J. Chem. Thermodynamics 73 (2014) 97–100

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Thermochemistry of methoxythiophenes: Measurement of their enthalpies of vaporization and estimation of their enthalpies of formation in the condensed phase

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ARTICLE INFO

Article history:
Available online 16 November 2013

This article is dedicated to the memory of the late Professor Manuel Ribeiro da Silva

Keywords:
2-Methoxythiophene
3-Methoxythiophene
Enthalpy of vaporization
Enthalpy of formation

ABSTRACT

Enthalpies of vaporization of 2- and 3-methoxythiophenes (48.32 ± 0.30 and 48.54 ± 0.22 kJ · mol^{-1}, respectively) have been measured by the transpiration method using nitrogen as the carrying and protecting stream. Combustion experiments leading to enthalpies of formation in the liquid phase, $\Delta_f H^0{}_m(l)$, for both isomers failed due to rapid darkening of freshly distilled samples even under a protecting atmosphere. However, combination of experimental vaporization enthalpies with values of the gaseous enthalpies of formation, $\Delta_f H^0{}_m(g)$, obtained by quantum-chemical calculations from our previous work Notario *et al.* (2012) [24] permits establishing estimated $\Delta_f H^0{}_m(l)$ values of $-(68.3 \pm 4.2)$ and $-(80.1 \pm 4.2)$ kJ · mol^{-1}, for 2- and 3-methoxythiophene, respectively.

1. Introduction

Thiophene is the simplest representative of an aromatic structure bearing sulfur. It is a chemically stable compound, easy to process and its applications have been a continuing matter of investigation. Several books and reviews are available on the chemistry of thiophenes [1–4]. The knowledge of the energetic properties of thiophenes was very sparse until recent years, but this situation has significantly improved subsequently. Since 2002, our group [5–10] in Spain and since 2007 the group of Ribeiro da Silva [8–23] in Portugal, have published thermochemical studies on thiophene derivatives with a variety of substituents in different positions on the ring.

Using the body of data on these species very recently published [24], it was possible to establish correlations between experimental and theoretical data that permitted a check on the reliability of experimental measurements and also allowed predictions of the enthalpies of formation of new thiophenes that are not available in the literature. In this paper, the gas-phase enthalpies of formation of 77 substituted thiophenes and other five-membered heterocycles containing sulfur derived from thiophene were calculated at the G3(MP2)//B3LYP and G3 levels using the atomization reaction method [25,26]. The G3(MP2)//B3LYP-calculated enthalpies of formation were corrected using the bond additivity correction (BAC) procedure developed by Anantharaman and Melius [27]. Very good linear correlations between experimental and calculated enthalpies of formation were obtained [24]:

$$\Delta_f H^0_m(\text{exp})/(\text{kJ} \cdot \text{mol}^{-1}) = (0.9973 \pm 0.0035)\Delta_f H^0_m(\text{G3(MP2)//B3LYP}) - (5.98 \pm 0.73) \quad (1)$$

$n = 48;\ R = 0.99971;\ sd = 4.9\ \text{kJ} \cdot \text{mol}^{-1}$,

$$\Delta_f H^0_m(\text{exp})/(\text{kJ} \cdot \text{mol}^{-1}) = (0.9879 \pm 0.0034)\Delta_f H^0_m(\text{G3}) + (1.89 \pm 0.72) \quad (2)$$

$n = 48;\ R = 0.99972;\ sd = 4.8\ \text{kJ} \cdot \text{mol}^{-1}$.

Both statistical correlations are of essentially the same level of quality with slopes and intercepts close to one and zero, respectively. They permit a correction of the calculated enthalpies of formation in order to estimate more reliable calculated values for the enthalpies of formation of substituted thiophenes.

A nice check on the reliability of these equations has been published very recently by Santos and Ribeiro da Silva [23] who measured the gas-phase enthalpy of formation of ethyl 2-thiophenecarboxylate. The same authors had measured this compound in 2009 [19] obtaining a value of $-(270.6 \pm 2.4)$ kJ · mol^{-1}. The

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http://dx.doi.org/10.1016/j.jct.2013.11.003

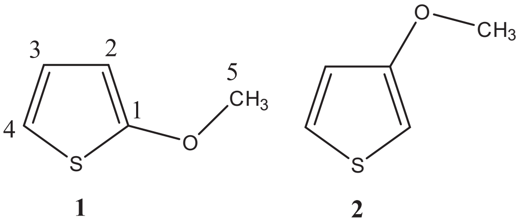

FIGURE 1. Schematic formulae of 2-methoxythiophene **1** and 3-methoxythiophene **2**.

values predicted by us [24], using equations (1) and (2), were $-277.9\ \text{kJ}\cdot\text{mol}^{-1}$, at the G3(MP2)//B3LYP level and $-279.6\ \text{kJ}\cdot\text{mol}^{-1}$, at the G3 level, significantly different from the experimental value. The same authors have re-measured the gas-phase enthalpy of formation of ethyl 2-thiophenecarboxylate in 2013 [23] obtaining a new value of $-(277.7 \pm 2.9)\ \text{kJ}\cdot\text{mol}^{-1}$, in very good agreement with our predicted values.

