



Experimental study on the thermochemistry of 2,5-dimethylthiophene and its acetyl derivative

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ARTICLE INFO

Article history:

Received 26 March 2008

Accepted 9 April 2008

Available online 15 April 2008

Keywords:

Enthalpy of combustion

Enthalpy of vaporization

Enthalpy of formation

2,5-Dimethylthiophene

3-Acetyl-2,5-dimethylthiophene

Combustion calorimetry

Calvet microcalorimetry

ABSTRACT

This paper reports the values of the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the gaseous phase, $\Delta_f H_m^\circ(g)$, at $T = 298.15$ K, of 2,5-dimethylthiophene and 3-acetyl-2,5-dimethylthiophene as $(50.6 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$ and $-(123.2 \pm 2.7) \text{ kJ} \cdot \text{mol}^{-1}$, respectively. These values were derived from experimental thermodynamic parameters, namely, the standard molar enthalpies of formation, in the liquid phase, $\Delta_f H_m^\circ(l)$, at $T = 298.15$ K, obtained from the standard molar enthalpies of combustion, $\Delta_c H_m^\circ$, measured by rotating bomb combustion calorimetry, and from the standard molar enthalpies of vaporization, $\Delta_v H_m^\circ$, at $T = 298.15$ K, measured by high temperature Calvet microcalorimetry.

The results are interpreted in terms of enthalpic increments, molecular structure and compared with structurally similar compounds.

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1. Introduction

The study of thiophene derivatives has been receiving great attention due to the presence of these units in some natural products, like fossil fuels [1], plants [2–9], and in biotin [10–12]. This tetrahydrothiophene (biotin) is the most important naturally occurring thiophene derivative; it is a water-soluble vitamin (also known as vitamin H or B₇), acts as a coenzyme in carboxylation and decarboxylation, *in vivo*, and is involved in the synthesis of long-chain fatty acids [13]. These organic sulphur heterocycles are used in the synthesis of new pharmaceutical drugs with high therapeutic potential. For example, the 3-acetyl-2,5-dimethylthiophene, studied in this work, is involved in the preparation of anti-bacterial [14] and anti-inflammatory [15] agents. The title compounds occur in boiled and cooked beef. They have a burnt, roasted flavour, being used to provide roasted and smoked flavourings [16].

Our research group has been involved in a systematic study of the thermochemistry of thiophene derivatives, being our main goal to analyse and evaluate the enthalpic increments and the structural effects produced by the different substituents in this class of compounds. In recent papers, we have published some experimental and computational results of several thiophene derivatives [17–23] and have established some relationships between structure, energetic and reactivity, and, in some cases, compared our results with others from structurally similar compounds.

The purpose of the present report is to investigate the enthalpic effects on 2,5-dimethylthiophene and its relationship with thiophene and 2-methylthiophene. A comparison is also made with the analogous benzene derivatives, more specifically benzene, toluene, and *p*-xylene. Moreover, we estimate the value of the standard molar enthalpy of formation, in the gaseous phase, of 3-acetyl-2,5-dimethylthiophene and compare it with the experimental one, obtained in this work. In this way, we report here the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in the gaseous phase, at $T = 298.15$ K, of the compounds represented in figure 1, obtained from combustion energies using a rotating-bomb combustion calorimeter and from the values of the enthalpies of vaporization, at $T = 298.15$ K, determined by high temperature Calvet microcalorimetry.

2. Experimental

2.1. Compounds and purity control

The two compounds studied were commercial samples: 2,5-dimethylthiophene [CAS 638-02-8] was supplied by Alfa Aesar with a mass fraction purity of 0.98. The 3-acetyl-2,5-dimethylthiophene [CAS 2530-10-1] was purchased from Lancaster Synthesis Ltd., with a mass fraction purity of 0.99. Before the calorimetric measurements, the liquid samples were purified by successive distillations under reduced pressure; the final purity of each one was assessed by gas–liquid chromatography, being found to be greater than 0.999 mass fraction.

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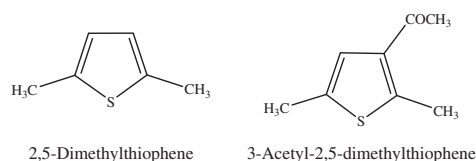


FIGURE 1. Structural formula of the compounds studied in this work.

