



# Thermochemical study of 2,5-dimethyl-3-furancarboxylic acid, 4,5-dimethyl-2-furaldehyde, and 3-acetyl-2,5-dimethylfuran

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3-Acetyl-2,5-dimethylfuran

## ABSTRACT

The standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation, in the gaseous state, at  $T = 298.15$  K, for 2,5-dimethyl-3-furancarboxylic acid, 3-acetyl-2,5-dimethylfuran, and 4,5-dimethyl-2-furaldehyde were derived from the values of the standard molar enthalpies of formation, in the condensed phase, and the standard molar enthalpies of phase transition from the condensed to the gaseous state. The values of the standard molar enthalpies of formation of the compounds in the condensed phases were calculated from the measurements of the standard massic energies of combustion obtained by static bomb combustion calorimetry. The enthalpies of vaporization/sublimation were measured by Calvet high temperature microcalorimetry. For 2,5-dimethyl-3-furancarboxylic acid the standard enthalpy of sublimation was also calculated, by the application of the Clausius–Clapeyron equation, to the temperature dependence of the vapor pressures measured by the Knudsen effusion technique.

Compound	$-\Delta_f H_m^\circ(\text{cr, l}) /$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )	$\Delta_{\text{cr, l}}^\circ H_m^\circ(T = 298.15 \text{ K}) /$ $\text{kJ} \cdot \text{mol}^{-1}$	
		Calvet	Knudsen
2,5-Dimethyl-3-furancarboxylic acid (cr)	$600.4 \pm 1.5$	$99.0 \pm 1.7$	$100.9 \pm 0.5$
3-Acetyl-2,5-dimethylfuran (l)	$352.1 \pm 1.8$	$57.5 \pm 1.5$	
4,5-Dimethyl-2-furaldehyde (l)	$294.5 \pm 1.7$	$57.7 \pm 0.6$	

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## 1. Introduction

This paper is part of a broad systematic investigation on the thermodynamic properties of furan derivatives, which is being carried out in our Research Group [1–4]. The aim of this work is to enlarge the thermochemical database for substituted furans by determining their experimental standard molar enthalpies of formation, in the gaseous phase, and so calculating the energetic effects caused by the introduction of different substituents into the furan ring, to interpret the relations between energetics and structure in this class of compounds.

In this paper, we report the standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation of 4,5-dimethyl-3-furancarboxylic acid,

in the crystalline state, 4,5-dimethyl-2-furaldehyde and 3-acetyl-2,5-dimethylfuran in the liquid state, at  $T = 298.15$  K, derived from the measurements, by static bomb combustion calorimetry, of the standard massic energies of combustion. The standard molar enthalpies of phase transition to the gaseous state, at a predefined temperature of the microcalorimeter, were measured by Calvet microcalorimetry, and corrected to  $T = 298.15$  K, using a group method. For the crystalline 2,5-dimethyl-3-furancarboxylic acid, vapor pressures were measured by the Knudsen effusion technique, at several temperatures and, by the application of the Clausius–Clapeyron equation, the standard molar enthalpy of sublimation, at the mean temperature of the experimental temperature range was calculated. The standard molar enthalpy, entropy and Gibbs energy of sublimation, at  $T = 298.15$  K, were calculated using estimated values for the heat capacity differences between the gas and the crystal phases.

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## 2. Experimental

### 2.1. Materials and purity control

The studied compounds, 2,5-dimethyl-3-furancarboxylic acid [CAS 636-44-2], 4,5-dimethyl-2-furaldehyde [CAS 52480-43-0], and 3-acetyl-2,5-dimethylfuran [CAS 10599-70-9], whose structural formula are shown in figure 1, were obtained commercially from Aldrich Chemical Co., with assessed mass fraction purities of, 0.98, 0.97, and 0.98, respectively. The liquids 4,5-dimethyl-2-furaldehyde and 3-acetyl-2,5-dimethylfuran were purified by repeated distillation under reduced pressure and the crystalline 2,5-dimethyl-3-furancarboxylic acid was purified by successive sublimations. Purity was checked by gas–liquid chromatography (GLC, HP-1890A), and found to be higher than 0.9998 (mass fraction) for each compound, as well as by the closeness to unity of the combustion experiments carbon dioxide recovery ratios for each compound. The average ratios of the mass of carbon dioxide recovered from the combustions to that calculated from the mass of samples were: 1.00025 for 2,5-dimethyl-3-furancarboxylic acid, 1.00033 for 3-acetyl-2,5-dimethylfuran and 1.00008 for 4,5-dimethyl-2-furaldehyde. The specific densities of the liquid compounds taken from the Aldrich catalogue [5] are  $1.038 \text{ g} \cdot \text{cm}^{-3}$  and  $1.016 \text{ g} \cdot \text{cm}^{-3}$ , respectively, for 3-acetyl-2,5-dimethylfuran and 4,5-dimethyl-2-furaldehyde. The specific density of 3-furoic acid,  $1.503 \text{ g} \cdot \text{cm}^{-3}$  [6], was assumed for 2,5-dimethyl-3-furancarboxylic acid.

### 2.2. Combustion calorimetry

An isoperibol calorimetric system was used to perform all combustion experiments. The bomb calorimeter, subsidiary apparatus and technique have been previously described [7,8].

