



Benchmark thermodynamic properties of methylanisoles: Experimental and theoretical study



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ABSTRACT

Accurate standard molar enthalpy of formation values in the liquid phase can be obtained by combining high-level quantum chemistry values of gas-phase enthalpies of formation with experimentally determined enthalpies of vaporisation. The procedure is illustrated for 2-, 3-, and 4-methyl-anisoles. Using the W1-F12 and G4 quantum-chemical methods, the gas-phase enthalpies of formation of these compounds at $T = 298.15$ K were computed. Molar enthalpies of vaporisation for these isomers were measured by the transpiration method. Combining the experimental and the high-level *ab initio* values, the standard molar enthalpies of formation in the liquid phase for all three isomers were derived and compared with those determined for 2- and 4-methyl-anisoles by using combustion calorimetry.

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1. Introduction

Electrophilic aromatic substitution is one of the most relevant synthetic pathways available for benzene rings, and the kind and location of the ring substituents exert a significant control on both reactivity and region-selectivity of this reaction [1]. A deep understanding of the substituent effect and its influence on the reactivity of aromatic systems requires the knowledge of their thermochemical properties, namely their standard enthalpies of formation, $\Delta_f H_m^\circ$ [2]. Although these values are known for a fairly large number of organic molecules [3,4], there are still important gaps for substituted benzenes, hindering a quantitative understanding of the reactivity of aromatic systems.

The three methylanisoles (figure 1) constitute one such gap.

Alkyl and alkoxy groups are far from being uncommon benzene substituents, yet much is unknown regarding the thermochemistry of even the simplest alkoxy-alkylbenzenes. While 3-methylanisole has been previously studied [3,5], the data for the whole series is required to fully understand the effect of these substituent groups. We therefore set out to perform a benchmark thermochemical

study of the methylanisoles. For this purpose, their vaporisation enthalpies were obtained from their vapour pressures, measured using the transpiration method [6], and the enthalpies of formation of 2- and 4-methylanisole in the liquid phase were determined by combustion calorimetry [2,7]. When combined, these data yielded the gas-phase enthalpy of formation for each compound, which were also obtained from high-level *ab initio* calculations.

In a previous work [8] we posited that quantum chemical methods have now reached a precision and accuracy that, for small- to mid-sized molecules, matches that of experimental techniques. We further stated that this notion implies that, when condensed phase data are unavailable, these properties can be obtained by combining theoretical gas-phase enthalpies of formation with experimental vaporisation or sublimation enthalpies. Comparison of the experimental and theoretical data provides a further test to the reliability of this approach.

2. Materials and methods

2.1. Materials

Samples of methylanisoles of commercial origin (see table 1) with 0.99 mass fraction purity were further purified by fractional distillation with a spinning-band column in vacuum. No impurities

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(greater than 0.01 mass per cent) could be detected in the samples used for the combustion experiments and the vapour pressure measurements. The degree of purity was determined using a GC equipped with FID. A capillary column HP-5 was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm . Provenance and final purity of the compound prepared for the thermochemical studies in this work are given in table 1.

2.2. Vapour pressure measurements. Transpiration method

Vapour pressures of methylanisoles were determined using the method of transpiration [6] in a saturated nitrogen stream. A total of about 0.5 g of the sample was mixed with small glass beads and placed in a thermostatted U-shaped saturator. A well-defined nitrogen stream was passed through the saturator at a constant temperature (± 0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample of each compound was determined by GC analysis using an external standard $n\text{-C}_{13}\text{H}_{28}$. The absolute vapour pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period. Assuming validity of the Dalton's law applied to the nitrogen stream saturated with the substance i , values of p_i were calculated with equation:

$$p_i = m_i R T_a / V M_i; \quad V = V_{\text{N}_2} + V_i; \quad (V_{\text{N}_2} \gg V_i), \quad (1)$$

where $R = 8.314462 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i its volume contribution to the gaseous phase. The V_{N_2} is the volume of the carrier gas and T_a is the temperature of the soap bubble meter used for measurement of the gas flow. The volume of the carrier gas V_{N_2} was determined from the flow rate and the time measurement. Experimental results are given in table 2.

The standard uncertainties (u) of the measured vapour pressures have been calculated to be $u(p/\text{Pa}) = 0.025 + 0.025(p/\text{Pa})$ for $p > 5$ to 3000 Pa. For validation of our uncertainty estimations we measured vapour pressures for series of aliphatic esters [6] where reliable data at $p = (20$ to 3000) Pa from different methods were available. It has turned out that vapour pressures of esters derived from the transpiration method were comparable with available high-precision vapour pressures generally within (1 to 3)% in agreement with our estimations.

