Thermodynamic study on six tricyclic nitrogen heterocyclic compounds by thermal analysis and effusion techniques

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ABSTRACT

The molar sublimation and vaporization enthalpies of acridine, phenanthridine, 1,7-phenanthroline, 1,10-phenanthroline, 4,7-phenanthroline and phenazine were determined at the averages of their respective experimental temperature ranges ($\Delta_{cr}^{g}H^{0}_{m}$ (<T>) and $\Delta_{l}^{g}H^{0}_{m}$ (<T>), respectively) from the temperature dependencies of vapor pressure determined using Knudsen Effusion Mass Loss (KEML), Torsion Effusion (TE) and Isothermal Thermogravimetry (ITG) above their solid and liquid phases. The fusion characteristics (melting temperatures and the molar standard enthalpies of fusion at their melting temperatures) measured by Differential Scanning Calorimetry (DSC) were compared with the available literature values. Solid and liquid vapor pressure data determined by KEML, TE and ITG techniques as well as $\Delta_{cr}^{g}H^{0}_{m}$ (<T>) and $\Delta_{l}^{g}H^{0}_{m}$ (<T>) values, adjusted at 298.15 K by using the values of $C_{p}(cr)$ and $C_{p}(l)$ calculated by a well-known group additivity method, were found to be fairly correlated and are consistent with the available literature data. Final $\Delta_{cr}^{g}H^{0}_{m}(298.15 K)$ values were also provided as weighted averages of all the available data.

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1. Introduction

This study is focused on compiling new thermodynamic data on sublimation and vaporization of six tricyclic nitrogen heterocyclic compounds. In this series, two compounds have a linear aromatic ring structure analogous to anthracene with one or two nitrogen atoms (acridine and phenazine), while four compounds have three fused benzene rings, like those of phenanthrene or naphthalene, with one nitrogen atom (phenanthridine) or two, in different positions of the two external rings 1,7-, 1,10- and 4,7-phenanthroline (Fig. 1). Compounds belonging to this class received increasing attention in the last years due to their properties, being probably the most important one its intercalating ability due to the presence of lone pair(s) on nitrogen atom(s) [1].

Acridine and its derivatives (i.e., the acridine-3,6-diamine, or its N,N,N′,N′ tetramethyl derivative, known as proflavin and acridine orange respectively) are disinfectant bacteriostatics against gram-positive bacteria or may be used as chemotherapeutic agents because of their ability to intercalate DNA, disrupt its synthesis and inhibit topoisomerase enzymes [2]. Similarly, several phenazine compounds found in nature and produced by pseudomonas, streptomyces, and pantoea agglomerans bacteria are biologically active [3]. Furthermore, preparation and use of acridine as a chemical intermediate, in the manufacture of dyes and in the synthesis of drugs may result in its release into the environment through various waste streams. Acridine's emissions are mainly originated by diesel exhaust, coal-burning effluent from residential furnaces, catalyst regeneration flue gas from a gas-oil stock of an oil refinery, and from coal tar and coke-oven. If released into the atmosphere, acridine will exist in the ambient atmosphere in both vapor and particulate phases due to its not negligible extrapolated vapor pressure (0.018 Pa at 298.15 [4]). Phenanthridine is an isomer of acridine, whose importance is due to the fact that it is the basis of DNA-binding fluorescent dyes through intercalation [5]. 1,10-phenanthroline (commonly known simply as phenanthroline) like their isomers 1,7- and 4,7-phenanthroline (all three compounds considered in this study) are extensively used as bidentate chelating ligand in coordination chemistry, due to their ability to form strong complexes with transition metal ions. Ferroin, which is the dication complex $[Fe(phen)_3]^{2+}$ (being

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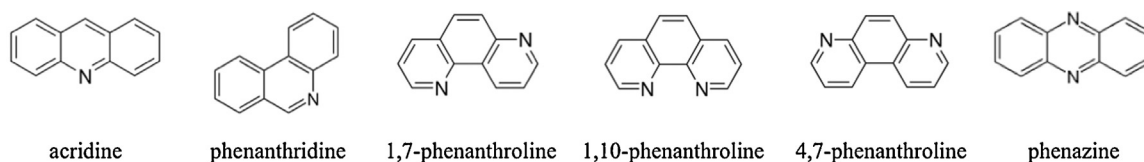E-mail address: stefano.vecchio@uniroma1.it (S. Vecchio Ciprioti).

Fig. 1. Structural formulas of the compounds investigated.

phen = 1,10-phenanthroline) is commonly used for the photometric determination of Fe(II).