The benzoic acid used in the calibration of the bomb was the NIST Standard Reference Material 39i. Thianthrene, the reference material for rotating bomb combustion calorimetry of organo-sulphur compounds, was supplied by Sigma-Aldrich Chemical Co, with a mass fraction purity of 0.99 and purified by zone melting. Undecane, with a mass fraction purity of 0.99+, was also obtained from Sigma-Aldrich Chemical Co.

The real mass of the samples was calculated from the apparent mass in air using the following specific densities: $\rho = 0.984 \text{ g} \cdot \text{cm}^{-3}$ [24] for 2,5-dimethylthiophene and $\rho = 1.086 \text{ g} \cdot \text{cm}^{-3}$ [24] for 3-acetyl-2,5-dimethylthiophene.

The relative atomic masses used for the elements were those recommended by the IUPAC Commission in 2005 [25].

2.2. Combustion calorimetry

The combustion experiments of the title compounds were performed in an isoperibol calorimeter equipped with a tantalum-lined rotating bomb, of internal volume 0.329 dm^3 . The apparatus and technique have been previously described [17,26–29].

Benzoic acid, NIST Thermochemical Standard 39i, with a certified massic energy of combustion, under bomb conditions, of $-(26,434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ was used to calibrate the isoperibol calorimeter, as described by Coops *et al.* [30]. From one set of 10 calibration experiments, that were performed in oxygen, at a pressure of 3.04 MPa, in the presence of 1.00 cm^3 of deionised water placed in the bomb, the value of the energy equivalent of the calorimeter was found to be $e(\text{calor}) = (20369.0 \pm 2.3 \text{ J} \cdot \text{K}^{-1})$ (0.011%), for an average mass of water added to the calorimeter of 3965.0 g , with the quoted uncertainty being the standard deviation of the mean.

The calorimeter temperatures were measured to 10^{-4} K , in time intervals of 10 s, using a quartz thermometer (Hewlett Packard HP 2804A) interfaced to a PC programmed to compute the adiabatic temperature change. In the fore and after periods 125 readings were taken, whereas in the main period the number of temperature readings was 100. Data acquisition and control of the calorimeter temperature were performed through the LABTERMO program [31].

In all experiments, the ignition temperature was chosen so that the final temperature was as close as possible to 298.15 K and the rotation of the bomb was started when the temperature rise in the main period reached about 63% of its final value and continued throughout the experiment, according the procedure described by Good *et al.* [32]. In this way, the frictional work produced by the bomb rotation is included in the correction for heat exchange and work of stirring. The electrical energy for the ignition was determined from the change in potential across a capacitor ($1281 \mu\text{F}$) when 40 V were discharged through a platinum ignition wire. The massic energy of combustion of the cotton thread fuse, for which the empirical formula is $\text{CH}_{1.686}\text{O}_{0.843}$, is $\Delta_c u^\circ = -16240 \text{ J} \cdot \text{g}^{-1}$ [32], a value that was confirmed in our laboratory.

The liquid samples of 3-acetyl-2,5-dimethylthiophene were burnt enclosed in previously weighed polyester bags made of melinex, with 0.025 mm in thickness, using the technique described by Skinner and Snelson [33], who determined the massic energy of combustion of dry melinex as $\Delta_c u^\circ = -(22902 \pm 5) \text{ J} \cdot \text{g}^{-1}$, a value that was also confirmed in our laboratory. The mass of melinex used in each experiment was corrected for the mass fraction of

water, $w = 0.0032$ [33] and the mass of carbon dioxide produced from it was calculated using the factor previously reported [33]. The liquid samples of 2,5-dimethylthiophene were burnt enclosed in polyethylene bags, for which we have determined the massic energy of combustion as $\Delta_c u^\circ = -(46315.8 \pm 2.7) \text{ J} \cdot \text{g}^{-1}$.

For the combustion of the two compounds studied, the procedure described by Waddington *et al.* [34] was followed. The experiments were carried out in oxygen, at a pressure of 3.04 MPa and with a volume of 15.00 cm^3 of deionised water added to the bomb.

The corrections for the nitric acid formed were determined by means of the Devarda's alloy method [35], based on $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$ for the standard molar energy of formation of $0.1 \text{ mol} \cdot \text{dm}^{-3}$ of aqueous HNO_3 from O_2 (g), N_2 (g) and H_2O (l) [36].

