

# Thermochemistry of hydroxymethylphenol isomers

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Portuguese Special Chapter

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**Abstract** The standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation in the crystalline state of the 2-, 3- and 4-hydroxymethylphenols,  $\Delta_f H_m^\circ(\text{cr}) = -(377.7 \pm 1.4)$  kJ mol $^{-1}$ ,  $\Delta_f H_m^\circ(\text{cr}) = -(383.0 \pm 1.4)$  kJ mol $^{-1}$  and  $\Delta_f H_m^\circ(\text{cr}) = -(382.7 \pm 1.4)$  kJ mol $^{-1}$ , respectively, were derived from the standard molar energies of combustion, in oxygen, to yield CO $_2$ (g) and H $_2$ O(l), at  $T = 298.15$  K, measured by static bomb combustion calorimetry. The Knudsen mass-loss effusion technique was used to measure the dependence of the vapour pressure of the solid isomers of hydroxymethylphenol with the temperature, from which the standard molar enthalpies of sublimation were derived using the Clausius–Clapeyron equation. The results were as follows:  $\Delta_{\text{cr}}^\circ H_m^\circ = (99.5 \pm 1.5)$  kJ mol $^{-1}$ ,  $\Delta_{\text{cr}}^\circ H_m^\circ = (116.0 \pm 3.7)$  kJ mol $^{-1}$  and  $\Delta_{\text{cr}}^\circ H_m^\circ = (129.3 \pm 4.7)$  kJ mol $^{-1}$ , for 2-, 3- and 4-hydroxymethylphenol, respectively. From these values, the standard molar enthalpies of formation of the title compounds in their gaseous phases, at  $T = 298.15$  K, were derived and interpreted in terms of molecular structure. Moreover, using estimated values for the heat capacity differences between the gas and the crystal phases, the standard ( $p^\circ = 0.1$  MPa) molar enthalpies, entropies and Gibbs energies of sublimation, at  $T = 298.15$  K, were derived for the three hydroxymethylphenols.

**Keywords** Energy of combustion · Enthalpy of sublimation · Enthalpy of formation · Combustion calorimetry · Knudsen effusion technique · Vapour

pressure · Entropy of sublimation · Gibbs energy of sublimation · Hydroxymethylphenol isomers

## Introduction

This work presents a thermochemical study of the hydroxymethylphenol isomers, which is a part of our broad interest on the thermochemistry of phenol derivatives, a class of chemical compounds that has generated continuing interest in the last century since they include a large number of synthetic and naturally occurring antioxidants, which play a major role in the chemistry of living organisms and life-supporting substances [1–3]. There are quite a few reports in the literature about the energetics and the thermochemistry of several phenol derivatives, namely, 4-nitrosophenol [4], *tert*-butyl- and di-*tert*-butylphenols [5, 6], cyanophenols [7], mono-, di- and trimethoxyphenols [8, 9], methoxynitrophenols [10]. For halogenated phenols, thermochemical parameters have been reported for pentafluorophenol [11], pentachlorophenol [12], chloronitrophenol isomers [13], cyanophenol and cyanothiophenol isomers [14], as well as for the mono- and dichlorophenol isomers [15, 16] and monofluorophenol isomers [17].

Hydroxymethylphenols, also known as hydroxybenzyl alcohol, are used as starting materials for the production of adhesives for manufacturing composite wood materials for structural use [18–20]. In 1920, Hirschfelder, Lundholm and Norrgaard [21] have shown that 2-hydroxymethylphenol (saligenin) possesses valuable properties as a local anaesthetic [22]. The 2-hydroxymethylphenol is also used in the synthesis of hirsutene [23], a triquinane metabolite isolated from Basidiomycete *Coriolus consors* [24], which can be used as biogenetic precursor to antibiotic and/or antitumor compounds. The salicin (2-(hydroxymethyl)

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phenyl- $\beta$ -D-glucopyranoside), which is an antirheumatic and analgetic drug [25], is enzymatically hydrolyzed by  $\beta$ -glucosidase to glucose and 2-hydroxymethylphenol, which is then slowly oxidized in the blood and in the liver to salicylic acid, well-known for their analgesic and antipyretic properties [1, 25].

The experimental determination of the standard ( $p^\circ = 0.1$  MPa) molar energies of combustion, in oxygen, at  $T = 298.15$  K, of the three hydroxymethylphenols, was done by static bomb combustion calorimetry, and the vapour pressures of the crystalline samples were measured at several temperatures, using the Knudsen mass-loss effusion technique. From the temperature dependence of the vapour pressure, the molar enthalpies and entropies of sublimation, at the mean temperature of the experimental temperature range, were derived. The standard molar enthalpies, entropies and Gibbs energies of sublimation, at  $T = 298.15$  K, were calculated estimating the heat capacity differences between the gas and the crystal phases for each compound.

From the experimental values of the standard molar enthalpies of formation, in the condensed phase, and the values of the standard molar enthalpies of sublimation, at  $T = 298.15$  K, the standard molar enthalpies of formation, in the gaseous phase, were derived for the three compounds.

