



## Experimental thermochemical study of 2,5- and 2,6-dichloro-4-nitroanilines

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### ABSTRACT

The standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation of 2,5- and 2,6-dichloro-4-nitroanilines, in the gaseous phase, at  $T = 298.15$  K, were derived from the combination of the values of the standard molar enthalpies of formation in the crystalline phase, at  $T = 298.15$  K, and the standard molar enthalpies of sublimation, of each compound, at the same temperature. The standard molar enthalpies of formation, in the crystalline phase, at  $T = 298.15$  K, were derived from the standard massic energies of combustion of the two isomers, in oxygen, at  $T = 298.15$  K, measured by rotating-bomb combustion calorimetry. The standard molar enthalpies of sublimation were calculated, by application of the Clausius–Clapeyron equation, to the vapour pressures at several temperatures measured by Knudsen effusion technique.

Compound	$\Delta_f H_m^\circ(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr}}^g H_m^\circ/(\text{kJ} \cdot \text{mol}^{-1})$
2,5-Dichloro-4-nitroaniline	$-85.6 \pm 1.9$	$114.3 \pm 0.9$
2,6-Dichloro-4-nitroaniline	$-107.3 \pm 1.4$	$109.2 \pm 0.9$

The values of the standard ( $p = 0.1$  MPa) molar enthalpies of formation of 2,5- and 2,6-dichloro-4-nitroanilines, in the gaseous phase, at  $T = 298.15$  K, were compared with those estimated by the Cox scheme.

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## 1. Introduction

Since William Henry Perkin discovered, in 1856, a process that converted aniline into a purple colorant, anilines went on to become fundamental products in the manufacture of synthetic dyes, pharmaceuticals, products for the processing of rubber and new polymers. Both 2,5- and 2,6-dichloro-4-nitroanilines are of interest as intermediaries in synthesis [1–3] and acid–base indicators [4]. 2,6-Dichloro-4-nitroaniline is also a well known fungicide, sold to the public under the name of Dichloran or Botran<sup>®</sup>. In an environmental health research, 2,6-dichloro-4-nitroaniline was found in 154 plasma samples collected at birth from 199 mothers and in 175 of 211 umbilical cord plasma samples [5].

The present work is a contribution to the thermochemical investigation of halogenated anilines and nitroanilines carried out by the Molecular Energetics Research Group of the University of Porto, following the studies of fluoroanilines [6,7], chloroanilines [8–11], bromoanilines [12], iodoanilines [13] and monochloronitroanilines [14,15].

This paper reports the standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation, of 2,5- and 2,6-dichloro-4-nitroanilines, in the crys-

talline phase, at  $T = 298.15$  K, derived from the standard massic energies of combustion, of those two compounds, in oxygen, at the same temperature, measured by rotating-bomb combustion calorimetry. This paper also reports the vapour pressures of both crystalline isomers, measured by Knudsen effusion technique, at several temperatures, allowing the calculation, by application of the Clausius–Clapeyron equation, of the standard molar enthalpies and entropies of sublimation, at the mean temperature of the experimental temperature range. The standard molar enthalpies, entropies and Gibbs energies of sublimation, at  $T = 298.15$  K, were calculated estimating the heat capacity differences between the gas and the crystal phases of each compound. The values of the standard molar enthalpies of formation, in the crystalline phase, and of the standard molar enthalpies of sublimation were combined to derive the standard molar enthalpies of formation, in the gaseous phase, at  $T = 298.15$  K, for each isomer.

## 2. Experimental details

### 2.1. Compounds and purity control

The isomers 2,5-dichloro-4-nitroaniline [CAS 6627-34-5] and 2,6-dichloro-4-nitroaniline [CAS 99-30-9] were obtained commercially from Aldrich Chemical Co., with an assessed mass fraction

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minimum purity of 0.97 and 0.96, respectively. The 2,5-dichloro-4-nitroaniline was purified by sublimation at 0.1 Pa background pressure and  $T = 405$  K. 2,6-Dichloro-4-nitroaniline was purified firstly by sublimation at 0.1 Pa background pressure and  $T = 363$  K, and then was recrystallized twice from toluene and twice from ethanol. The final purity of each isomer was checked by gas liquid chromatography, performed on an Agilent 4890D gas chromatograph equipped with an HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane (15 m  $\times$  0.530 mm i.d.  $\times$  1.5  $\mu$ m film thickness), and with nitrogen as carrier gas. The temperature of the injector was set at 473 K and the oven temperature was programmed as follows: 323 K (1 min), ramp at 10 K  $\cdot$  min $^{-1}$ , 423 K (5 min). No impurities greater than  $10^{-3}$  in mass fraction could be detected in the samples of both isomers used for the rotating-bomb combustion calorimetry and for the Knudsen effusion technique.

