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Thermochemical study of cyanopyrazines: Experimental and theoretical approaches

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Abstract

The standard ($p^\circ = 0.1$ MPa) molar energy of combustion, at $T = 298.15$ K, of crystalline 2,3-dicyanopyrazine was measured by static bomb calorimetry, in oxygen atmosphere. The standard molar enthalpy of sublimation, at $T = 298.15$ K, was obtained by Calvet Microcalorimetry, allowing the calculation of the standard molar enthalpy of formation of the compound, in the gas phase, at $T = 298.15$ K: $\Delta_f H_m^\circ$ (g) = (518.7 ± 3.4) $\text{kJ} \cdot \text{mol}^{-1}$.

In addition, the geometries of all cyanopyrazines were obtained using density functional theory with the B3LYP functional and two basis sets: 6-31G* and 6-311G**. These calculations were then used for a better understanding of the relation between structure and energetics of the cyanopyrazine systems. These calculations also reproduce measured standard molar enthalpies of formation with some accuracy and do provide estimates of this thermochemical parameter for those compounds that could not be studied experimentally, namely the tri- and tetracyanopyrazines: the strong electron withdrawing cyano group on the pyrazine ring makes cyanopyrazines highly destabilized compounds.

Keywords: Cyanopyrazines; Energy of combustion; Enthalpy of sublimation; Enthalpy of formation; Theoretical calculations

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1. Introduction

The thermochemical study of pyrazine derivatives has been a continuing interest of researchers in our laboratory, in order to establish relationships among the structural and energetical properties in this kind of compounds [1–7]. It is our aim with this paper to enlarge the thermochemical database as well as to predict theoretically thermochemical parameters for other compounds whose experimental study is impossible due to difficulties in their synthesis and/or in obtaining them pure in the needed quantity.

We have performed the experimental study of cyanopyrazine [7] and in the present work we report the standard molar enthalpy of formation of 2,3-dicyanopyrazine (2,3-DCNPz) in the gaseous phase, obtained from measurements of the combustion energy using a static bomb calorimeter and from the enthalpy of sublimation of the compound measured by microcalorimetry Calvet. Experimental determinations for tri- and tetracyanopyrazine were precluded due to the impossibility to obtain pure samples of the compounds in the needed quantity. So, we have decided to perform theoretical calculations as a complement to the experimental work. Density functional theory (DFT) calculations were performed in order to obtain the optimized geometry of 2,3-dicyanopyrazine and of all the other possible isomers, as well as, all the other cyanopyrazines. Estimates of the

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enthalpies of formation for all the cyanopyrazines were thus obtained from the DFT calculations.

The 2,3-dicyanopyrazine derivatives are very powerful electron acceptors and valuable in a broad range of chemistry fields for their application to dyestuff and non-linear optical materials [8]. Compounds containing the 2,3-dicyanopyrazine unity are especially suitable building blocks for the strong intramolecular charge-transfer chromophoric system which is necessary for second order nonlinear optical materials [9]. The 2,3-dicyano-5-methylpyrazines can be used as convenient precursors for fluorescent dyes, and can be applied jointly with other compounds as emitters for electroluminescence devices [9].

2. Experimental

2.1. Materials

The 2,3-DCNPy obtained commercially from Aldrich Chemical Co. [13481-25-9], with the minimum mass fraction of purity of 0.99, was further purified by repeated sublimation under reduced pressure until the combustion results were consistent and the carbon dioxide recovery ratios were satisfactory. The average ratio, together with the standard deviation of the mean, of the mass of carbon dioxide recovered to that calculated from the mass of sample was (0.9999 ± 0.0001). The final purity of the compound was further assessed by differential scanning calorimetry (DSC) using the fractional fusion technique [10]. The mass fraction of impurities found was less than 1×10^{-3}. The temperature and the enthalpy of fusion of the purified samples (hermetically sealed in steel crucibles) were measured using a Setaram DSC 141 apparatus under a heating rate of $3.3 \times 10^{-2}\ \mathrm{K \cdot s^{-1}}$. The power scale of the calorimeter was calibrated with high-purity indium (mass fraction > 0.99999) and its temperature scale was calibrated by measuring the melting temperature of the following high purity reference materials [11]: naphthalene, benzoic acid and indium. The recorded thermograms do not show any phase transitions between $T = 298$ K and the melting temperature of the samples. The temperature of fusion (observed at the onset of the calorimetric peaks), T_{fus}, and the molar enthalpy of fusion were computed from the DSC thermograms, $\Delta_{\mathrm{cr}}^{l} H_{\mathrm{m}}\ (T_{\mathrm{fus}} = (405.06 \pm 0.05\ \mathrm{K})) = (19.80 \pm 0.31)\ \mathrm{kJ \cdot mol^{-1}}$. The uncertainties assigned to the last values are twice the standard deviation of the mean of five independent runs. The density for 2,3-DCNPz was estimated as $\rho = 1.13\ \mathrm{g \cdot cm^{-3}}$ at $T = 298$ K.

