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Thermochemistry of 2,2′-dipyridil *N*-oxide and 2,2′-dipyridil *N*,*N*′-dioxide. The dissociation enthalpies of the N–O bonds

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ABSTRACT

In this paper, the first, second and mean (N–O) bond dissociation enthalpies (BDEs) were derived from the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the gaseous phase, $\Delta_f H^\circ_m(\text{g})$, at $T = 298.15$ K, of 2,2′-dipyridil *N*-oxide and 2,2′-dipyridil *N*,*N*′-dioxide. These values were calculated from experimental thermodynamic parameters, namely from the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the crystalline phase, $\Delta_f H^\circ_m(\text{cr})$, at $T = 298.15$ K, obtained from the standard molar enthalpies of combustion, $\Delta_c H^\circ_m$, measured by static bomb combustion calorimetry, and from the standard molar enthalpies of sublimation, at $T = 298.15$ K, determined from Knudsen mass-loss effusion method.

1. Introduction

Experimental and theoretical energetic studies on compounds containing a terminal N–O bond, in different molecular environments, have been developed in our Research Group [1–9], with the main goal to compile and place them, together with other oxygenated species, in a simple reactivity scale for primary oxo transfer reactions in chemical and biochemical conversions, as it has been introduced/suggested by Holm *et al.* [10,11].

Among the classes of molecules extensively studied are the pyridine *N*-oxide [1,7,9,12–15], derivatives and the quinoxaline-*N*,*Ń*-dioxides [1–5,16,17], for which our research has been also embracing the evaluation of the energetic effect of the substituents on the ring of the nitrogen heterocycle *N*-oxides, upon the dissociation enthalpy of the (N–O) bonds.

The present work reports an experimental study of one mono-*N*-oxide and one *N*,*Ń*-dioxide bipyridine, namely, 2,2′-dipyridil *N*-oxide and 2,2′-dipyridil *N*,*N*′-dioxide, whose structures are shown in figure 1. Bipyridine derivatives are compounds containing two pyridyl donor units, which have been found to be useful bridging ligands in the construction of inorganic networks and crystal engineering, resulting in many assemblies, as it has been demonstrated by the use of 4,4-bipyridine *N*,*N*-dioxide in the construction of lanthanide coordination polymers [18].

The standard ($p^\circ = 0.1$ MPa) massic energies of combustion, in oxygen, of these two compounds were measured by high precision static bomb calorimetry, from which the values of the standard molar enthalpies of formation, in the crystalline phase, at $T = 298.15$ K, were derived. The enthalpies of sublimation of both compounds were derived from their vapor pressures, at different temperatures, measured by the Knudsen effusion technique. Combining the standard molar enthalpies of formation in the crystalline phase and the corresponding enthalpies of sublimation allowed us to derive the standard molar enthalpies of formation in the gas phase, at $T = 298.15$ K, for the two compounds. These results were used to obtain the experimental values for the N–O bond dissociation enthalpy in the 2,2′-dipyridil *N*-oxide and the first N–O bond dissociation enthalpy in the 2,2′-dipyridil *N*,*N*′-dioxide.

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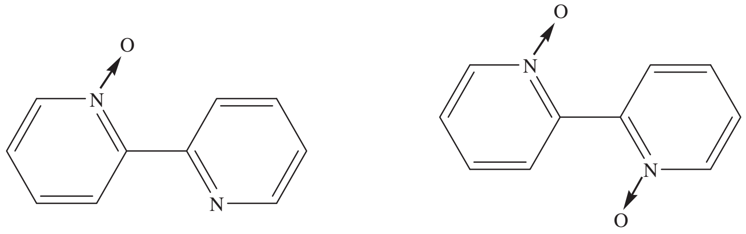

(A) (B)

FIGURE 1. Structural formula for 2,2′-dipyridil *N*-oxide (A) and 2,2′-dipyridil *N*,*N*′-dioxide (B).

2. Experimental

2.1. Compounds and purity control

The 2,2′-dipyridil *N*-oxide was prepared by oxidation of 2,2′-bipyridine with *m*-chloroperoxybenzoic acid in chloroform according to the synthetic method of Wenkert and Woodward [19]. The reaction mixture was then washed several times with a 5% aqueous sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and the chloroform removed under reduced pressure. The residual oil was then extracted with boiling hexane to remove any unreacted starting materials. The crude was dried for several days in a vacuum oven and further purified by vacuum sublimation. Elemental analysis was in agreement with calculated value. Mass fractions for $C_{10}H_8N_2O$: found C, 0.6963; H, 0.0479; N, 0.1614; calculated: C, 0.6976; H, 0.0468; N, 0.1627.