The specific densities used to calculate the true mass from the apparent mass in air were, 1.54 g  $\cdot$  cm $^{-3}$  for 2,5-dichloro-4-nitroaniline, determined from the mass and the dimensions of the pellet of the crystalline compound, using a digital palmer (323-511N Mitutoyo), and 1.754 g  $\cdot$  cm $^{-3}$  [16] for 2,6-dichloro-4-nitroaniline.

The relative atomic masses used in the calculation of all molar quantities throughout this paper were those recommended by the IUPAC Commission in 2005 [17], yielding 207.0152 g  $\cdot$  mol $^{-1}$  for the molar mass of the dichloronitroaniline isomers.

## 2.2. Combustion calorimetry measurements

The standard ( $p^\circ = 0.1$  MPa) massic energies of combustion of 2,5- and 2,6-dichloro-4-nitroaniline, were determined using an isoperibol rotating-bomb calorimeter that was formerly at the National Physical Laboratory, Teddington, UK [18,19]. This apparatus, after having been installed in the University of Manchester, UK [20], has been transferred to Porto University, where some changes were made in the auxiliary equipment, as described by Ribeiro da Silva *et al.* [21]. The rotating-bomb calorimeter was used with a tantalum-lined bomb of internal volume 0.329 dm $^3$  and a tantalum head.

For each experiment, water was added to the calorimeter from a weighed glass vessel. The vessel was weighed with a Mettler PC 8000 balance with a sensitivity of  $\pm 10^{-1}$  g, before and after the water was added, and a correction to the energy equivalent,  $\varepsilon(\text{calor})$ , was made for the deviation of the mass of water from 3969.2 g. The water in the calorimeter, before the experiment, was heated electrically to such a value so that the final temperature after the combustion experiment would be close to 298.15 K. Calorimeter temperatures were measured with an uncertainty within the bounds of  $\pm 10^{-4}$  K, at time intervals of 10 s, using a quartz thermometer (Hewlett Packard HP 2804A) interfaced to a PC programmed to compute the adiabatic temperature change. In the fore, main, and after periods, 125, 100, 125 temperature readings were taken, respectively. Data acquisition and control of the calorimeter was performed using the program LABTERMO [22]. Rotation of the bomb, about its axial and longitudinal axis, was started when the temperature in the main period had risen to about 63% of its total value and continued throughout the rest of the experiment, so that the frictional work of bomb rotation was automatically included in the corrections for the work of water stirring and the heat exchange with the surrounding isothermal jacket, as shown by Good *et al.* [23].

The calorimetric system was calibrated, according to the procedure suggested by Coops *et al.* [24], by the combustion, without bomb rotation, of benzoic acid (NIST Standard Reference Material 39i) having a standard massic energy of combustion, under bomb conditions, of  $\Delta_c u^\circ = -(26434 \pm 3)$  J  $\cdot$  g $^{-1}$  [25]. Calibration experiments were carried out in oxygen, at the pressure

of 3.04 MPa, with 1.00 cm $^3$  of deionised water added to the bomb. From ten calibration experiments, the energy equivalent of the calorimeter obtained was  $\varepsilon(\text{calor}) = (20369.0 \pm 2.3)$  J  $\cdot$  K $^{-1}$ , (0.011%), where the quoted uncertainty is the standard deviation of the mean.

