



Experimental and computational thermochemical study of the tri-, tetra-, and pentachloronitrobenzene isomers

Manuel A.V. Ribeiro da Silva*, Ana I.M.C. Lobo Ferreira, Joana I.T.A. Cabral, Ana Filipa L.O.M. Santos, Ana Rita G. Moreno, Tiago L.P. Galvão, Inês M. Rocha, Paula M.V. Fernandes, Sílvia Q. Salgueiro, Vanessa A.F. de Moura, Isabel M.S.C. Oliveira, Paula C. Cotelo, Mariana R.A. Ribeiro

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

ARTICLE INFO

Article history:

Received 9 March 2009

Accepted 27 March 2009

Available online 5 April 2009

Keywords:

Thermochemistry

Energy of combustion

Enthalpy of sublimation

Enthalpy of formation

Rotating-bomb combustion calorimetry

Calvet microcalorimetry

Knudsen effusion

Vapour pressure

Entropy of sublimation

Gibbs energy of sublimation

2,4,6-Trichloronitrobenzene

2,3,5,6-Tetrachloronitrobenzene

Pentachloronitrobenzene

ABSTRACT

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of 2,4,6-trichloronitrobenzene, 2,3,5,6-tetrachloronitrobenzene, and pentachloronitrobenzene, in the crystalline state, at $T = 298.15$ K, were derived from the standard massic energies of combustion, in oxygen, at $T = 298.15$ K, measured by rotating-bomb combustion calorimetry.

The standard molar enthalpies of sublimation, at $T = 298.15$ K, of 2,4,6-trichloronitrobenzene and pentachloronitrobenzene, were determined from the dependence with the temperature of the vapour pressures, measured by the Knudsen mass-loss effusion method, whereas for 2,3,5,6-tetrachloronitrobenzene, the Calvet drop microcalorimetric technique was used.

| | $-\Delta_c U_m^{\circ}(\text{cr})/$ ($\text{kJ} \cdot \text{mol}^{-1}$) | $-\Delta_f H_m^{\circ}(\text{cr})/$ ($\text{kJ} \cdot \text{mol}^{-1}$) | $\Delta_{\text{cr}}^{\circ} H_m^{\circ}/$ ($\text{kJ} \cdot \text{mol}^{-1}$) |
|---------------------------------|--|--|--|
| 2,4,6-Trichloronitrobenzene | 2663.5 ± 1.1 | 58.6 ± 1.3 | 86.7 ± 1.1 |
| 2,3,5,6-Tetrachloronitrobenzene | 2537.1 ± 1.7 | 67.0 ± 1.9 | 91.3 ± 2.5 |
| Pentachloronitrobenzene | 2387.4 ± 2.4 | 98.6 ± 2.5 | 94.5 ± 0.4 |

The experimental values are also compared with estimates based on G3(MP2)//B3LYP computations, which have also been extended to all the isomers of the trichloro- and tetrachloronitrobenzene that were not studied experimentally.

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1. Introduction

The natural formation of polychloronitrobenzenes [1] is rare and most of these compounds are frequently produced in industrial processes. They have been used for many years in the synthesis of fungicides and pharmaceuticals, and are also starting materials for the production of azo and sulphur dyes. These compounds are characterized by their long life, chemical stability and, across the years, they have become a serious environmental issue [2]. Despite their large application in industry and agriculture, these chemicals are intentional released into the soils and, sometimes, into the water courses [3]. The nitroaromatic compounds are biodegraded by bacteria and so do not accumulate in the environment, unless the concentrations exceed the assimilation capacity of the ecosystem [4].

Pentachloronitrobenzene is especially important in industry, preventing the formation of slime in residual waters. It is also largely used as a fungicide in gardens and agricultural areas, protecting cotton, grain seeds, potatoes, onions, and rice from the growth of fungi. According to the Environmental Protection Agency (EPA) [5], pentachloronitrobenzene may represent a health hazard, given its extensive use on a multitude of crops which leads to cumulative exposure and potential liver damage. As a technical impurity of pentachloronitrobenzene, 2,3,5,6-tetrachloronitrobenzene may be released to the environment during pentachloronitrobenzene production and use. Although, 2,3,5,6-tetrachloronitrobenzene is also a fungicide, it is only applied to potatoes, post-harvest, intended for long-term storage, for the control of sprouting and the prevention of weight loss in store. Their exposure to the general population is expected to be mainly through residues in food.