Combustion of certificated benzoic acid NBS Standard Reference Material, Sample 39j, was used for calibration of the bomb. Its massic energy of combustion is  $(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ , under certificate conditions. The calibration results were corrected to give the energy equivalent  $\varepsilon(\text{calor})$  corresponding to the average mass of water added to the calorimeter: 3119.6 g. One set of six calibration experiments was performed leading to the value of the energy equivalent of the calorimeter,  $\varepsilon(\text{calor}) = (15917.4 \pm 1.4) \text{ J} \cdot \text{K}^{-1}$ , where the uncertainty quoted is the standard deviation of the mean. For the 2,5-dimethyl-3-furancarboxylic acid, which was studied later, the energy equivalent of the calorimeter was,  $\varepsilon(\text{calor}) = (15906.6 \pm 1.9) \text{ J} \cdot \text{K}^{-1}$ .

In all combustion experiments,  $1.00 \text{ cm}^3$  of water was introduced into the bomb, a twin-valve static combustion bomb, Type 1105 from Parr Instrument Company, made of stainless steel, with an internal volume of  $0.340 \text{ cm}^3$ . The bomb was purged twice to remove air, before being charged with 3.04 MPa of oxygen.

For all experiments, the calorimeter temperatures were measured to  $\pm(1 \cdot 10^{-4}) \text{ K}$ , at time intervals of 10 s, with a quartz crystal thermometer (Hewlett Packard HP 2804A), interfaced to a PC. Data acquisition and control of the calorimeter were performed using the program LABTERMO [9]. At least 100 readings of the temperature were taken before the ignition of the samples which was made

at  $T = (298.150 \pm 0.001) \text{ K}$  by the discharge of a  $1400 \mu\text{F}$  capacitor through the platinum ignition wire. After the ignition, 100 readings were taken for each the main and after periods.

The liquid samples were enclosed in melinex bags using the technique described by Skinner and Snelson [10], who determined the specific energy of combustion of dry melinex as  $\Delta_c u^\circ = -(22902 \pm 5) \text{ J} \cdot \text{g}^{-1}$ . This value was confirmed in our laboratory. The mass of melinex used in each experiment was corrected for the mass fraction of water (0.0032). The 2,5-dimethyl-3-furancarboxylic samples were burnt in pellets form. For the cotton thread fuse of empirical formula  $\text{CH}_{1.686}\text{O}_{0.843}$ , the massic energy of combustion was assigned to  $-\Delta_c u^\circ = 16240 \text{ J} \cdot \text{g}^{-1}$  [11]. This value has been previously confirmed in our laboratory. *n*-Hexadecane (Aldrich Gold Label, mass fraction  $>0.999$ ), stored under nitrogen, was used as auxiliary combustion aid for 2,5-dimethyl-3-furancarboxylic acid due to carbon formation during previous test combustion experiments. The massic energy of combustion of the particular sample used, was determined in our laboratory as  $-\Delta_c u^\circ = 47132.7 \pm 2.6) \text{ J} \cdot \text{g}^{-1}$ . The corrections for nitric acid formation were based on  $59.7 \text{ kJ} \cdot \text{mol}^{-1}$  [12], for the molar energy of formation of  $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3(\text{aq})$  from  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}(\text{l})$ . An estimated pressure coefficient of specific 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 for most organic compounds [13] was assumed. For each compound, the massic energy of combustion,  $\Delta_c u^\circ$ , was calculated by the procedure, given by Hubbard *et al.* [14]. The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after the allowance for that formed from the cotton thread fuse and melinex or *n*-hexadecane. All the necessary weighing was made in a Mettler Toledo AT201 balance, sensitivity  $\pm(1 \cdot 10^{-5}) \text{ g}$  and corrections from the apparent mass to true mass were made.

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2007 [15], yielding for 2,5-dimethyl-3-furancarboxylic acid,  $\text{C}_7\text{H}_8\text{O}_3$ ,  $M = 140.1366 \text{ g} \cdot \text{mol}^{-1}$ , for 3-acetyl-2,5-dimethylfuran,  $\text{C}_8\text{H}_{10}\text{O}_2$ ,  $M = 138.1638 \text{ g} \cdot \text{mol}^{-1}$  and for 4,5-dimethyl-2-furaldehyde,  $\text{C}_7\text{H}_8\text{O}_2$ ,  $M = 124.1372 \text{ g} \cdot \text{mol}^{-1}$ .

### 2.3. Microcalorimetry Calvet

The standard molar enthalpies of phase transition of the compounds were determined by microcalorimetry, using for liquids a similar technique [16] to that described for sublimation of solids, the so called “vacuum sublimation drop-microcalorimetric technique” [17,18]. The apparatus and technique have been already described [18]. Each sample contained in a small thin glass capillary tube sealed at one end, was dropped at room temperature into the hot reaction vessel in the Calvet High-Temperature Microcalorimeter (Setaram HT 1000), held at a predefined temperature, and then removed from the hot zone by vacuum sublimation/vaporization. Simultaneously, an empty capillary tube of similar mass was dropped in the reference cell. The thermal corrections for the glass capillary tubes were determined in separate experiments, and were minimized, as far as possible, by dropping tubes of nearly equal mass, to within  $\pm 10 \mu\text{g}$ , into each of the twin calorimeter cells.

