J. Chem. Thermodynamics 91 (2015) 186–193

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

# Benchmark thermochemistry of methylbenzonitriles: Experimental and theoretical study

Ksenia V. Zaitseva [a], Vladimir N. Emel'yanenko [a,b], Filipe Agapito [c], Andrey A. Pimerzin [d], Mikhail A. Varfolomeev [a], Sergey P. Verevkin [a,b,*]

[a] Department of Physical Chemistry, Kazan Federal University, 420008 Kazan, Russia
[b] Department of Physical Chemistry and Department "Science and Technology of Life, Light and Matter", University of Rostock, D-18059 Rostock, Germany
[c] Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal
[d] Chemical Technology Department, Samara State Technical University, Samara 443100, Russia

ARTICLE INFO

*Article history:*
Received 29 April 2015
Received in revised form 15 July 2015
Accepted 18 July 2015
Available online 31 July 2015

*Keywords:*
Methylbenzonitrile
Combustion calorimetry
Transpiration method
Enthalpy of formation
Vapor pressure
Enthalpy of vaporization
Group additivity

ABSTRACT

The gas-phase enthalpies of formation of 2-, 3-, and 4-methylbenzonitrile at $T = 298.15$ K were studied by combustion calorimetry, and their vaporization enthalpies were determined using the transpiration method. The composite ab initio methods W1-F12 and G4 were used to calculate the gas-phase enthalpies of formation for these three methylbenzonitriles. These theoretical values were found to be in excellent agreement with the corresponding experimental data. The analysis of these data revealed that the interaction between cyano and methyl groups is slightly stabilizing. Using the experimental data a set of group-additivity terms, which allows to estimate thermochemical properties for methyl and cyano substituted benzenes, was proposed. These terms, together with theoretical data, were subsequently used to reassess the thermochemical properties of 2,6-dimethylbenzonitrile and 2,4,6-trimethylbenzonitrile.



## 1. Introduction

Several chemical properties of the benzene moiety are dependent on its aromaticity, which varies with the number and nature of its substituents [1]. The cyano group, CN, is a prototypical electron withdrawing substituent. Because of their rich chemistry, cyano substituted benzenes (*i.e.*, benzonitriles) are important intermediates in organic synthesis [1]. While the thermochemical properties of some benzonitriles of interest are known [2–7], those for several other simple CN substituted benzenes have yet to be determined. This hinders our knowledge of these aromatic compounds, and prevents the quantitative study of the chemical reactions in which they take part. Group additivity schemes can provide rough estimates of the thermochemical properties of substituted benzene rings [8]. Nevertheless, a deeper understanding of such species and of their reactivity requires high-accuracy thermochemical data. Furthermore, benchmark quality thermochemical data are crucial for the testing of high-accuracy ab initio methods. This is particularly relevant since these theoretical gas-phase data, together with experimental phase change values, can now be used in the determination of condensed phase properties [9,10].

The methylbenzonitriles, which feature a cyano group and an electron donating methyl group, are a simple family of benzonitriles for which experimental data is unavailable. In this work we report a new experimental study of the thermochemistry of 2-, 3-, and 4-methylbenzonitriles by combustion calorimetry [11] and the transpiration method [12]. Experimental values for the liquid and gaseous enthalpies of formation were evaluated and recommended as benchmark values. These data were compared with those determined by G4 [13] and W1-F12 [14] quantum chemical calculations. Using this information, group additivity parameters were derived for the estimation of the thermochemical properties of similar compounds.

## 2. Experimental

### 2.1. Materials

Samples of 2-, 3-, and 4-methylbenzonitrile of commercial origin were used (see table 1). Liquid samples were additionally purified by fractional distillation in vacuum. The solid sample of

* Corresponding author at: Department of Physical Chemistry and Department "Science and Technology of Life, Light and Matter", University of Rostock, D-18059 Rostock, Germany. Tel.: +49 381 498 6508; fax: +49 381 498 6502.
*E-mail address:* sergey.verevkin@uni-rostock.de (S.P. Verevkin).

http://dx.doi.org/10.1016/j.jct.2015.07.025
0021-9614/