The 2,2′-dipyridil *N*,*N*′-dioxide was prepared by the peroxyacetic acid oxidation of 2,2′-bipyridine according to the published procedure of Simpson and co-workers [20]. The 2,2′-bipyridine and 30% hydrogen peroxide were dissolved in glacial acetic acid, and the resulting mixture was heated at $T = (343 \text{ to } 353)$ K for 15 hours, with additional 30% hydrogen peroxide being added at the 5 h mark. The reaction mixture was then cooled and basified with KOH solution. On addition of acetone, 2,2′-dipyridil *N*,*N*′-dioxide precipitated. The crude sample was further purified by re-crystallization from aqueous-acetone mixture. Elemental analysis was in agreement with calculated value. Mass fractions for $C_{10}H_8N_2O_2$: found C, 0.6371; H, 0.0430; N, 0.1472; calculated: C, 0.6382; H, 0.0428; N, 0.1489.

Before the measurements, both compounds were purified by successive vacuum sublimations under reduced pressure. As they are sensitive to moisture, the samples were dried in vacuum and handled under nitrogen atmosphere.

The purity of both compounds was confirmed by the mass of carbon dioxide recovered in the combustion experiments compared to that calculated from the mass of the sample; the average ratios, together with the respective uncertainties (twice the standard deviation of the mean), were: 2,2′-dipyridil *N*-oxide (0.9987 ± 0.0021) and 2,2′-dipyridil *N*,*N*′-dioxide (0.9992 ± 0.0005).

The specific densities of both samples were assumed to be $\rho = 1.0 \text{ g} \cdot \text{cm}^{-3}$, estimated from the mass and volume of a pellet for each compound.

The relative atomic masses used for the elements were those recommended by the IUPAC Commission in 2007 [21].

2.2. Combustion calorimetry

The standard ($p^\circ = 0.1$ MPa) molar energies of combustion of 2,2′-dipyridil *N*-oxide and 2,2′-dipyridil *N*,*N*′-dioxide were measured in two different isoperibol static bomb calorimetric systems. Two different calorimeters were used as the study was carried out at different time periods by different researchers. The availability of the equipment was also a factor.

(i) The calorimetric study of 2,2′-dipyridil *N*-oxide was carried out in an isoperibol combustion calorimeter, previously described in the literature [22,23], equipped with a twin valve static bomb made of stainless steel and with an internal volume of 0.342 dm^3. This system was calibrated with benzoic acid NIST Thermochemical Standard 39j, with a certified massic energy of combustion, under bomb conditions of $-(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ [24]. The value of the energy equivalent of the calorimeter was found to be $\varepsilon(\text{calor}) = (15995.3 \pm 2.0) \text{ J} \cdot \text{K}^{-1}$ (where the uncertainty quoted is the standard deviation of the mean), for an average mass of water of 3119.6 g added to the calorimeter.

The crystalline samples of 2,2′-dipyridil *N*-oxide were burnt in pellet form, at $T = 298.15$ K, enclosed in sealed polyester bags made of Melinex (0.025 mm thickness, $\Delta_c u^\circ = -(22902 \pm 5) \text{ J} \cdot \text{g}^{-1}$), using the technique described by Skinner and Snelson [25], and with 1.00 cm^3 of deionised water introduced into the bomb, which was purged twice to remove air, before being charged with 3.04 MPa of oxygen. The mass of carbon dioxide produced from the Melinex combustion was calculated using the factor previously reported [25]. In all combustion experiments, the calorimeter temperatures were measured with a precision of $\pm(1 \cdot 10^{-4})$ K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett Pachard HP 2804 A).

(ii) The enthalpy of combustion of 2,2′-dipyridil *N*,*N*′-dioxide was measured in another static bomb calorimeter, equipped with a twin valve bomb, whose internal volume is 0.290 cm^3. The apparatus and the detailed procedure have been described previously [26–28]. Benzoic acid NIST Thermochemical Standard 39j [24] was also used for calibration of this bomb. From 12 calibration experiments the value of the energy equivalent of the calorimeter was determined as $\varepsilon(\text{calor}) = (15546.5 \pm 1.1) \text{ J} \cdot \text{K}^{-1}$, for an average mass of water added to the calorimeter of 2900.0 g; the quoted uncertainty is the standard deviation of the mean.

Samples of 2,2′-dipyridil *N*,*N*′-dioxide, in pellet form, were ignited at $T = 298.15$ K, under oxygen at $p = 3.04$ MPa and with 1.00 cm^3 of deionised water placed into the bomb. The calorimetric liquid temperature readings were collected at time intervals of 10 s, with a precision of $\pm(1 \cdot 10^{-4})$ K, with a using a S10 four wire calibrated ultra-stable thermistor probe (Thermometrics, Standard Serial No. 1030) and recorded by a high sensitivity nanovolt/micro-ohm meter (Agilent 34420A) interfaced to a computer.

For both calorimetric systems, the 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, according to the method described by Coops *et al.* [29]. The LABTERMO [30] program was used to acquire data, control the calorimeters temperatures and to compute the adiabatic temperature change.

The electrical energy for the ignition was determined from the change in potential difference across a capacitor when *ca.* 40 V