J. Chem. Thermodynamics 41 (2009) 1247–1253

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Experimental thermochemical study of 4,5-dichloro-2-nitroaniline

Manuel A.V. Ribeiro da Silva *, Maria D.M.C. Ribeiro da Silva, Ana I.M.C. Lobo Ferreira,
Ana Filipa L.O.M. Santos, Tiago L.P. Galvão

Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

ARTICLE INFO

Article history:
Received 18 May 2009
Received in revised form 22 May 2009
Accepted 25 May 2009
Available online 31 May 2009

Keywords:
Thermochemistry
Enthalpy of formation
Rotating-bomb combustion calorimetry
Enthalpy of sublimation
Vapour pressure
Knudsen effusion
Cox Scheme
Dichloronitroaniline isomers

ABSTRACT

The standard ($p^\circ = 0.1$ MPa) molar enthalpy of formation of 4,5-dichloro-2-nitroaniline, in the gaseous phase, at $T = 298.15$ K, was derived from the combination of the values of the standard molar enthalpy of formation, in the crystalline phase, at $T = 298.15$ K, and the standard molar enthalpy of sublimation, at the same temperature. The standard molar enthalpy of formation, in the crystalline phase, at $T = 298.15$ K, was derived as $-(99.7 \pm 1.6)$ $\text{kJ} \cdot \text{mol}^{-1}$ from the standard massic energy of combustion, in oxygen, measured by rotating-bomb combustion calorimetry. The standard molar enthalpy of sublimation was calculated, (109.4 ± 0.9) $\text{kJ} \cdot \text{mol}^{-1}$ by the application of the Clausius–Clapeyron equation, to the vapour pressures measured at several temperatures by Knudsen effusion technique.

The standard molar enthalpies of formation, in the gaseous phase, of the six dichloro-2-nitroaniline isomers and of the four dichloro-4-nitroaniline isomers were estimated by the Cox Scheme and by the Domalski and Hearing group additivity method and compared with the available experimental values. For the Domalski and Hearing group additivity method four new correction terms were derived.

1. Introduction

The 4,5-dichloro-2-nitroaniline is of interest as an intermediary in synthesis [1] and its molecular structure has already been studied [2]. The amino and nitro groups are coplanar with the aromatic ring and linked by an intramolecular N–H···O hydrogen bond. The molecules are staked in layers and held together by intermolecular N–H···O and C–H···O hydrogen bonds.

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, from which the fluoroanilines [3,4], chloroanilines [5–8], bromoanilines [9], iodoanilines [10], monochloronitroanilines [11,12], and two dichloro-4-nitroaniline isomers [13] have already been studied.

This paper reports the standard ($p^\circ = 0.1$ MPa) molar enthalpy of formation, of 4,5-dichloro-2-nitroaniline, in the crystalline phase, at $T = 298.15$ K, derived from the standard massic energy of combustion, in oxygen, at the same temperature, measured by rotating-bomb combustion calorimetry. The vapour pressures at several temperatures, measured by Knudsen effusion technique, are also reported, allowing the calculation, by application of the Clausius–Clapeyron equation, of the standard molar enthalpy and entropy of sublimation, at the mean temperature of the experimental temperature range. The standard molar enthalpy, entropy, and Gibbs free energy of sublimation, at $T = 298.15$ K, were calculated along with the estimated heat capacity difference between the gas and the crystal phases of the compound. The values of the standard molar enthalpy of formation, in the crystalline phase, and of the standard molar enthalpy of sublimation were combined to derive the standard molar enthalpy of formation of the compound, in the gaseous phase, at $T = 298.15$ K. The same parameter was estimated by the Cox Scheme and by the Domalski and Hearing group additivity method for all dichloro-2-nitroaniline and dichloro-4-nitroaniline isomers.

2. Experimental

2.1. Compound and purity control

The 4,5-dichloro-4-nitroaniline [CAS 6641-64-1] was obtained commercially from Aldrich Chemical Co., with an assessed mass fraction minimum purity of 0.96. The compound was purified firstly by sublimation at 0.1 Pa background pressure and $T = 410$ K, then recrystallized from ethanol, and sublimated again at the former conditions. The final purity was checked by gas chromatography, performed on an Agilent 4890D gas chromatograph. No impurities greater than 10^{-3} in mass fraction could be detected in the sample of the compound used for the rotating-bomb combustion calorimetry and for the Knudsen effusion experiments.

---

* Corresponding author. Tel.: +351 22 0402 521; fax: +351 22 0402 522.
E-mail address: risilva@fc.up.pt (M.A.V. Ribeiro da Silva).

0021-9614/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2009.05.013

The specific density used to calculate the true mass from the apparent mass in air for 4,5-dichloro-2-nitroaniline was 1.764 $g \cdot cm^{-3}$ [2].

The relative atomic masses used in the calculation of all molar quantities throughout this paper were those recommended by the IUPAC Commission in 2005 [14], yielding for the molar mass of 4,5-dichloro-2-nitroaniline 207.0152 $g \cdot mol^{-1}$.

2.2. Combustion calorimetry measurements

The standard ($p^\circ = 0.1$ MPa) massic energy of combustion of 4,5-dichloro-2-nitroaniline was determined using an isoperibol rotating-bomb calorimeter that was formerly at the National Physical Laboratory, Teddington, UK [15]. The rotating-bomb calorimeter, previously described in the literature [16–18] 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 acrylic vessel and a correction to the energy equivalent, ε(calor), was made for the deviation in the mass of water from 3969.2 g. 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 [19]. Rotation of the bomb was started when the temperature in the main period had risen to approximately 63% of its total value and continued throughout the rest of the experiment, so that the frictional work of the 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.* [20].