The establishment of relations between the energetic and the structural properties of the compounds is important to explain their behaviour in terms of reactivity. In the last few years, our Research Group, has been involved in the study of the thermochemistry of

* 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).

polychloronitrobenzenes derivatives [6–9], and so the experimental work reported here represents an additional contribution to this study.

The gas-phase standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of 2,4,6-trichloronitrobenzene, 2,3,5,6-tetrachloronitrobenzene, and pentachloronitrobenzene here reported, have been obtained experimentally since high purity samples of these compounds were available for experimental determinations. In the experimental investigation, the determination of the standard molar energies of combustion, in oxygen, at $T = 298.15$ K, of these three compounds was done by rotating-bomb combustion calorimetry, from which the values of the standard molar enthalpies of formation, in the crystalline phase, were derived. The determination of the standard molar enthalpies of sublimation of the three chloronitrobenzene derivatives was done by Calvet microcalorimetry using the high-temperature vacuum sublimation technique. The Knudsen mass-loss effusion technique was used to measure the vapour pressures as a function of temperature of the 2,4,6-trichloronitrobenzene and of the pentachloronitrobenzene, from which the molar enthalpies and entropies of sublimation, at the mean temperature of the experimental temperature range, were derived. Standard molar enthalpies, entropies, and Gibbs energies of sublimation, at $T = 298.15$ K, were calculated using estimated values for the heat capacity differences between the gas and the crystal phases of each compound. These two sets of experimental values allowed the derivation of the standard molar enthalpies of formation, in the gaseous state, of these three compounds.

For the experimental studied compounds and for the other tri- and tetrachlorinated isomers for which high purity samples were not available, the standard molar enthalpies of formation in the gaseous phase have been estimated by computational thermochemistry by means of the G3(MP2)//B3LYP method.

2. Experimental details

2.1. Compounds and purity control

The studied compounds were commercially obtained from Sigma-Aldrich Chemical Co. with the following assessed purities: 2,4,6-trichloronitrobenzene [CAS 18708-70-8] mass fraction 0.98; 2,3,5,6-tetrachloronitrobenzene [CAS 117-18-0] mass fraction 0.99; and pentachloronitrobenzene [CAS 82-68-8] mass fraction 0.99. The compounds were further purified by successive vacuum sublimations and their purity control assessed by gas chromatography, performed on an Agilent 4890D Gas Chromatograph, being found to be greater than 0.9990.

The specific densities used to calculate the true mass from the apparent mass in air, were taken as (1.73, 1.81, and 1.93) $\text{g} \cdot \text{cm}^{-3}$, respectively, for 2,4,6-trichloronitrobenzene, 2,3,5,6-tetrachloronitrobenzene, and pentachloronitrobenzene, determined from the ratio mass/volume of pellets of the compounds (made in vacuum, with an applied pressure of 10^5 $\text{kg} \cdot \text{cm}^{-2}$).

The relative atomic masses used in the calculation of all molar quantities throughout this paper were those recommended by the IUPAC Commission in 2005 [10]; using those values, the molar masses are (226.4446, 260.8896, and 295.3347) $\text{g} \cdot \text{mol}^{-1}$, respectively, for 2,4,6-trichloronitrobenzene, 2,3,5,6-tetrachloronitrobenzene, and pentachloronitrobenzene.