2.3. Combustion calorimetry

The molar enthalpies of combustion of 2- and 4-methylanisole were measured with an isoperibolic calorimeter with a static bomb and a stirred water bath. The liquid sample was burned in a polythene ampoule (Fa. NeoLab, Heidelberg, Germany). The sample was transferred into the polyethylene bulb with a syringe under nitrogen stream in a glove-box. The fine neck of the container was compressed with a special tweezers and was sealed outside the glove-box by heating of the neck in a close proximity to a glowing wire. Then, the container was placed in the crucible and was

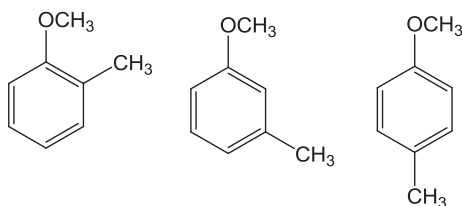


FIGURE 1. The structures of 1-methoxy-2-methylbenzene (left), 1-methoxy-3-methylbenzene (centre), and 1-methoxy-4-methylbenzene (right).

burned in oxygen at a pressure 3.04 MPa. The detailed procedure has been described previously [7]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither were detected. The energy equivalent of the calorimeter $\varepsilon_{\text{calor}} = (14810.1 \pm 0.9) \text{ J} \cdot \text{K}^{-1}$ was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). For the reduction of the data to standard conditions, conventional procedures [10] were used. Auxiliary data are collected in table 3. Correction for nitric acid formation was based on titration with 0.1 $\text{mol} \cdot \text{dm}^{-3}$ NaOH (aq). The residual water content in the samples was determined by Karl Fischer titration before starting experiments and appropriate corrections have been made for combustion results. Results for combustion experiments are summarised in tables 4 and 5.

3. Results and discussion

3.1. Vapour pressures of isomeric methylanisoles

Vapour pressures of 2-, 3-, and 4-methylanisoles have been measured for the first time. Temperature dependence of the measured vapour pressures p_i were fitted with the following equation [6]:

$$R \cdot \ln p_i = a + \frac{b}{T} + \Delta_1^{\text{g}} C_{p,m}^{\text{c}} \cdot \ln \left(\frac{T}{T_0} \right), \quad (2)$$

where a and b are adjustable parameters and $\Delta_1^{\text{g}} C_{p,m}^{\text{c}}$ is the difference of the molar heat capacities of the gaseous and the liquid phase respectively, T_0 is an arbitrarily chosen reference temperature (which has been chosen to be $T = 298.15 \text{ K}$), and R is the molar gas constant. Uncertainties of absolute vapour pressures measured by the transpiration method were estimated according to the procedure described in detail in reference [13]. They are governed mostly by the reproducibility of the GC analysis as well as by the V_{N_2} volume determination. The combined uncertainties $u(p)$ of vapour pressures derived from the transpiration method are generally on the level (1 to 3)% and the corresponding deviations from the smoothed equations are adequate estimates of the uncertainty [13].

The experimental vapour pressures of all three isomers are compared in figure 2. The vapour pressures of 2-methyl isomer are highest among the series. The vapour pressures for the 4-methyl isomer are between those of the 2- and 3-methyl substituted isomers of anisole.

3.2. Vaporisation enthalpies of methylanisoles

In this work the vaporisation enthalpies of methylanisoles at temperature T were indirectly derived from the temperature dependences of vapour pressures measured by the transpiration using equation (3), where b is the adjustable parameter of equation (2):

$$\Delta_1^{\text{g}} H_m^{\text{c}}(T) = -b + \Delta_1^{\text{g}} C_{p,m}^{\text{c}} \cdot T. \quad (3)$$

A value of $\Delta_1^{\text{g}} C_{p,m}^{\text{c}} = -69.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ has been calculated by the procedure developed by Chickos and Acree [11] based on the isobaric molar heat capacity $C_{p,m}^{\text{c}}(1, T = 298.15 \text{ K}) = 227.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ calculated according to the group-contribution method suggested by Chickos *et al.* [12]. Experimental absolute vapour pressures for methylanisoles from the transpiration method and coefficients a and b of equation (2) are given in table 2. The procedure for calculation of the combined uncertainties of the vaporisation enthalpy has been described elsewhere [13]. They include uncertainties from the transpiration experimental conditions, uncertainties of vapour pressure, and uncertainties from temperature adjustment to $T = 298.15 \text{ K}$.

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