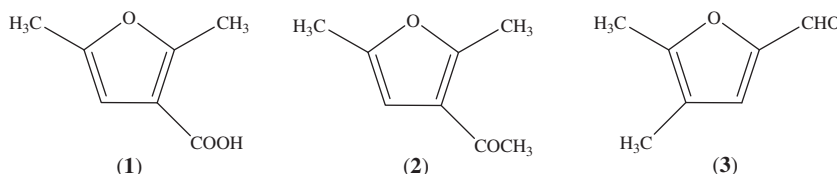


FIGURE 1. Structural formula of 2,5-dimethyl-3-furancarboxylic acid, (1), 3-acetyl-2,5-dimethylfuran (2), and 4,5-dimethyl-2-furaldehyde (3).

TABLE 1

Typical combustion results, at  $T = 298.15$  K, for the studied furan derivatives.

	2,5-Dimethyl-3-furancarboxylic acid	3-Acetyl-2,5-dimethylfuran	4,5-Dimethyl-2-furaldehyde
$m(\text{CO}_2)/\text{g}$	1.93182	1.50216	1.45172
$m'(\text{cpd})/\text{g}$	0.51796	0.54393	0.53178
$m''(\text{fuse})/\text{g}$	0.00247	0.00242	0.00319
$m'''(\text{aux})/\text{g}$	0.25378	0.04899	0.05540
$\Delta T_{\text{ad}}/\text{K}$	1.51989	1.11673	1.05158
$\epsilon_f/(\text{J} \cdot \text{K}^{-1})$	17.18	16.22	16.05
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.0	0.0	0.0
$-\Delta U(\text{IBP})^a/\text{J}$	24201.74	17792.77	16754.38
$\Delta U(\text{aux})/\text{J}$	11961.54	1121.91	1268.80
$\Delta U(\text{fuse})/\text{J}$	40.11	39.30	51.81
$\Delta U(\text{HNO}_3)/\text{J}$	0.32	0.78	2.01
$\Delta U(\text{ign})/\text{J}$	0.65	0.78	0.92
$\Delta U_{\Sigma}/\text{J}$	11.99	10.00	10.14
$-\Delta_c u^\circ/(\text{J} \cdot \text{g}^{-1})$	23530.35	30556.84	29000.00

$m(\text{CO}_2)$  is the mass of  $\text{CO}_2$  formed in each combustion experiments,  $m'(\text{cpd})$  is the mass of compound burnt in each experiment;  $m''(\text{fuse})$  is the mass of the fuse (cotton) used in each experiment;  $m'''(\text{aux})$  is the mass of *n*-hexadecane used in the case of 2,5-dimethyl-3-furancarboxylic acid, or the mass of melinex bags used in the case of the other two compounds;  $\Delta T_{\text{ad}}$  is the corrected temperature rise;  $\epsilon_f$  is the energy equivalent of the contents in the final state;  $\Delta m(\text{H}_2\text{O})$  is the deviation of mass of water added to the calorimeter from the mass assigned for  $\epsilon(\text{calor})$ ;  $\Delta U(\text{IBP})$  is the energy change for the isothermal combustion reaction under actual bomb conditions;  $\Delta U(\text{aux})$  is the energy of combustion of the *n*-hexadecane or melinex;  $\Delta U(\text{fuse})$  is the energy of combustion of the fuse (cotton);  $\Delta U(\text{HNO}_3)$  is the energy correction for the nitric acid formation;  $\Delta U(\text{ign})$  is the electric energy for the ignition;  $\Delta U_{\Sigma}$  is the standard state correction;  $\Delta_c u^\circ$  is the standard massic energy of combustion.

<sup>a</sup>  $U(\text{IBP})$  includes  $\Delta U(\text{ignition})$ .

The observed enthalpies of sublimation/vaporization,  $\Delta_{\text{cr},1,298.15\text{K}}^{\text{g},\text{T}} H_{\text{m}}$ , were corrected to  $T = 298.15$  K using values of  $\Delta_{298.15\text{K}}^{\text{g},\text{T}} H_{\text{m}}^\circ(\text{g})$  estimated by a group method that is: 2,5-dimethyl-3-furancarboxylic acid = furan + 1,3-dimethylcyclopentane – cyclopentane + benzoic acid – benzene; 3-acetyl-2,5-dimethylfuran = furan + 1,3-dimethylcyclopentane – cyclopentane + 2-butanone – ethane; and 4,5-dimethyl-2-furaldehyde = furan + 1,2-dimethylcyclopentane – cyclopentane + propionaldehyde – ethane, based on data of Stull *et al.* [19]. For the vaporization measurements, the microcalorimeter was calibrated *in situ* using the reported standard molar enthalpy of vaporization of *n*-undecane ( $56.58 \pm 0.57$ )  $\text{kJ} \cdot \text{mol}^{-1}$  [20] and for the sublimation measurements using naphthalene for which  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(T = 298.15 \text{ K}) = (72.6 \pm 0.6)$   $\text{kJ} \cdot \text{mol}^{-1}$  [20].

#### 2.4. Knudsen effusion method

For the 2,5-dimethyl-3-furancarboxylic acid compound, the vapor pressures were measured at several temperatures using a Knudsen effusion apparatus which enables the simultaneous operation of nine aluminium effusion cells [21]. This apparatus has been tested by measuring vapor pressures between 0.1 Pa and 1.0 Pa, over temperature ranges of *ca.* 20 K, of benzoic acid, phenanthrene, anthracene, benzanthrene, and 1,3,5-triphenylbenzene. Both the measured vapor pressures and the derived enthalpies of sublimation of the test substances are in excellent agreement with the literature results for those compounds. The nine effusion cells are contained in cylindrical holes inside three aluminium blocks, three cells per block. Each block is kept at a constant temperature, different from the other two blocks.