The accuracies of the experimental procedure and of the calorimeter were checked by measuring the standard massic energy of combustion of 4-chlorobenzoic acid, recommend as a test substance for the bomb combustion calorimetry of organochlorine compounds [26]. From six combustion experiments done with 4-chlorobenzoic acid in pellet form and enclosed in polyester bags made from melinex (0.025 mm thickness), using the technique described by Snelson and Skinner [27], at a pressure of 3.04 MPa and in the presence of 15.00 cm $^3$  of aqueous solution of As $_2$ O $_3$  ( $\approx 0.09$  mol  $\cdot$  dm $^{-3}$ ), the standard massic energy of combustion was  $\Delta_c u^\circ = -(19568.6 \pm 2.4)$  J  $\cdot$  g $^{-1}$  [28], where the quoted uncertainty is the standard deviation of the mean. Our experimental value is in excellent agreement with the recommended value [29],  $\Delta_c u^\circ = -(19566.4 \pm 1.5)$  J  $\cdot$  g $^{-1}$ .

Both 2,5- and 2,6-dichloro-4-nitroanilines were burned in pellet form. Each pellet was enclosed in a sealed polyester bag made from melinex using the technique described by Skinner and Snelson [27]. The combustion experiments of the compounds were carried out in oxygen, at  $p = 3.04$  MPa, in the presence of 35.00 cm $^3$  and 40.00 cm $^3$  of aqueous solutions of As $_2$ O $_3$  (0.09046, 0.09022, and 0.09096 mol  $\cdot$  dm $^{-3}$ ). The presence of the As $_2$ O $_3$  solution insured that all the Cl $_2$  formed in the combustion experiment was reduced to aqueous HCl.

The electrical energy for the ignition was determined from the change in potential difference on the discharge of a capacitor (1281  $\mu$ F) when 40 V were discharged through a platinum ignition wire ( $\phi = 0.05$  mm, Goodfellow, mass fraction 0.9999). The cotton thread fuse (empirical formula CH $_{1.686}$ O $_{0.843}$ ) has a standard massic energy of combustion assigned to  $\Delta_c u^\circ = -16,240$  J  $\cdot$  g $^{-1}$  [24].

The energy of combustion of the melinex,  $\Delta U(\text{melinex})$ , was calculated using  $\Delta_c u^\circ(\text{melinex}) = -(22,902 \pm 5)$  J  $\cdot$  g $^{-1}$  [27]. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032) and the mass of carbon dioxide produced from it was calculated using the factor previously reported [27].

The values of the standard massic energies of combustion of both the cotton thread fuse and of the melinex have been previously confirmed in our Laboratory.

The HNO $_3$  formed from the combustion of the compounds and from traces of atmospheric N $_2$  remaining inside the bomb was analyzed by the Devarda's alloy method [30]. The corrections for the HNO $_3$  formed were based on  $\Delta_f U_m^\circ$  (HNO $_3$ , aq, 0.1 mol  $\cdot$  dm $^{-3}$ ) =  $-59.7$  kJ  $\cdot$  mol $^{-1}$  [31], from 0.5N $_2$ (g), 1.25O $_2$ (g) and 0.5H $_2$ O(l).

The extent of As $_2$ O $_3$  oxidation was determined by titration with a standardized iodine solution [30]. For the calculation of  $\Delta U$  (As $_2$ O $_3$ ), corresponding to the energy of oxidation of As $_2$ O $_3$  to As $_2$ O $_5$  in aqueous solution, the procedure described by Hu *et al.* [26] using the enthalpies of oxidation of As $_2$ O $_3$ (aq) by Cl $_2$  [32] and the thermal effects of mixing As $_2$ O $_5$ (aq) with strong acids [33] was followed. Within the precision of the analytical method, no evidence was found for the oxidation of the aqueous solution of As $_2$ O $_3$  after the bomb had been charged with oxygen at  $p = 3.04$  MPa and left up to 5 h at room temperature [34].

The amount of H $_2$ PtCl $_6$ (aq) formed was determined from the loss of mass of platinum from the crucible and its supporting parts. The energy correction was made using  $\Delta_f H_m^\circ$ (H $_2$ PtCl $_6$ , aq) =  $-(676.1 \pm 0.1)$  kJ  $\cdot$  mol $^{-1}$  [31].

The necessary weighings for the combustion experiments were made in a Mettler Toledo 245 balance with a sensitivity of  $\pm 10^{-5}$  g.

An estimated pressure coefficient of massic energy,  $(\partial u / \partial p)_T = -0.2$  J  $\cdot$  g $^{-1}$   $\cdot$  MPa $^{-1}$ , at  $T = 298.15$  K, was assumed for the two studied compounds [35].

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