J. Chem. Thermodynamics 41 (2009) 904–910

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Experimental and computational thermochemical study of the dichloronitrobenzene isomers

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ARTICLE INFO

Article history:
Received 2 March 2009
Accepted 10 March 2009
Available online 20 March 2009

Keywords:
Thermochemistry
Energy of combustion
Enthalpy of sublimation
Enthalpy of formation
Rotating bomb combustion calorimetry
Calvet microcalorimetry
Cox scheme
Dichloronitrobenzene isomers

ABSTRACT

The standard (p° = 0.1 MPa) molar enthalpies of formation of 2,4-, 2,5-, 3,4- and 3,5-dichloronitrobenzene isomers, in the crystalline state, at T = 298.15 K, were derived from the standard (p° = 0.1 MPa) massic energies of combustion, in oxygen, at T = 298.15 K, measured by rotating bomb combustion calorimetry. The standard molar enthalpies of sublimation of the four isomers, at T = 298.15 K, were obtained by high-temperature Calvet microcalorimetry.

	$-\Delta_c U^\circ_m(cr)/(kJ \cdot mol^{-1})$	$-\Delta_f H^\circ_m(cr)/(kJ \cdot mol^{-1})$	$\Delta^g_{cr} H^\circ_m/(kJ \cdot mol^{-1})$
2,4-Dichloronitrobenzene	2792.8 ± 0.9	47.4 ± 1.2	87.8 ± 1.7
2,5-Dichloronitrobenzene	2793.0 ± 1.8	47.2 ± 2.0	87.4 ± 2.5
3,4-Dichloronitrobenzene	2774.1 ± 1.2	66.1 ± 1.4	85.8 ± 2.5
3,5-Dichloronitrobenzene	2769.6 ± 0.9	70.6 ± 1.2	83.2 ± 1.5

From the determined experimental results, the values of the gaseous standard (p° = 0.1 MPa) molar enthalpies of formation were derived. The gas-phase enthalpies of formation of all the six chloronitrobenzene isomers were also estimated by the Cox scheme and by computational thermochemistry methods and compared with the available experimental values.

1. Introduction

The chlorinated nitroaromatic compounds are characterized by their long life, chemical stability and non-biodegradability and over the years have become a serious environmental issue [1,2]. They are environmental pollutants released from automobile exhausts and industrial areas and shown to be potential mutagens or carcinogens. Toxicity induced by the various chloronitrobenzene isomers *in vivo* includes hematotoxicity, immunotoxicity, hepatotoxicity, and nephrotoxicity [3,4], and they are also suspected to have genotoxic and carcinogenic potential, being identified as priority pollutants by the Environmental Protection Agency (EPA) [5].

The natural formation of these compounds is rare, with their vast presence in the environment resulting from massive industrial production, which conducted to an extensive research work in the study of means of quick and reliable detection of these substances in aqueous phase and soil [6,7] and on methodologies for their elimination, such as advanced oxidation process or biological degradation process [8–11].

Thermodynamic properties of some chloronitrobenzenes have been studied [12–15]. To the best of our knowledge, however, in what concerns the dichloronitrobenzenes there are only available, experimental results of the vapour pressure, enthalpy of sublimation, and enthalpy of fusion of the 3,4-dichloronitrobenzene, recently reported by Verevkin *et al.* [16].

In this work, the standard (p° = 0.1 MPa) molar enthalpies of formation, in the gaseous state, at T = 298.15 K, of four dichlorinated nitrobenzenes isomers were experimentally determined, whereas the gas-phase standard molar enthalpies of formation of the other two dichloronitrobenzenes isomers, which were not available, were estimated by means of the empirical methodology developed by Cox and by computational methods. The choice of these molecules is due to the fact that the effects of the introduction of chlorine atoms in benzene rings [15,17–23] as well as the effect of the same substituents into heterocycles [24–30] has been, for some years, one of the research objectives of our Research Group on thermochemical properties. The experimental investigation includes the determination of the standard molar energies of combustion, in oxygen, at T = 298.15 K, of four dichloronitrobenzene isomers, using a rotating bomb combustion calorimeter, from which the values of the standard molar enthalpies of formation, in the condensed phase, were derived. The determination of the

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doi:10.1016/j.jct.2009.03.001

standard molar enthalpies of sublimation, at T = 298.15 K, was performed by Calvet microcalorimetry using the high-temperature vacuum sublimation technique. These experimental values allowed the derivation of the standard molar enthalpies of formation, in the gaseous state, of 2,4-dichloronitrobenzene [CAS 611-06-3], 2,5-dichloronitrobenzene [CAS 89-61-2], 3,4-dichloronitrobenzene [CAS 99-54-7] and 3,5-dichloronitrobenzene [CAS 618-62-2], which were compared with values estimated from the Cox scheme [31] and those obtained by computational thermochemistry.

2. Experimental

2.1. Compounds and purity control

The isomers 2,4-dichloronitrobenzene [2,4-Cl2NO2Benz], 2,5-dichloronitrobenzene [2,5-Cl_2NO_2Benz], 3,4-dichloronitrobenzene [3,4-Cl_2NO_2Benz] and 3,5-dichloronitrobenzene [3,5-Cl_2NO_2Benz], were commercially available from Aldrich Chemical Co., with an assessed mass fraction minimum purity of 0.97, and were purified by repeated sublimations at 0.1 Pa background pressure. The final purity of each isomer was checked by gas chromatography, performed on an Agilent 4890D gas chromatograph equipped with an HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane (15 m × 0.530 mm i.d. × 1.5 μm 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 · min^{-1}, 423 K (5 min). No impurities greater than 10^{-3} in mass fraction could be detected in the samples of the chloronitrobenzene isomers used for the rotating bomb combustion calorimetry and Calvet microcalorimetry measurements.

