p. of 64°C, (lit. 64°C). A DSC determination showed the purity to be 99.9%.

*Combustion calorimeter*

This was a commercial instrument (Gallenkamp Automatic Bomb Calorimeter, Model CB-110) with modifications as described previously [9]. Experimental and calculational procedures were as given before. Calibration experiments with benzoic acid and test runs with acetanilide were made.

*Esf Value*

The mean of 11 calibration experiments using benzoic acid gave the energy equivalent of the uncharged calorimeter as $8.6186 \pm 0.0026$ kJ $K^{-1}$ [9].

*Acetanilide*

The mean of seven experiments using acetanilide as a test substance [10] gave a value of $\Delta u_c^{\ominus} = -31.221 \pm 0.013$ kJ $g^{-1}$, in good agreement with the recommended values [11] ($-31.2300 \pm 0.0069$ kJ $g^{-1}$).

## RESULTS AND DISCUSSION

The standard energies of combustion of the 2,4- and 2,6-dinitrophenols were found to be $-2703.42$ and $-2729.28 \pm 3.18$ kJ $mole^{-1}$, respectively. (For 2,4-DNP, two experiments only were performed, hence error limits are not given.)

Using

$$C_6H_4N_2O_5(c) + \tfrac{9}{2}\ O_2(g) = 6\ CO_2(g) + 2\ H_2O(l) + N_2(g)$$

$$\left(\Delta n = \tfrac{5}{2}\right)$$

TABLE 1

Thermochemical data for dinitrophenols

| Isomer | $-\Delta H_f^{\ominus}$ (kJ $mole^{-1}$) | Ref. |
|---|---|---|
| 2,4- | $235.81 \pm 2.72$ | 1 |
| | $229.66 \pm 2.72$ | 2 |
| | 235.50 | This work |
| 2,6- | $209.91 \pm 2.76$ | 1 |
| | $209.64 \pm 3.27$ | This work |

TABLE 2

Combustion calorimetry results for 2,6-dinitrophenol ($d = 1.68$ g cm$^{-3}$)

| | Sample | | | |
|---|---|---|---|---|
| | A | B | C | D |
| $m$(sample) (g) | 2.113761 | 2.091199 | 1.351735 | 1.485270 |
| $m$(fuse) (g) | 0.00523 | 0.00498 | 0.00436 | 0.00449 |
| $m$(Pt wire) (g) | 0.00675 | 0.00946 | 0.00794 | 0.00593 |
| $m$(silica crucible) (g) | 4.639056 | 4.449399 | 4.449230 | 4.638936 |
| $m$(soot) (g) | 0.00045 | 0.00093 | 0.00047 | 0.00089 |
| $m(H_2O)$ (g) | 10.8 | 10.8 | 10.8 | 10.8 |
| $q_i$(kJ) | 0.093303 | 0.088930 | 0.078086 | 0.078530 |
| $q_n$(kJ) | 0.081219 | 0.082115 | 0.078830 | 0.081219 |
| $q_c$(kJ) | 0.01485 | 0.03069 | 0.01551 | 0.02937 |
| $q_w$(kJ) | 0.061354 | 0.060623 | 0.037747 | 0.041764 |
| $\Delta T$(K) | 3.6401 | 3.5958 | 2.3260 | 2.5571 |
| $e_f$(kJ K$^{-1}$) | 8.6795 | 8.6793 | 8.6784 | 8.6787 |
| $e_{cf}$(kJ K$^{-1}$) | 0.060878 | 0.060705 | 0.059741 | 0.060050 |
| $-\Delta u_c^{\ominus}$(298.15 K) (kJ g$^{-1}$) | 14.8424 | 14.8279 | 14.8008 | 14.8257 |

Mean $= -14.8242 \pm 0.017$ kJ g$^{-1}$.

the standard enthalpies of combustion are $-2697.22$ (2,4-DNP) and $-2723.08 \pm 3.18$ (2,6-DNP) kJ mole$^{-1}$ and hence standard enthalpies of formation are as shown in Table 1. These results compare favourably with those obtained by Badoche [1]. Detailed results for each set of combustion experiments are shown in Tables 2 and 3.

TABLE 3

Combustion calorimetry results for 2,4-dinitrophenol ($d = 1.68$ g cm$^{-3}$)

| | Sample | |
|---|---|---|
| | A | E |
| $m$(sample) (g) | 1.79415 | 1.78644 |
| $m$(fuse) (g) | 0.00478 | 0.00458 |
| $m$(Pt wire) (g) | 0.00832 | 0.00867 |
| $m$(silica crucible) (g) | 4.44983 | 4.63888 |
| $m$(soot) (g) | 0.00006 | 0.00000 |
| $m(H_2O)$ (g) | 10.8 | 10.8 |
| $q_i$(kJ) | 0.08543 | 0.08193 |
| $q_n$(kJ) | 0.09824 | 0.09782 |
| $q_c$(kJ) | 0.00198 | 0.00000 |
| $q_w$(kJ) | 0.05107 | 0.05090 |
| $\Delta T$(K) | 3.0625 | 3.0488 |
| $e_f$(kJ K$^{-1}$) | 8.6789 | 8.6790 |
| $e_{cf}$(kJ K$^{-1}$) | 0.06032 | 0.06045 |
| $-\Delta u_c^{\ominus}$(298.15 K) (kJ g$^{-1}$) | 14.6846 | 14.6829 |

Mean $= 14.6837$ kJ g$^{-1}$.

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