The measurements were extended through a chosen temperature interval corresponding to measured vapor pressures in the range 0.1 Pa to 1.0 Pa. In each effusion experiment, the mass loss,  $\Delta m$ , of the samples, during a convenient effusion time period,  $t$ , is determined by weighing the effusion cells to  $\pm 0.01$  mg, before and after the effusion period in a system evacuated to a pressure near  $1 \cdot 10^{-4}$  Pa. At the temperature,  $T$ , of the experiment, the vapor pressure,  $p$ , is calculated by the equation

$$p = (\Delta m / A_0 w_0 t) (2\pi RT / M)^{1/2}, \quad (1)$$

where  $M$  is the molar mass of the effusing vapor,  $R$  is the gas constant,  $A_0$  is the area of the effusion hole and  $w_0$  is the respective Clausing factor calculated by equation (2) where  $l$  is the thickness of the effusion hole and  $r$  its radius:

$$w_0 = \{1 + (3l/8r)\}^{-1}. \quad (2)$$

The areas and Clausing factors of the effusion orifices, made in platinum foil of 0.0125 mm thickness, are presented in the Supplementary Information, table S1.

### 3. Results

Results for one typical combustion experiment of each studied compound are given in table 1, where  $\Delta m(\text{H}_2\text{O})$  is the deviation of the mass of water added to the calorimeter from 3119.6 g, the mass assigned to  $\epsilon(\text{calor})$ ,  $\Delta U_{\Sigma}$  is the energy correction to the standard state and  $\Delta_c u^\circ$  refers to the idealized combustion reaction yielding  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$ . The remaining quantities are as previously defined [14].

TABLE 2

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

2,5-Dimethyl-3-furancarboxylic acid	3-Acetyl-2,5-dimethylfuran	4,5-Dimethyl-2-furaldehyde
	$-\Delta_c u^\circ/(\text{J} \cdot \text{g}^{-1})$	
23515.22	30552.95	29016.40
23520.05	30559.80	28997.85
23530.35	30556.84	29013.02
23518.30	30542.24	28993.09
23526.99	30556.58	29000.00
23516.90	30550.25	29018.46
		29009.31
		29005.70
	$-(\Delta_c u^\circ)/(\text{J} \cdot \text{g}^{-1})^a$	
23521.3 $\pm$ 2.4	30553.1 $\pm$ 2.6	29006.7 $\pm$ 3.2

<sup>a</sup> Mean value and standard deviation of the mean.

**TABLE 3**

Derived standard ( $p^\circ = 0.1$  MPa) molar energies of combustion,  $\Delta_c U_m^\circ$ , standard molar enthalpies of combustion,  $\Delta_c H_m^\circ$ , and standard molar enthalpies of formation,  $\Delta_f H_m^\circ$ , for the compounds, at  $T = 298.15$  K.

Compound	$-\Delta_c U_m^\circ(\text{cr, l})/(\text{kJ} \cdot \text{mol}^{-1})$	$-\Delta_c H_m^\circ(\text{cr, l})/(\text{kJ} \cdot \text{mol}^{-1})$	$-\Delta_f H_m^\circ(\text{cr, l})/(\text{kJ} \cdot \text{mol}^{-1})$
2,5-Dimethyl-3-furancarboxylic acid	3296.2 $\pm$ 1.2	3297.5 $\pm$ 1.2	600.4 $\pm$ 1.5
3-Acetyl-2,5-dimethylfuran	4221.4 $\pm$ 1.4	4225.1 $\pm$ 1.4	352.1 $\pm$ 1.8
4,5-Dimethyl-2-furaldehyde	3600.9 $\pm$ 1.4	3603.4 $\pm$ 1.4	294.5 $\pm$ 1.7

**TABLE 4**

Microcalorimetric standard ( $p^\circ = 0.1$  MPa) molar enthalpies of phase transition at  $T = 298.15$  K.

Compound	Number of expts	$T/\text{K}$	$\Delta_{\text{cr,l}}^{g,T} H_m^\circ(T)/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{298.15\text{K}}^{g,T} H_m^\circ(\text{g})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr,l}}^{g,T} H_m^\circ(T = 298.15 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1})$
2,5-Dimethyl-3-furancarboxylic acid	7	376	111.2 $\pm$ 0.1	12.24	99.0 $\pm$ 1.7
3-Acetyl-2,5-dimethylfuran	7	325	62.5 $\pm$ 0.5	4.98	57.5 $\pm$ 1.5
4,5-Dimethyl-2-furaldehyde	6	335	63.7 $\pm$ 0.2	5.99	57.7 $\pm$ 0.6

**TABLE 5**

Knudsen effusion results for 2,5-dimethyl-3-furancarboxylic acid.