The specific densities used to calculate the true mass from the apparent mass in air, were for 2,4-, 3,4-, and 3,5-dichloronitrobenzene, respectively, 1.69 g · cm^{-3}, 1.64 g · cm^{-3} and 1.63 g · cm^{-3}, determined from the ratio mass/volume of the pellet, made in vacuum, with an applied pressure of 10^5 kg · cm^{-2}, and were of 1.442 g · cm^{-3} for 2,5-dichloronitrobenzene [32].

The relative atomic masses used in the calculation of all molar quantities throughout this paper were those recommended by the IUPAC Commission in 2005 [33], yielding for the molar mass of the dichloronitrobenzene isomers 192.0005 g · mol^{-1}.

2.2. Combustion calorimetry measurements

The combustion experiments were performed with an isoperibol rotating bomb calorimeter, already described [34,35], which was originally constructed at the University of Lund, Sweden, according to the design of Professor Stig Sunner [36]. The stainless steel combustion bomb with internal volume of 0.258 dm^{-3} and wall thickness of 1 cm, is a twin valve bomb lined with platinum, with the internal fittings machined from platinum. The bomb is suspended from the lid of the calorimeter can, to which a mass of nearly 5222.5 g of water, previously weighed in a Perspex vessel, is added. A Mettler PM 11-N balance, sensitivity ±10^{-1} g, was used to weigh the amount of distilled water added to the calorimeter from a weighed acrylic vessel. Calorimetric temperatures were measured to ±10^{-4} K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett–Packard HP 2804A), interfaced to a PC programmed to compute the adiabatic temperature change.

The calorimetric system was calibrated, in the conventional way, without bomb rotation, according to the procedure suggest by Coops *et al.* [37], by combustion of benzoic acid (NIST Standard Reference Material 39j) having a massic energy of combustion under bomb conditions of −(26434 ± 3) J · g^{-1} [38]. Calibration experiments were carried out in oxygen, at a pressure of 3.04 MPa, with 1.00 cm^3 of deionised water added to the bomb. The obtained value of the energy equivalent of the calorimeter was ε(calor) = (25164.0 ± 2.1) J · K^{-1}, (0.0083%), as a mean of seven calibration experiments, where the uncertainty quoted is the standard deviation of the mean. This value was used for the experiments carried out for the 2,4-Cl_2NO_2Benz, 2,5-Cl_2NO_2Benz, and 3,4-Cl_2NO_2Benz. Then, since the equipment was subject to maintenance works, a new calibration constant ε(calor) = (25157.4 ± 1.1) J · K^{-1}, (0.0044%), was used for the 3,5-Cl_2NO_2Benz. The uncertainty quoted for the calibration constants is the standard deviation of the mean.

For each combustion experiment, the ignition temperature was chosen so that the final temperature would be close to T = 298.15 K. The ignition energy was measured by the change in potential difference on the discharge of a capacitor (1400 μF) across a platinum wire (ϕ = 0.05 mm, Goodfellow, mass fraction 0.9999). At least 100 temperature readings were taken for the main period and for both the fore and after periods. Data acquisition and control of the calorimeter were performed using the program LABTERMO [39].

The calibration results, as well as the results of the combustion experiments of the studied compounds, were corrected to give the energy equivalents corresponding to the average mass of water added to the calorimeter: 5222.5 g. The accuracy of the calorimeter was checked in our laboratory by measuring the energy of combustion of 4-chlorobenzoic acid [17,18]. 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 [17,35].

The four isomers of dichloronitrobenzene were burned in pellet form. Since the first experiments of combustion of the 3,4- and 3,5-dichloronitrobenzene compounds yielded considerable amounts of carbon soot, the combustion experiments were performed enclosing the pellet of the compounds in sealed polyester bags made from Melinex (0.025 mm thickness) using the technique described by Skinner and Snelson [40]. One of the combustion experiments with 3,5-dichloronitrobenzene was performed enclosing the pellet in a polyethylene bag. The combustion experiments of the dichloronitrobenzenes were carried out in oxygen, at p = 3.04 MPa and in the presence of 30.00 cm^3 of aqueous solution of As_2O_3 (≈0.09 mol · dm^{-3}), insuring that all the free chlorine formed in the combustion experiment was reduced to aqueous hydrochloric acid.

For each combustion experiment of the studied compounds, the 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 this procedure, the frictional work due to the rotation of the bomb is automatically accounted in the temperature corrections for the work of water stirring and for the heat exchanged with the surrounding isothermal jacket [41]. The rotating mechanism allows the simultaneous axial and end-over-end rotation of the bomb, causing the aqueous solution of As_2O_3 placed in the bomb to wash all internal surfaces of the bomb, yielding a homogeneous final solution.

At the end of some experiments a small residue of carbon was found due to incomplete combustion. If the carbon soot formed stays only on the walls of the platinum crucible, and not in the combustion solution or on the walls of the bomb, an energy correction for the carbon soot was done by weighing the crucible before and after calcinations. Otherwise, the experiments were discarded. Corrections for carbon soot formation were based on the standard massic energy of combustion of carbon, $\Delta_c u^\circ = -33$ · kJ · g^{-1} [37].

The HNO_3 formed from the combustion of the chloronitrobenzene samples and from traces of atmospheric nitrogen remaining