## Experimental section

### Materials and purity control

2-Hydroxymethylphenol, CAS [2444-36-2], 3-hydroxymethylphenol, CAS [1878-65-5], and 4-hydroxymethylphenol, CAS [1878-66-6], were commercially obtained from Aldrich Chemical Co. with the assessed minimum purity of 0.99 (mass fraction). They were purified by successive vacuum sublimations at 0.1 Pa background pressure, and their final purity was checked by gas chromatography (Agilent 4890D), and also by the consistent results obtained from the combustion experiments, as well as by the closeness to unity of the carbon dioxide recovery ratios. The average ratio of the mass of carbon dioxide recovered after combustion to that calculated from the mass of sample of 2-, 3- and 4-hydroxymethylphenol were  $(0.99979 \pm 0.00030)$ ,  $(0.99972 \pm 0.00028)$  and  $(0.99983 \pm 0.00039)$ , respectively, where the uncertainty is the standard deviation of the mean.

The specific density used to calculate the true mass from the apparent mass in air, of the 3-hydroxymethylphenol was  $\rho = 1.325$  g cm<sup>-3</sup> [26], and for the 2- and 4-hydroxymethylphenol, the specific densities were determined as  $\rho = 1.27$  g cm<sup>-3</sup> and  $\rho = 1.17$  g cm<sup>-3</sup>, respectively,

estimated from the mass and the dimensions of pellets of the crystalline compounds, made in vacuum, with an applied pressure of  $10^5$  kg cm<sup>-2</sup>.

The relative atomic masses used in the calculation of all molar quantities throughout this article were those recommended by the IUPAC Commission in 2005 [27]; using those values, the molar mass for the 2-, 3- and 4-hydroxymethylphenol isomers is 124.1379 g mol<sup>-1</sup>.

### Combustion calorimetry measurements

The energies of combustion of the title compounds were measured using an isoperibolic static bomb calorimeter previously described [28, 29], with a twin valve combustion bomb Type 1105, Parr Instrument Company, made of stainless steel, with an internal volume of 0.340 dm<sup>3</sup>.

The calorimetric system was calibrated using benzoic acid (NIST Standard Reference Material 39j), having a massic energy of combustion under bomb conditions of  $-(26434 \pm 3)$  J g<sup>-1</sup>. Six calibration experiments were made in oxygen, at  $p = 3.04$  MPa, with 1.00 cm<sup>3</sup> of water added to the bomb, according to the procedure suggest by Coops et al. [30], leading to the value of the energy equivalent of the calorimeter:  $\varepsilon(\text{calor}) = (15905.72 \pm 0.96)$  J K<sup>-1</sup>, for the combustion experiments of the 3-hydroxymethylphenol, and  $\varepsilon(\text{calor}) = (15917.4 \pm 1.4)$  J K<sup>-1</sup> for the 2- and 4-hydroxymethylphenol. The quoted uncertainty refers to the standard deviation of the mean. The calibration results as well as the results of the combustion experiments of the compounds were corrected to give the energy equivalents corresponding to the average mass of water added to the calorimeter (3119.6 g). In all combustion experiments, the bomb was purged twice to remove air, before being charged with 3.04 MPa of oxygen.

The crystalline samples of 2- and 3-hydroxymethylphenol in pellet form were ignited at  $T = (298.150 \pm 0.001)$  K, in oxygen, at a pressure  $p = 3.04$  MPa, with a volume of 1.00 cm<sup>3</sup> of water added to the bomb, whereas in the case of 4-hydroxymethylphenol, the combustion experiments were performed enclosing the pellet of the compound in sealed polyester bags made from Melinex (0.025 mm thickness) using the technique described by Skinner and Snelson [31].

For all experiments, the calorimeter temperatures were measured to  $\pm 10^{-4}$  K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett-Packard HP 2804A), interfaced to a PC programmed to compute the adiabatic temperature change. At least 100 readings were taken for the main period and for both the fore and after periods. Data acquisition and control of the calorimeter were performed using the program LABTERMO [32].

After the combustions, the CO<sub>2</sub> was collected in absorption tubes filled with Carbosorb AS Self-Indicating, previously weighed with a Mettler AT201 balance, sensitivity  $\pm 10^{-5}$  g, and the quantity of nitric acid was determined by titration. From the total mass of carbon dioxide produced, the amount of substance used in each experiment was determined, taken into account that the CO<sub>2</sub> formed from the combustion of the cotton-thread and of the Melinex bags.

The ignition energy was measured by the degree of discharge of a capacitor (1400  $\mu$ F) throughout a platinum wire of 0.05 mm diameter (Goodfellow, mass fraction 0.9999).

For the cotton-thread fuse of empirical formula CH<sub>1.686</sub>O<sub>0.843</sub>,  $\Delta_c u^\circ = -16,240$  J g<sup>-1</sup> [30] and for dry Melinex,  $\Delta_c u^\circ = -(22902 \pm 5)$  J g<sup>-1</sup> [31]; these values have been previously confirmed in our Laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032), and the mass of carbon dioxide produced from it was calculated using the factor previously reported [31]. Corrections for the nitric acid formed were based on  $\Delta_f U_m^\circ(\text{HNO}_3, \text{aq}, 0.1 \text{ mol dm}^{-3}) = -59.7$  kJ mol<sup>-1</sup> [33], from 1/2 N<sub>2</sub>(g), 5/4 O<sub>2</sub>(g) and 1/2 H<sub>2</sub>O(l).