$T/\text{K}$	$t/\text{s}$	Orifices	$p/\text{Pa}$			$10^2 \cdot \Delta \ln(p/\text{Pa})$		
			Small	Medium	Large	Small	Medium	Large
309.189	25453	A3-B6-C9	0.1409	0.1320	0.1359	-0.1	3.1	0.7
311.125	25453	A2-B5-C8	0.1806	0.1768	0.1708	-0.8	-1.8	0.9
313.085	25453	A1-B4-C7	0.2273	0.2279	0.2259	-0.2	-3.2	-1.3
315.182	17862	A3-B6-C9	0.2914	0.2809	0.2804	-0.1	1.2	-0.4
317.115	17862	A2-B5-C8	0.3673	0.3617	0.3524	-0.1	-0.6	0.2
319.082	17862	A1-B4-C7	0.4503	0.4556	0.4490	2.4	-0.6	-0.5
321.183	10212	A3-B6-C9	0.5801	0.5612	0.5670	1.1	3.0	0.9
323.094	10212	A2-B5-C8	0.7336	0.7218	0.7101	-0.6	-0.1	0.5
325.075	10212	A1-B4-C7	0.9185	0.9080	0.8953	-0.7	-0.5	-2.8
325.186	11267	A3-B6-C9	0.9292	0.9270	0.8864	-0.6	-1.3	1.5
327.102	11267	A2-B5-C8	1.1471	1.1284	1.1017	-0.2	0.8	0.3

**TABLE 6**

Experimental results for 2,5-dimethyl-3-furancarboxylic acid, where  $a$  and  $b$  are from Clausius–Clapeyron equation,  $\ln(p/\text{Pa}) = a - b/(T)$  and  $b = \Delta_{\text{cr,l}}^{g,T} H_m^\circ(T)/R$ ;  $R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

Orifices	$a$	$b$	$\langle T \rangle/\text{K}$	$\langle p \rangle/\text{Pa}$	$\Delta_{\text{cr,l}}^{g,T} H_m^\circ(T)/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr,l}}^{g,T} S_m^\circ(T, p(T))/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
A1-A2-A3	36.21 $\pm$ 0.17	11820 $\pm$ 53			98.3 $\pm$ 0.4	
B4-B5-B6	36.74 $\pm$ 0.33	11975 $\pm$ 106			99.6 $\pm$ 0.9	
C7-C8-C9	36.26 $\pm$ 0.21	11828 $\pm$ 67			99.3 $\pm$ 0.6	
Global results	36.42 $\pm$ 0.19	11874 $\pm$ 60	318.145	0.406	98.7 $\pm$ 0.5	310.2 $\pm$ 1.6

As samples were ignited at  $T = (298.150 \pm 0.001) \text{ K}$ ,

$$\Delta U(\text{IPB}) = -\{\varepsilon(\text{calor}) + \Delta m(\text{H}_2\text{O})c_p(\text{H}_2\text{O}, \text{l}) + \varepsilon_f\}\Delta T_{\text{ad}} + \Delta U(\text{ign}), \quad (3)$$

where  $\Delta U(\text{IPB})$  is the energy associated to the isotherm bomb process,  $\varepsilon_f$  is the energy of the bomb contents after ignition,  $\Delta U(\text{ign})$  is the ignition energy and  $\Delta T_{\text{ad}}$  is the adiabatic temperature rise.

Detailed results for each combustion calorimetric experiment performed for each compound are given as Supplementary Information (tables S2 to S4).

The individual values of  $\Delta_c u^\circ$ , together with their means and standard deviations, are given in table 2 and refer to the combustion reactions represented by equation (4) for 2,5-dimethyl-3-furancarboxylic acid, equation (5) for 3-acetyl-2,5-dimethylfuran and equation (6) for 4,5-dimethyl-2-furaldehyde:

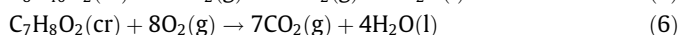
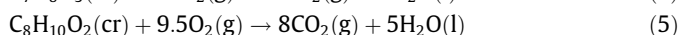
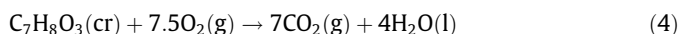
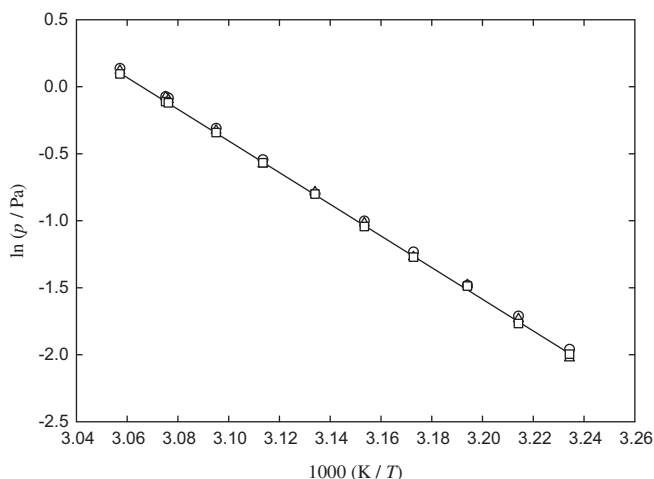


Table 3 lists the derived standard molar energies and enthalpies of combustion and the standard molar enthalpies of formation for 4,5-dimethyl-2-furaldehyde and 3-acetyl-2,5-dimethylfuran, in the liquid state, and for 2,5-dimethyl-3-furancarboxylic acid, in the crystalline state, at  $T = 298.15$  K. In accordance with normal thermochemical practice [22,23], the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of auxiliary quantities used. To derive  $\Delta_f H_m^\circ(\text{cr, l})$  from  $\Delta_c H_m^\circ(\text{cr, l})$  the standard molar enthalpies of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$ , at  $T = 298.15$  K,  $-(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$  [24], and  $-(285.830 \pm 0.040) \text{ kJ} \cdot \text{mol}^{-1}$  [24], respectively, were used.