Following our previous studies, we present here the thermochemical study of two new compounds, 2- and 3-methoxythiophenes (see figure 1), because of the interest in the properties of electron-rich thiophenes substituted with oxygen-containing substituents [28]. We have measured their vaporization enthalpies and because of the difficulty to obtain sufficiently pure samples to measure their enthalpies of formation in the condensed phase, we have estimated these values using the gas-phase enthalpies of formation calculated at the G3(MP2)//B3LYP and G3 levels from our previous work [24].

2. Experimental

2.1. Compounds and purity control

Commercial samples of 2- and 3-methoxythiophene were obtained from Lancaster at a stated mass fraction purity of 0.99. To obtain dry and pure samples of both isomers, the commercial compounds were dried over $4\cdot 10^{-10}$ m molecular sieves before and after fractional distillation in a packed column under reduced pressure. This procedure was repeated several times. The transparent distilled samples rapidly become dark with time and therefore, it was not possible to obtain samples with the required purity to determine the enthalpy of combustion and hence to derive the enthalpy of formation in the liquid phase. To assess the purity of the compounds, a standard gas chromatograph with a 60 m BPX70 fused silica SGE capillary column was used and the results obtained are shown in table 1.

2.2. Vapour pressure measurements

The vapour pressure and enthalpies of vaporization of methoxythiophenes were determined using the method of transpiration in a saturated N_2-stream [29,30] and applying the Clausius–Clapeyron equation. About 0.5 g of fresh distilled sample of the methoxythiophene was mixed with glass beads and was loaded in the saturator under protecting nitrogen stream in a glove box. The saturator with the sample was immediately connected to the carrier gas line. Thus, in the transpiration experiments the sample was handled always under a protecting gas stream. No change in color of the material in the saturator as well as in the transported material was observed. At constant temperature (±0.1 K), a nitrogen stream was passed through the saturator within a definite time and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the nitrogen stream was measured using a soap bubble flow meter and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. Experiments were carried out in the flow rate interval of $(0.28\ \text{to}\ 0.52)\ \text{cm}^3\cdot\text{s}^{-1}$ which has ensured that transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. The amount of condensed substance was determined by GC analysis using an external standard (hydrocarbon $n\text{–}C_nH_{2n+2}$). The saturation vapour pressure p_i at each temperature T_i was calculated from the amount of product collected within a definite period of time. Assuming that Dalton‘s law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i were calculated assuming:

$$p_i = m_i\cdot R\cdot T_a/V\cdot M_i;\quad V = V_{N2} + V_i;\quad (V_{N2} \gg V_i), \tag{3}$$

where R is the universal gas constant; m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i; its volume contribution to the gaseous phase. The V_{N2} is the volume of transporting gas, and T_a is the temperature of the soap bubble meter. The volume of transporting gas V_{N2} was determined from the flow rate and time measurements. The flow rate was maintained constant with help of the high precision needle valve (Hoke, C1335G6BMM-ITA). The accuracy of the volume V_{N2} measurements from flow rate was established to be $(\pm 0.001\ \text{dm}^3)$. Data of p_i were obtained as a function of temperature and were fitted using following equation [29,30]:

$$R\cdot \ln p_i = a + \frac{b}{T} + \Delta_l^g C_p \cdot \ln\left(\frac{T}{T_0}\right), \tag{4}$$

were a and b are adjustable parameters and $\Delta_l^g C_p$ is the difference of the molar heat capacities of the gaseous and the liquid phase, respectively. The T_0 appearing in equation (4) is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from equation (4) the expression for the vaporization enthalpy at temperature T is derived:

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p \cdot T. \tag{5}$$

Values of $\Delta_l^g C_p$ have been derived according to a procedure developed by Chickos [31,32]. All results together with the parameters a and b are listed in table 2.

3. Results and discussion

3.1. Molecular structures

The crystal structures of both methoxythiophenes were determined by X-ray diffraction by Blake *et al.* in 1999 [28]. The structure of 2-methoxythiophene had been previously reported [33] but as a solvate of a rhodium complex. The 2-methoxythiophene is close to being planar, and the methyl group of the methoxy substituent lies Z to the C1–C2 bond as shown in table 3. The

TABLE 1
Purity and provenance of the materials used in the study.

Chemical name	CAS	Provenance	Mass fraction purity	Analysis method
2-Methoxythiophene	16839-97-7	Lancaster	0.9915	GC
3-Methoxythiophene	17573-92-1	Lancaster	0.9923	GC