2.2. Combustion calorimetry

The combustion experiments were performed with a static bomb calorimeter. The apparatus and technique have been described previously [12,13]. Benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190r) was used for calibration of the bomb. Its massic energy of combustion is $\Delta_{\mathrm{c}} u = -(26432.3 \pm 3.8)\ \mathrm{J \cdot g^{-1}}$, under certificate conditions. The calibration results were corrected to give the energy equivalent $\varepsilon_{\mathrm{cal}}$ corresponding to the average mass of water added to the calorimeter: 3119.6 g. From six calibration experiments, $\varepsilon_{\mathrm{cal}} = (16007.3 \pm 0.7)\ \mathrm{J \cdot K^{-1}}$, where the uncertainty quoted is the standard deviation of the mean. The 2,3-DCNPz was burnt, in pellet form, in oxygen at the pressure 3.04 MPa with $1.00\ \mathrm{cm^3}$ of water added to the bomb. For all experiments, ignition was made at $T = (298.150 \pm 0.001)$ K. The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton-thread fuse, empirical formula $\mathrm{CH_{1.686}O_{0.843}}$, the standard massic energy of combustion is $\Delta_{\mathrm{c}} u^{\circ} = -16250\ \mathrm{J \cdot g^{-1}}$ [14]. This value has been confirmed by previous combustion of cotton-thread samples in our laboratory. The corrections for nitric acid formation were based on $-59.7\ \mathrm{kJ \cdot mol^{-1}}$ [15], for the molar energy of formation of $0.1\ \mathrm{mol \cdot dm^{-3}}$ $\mathrm{HNO_3(aq)}$ from $\mathrm{N_2(g)}$, $\mathrm{O_2(g)}$, and $\mathrm{H_2O(l)}$. The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton thread fuse. An estimated pressure coefficient of massic energy: $(\partial u/\partial p)_T = -0.2\ \mathrm{J \cdot g^{-1} \cdot MPa^{-1}}$ at $T = 298.15$ K, a typical value for most organic compounds [16], was assumed. The standard massic energy of combustion, $\Delta_{\mathrm{c}} u^{\circ}$, for 2,3-DCNPy was calculated using the procedure given by Hubbard *et al.* [17]. The molar masses used for the elements were those recommended by the IUPAC commission [18].

2.3. Microcalorimetry Calvet

The standard molar enthalpy of sublimation of 2,3-DCNPz was measured using the "vacuum sublimation" drop microcalorimetric method [19]. Samples, about 3 mg of the crystalline compound, contained in thin glass capillary tubes sealed at one end, were dropped, at room temperature, into the hot reaction vessel, in the Calvet high temperature microcalorimeter (SETARAM HT 1000) held at a convenient temperature of 385 K, and then removed from the hot zone by vacuum sublimation. Simultaneously, an empty capillary tube was dropped in the reference calorimetric cell. The observed standard molar enthalpy of sublimation $\Delta_{\mathrm{cr},298.15\ \mathrm{K}}^{\mathrm{g}T} H_{\mathrm{m}}^{\circ}$ was corrected to $T = 298.15$ K using the value of $\Delta_{298.15\ \mathrm{K}}^{T} H_{\mathrm{m}}^{\circ}(\mathrm{g})$ estimated by a group method with values from Stull *et al.* [20]. The microcalorimeter was calibrated *in situ* for these measurements using the reported standard molar enthalpy of sublimation of naphthalene [21].