Measurements of the standard molar enthalpies of sublimation/vaporization of the three studied compounds by Calvet microcalorimetry, as well as the uncertainties given by their standard deviations of the mean, are given in table 4. The uncertainties associated to the standard molar enthalpies of sublimation/vaporization, at  $T = 298.15$  K, are twice the standard deviation of the



**FIGURE 2.** Plots of  $\ln(p/\text{Pa})$  against  $1/T$  for 2,5-dimethyl-3-furancarboxylic acid:  $\circ$ , smaller orifices;  $\Delta$ , medium orifices;  $\square$ , larger orifices.

mean and include the uncertainties associated with the calibration process.

For 2,5-dimethyl-3-furancarboxylic acid, vapor pressures were measured at several temperatures by the Knudsen effusion method. The integrated form of the Clausius–Clapeyron equation,  $\ln(p/\text{Pa}) = a - b \cdot (T/\text{K})^{-1}$ , where  $a$  is a constant and  $b = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/R$ , was used to derive the standard molar enthalpy of sublimation at the mean temperature of the experimental temperature range. The experimental results obtained from each effusion cell, together with the residuals of the Clausius–Clapeyron equation derived from least squares adjustments, are presented in table 5. Table 6 presents for each hole used and for the global treatment of all the  $(p, T)$  points obtained for the studied compound, the detailed parameters of the Clausius–Clapeyron equation together with the calculated standard deviations and the standard molar enthalpies of sublimation at the mean temperature of the experiments  $T = \langle T \rangle$ . The calculated enthalpies of sublimation obtained from each individual orifice are in agreement within experimental associated uncertainty. The equilibrium pressure at the mean tem-

perature range  $p(T = \langle T \rangle)$  and the entropies of sublimation, at equilibrium conditions are also presented in table 6.

The entropies of sublimation, at equilibrium conditions, were calculated as

$$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}\{\langle T \rangle, p(T = \langle T \rangle)\} = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/\langle T \rangle. \quad (7)$$

The plots of  $\ln p = f(1/T)$  for the global results are presented in figure 2.

Table 7 lists the  $(p, T)$  values calculated from the  $(p, T)$  equations for the crystalline compound within the experimental range of pressures used: 0.1 Pa to 1 Pa. The standard molar enthalpy of sublimation, at the temperature 298.15 K, was derived from the sublimation enthalpy calculated at the mean temperature of the experiments, by the equation

$$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(T = 298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle) + \Delta_{\text{cr}}^{\text{g}} C_{p, \text{m}}^{\circ}(298.15 \text{ K} - \langle T \rangle). \quad (8)$$

The value of  $\Delta_{\text{cr}}^{\text{g}} C_{p, \text{m}}^{\circ}$  was estimated as  $-50 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for the studied compound, in accordance with similar estimations made by other authors [25], which we have already used in previous papers for other organic compounds [1,3,26–52].

Table 8 presents the values, at  $T = 298.15 \text{ K}$ , of the standard molar enthalpy of sublimation, the standard molar entropy of sublimation calculated by equation (9), were  $p^{\circ} = 10^5 \text{ Pa}$ , and the standard molar Gibbs energy of sublimation. The value of the standard molar enthalpy of sublimation, at  $T = 298.15 \text{ K}$ , of 2,5-dimethyl-3-furancarboxylic acid, derived from the Knudsen effusion method (table 9) is in agreement with the one determined by Calvet microcalorimetry (table 4)

$$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^{\circ}(T = 298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} S_{\text{m}}\{\langle T \rangle, p(\langle T \rangle)\} + \Delta_{\text{cr}}^{\text{g}} C_{p, \text{m}}^{\circ} \ln(298.15 \text{ K}/\langle T \rangle) - R \ln\{p^{\circ}/p(\langle T \rangle)\} \quad (9)$$

For the three studied compounds, the standard molar enthalpies of formation in the gaseous state, at  $T = 298.15 \text{ K}$ , obtained by the addition of the derived standard molar enthalpies of formation in the condensed state with the standard molar enthalpies of sublimation/vaporization, are summarized in table 9. For 2,5-dimethyl-3-furancarboxylic acid, the Knudsen value was used for the calculation of the standard molar enthalpy of formation in the gaseous state.

**TABLE 7**

Calculated  $(p, T)$  values from the vapor pressure equations for 2,5-dimethyl-3-furancarboxylic acid.

$p/\text{Pa}$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$T/\text{K}$	306.6	312.2	315.6	318.0	319.9	321.5	322.9	324.0	325.1	326.0

**TABLE 8**

Values of the standard ( $p^{\circ} = 0.1 \text{ MPa}$ ) molar enthalpies,  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}$ , entropies,  $\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^{\circ}$ , and Gibbs free energies  $\Delta_{\text{cr}}^{\text{g}} G_{\text{m}}^{\circ}$ , of sublimation, at  $T = 298.15 \text{ K}$ , for 2,5-dimethyl-3-furancarboxylic acid.

Compound	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^{\circ}/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr}}^{\text{g}} G_{\text{m}}^{\circ}/(\text{kJ} \cdot \text{mol}^{-1})$
2,5-Dimethyl-3-furancarboxylic acid	$100.9 \pm 0.5$	$210.2 \pm 1.6$	$38.2 \pm 0.7$

**TABLE 9**

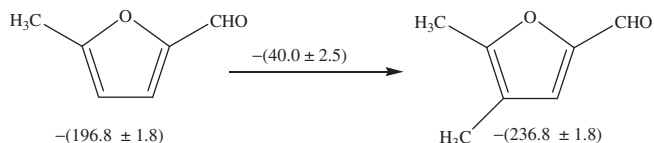
Standard ( $p^{\circ} = 0.1 \text{ MPa}$ ) molar enthalpies of formation, in both liquid or crystalline and gaseous phases, and standard molar enthalpies of vaporization/sublimation, at  $T = 298.15 \text{ K}$ .