An estimated value of the pressure coefficient of massic energy, $(\partial u / \partial p)_T = -0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$, at $T = 298.15 \text{ K}$, a typical value or most organic compounds [37], was assumed.

For each compound, the corrections to the standard state, ΔU_Σ , were calculated by the procedures given by Hubbard *et al.* [38] and by Good and Scott [39].

The quantity of distilled water used as calorimetric liquid was weighed in a Mettler PC 8000 balance, sensitivity $\pm 10^{-1} \text{ g}$, whereas a Mettler Toledo 245 balance, sensitivity $\pm 10^{-5} \text{ g}$, was used to all the necessary weighing for the combustion experiments.

2.3. High temperature calvet microcalorimetry

The enthalpies of vaporization of the compounds studied were measured in a Calvet high temperature microcalorimeter from Setaram, model HT 1000. The "vacuum sublimation" drop microcalorimetry technique was used [40], having been previously tested in our laboratory, for liquid vaporizations [41]. The apparatus and the experimental technique have been recently described [42].

In each experiment, two thin glass capillary tubes sealed at one end, one containing 4–6 mg of the sample of the liquid compound and the other acting as reference tube, were simultaneously dropped into the hot reaction vessels, held at a suitable predefined temperature T , for the study of the vaporization of the compounds. After the tubes reached thermo stability, samples are removed from the hot zone by vacuum vaporization. The thermal corrections for the differences in the mass of both capillary tubes and different sensibilities of the two measuring cells were obtained by making individual blank correction experiments, dropping empty tubes of nearly equal mass into each of the twin cells [42].

The *n*-undecane ($\text{C}_{11}\text{H}_{24}$), mass fraction purity 0.99+, with a standard molar enthalpy of vaporization, at $T = 298.15 \text{ K}$, of $(56.580 \pm 0.566) \text{ kJ} \cdot \text{mol}^{-1}$ [43] was used to calibrate the Calvet microcalorimeter. The values of the calibration constants were $k_{(T=350 \text{ K})} = (0.9969 \pm 0.0026)$ for 2,5-dimethylthiophene and $k_{(T=350 \text{ K})} = (0.9982 \pm 0.0012)$ for 3-acetyl-2,5-dimethylthiophene; the quoted uncertainty are the standard deviations of the means.

The standard molar enthalpies of vaporization, at $T = 298.15 \text{ K}$, were calculated from the same thermodynamic parameter, at the temperature T , corrected to $T = 298.15 \text{ K}$, using $\Delta_{298.15 \text{ K}}^T H_m^\circ$ (g) estimated by a group additivity scheme based on values of Stull *et al.* [44], presented in figure 2.

All the necessary weighing for the Calvet experiments was made with a precision of $\pm 10^{-6} \text{ g}$, in a Mettler CH-8608 analytical balance.

3. Results

Detailed results of each combustion experiment, for the two compounds studied, are given in Supplementary information, tables S1 and S2. In table 1, the results of one combustion experiment of

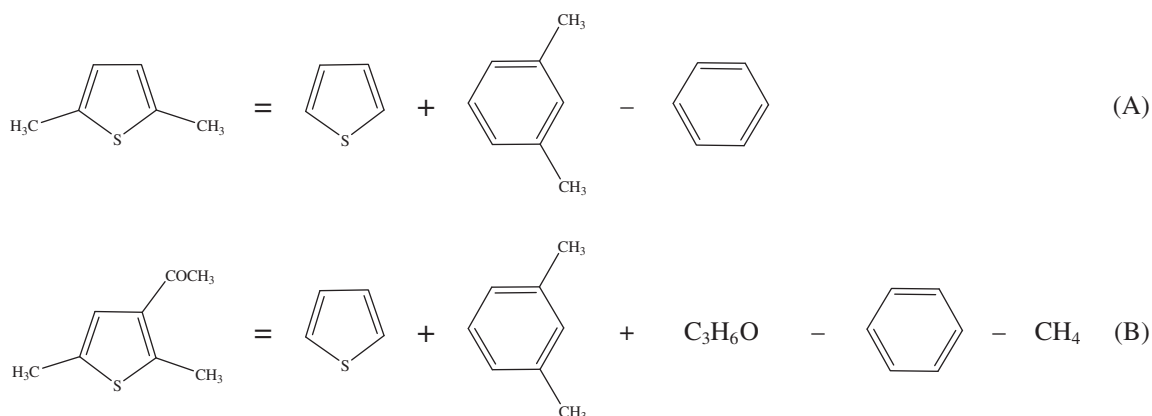


FIGURE 2. Group additivity scheme for the estimation of $\Delta_{298.15\text{K}}^{\circ} H_{\text{m}}^{\circ}$ (g) for 2,5-dimethylthiophene and 3-acetyl-2,5-dimethylthiophene.