So, in order to better understand the environmental risks due to their possible presence in the atmosphere the thermodynamic properties of these six tricyclic nitrogen heterocyclic compounds, with particular reference to vapor pressure and enthalpy related to sublimation and vaporization, should be known. On the other hand, a reliable determination of vapor pressure can be done by performing experiments using two or even more different techniques in suitable temperature ranges above the same phase or on two different phases (i.e., above the solid and the liquid), like our group already made in the recent past [6,7] and in the present study. In this context, the aim of this investigation is to present our contribution for providing recommended standard sublimation enthalpies and entropies of these six compounds adjusted at 298.15 K, once the sublimation and vaporization enthalpies were determined at the averages of their respective experimental temperature ranges from the temperature dependencies of vapor pressure. These trends were determined using both effusion (Knudsen Effusion Mass loss, and Torsion Effusion, KEML and TE, respectively) and Isothermal Thermogravimetry (ITG). Effusion experiments were performed above the solids (in the range $T < T_m$, where T_m is the melting temperature extrapolated from the corresponding onset DSC peak), while for ITG experiments the temperatures were selected above the liquid phase in the range $T > T_m$. Comparing the results obtained using the above-mentioned two different approaches (in particular the intersection of both the solid and liquid lines at $T = T_m$) the internal consistency of the obtained vapor pressure data was checked.

2. Experimental and method

2.1. Chemicals

All substances were purchased by Aldrich and needed a further purification by vacuum sublimation. Detailed information concerning molecular formulas, molar masses, CAS numbers and final purities (expressed as mass fraction) are reported in Table 1. Fig. 1 reports their structural formulas.

2.2. Instruments

2.2.1. DSC experiments for melting characterization

DSC experiments were carried out using a Stanton Redcroft STA-625 simultaneous TG/DSC apparatus, consisting of two open aluminium crucibles of cylindrical shape, one empty for the reference and the other filled with an appropriate amount of the sample. DSC experiments were carried out at 2 K min^{-1} under argon flow rate of 20 ml min^{-1}. Raw data were acquired using a personal computer (operating system being Windows 98) through the RSI Orchestrator software (Rheometric Scientific) and subsequently processed by means of Excel spreadsheets. Calibration of temperature and heat flux $q^.$ ($q^. = dq/dt$) was made using recommended high purity reference materials, benzoic acid and indium, whose melting temperatures T_m and enthalpies of fusion $\Delta_{cr}^l H_m^0$ are well known [8,9].

2.2.2. KEML measurements

Vapor pressure measurements of acridine, 1,10 phenanthroline, and phenazine were carried out using an Ugine-Eyraud Model B60 Setaram thermobalance, whose main details were accurately described in a previous paper [10]. The temperature dependency of vapor pressure was determined according to the well-known Knudsen equation [11]:

$$p(T) = K_K \times \Delta m / \Delta t \times (T/M)^{1/2} \tag{1}$$

where K_K is a constant that includes the geometrical characteristics of the used effusion orifice of the cell, $\Delta m / \Delta t$ the rate of mass loss of the sample and M the molar mass of the effusing vapor. A brief description of this apparatus is conveniently provided: it consists of a furnace, a microbalance and a vacuum system. The pyrophyllite effusion cell (with an internal diameter of 8 mm and two different possible orifice with diameters of 1 or 3 mm) is inserted into a copper cylinder with a cap that equalizes the sample temperature in order to allow an optimal temperature measurement. The copper cylinder is suspended to the arm of a microbalance and a standard mass uncertainty of $u(m) = 0.01$ mg can be estimated. Temperature was measured via a Pt100 Platinum Resistance Thermometers inserted in the copper cylinder, with standard measurements uncertainty (Type B) estimated to be less than $u(T) = 0.2$ K. The temperature control and the mass loss measurements are made through a data logger (HP 34970A) driven by the Labview software that permits the continuous control of the system. The standard uncertainties (Type B) of vapor pressures are estimated according to the following relation: $u(p) = 0.1p$. Before making the experiments on the compounds tested, some calibration runs were made under the same experimental conditions using both the pyrophyllite effusion cells to determine the two values of K_K of the Knudsen equation (one for each effusion orifice) (Eq. (1)). Very pure recommended reference compounds with well-known vapor pressures were used for the calibration runs (in this study, benzoic acid [12,13] and cadmium [14]). The temperature was changed during measurements to obtain isotherm periods to evaluate the mass loss rate at different constant temperatures. For each cell the experiments were carried by selecting two times the working temperature from its highest to its lowest value, with the aim to verify (if any) possible changes in the composition of the examined sample caused by volatile decomposition products or impurities, causing a gradual variation of the vapor pressures and therefore two non-overlapping data sets. In the study, it seems that these problems have not been encountered.

2.2.3. TE measurements

The vapor pressure measurements on phenantridine, 1,7 phenanthroline and 4,7 phenanthroline above the solid state ($T < T_m$) were carried out by means of a torsion–effusion instrument, previously described in detail in Ref. [15]. In this system a pyrophyllite cell (whose effusion orifice diameter is of about 1.0 mm) was suitably suspended from a tungsten wire (whose length and diameter are 30 cm and 30 μm, respectively). The vapor effusion through the cell orifice produces a twist in the wire, which is proportional to the vapor pressure (p) by the torsion angle of the assembly (α) according to the simple equation: $p = K_T$ α, where