Compound	$-\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{cr, l})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr, l}}^{\text{g}} H_{\text{m}}^{\circ}/(\text{kJ} \cdot \text{mol}^{-1})$	$-\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{g})/(\text{kJ} \cdot \text{mol}^{-1})$
2,5-Dimethyl-3-furancarboxylic acid	$600.4 \pm 1.5$	$100.9 \pm 0.5$	$499.5 \pm 1.6$
3-Acetyl-2,5-dimethylfuran	$352.1 \pm 1.8$	$57.5 \pm 1.5$	$294.6 \pm 2.3$
4,5-Dimethyl-2-furaldehyde	$294.5 \pm 1.7$	$57.7 \pm 0.6$	$236.8 \pm 1.8$

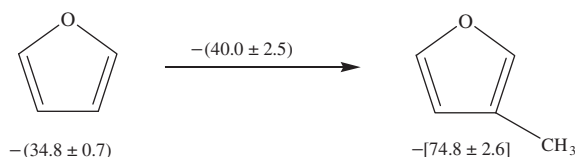
#### 4. Discussion

In a previous paper, we determined the standard molar enthalpy of formation of 2-methylfuran as  $\Delta_f H_m^\circ(\text{g}) = -(76.4 \pm 1.2) \text{ kJ} \cdot \text{mol}^{-1}$  [4] which, together with  $\Delta_f H_m^\circ(\text{furan, g}) = (34.8 \pm 0.7) \text{ kJ} \cdot \text{mol}^{-1}$  [53], allowed us to calculate the enthalpic increment for the entrance of a methyl group in the *ortho* position of the furan ring as  $(41.6 \pm 1.4) \text{ kJ} \cdot \text{mol}^{-1}$  [4]. Considering now the values of  $\Delta_f H_m^\circ(5\text{-methyl-2-furaldehyde, g}) = -(196.8 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$  [4] and of  $\Delta_f H_m^\circ(4, 5\text{-dimethyl-2-furaldehyde, g}) = -(236.8 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$ , derived in this paper, we calculate the enthalpic increment for the entrance of a methyl group in the *meta* position of the furan ring as  $-(40.0 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$ , as shown in scheme 1.

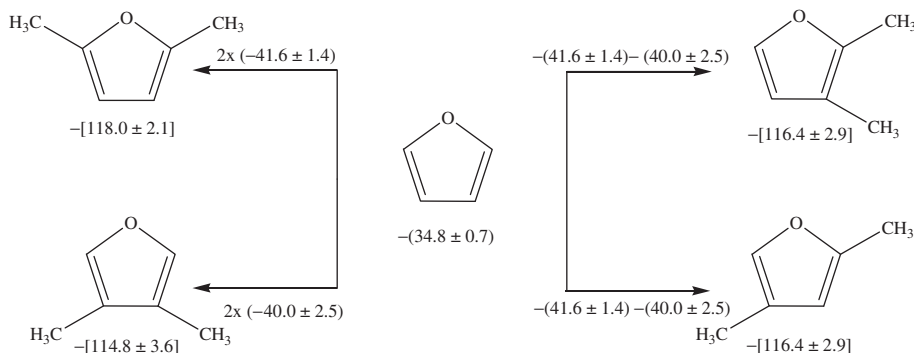
The calculated increments of the entrance of a methyl group in the *ortho* and *meta* positions of the furan ring allows us to estimate the standard molar enthalpies of formation of the 3-methylfuran (g) as  $-(74.8 \pm 2.6) \text{ kJ} \cdot \text{mol}^{-1}$ , as shown in scheme 2 and of all the dimethylfuran isomers, as shown in scheme 3.



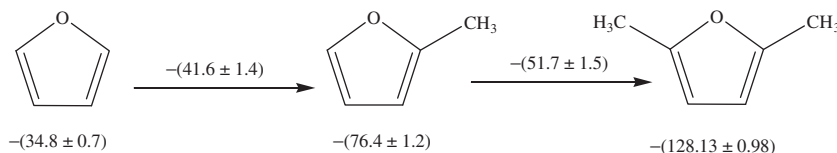
**Scheme 1.** Estimation of the enthalpic increment for the entrance of a methyl group in the *meta* position of the furan ring (all values in  $\text{kJ} \cdot \text{mol}^{-1}$ ).



**Scheme 2.** Estimation of the standard molar enthalpy of formation of 3-methylfuran (all values in  $\text{kJ} \cdot \text{mol}^{-1}$ ).



**Scheme 3.** Estimation of the standard molar enthalpies of formation of the dimethylfuran isomers (all values in  $\text{kJ} \cdot \text{mol}^{-1}$ ).



**Scheme 4.** Enthalpic increments for the introduction of one  $-\text{CH}_3$  group into the 2-position of furan and one  $-\text{CH}_3$  group into the 5-position of 2-methylfuran. (all values in  $\text{kJ} \cdot \text{mol}^{-1}$ ).