each compound are presented. Here, the $\Delta m(\text{H}_2\text{O})$ represents the deviation of the mass of water added to the calorimeter from 3965.0 g, the mass assigned to $\varepsilon(\text{calor})$, $\Delta U(\text{IBP})$ is the internal energy for the isothermal combustion reaction, under bomb conditions, calculated through:

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + c_p(\text{H}_2\text{O}, \text{l})\Delta m(\text{H}_2\text{O})\}\Delta T_{\text{ad}} + (T_i - 298.15)\varepsilon_i + (298.15 - T_i - \Delta T_{\text{ad}})\varepsilon_f + \Delta U(\text{ign}), \quad (1)$$

where ΔT_{ad} is the calorimeter temperature change corrected for the heat exchange, work of stirring and frictional work of bomb rotation and the other symbols have the same meaning as those previously defined by Hubbard *et al.* [38] and Westrum [45]. The standard state

corrections, ΔU_{S} , (Washburn corrections) were calculated as recommended in the literature for organic sulphur compounds [38,39].

Table 2 lists, for each compound, the individual values of $\Delta_c u^{\circ}$, together with its mean value, $\langle \Delta_c u^{\circ} \rangle$, and the standard deviation of the mean. The values of $\Delta_c u^{\circ}$ refer to the reactions represented by equations (2) and (3), for 2,5-dimethylthiophene and 3-acetyl-2,5-dimethylthiophene, respectively.

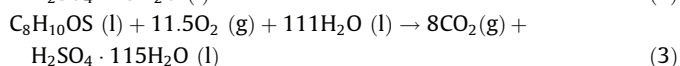
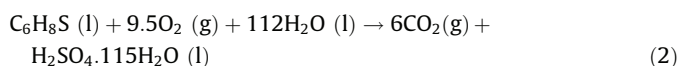


Table 3 lists the derived standard molar values for the energy, $\Delta_c U_{\text{m}}^{\circ}$ (l), and enthalpy, $\Delta_c H_{\text{m}}^{\circ}$ (l), of combustion reactions (2) and (3), as well as the standard molar enthalpies of formation, in the liquid phase, $\Delta_f H_{\text{m}}^{\circ}$ (l), at $T = 298.15$ K.

The uncertainties of the standard molar energies and enthalpies of combustion are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of auxiliary quantities used [46,47].

To derive $\Delta_f H_{\text{m}}^{\circ}$ (l), at $T = 298.15$ K, from $\Delta_c H_{\text{m}}^{\circ}$ (l), the standard molar enthalpies of formation of H_2O (l), $-(285.830 \pm 0.042)$ $\text{kJ} \cdot \text{mol}^{-1}$ [48], CO_2 (g), $-(393.51 \pm 0.13)$ $\text{kJ} \cdot \text{mol}^{-1}$ [48] and H_2SO_4 in 115 H_2O (l), $-(887.81 \pm 0.01)$ $\text{kJ} \cdot \text{mol}^{-1}$ [36], were used.

Values of the standard molar enthalpies of vaporization, at the experimental temperature T , together with the corrective enthalpic term, $\Delta_{298.15\text{K}}^{\circ} H_{\text{m}}^{\circ}$ (g), estimated by a group additivity scheme based on values of Stull *et al.* [44] and the standard molar enthalpy of vaporization for each compound, at $T = 298.15$ K, are given in table 4. The uncertainties associated to the values of $\Delta_f H_{\text{m}}^{\circ}$ ($T = 298.15$ K) are twice the overall standard deviation of the mean and include the uncertainties in calibration.