2.2. Combustion calorimetry measurements

The standard molar energies of combustion of the 2,4,6-trichloronitrobenzene, 2,3,5,6-tetrachloronitrobenzene, and pentachloronitrobenzene were determined in two different isoperibol systems:

- (I) The calorimetric studies of 2,4,6-trichloronitrobenzene and pentachloronitrobenzene were performed in an isoperibolic rotating-bomb calorimeter, already described in literature [11,12]. A tantalum-lined combustion bomb with an internal volume of 0.329 dm^3 was used. The calibration of the calorimeter was made by combustion of benzoic acid NBS Calorimetric Standard 39i, with a certified massic energy of combustion, when burnt under the bomb conditions, of $-(26434 \pm 3) \text{J} \cdot \text{g}^{-1}$ [13]. From 10 calibration experiments, that were made in oxygen, at $p = 3.04$ MPa, with 1.00 cm^3 of deionised water added to the bomb, the value of the energy equivalent of the calorimeter was found to be $\varepsilon(\text{calor}) = (20369.0 \pm 2.3) \text{J} \cdot \text{K}^{-1}$ (0.011%), for an average mass of water added to the calorimeter of 3969.2 g; the quoted uncertainty is the standard deviation of the mean.
- (II) The combustion experiments of the 2,3,5,6-tetrachloronitrobenzene were also performed in an isoperibolic rotating-bomb calorimeter, using a twin valve bomb lined with platinum, and made of stainless steel, having an internal volume of 0.258 dm^3 . The apparatus and technique have been detailed elsewhere [6,14,15]. Combustion of benzoic acid NIST Thermochemical Standard 39j was used for calibration of this rotating-bomb. Its massic energy of combustion is $-(26434 \pm 3) \text{J} \cdot \text{g}^{-1}$, under certificate conditions [16]. The calibration results were corrected to give the energy equivalent of the calorimeter, $\varepsilon(\text{calor})$, corresponding to the average mass of 5222.5 g of water added to this calorimeter. From seven calibration experiments, $\varepsilon(\text{calor})$ was found to be $(25164.0 \pm 2.1) \text{J} \cdot \text{K}^{-1}$ (0.0084%), where the uncertainty quoted is the standard deviation of the mean.

In both calorimetric systems the calibration experiments were performed in the conventional way, without bomb rotation, and according to the procedure suggest by Coops *et al.* [17].

Samples of the compounds in pellet form, were ignited in oxygen at a pressure $p = 3.04$ MPa, with volumes of (15.00, 35.00, and 30.00) cm^3 of an aqueous solution of $\text{As}_2\text{O}_3 \approx 0.09$ $\text{mol} \cdot \text{dm}^{-3}$ added to the bombs, respectively, for the combustion experiments of 2,4,6-trichloronitrobenzene, 2,3,5,6-tetrachloronitrobenzene, and pentachloronitrobenzene. The presence of the arsenious oxide solution insures that all the free chlorine formed in the combustion experiments was reduced to aqueous hydrochloric acid. Since the first experiments of combustion yielded considerable amounts of carbon soot, dried paraffin oil (Aldrich, Gold label, mass fraction purity >0.999) was used as auxiliary of combustion in all the combustion experiments of the three compounds.

For each combustion experiment, the ignition temperature was chosen so that the final temperature would be close to $T = 298.15$ K. The electrical energy for ignition was measured from the change in potential difference across a capacitor when discharged through the platinum ignition wire ($\phi = 0.05$ mm, Goodfellow, mass fraction 0.9999). Temperature measurements of both calorimeters were automatically collected every 10 s, within the bounds of $\pm(1 \cdot 10^{-4})$ K, using a Hewlett-Packard (HP-2804A) quartz crystal thermometer interfaced to a PC programmed for data acquisition and to compute the adiabatic temperature change, by means of a version of LABTERMO program [18]. For the 2,4,6-trichloronitrobenzene and pentachloronitrobenzene, 125 readings were taken for the fore, and the after periods, and 100 readings for the main period, while for the 2,3,5,6-tetrachloronitrobenzene 100 readings were taken for each the fore, the main and the after periods.

For each combustion experiment of the compounds, rotation of the bomb was started when the temperature rise of the main period reached about 0.63 of its total value and then continued throughout the experiment. It has been shown that by adopting

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