These estimated values are in agreement, within the associated uncertainties, to those obtained by Simmie and Curran [54] from theoretical calculations,  $\Delta_f H_m^\circ(2, 3\text{-dimethylfuran, g}) = -(116.5 \pm 1.1) \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\Delta_f H_m^\circ(2, 4\text{-dimethylfuran, g}) = -(117.6 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\Delta_f H_m^\circ(3, 4\text{-dimethylfuran, g}) = -(107.6 \pm 1.1) \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_f H_m^\circ(3\text{-methylfuran, g}) = -(69.5 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$ , but our estimated values for 3-methylfuran and 3,4-dimethylfuran are more negative than the theoretical values.

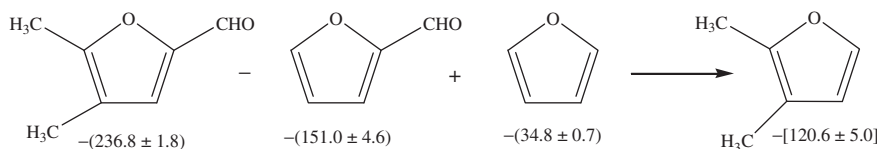
For the 2,5-dimethylfuran isomer, the estimated value is not in good agreement with the experimental one,  $\Delta_f H_m^\circ(\text{g}) = -(128.13 \pm 0.98) \text{ kJ} \cdot \text{mol}^{-1}$  [55]. It seems that the 2,5-dimethylfuran is more stable than the other dimethyl isomers. This effect can be seen if we compare the enthalpic increment of the introduction of a  $-\text{CH}_3$  group in the 2-position of the furan ring,  $(41.6 \pm 1.4) \text{ kJ} \cdot \text{mol}^{-1}$ , with the enthalpic increment relative to the entrance of a second  $-\text{CH}_3$  group in the 5-position of 2-methylfuran,  $(51.7 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$ , to yield the 2,5-dimethylfuran as shown in scheme 4.

The addition of a second  $-\text{CH}_3$  group in the *ortho* position of furan has a greater stabilizing effect than the same entrance in the 3- and 4-positions. The interactions between the alkyl substituents and the furan ring may change the ring geometry and cause better conjugation between the double bonds and the attached oxygen atom.

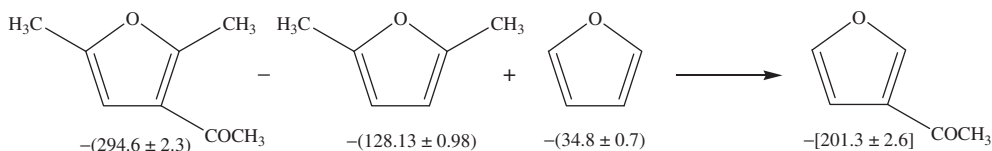
The standard molar enthalpy of formation of 4,5-dimethyl-2-furaldehyde,  $\Delta_f H_m^\circ(\text{g}) = -(236.8 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$ , derived in this paper, together with the literature values of 2-furaldehyde,  $\Delta_f H_m^\circ(\text{g}) = -(151.0 \pm 4.6) \text{ kJ} \cdot \text{mol}^{-1}$  [53], and furan,  $\Delta_f H_m^\circ(\text{g}) = -(34.8 \pm 0.7) \text{ kJ} \cdot \text{mol}^{-1}$  [53] allows us to estimate the standard molar enthalpy of formation of 2,3-dimethylfuran as,  $\Delta_f H_m^\circ(\text{g}) = -(120.6 \pm 5.0) \text{ kJ} \cdot \text{mol}^{-1}$ , as shown in scheme 5, which is in agreement with the estimated value obtained above.

Previously [2], from the 2- to 3-isomerisation enthalpy of acetylpyridine  $-(6.1 \pm 4.0) \text{ kJ} \cdot \text{mol}^{-1}$ , and the 2- to 3-isomerisation of acetylthiophene  $-(4.7 \pm 2.8) \text{ kJ} \cdot \text{mol}^{-1}$ , we have estimated the standard molar enthalpy of formation of 3-acetylfuran in the gaseous phase as  $(201 \text{ to } 202) \text{ kJ} \cdot \text{mol}^{-1}$ , from comparison with the corresponding value of  $\Delta_f H_m^\circ(2\text{-acetylfuran, g}) = -(207.4 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ . This estimated value is in agreement to the estimated





**Scheme 5.** Estimation of the standard molar enthalpy of formation of 2,3-dimethylfuran (all values in  $\text{kJ} \cdot \text{mol}^{-1}$ ).



**Scheme 6.** Estimation of the standard molar enthalpy of formation of 3-acetylfuran (all values in  $\text{kJ} \cdot \text{mol}^{-1}$ ).

value,  $\Delta_f H_m^\circ(3\text{-acetylfuran, g}) = -(201.3 \pm 2.6) \text{ kJ} \cdot \text{mol}^{-1}$  obtained from the literature values of 2,5-dimethylfuran,  $\Delta_f H_m^\circ(\text{g}) = -(128.13 \pm 0.98) \text{ kJ} \cdot \text{mol}^{-1}$  [55], furan,  $\Delta_f H_m^\circ(\text{g}) = -(34.8 \pm 0.7) \text{ kJ} \cdot \text{mol}^{-1}$  [53] and the value of 3-acetyl-2,5-dimethylfuran obtained in this work, as shown in scheme 6.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jct.2010.07.006](https://doi.org/10.1016/j.jct.2010.07.006).

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