TABLE 1

Typical combustion results, at $T = 298.15$ K ($p^{\circ} = 0.1$ MPa), for the studied compounds

	2,5-Dimethylthiophene	3-Acetyl-2,5-dimethylthiophene
$m(\text{cpd})/\text{g}$	0.51564	0.72229
$m'(\text{fuse})/\text{g}$	0.00376	0.00289
$m''(\text{pol})/\text{g}$	0.24157	
$m'''(\text{melinex})/\text{g}$		0.04419
T_i/K	296.6544	296.9161
T_f/K	298.1652	298.1473
$\Delta T_{\text{ad}}/\text{K}$	1.47784	1.19644
$\varepsilon_i/(\text{J} \cdot \text{K}^{-1})$	74.60	74.42
$\varepsilon_f/(\text{J} \cdot \text{K}^{-1})$	74.66	73.96
$\varepsilon_{\text{corr}}/(\text{J} \cdot \text{K}^{-1})$	20370.67	20375.28
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.4	1.5
$-\Delta U(\text{IBP})^a/\text{J}$	30213.73	24465.78
$\Delta U(\text{fuse})/\text{J}$	61.06	46.93
$\Delta U(\text{pol})/\text{J}$	11188.71	
$\Delta U(\text{melinex})/\text{J}$		1012.02
$\Delta U(\text{HNO}_3)/\text{J}$	47.76	25.79
$\Delta U(\text{ign})/\text{J}$	1.11	1.08
$\Delta U_{\text{S}}/\text{J}$	33.46	32.12
$-\Delta_c u^{\circ}/(\text{J} \cdot \text{g}^{-1})$	36620.01	32326.24

$m(\text{cpd})$ is the mass of compound burnt in each experiment; $m'(\text{fuse})$ is the mass of the fuse (cotton) used in each experiment; $m''(\text{pol})$ is the mass of polyethylene used in each experiment; $m'''(\text{melinex})$ is the mass of melinex used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise; ε_i is the energy equivalent of the contents in the initial state; ε_f is the energy equivalent of the contents in the final state; $\varepsilon_{\text{corr}}$ is the energy equivalent of the calorimeter corrected for the deviation of mass of water added to the calorimeter; $\Delta m(\text{H}_2\text{O})$ is the deviation of mass of water added to the calorimeter from 3965.0 g; $\Delta U(\text{IBP})$ is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta_c U(\text{fuse})$ is the energy of combustion of the fuse (cotton); $\Delta U(\text{pol})$ is the energy of combustion of the polyethylene; $\Delta U(\text{melinex})$ is the energy of combustion of the melinex; $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; $\Delta U(\text{ign})$ is the electric energy for the ignition; ΔU_{S} is the standard state correction; $\Delta_c u^{\circ}$ is the standard massic energy of combustion.

^a $\Delta U(\text{IBP})$ includes $\Delta U(\text{ignition})$.

TABLE 2

Individual values of standard ($p^{\circ} = 0.1$ MPa) massic energies of combustion, $\Delta_c u^{\circ}$, of the studied compounds, at $T = 298.15$ K

2,5-Dimethylthiophene	3-Acetyl-2,5-dimethylthiophene
$-\Delta_c u^{\circ}/(\text{J} \cdot \text{g}^{-1})$	
36620.01	32326.24
36609.39	32332.67
36613.64	32337.47
36614.12	32323.42
36618.70	32318.12
36621.55	32334.22
$-\langle \Delta_c u^{\circ} \rangle/(\text{J} \cdot \text{g}^{-1})$	
36616.2 ± 1.9	32328.7 ± 3.0

^a Mean value and standard deviation of the mean.

TABLE 3

Derived standard ($p^\circ = 0.1$ MPa) molar values of the studied compounds, in the condensed phase, at $T = 298.15$ K

Compound	$-\Delta_c U_m^\circ(l)/(\text{kJ} \cdot \text{mol}^{-1})$	$-\Delta_c H_m^\circ(l)/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f H_m^\circ(l)/(\text{kJ} \cdot \text{mol}^{-1})$
2,5-Dimethylthiophene	4108.1 ± 1.5	4116.8 ± 1.5	10.4 ± 1.7
3-Acetyl-2,5-dimethylthiophene	4986.0 ± 2.1	4994.7 ± 2.1	-184.5 ± 2.4

The standard molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K, for the two studied compounds, derived from the respective standard molar enthalpies of formation, in the liquid phase, and the standard molar enthalpies of vaporization, are summarized in table 5.

