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Thermodynamic properties of methylquinolines: Experimental results for 2,6-dimethylquinoline and mutual validation between experiments and computational methods for methylquinolines ☆

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Abstract

Measurements leading to the calculation of the standard thermodynamic properties for gaseous 2,6-dimethylquinoline (Chemical Abstracts registry number [877-43-0]) are reported. Experimental methods included adiabatic heat-capacity calorimetry, vibrating-tube densimetry, comparative ebulliometry, inclined-piston gauge manometry, differential-scanning calorimetry (d.s.c.), and combustion calorimetry. The critical temperature was measured with d.s.c. The critical pressure and critical density were estimated. Molar entropies, molar enthalpies, and molar Gibbs free energies of formation for the ideal gas state were derived at selected temperatures between 298.15 K and 700 K. Results are compared with experimental property values reported previously in the literature. Independent calculations of the ideal gas entropies were performed at the B3LYP/6-31+G(d,p) model chemistry for 2,6-dimethylquinoline and other methylquinolines (including hindered internal rotations) and are shown to be in excellent accord with the calorimetric results. Implications of these results are discussed.
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Keywords: 2,6-Dimethylquinoline; Heat capacity; Vapor pressure; Density; Critical properties; Enthalpy of formation; Ideal gas properties; Computational chemistry

1. Introduction

Properties of cyclic aromatics are required in the analysis of technological problems in a wide variety of fields from pharmaceuticals to ‘science based’ environmental regulations and ecosystem restoration, as well as to the processing of fossil fuels. The high-precision measurements reported here provide the basis for improved and extended estimation and correlation methods necessary to provide reliable property values. This work is a product of research funded by the US Department of Energy Office of Fossil Energy, Advanced Oil Recovery (AOR) program. Within a portion of this research program, thermochemical and thermophysical properties are determined for key aromatics and hydroaromatics present in the spectrum of fossil-fuel materials. The results of the thermodynamic property

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measurements can be used to provide insights into the reaction networks and relative reactivities of polycyclic aromatics and hydroaromatics within the complex processes operating in hydroprocessing.

The increased demand for clean fuels (including gasolines and diesels) has given rise to an increase in the amounts of heavier feedstock used within the refinery system. These heavier oils contain larger amounts of sulfur and nitrogen. This means that not only hydrodesulfurization (HDS), but also hydrodenitrogenation (HDN) of the heavier feedstock is required to obtain the lighter clean oils that can meet strict modern environmental requirements. Many reviews on the subject of HDN have been published (*cf.* [1,2]). Reference [2] contains detailed discussions of HDN including the effects of compound structure, the need for N-ring hydrogenation prior to the denitrogenation step, and the structure of novel HDN catalysts.

In a previous publication, the thermodynamic properties of 2-methylquinoline and 8-methylquinoline were reported [3]. The methylquinolines were chosen for study following completion of work on the parent compound quinoline [4]. Results of that study showed the possible existence of a glassy crystalline phase at low temperatures. Agreement between statistical and experimental determinations of ideal gas entropies for quinoline was good (within 0.1% to 0.2%), but was not as good as numerous similar comparisons for other aromatics studied as part of this research program. Agreement in each of those cases was well within 0.1%. An extensive list of citations to more than 15 compounds, including pyridine, the xylenes, methylpyridines, and dimethylpyridines, was given recently [5]. Contributions of methyl groups to the ideal gas properties of aromatics can often be estimated with the free-rotor approximation. In this way, measurements for methyl derivatives provide results that can be used to substantiate those for the parent compound. The present article, which includes experimental thermodynamic properties for 2,6-dimethylquinoline, completes our series of reports for the methylquinolines.

Extensive exploitation of modern computational methods for the calculation of thermodynamic properties is often limited by the inability to quantify uncertainties associated with the calculated values. The relatively rigid nature of the fused ring systems in the methyl quinolines, together with the apparent absence of significant barriers to the methyl rotations, makes these molecules particularly good candidates for accurate calculation of thermodynamic properties, particularly entropies for the ideal gas state. In the present paper, entropies for the ideal gas state derived from the reported property measurements are compared with independently calculated values derived with the methods of computational chemistry. The excellent accord achieved provides a mutual validation of the two independent methods, and demonstrates an important path to the quantification of uncertainties for the computational methods.

The thermodynamic properties of 2,6-dimethylquinoline reported here were measured with oxygen bomb calorimetry, adiabatic heat-capacity calorimetry, comparative ebulliometry, inclined-piston gauge manometry, vibrating tube densimetry, and differential-scanning calorimetry (d.s.c.). Standard molar formation properties (Gibbs free energies, enthalpies, and entropies) in the ideal gas state were derived. All measured or derived thermodynamic property values are compared with those reported in the literature. Complete discussion of the topic of property consistency within the family of methylquinolines is provided herein.

2. Experimental

2.1. Materials

The research group of Professor E.J. "Pete" Eisenbraun (retired) of Oklahoma State University synthesized and purified the calorimetric sample of 2,6-dimethylquinoline. The mole fraction impurity x of the sample used in this research ($x = 0.0005_6$) was determined by fractional melting as part of the adiabatic heat-capacity calorimetric studies reported here. The purity level was further corroborated in ebulliometric vapor-pressure studies reported here by the small differences observed between the boiling and condensation temperatures of the sample. All purified samples were transferred under nitrogen or helium or by vacuum distillation. Purification of the water and decane used as reference materials in the ebulliometric vapor-pressure measurements has been described [5].

2.2. Physical constants and standards

Molar values are reported in terms of $M = 157.212$ for $C_{11}H_{11}N$ [6], and the gas constant $R = 8.314472\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ adopted in 2002 by CODATA [7]. The platinum resistance thermometers used in these measurements were calibrated by comparison with standard thermometers whose constants were determined at the National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST). All temperatures were measured in terms of IPTS-68 [8] and were converted to ITS-90 with published temperature increments [9]. The platinum resistance thermometer used in the adiabatic heat-capacity studies was calibrated below $T = 13.81$ K with the method of McCrackin and Chang [10]. Mass, time, electrical resistance, and potential difference were measured in terms of standards traceable to calibrations at NIST.

2.3. Apparatus and procedures

Heat capacities and enthalpy increments were measured with an adiabatic calorimetric system that has been described previously [4]. The calorimeter characteristics and sealing conditions are given in table 1. Energies were measured with a repeatability of 0.01%, and temperatures were measured with a repeatability of 0.0001 K. The energy