The calorimetric system was calibrated, according to the procedure suggested by Coops *et al.* [21], by the combustion of benzoic acid (NIST Standard Reference Material 39i) having a standard massic energy of combustion, under bomb conditions, of $\Delta_c u = -(26434 \pm 3)\ J \cdot g^{-1}$ [22]. Calibration experiments were carried out in oxygen, at $p = 3.04$ MPa, with 1.00 cm^3 of deionised water added to the bomb. From 10 calibration experiments, the energy equivalent of the calorimeter was obtained as $\varepsilon(\text{calor}) = (20369.0 \pm 2.3)\ J \cdot K^{-1}$, (0.011%), where the quoted uncertainty is the standard deviation of the mean.

The accuracy of the experimental procedure and of the calorimeter was checked by measuring the standard massic energy of combustion of 4-chlorobenzoic acid, recommend as the test substance for the bomb combustion calorimetry of organochlorine compounds [23]. From six combustions done with 4-chlorobenzoic acid, in the pellet form, and enclosed in polyester bags made from melinex (0.025 mm thickness), using the technique described by Snelson and Skinner [24], at $p = 3.04$ MPa and in the presence of 15.00 cm^3 of aqueous solution of As_2O_3 ($\approx 0.09\ mol \cdot dm^{-3}$), the standard massic energy of combustion was found to be $\Delta_c u^\circ = -(19568.6 \pm 2.4)\ J \cdot g^{-1}$ [25], where the quoted uncertainty refers to the standard deviation of the mean. This experimental value is in excellent agreement with the recommended value [26], $\Delta_c u^\circ = -(19566.4 \pm 1.5)\ J \cdot g^{-1}$.

The 4,5-dichloro-2-nitroaniline was burnt in the pellet form. Each pellet was enclosed in a sealed polyester bag made from melinex (0.025 mm thickness). The combustion experiments of the compound were carried out in oxygen, at $p = 3.04$ MPa, in the presence of 30.00 cm^3 of aqueous solution of As_2O_3 ($0.09096\ mol \cdot dm^{-3}$). The presence of the As_2O_3 solution insured that all the Cl_2 formed in the combustion experiments was reduced to aqueous HCl.

The electrical energy for the ignition was determined from the change in potential difference of a capacitor (1281 μF) 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 $\Delta_c u^\circ = -16240\ J \cdot g^{-1}$ [21].

The energy of combustion of the melinex, ΔU(melinex), was calculated using $\Delta_c u^\circ(\text{melinex}) = -(22902 \pm 5)\ J \cdot g^{-1}$ [24]. 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 [24].

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 [27]. The corrections for the HNO_3 formed were based on $\Delta_f U^\circ_m(HNO_3, aq, 0.1\ mol \cdot dm^{-3}) = -59.7\ kJ \cdot mol^{-1}$ [28], from 0.5 N_2(g), 1.25 O_2(g), and 0.5 H_2O(l).

The extent of the As_2O_3 oxidation was determined by titration with a standardized iodine solution [27]. For the calculation of $\Delta U(As_2O_3)$, corresponding to the energy of oxidation of As_2O_3 to As_2O_5 in aqueous solution, the procedure described by Hu *et al.* [23] using the enthalpies of oxidation of As_2O_3(aq) by Cl_2 [29] and the thermal effects of mixing As_2O_5(aq) with strong acids [30] was followed. Within the precision of the analytical method, no evidence was found for the oxidation of the aqueous solution of As_2O_3 after the bomb had been charged with oxygen at $p = 3.04$ MPa and left up to 5 h at room temperature [31].

At the end of some experiments, a small residue of carbon was found due to incomplete combustion. If the carbon soot stayed only on the walls of the platinum crucible, it was possible to determine its amount by weighing the crucible before and after calcinations and so corrections for carbon soot formation were made, based on the standard massic energy of combustion of carbon, $\Delta_c u^\circ = -33\ kJ \cdot g^{-1}$ [21].

The amount of H_2PtCl_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 $\Delta_f H^\circ_m(H_2PtCl_6, aq) = -(676.1 \pm 0.1)\ kJ \cdot mol^{-1}$ [28].

The necessary weighings for the combustion experiments were made with 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 studied compound [32].

The standard state corrections, ΔU_Σ, and the heat capacities of the bomb contents, ε_i and ε_f, were calculated by the procedure given by Hubbard *et al.* [33] using the solubility constants and energies of solution of CO_2 and O_2 as given by Hu *et al.* [23].

2.3. Knudsen effusion measurements

The vapour pressures of 4,5-dichloro-2-nitroaniline, over the range of (0.1 to 1.0) Pa, were measured, at several temperatures, using a Knudsen effusion apparatus. The detailed description of the apparatus, procedure, and technique, and the results obtained with test substances (benzoic acid and ferrocene) have been reported by Ribeiro da Silva and Monte [34]. This apparatus enables the simultaneous operation of three aluminium effusion cells, with different orifice diameters, at the same temperature.

In each effusion experiment, the sample was placed at the base of the Knudsen cells, which were immersed in a thermostatically controlled silicone oil bath; the system was evacuated to a pressure near 10^{-4} Pa and, during a convenient effusion time period t, the vapour effused into the vacuum outside the cell. The mass loss, Δm, of the sample was determined by weighing the effusion cells to ±0.01 mg, in a Mettler AE 163 balance, before and after