4. Discussion

Richard [49] published a paper with thermodynamic properties of some geochemically important organic sulphur compounds, some of which are thiophene derivatives. In that report, he presents the standard molar enthalpies of formation of 2,5-dimethylthiophene in the liquid and in the gaseous phase as being, respectively, $10.3 \text{ kJ} \cdot \text{mol}^{-1}$ and $52.1 \text{ kJ} \cdot \text{mol}^{-1}$, values that are in very good agreement with the ones determined in this work ($10.4 \pm 1.7 \text{ kJ} \cdot \text{mol}^{-1}$ and $(50.6 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$, respectively. The

uncertainties associated with these values are of the order of $(0.6$ to $1.9) \text{ kJ} \cdot \text{mol}^{-1}$ for the liquid phase and $(0.6$ to $2.1) \text{ kJ} \cdot \text{mol}^{-1}$ for the gaseous phase.

Using the literature values of the standard molar enthalpies of formation, in the gaseous state, for thiophene ($115.0 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ [50] and 2-methylthiophene ($84.35 \pm 0.92 \text{ kJ} \cdot \text{mol}^{-1}$ [51], the enthalpic increment of the substitution of an H atom by a $-\text{CH}_3$ group in the 2 position of the thiophene ring is $-(30.7 \pm 1.4) \text{ kJ} \cdot \text{mol}^{-1}$. Using the value of the standard molar enthalpy of formation, in the gaseous phase, of 2,5-dimethylthiophene, reported in this paper, one calculates the enthalpic increment relative to the entrance of a second $-\text{CH}_3$ group in the 5 position of the thiophene ring to yield the 2,5-dimethylthiophene, as $-(33.8 \pm 2.1) \text{ kJ} \cdot \text{mol}^{-1}$, as shown in the scheme of figure 3, where all the values are in $\text{kJ} \cdot \text{mol}^{-1}$.

Within the associated uncertainties, we can conclude that there is no significant energetic effect caused by the introduction of a second methyl group in 2-methylthiophene to yield 2,5-dimethylthiophene, neither when an H atom, in the 2 position of the thiophene ring is substituted by a methyl group to give the 2-methylthiophene.

Our experimental results allow us to make a comparative analysis with the analogous substituted benzenes. From the literature values of the standard molar enthalpies of formation, in the gaseous state, of benzene ($82.6 \pm 0.7 \text{ kJ} \cdot \text{mol}^{-1}$ [52], toluene

TABLE 4

Standard ($p^\circ = 0.1$ MPa) molar enthalpies of vaporization, $\Delta_f^\circ H_m^\circ$, for the two studied compounds at $T = 298.15$ K, determined by Calvet microcalorimetry

Compound	Number of experiments	T/K	$\Delta_{f,298.15\text{ K}}^\circ H_m^\circ/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{f,298.15\text{ K}}^\circ H_m^\circ(\text{g})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f^\circ H_m^\circ(298.15\text{ K})/(\text{kJ} \cdot \text{mol}^{-1})$
2,5-Dimethylthiophene	5	349.8	47.7 ± 0.1	7.51	40.2 ± 0.9
3-Acetyl-2,5-dimethylthiophene	5	350.0	71.4 ± 0.2	10.08	61.3 ± 1.3

TABLE 5

Standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in both condensed and gaseous phase, and standard molar enthalpies of vaporization, at $T = 298.15$ K

Compound	$\Delta_f H_m^\circ(l)/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f^\circ H_m^\circ(298.15\text{ K})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f H_m^\circ(\text{g})/(\text{kJ} \cdot \text{mol}^{-1})$
2,5-Dimethylthiophene	10.4 ± 1.7	40.2 ± 0.9	50.6 ± 1.9
3-Acetyl-2,5-dimethylthiophene	-184.5 ± 2.4	61.3 ± 1.3	-123.2 ± 2.7

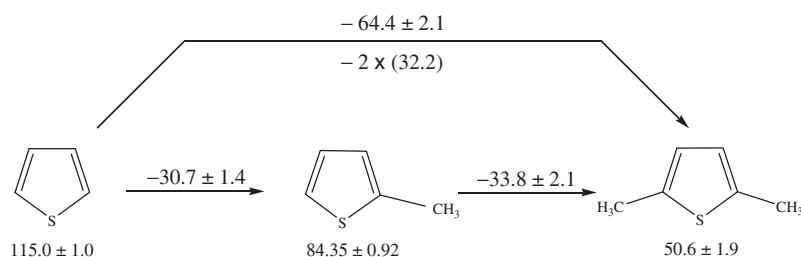


FIGURE 3. Enthalpic increments for the formation of 2,5-dimethylthiophene from thiophene or 2-methylthiophene.

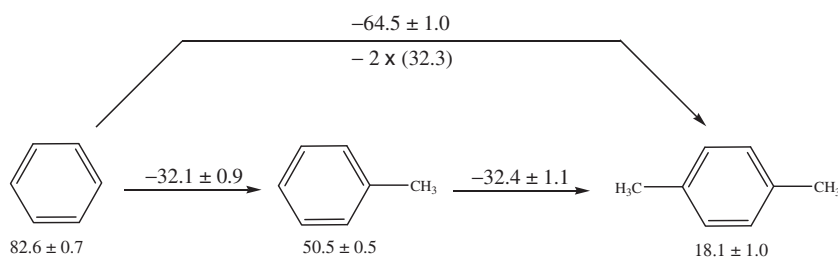


FIGURE 4. Enthalpic increments for the formation of *p*-xylene from benzene or toluene.

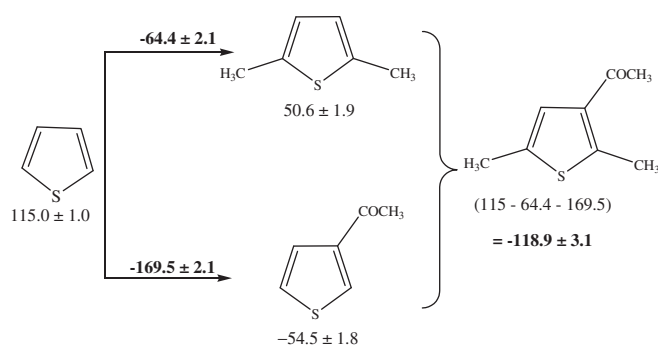


FIGURE 5. Estimation of the standard molar enthalpy of formation of 3-acetyl-2,5-dimethylthiophene, using enthalpic increments.

(50.5 ± 0.5) kJ · mol⁻¹ [52] and *p*-xylene (18.1 ± 1.0) kJ · mol⁻¹ [52], we obtain the values given in the scheme of figure 4.

Within the experimental uncertainties associated, the resulting enthalpic increments of the addition of a -CH₃ group in the 2 position and of a second -CH₃ group in the 5 position of the thiophene ring are equal to the respective additions to the benzene ring, that is, the energetic effects obtained from the conversion of benzene → toluene → *p*-xylene are similar to the same effects of the conversion of thiophene → 2-methylthiophene → 2,5-dimethylthiophene. We can conclude that the energetic effects involved in the stabilization due to the substitution of two H atoms by two -CH₃ groups in the 2 and 5 positions of thiophene and in the 1,4 positions of benzene are equal, -(64.4 ± 2.1) kJ · mol⁻¹ and -(64.5 ± 1.0) kJ · mol⁻¹, respectively, showing that these substitutions do not induce different specific enthalpic effects.

From the literature value of the standard molar enthalpy of formation, in the gaseous phase, of 3-acetylthiophene -(54.5 ± 1.8) kJ · mol⁻¹ [19] and the enthalpic increment of the entrance of two -CH₃ groups in the 2 and 5 positions of thiophene ring -(64.4 ± 2.1) kJ · mol⁻¹, as shown in the scheme of figure 3, one estimates the standard molar enthalpy of formation, in the gaseous phase, of 3-acetyl-2,5-dimethylthiophene as -(118.9 ± 3.1) kJ · mol⁻¹ (figure 5), a value that is in good agreement with the experimental value of -(123.2 ± 2.7) kJ · mol⁻¹, determined in this work.

Acknowledgements

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal and to FEDER for financial support to Centro de Investigação em Química, University of Porto. A.F.L.O.M.S. thanks FCT and the European Social Fund (ESF) under the Community Support Framework (CSF) for the award of a Ph.D. Research Grant (SFRH/BD/12886/2003).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2008.04.005.

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