At the end of some experiments performed with 2- and 4-hydroxymethylphenol, a small residue of carbon was found due to incomplete combustion. If the carbon soot formed stayed only on the walls of the platinum crucible, and not in the combustion solution or on the walls of the bomb, an energy correction for the carbon soot was done by weighing the crucible before and after calcinations. Otherwise, the experiments were discarded. Corrections for carbon soot formation were based on the standard massic energy of combustion of carbon,  $\Delta_c u^\circ = -33$  kJ g<sup>-1</sup> [30].

An estimated pressure coefficient of massic energy:  $(\partial u/\partial p)_T = -0.2$  J g<sup>-1</sup> MPa<sup>-1</sup>, at  $T = 298.15$  K, a typical value for most organic compounds [34], was used for all the studied compounds. The standard massic energy of combustion  $\Delta_c u^\circ$ , for the hydroxymethylphenol isomers was calculated considering the procedure given by Hubbard et al. [35]. All the necessary weighings for the combustion experiments were made with a precision of  $\pm 10^{-5}$  g in a Mettler Toledo AE 240 analytical balance, and corrections from apparent mass to true mass were introduced.

### Vapour pressures measurements

The vapour pressures of the crystalline samples of 2-, 3- and 4-hydroxymethylphenols were measured at several temperatures, using the Knudsen mass-loss effusion technique. The apparatus enables the simultaneous operation of nine aluminium effusion cells with three different

effusion orifice diameters, at three different temperatures. The measuring procedure and the detailed description of the apparatus have been recently reported [36], as well as the experimental results obtained during its testing by measuring reference compounds (benzoic acid, phenanthrene, anthracene, benzanthrone, and 1,3,5-triphenylbenzene). For each compound, the measurements were extended through a chosen temperature interval corresponding to measured vapour pressures in the range 0.1–1.0 Pa. In each effusion experiment, in a system evacuated to a pressure near ( $1 \times 10^{-4}$ ) Pa, the loss of mass  $\Delta m$  of the samples, during the convenient effusion time period  $t$ , is determined by weighing the effusion cells to  $\pm 10^{-5}$  g (Mettler Toledo EA 163 balance) before and after the effusion period.

The vapour pressure  $p$  of the crystalline sample contained in each effusion cell is calculated by the equation

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

where  $T$  is the temperature of the effusion experiment,  $A_o$  is the area of the effusion hole,  $R$  is the gas constant ( $R = 8.314472$  J K<sup>-1</sup> mol<sup>-1</sup>),  $M$  is the molar mass of the sample and  $w_o$  is the Clausing probability factor, calculated as

$$w_o = \{1 + [3l/(4\phi)]\}^{-1} \quad (2)$$

where  $l$  is the thickness of the effusion orifice and  $\phi$  is its diameter. There are three different groups of effusion cells, according to their different areas of effusion orifices: series A (small orifices;  $A_o \approx 0.5$  mm<sup>2</sup>), series B (medium orifices;  $A_o \approx 0.8$  mm<sup>2</sup>), series C (large orifices;  $A_o \approx 1.1$  mm<sup>2</sup>). The exact diameters and the Clausing factors of each effusion orifice, made in platinum foil of  $l = 0.0125$  mm thickness, are, respectively, 0.7998 mm and 0.988 (oven 1, small orifice), 0.9924 mm and 0.991 (oven 1, medium orifice), 1.1830 mm and 0.992 (oven 1, large orifice), 0.8050 mm and 0.988 (oven 2, small orifice), 0.9986 mm and 0.991 (oven 2, medium orifice), 1.1970 mm and 0.992 (oven 2, large orifice), 0.8160 mm and 0.988 (oven 3, small orifice), 1.0040 mm and 0.991 (oven 3, medium orifice), and 1.2000 mm and 0.992 (oven 3, large orifice).

## Results

### Experimental enthalpies of formation

Detailed results for all the combustion experiments of each studied compound are given in Tables 1, 2, and 3, together with the mean values of the standard massic energies of combustion,  $\Delta_c u^\circ$ , where  $\Delta m(\text{H}_2\text{O})$  is the deviation of the

**Table 1** Standard massic energy of combustion of 2-Hydroxymethylphenol, at  $T = 298.15$  K

Experiment	1	2	3	4	5	6
$m^*$ (cpd)/g	0.68538	0.69854	0.67734	0.81790	0.74409	0.76818
$m^{**}$ (fuse)/g	0.00334	0.00281	0.00348	0.00252	0.00274	0.00355
$T_i$ /K	298.1494	298.1505	298.1512	298.1513	298.1507	298.1516
$T_f$ /K	299.4822	299.5076	299.4696	299.7067	299.5798	299.6202
$\Delta T_{ad}$ /K	1.22376	1.24700	1.20962	1.45873	1.32708	1.37003
$\varepsilon_i$ /J K <sup>-1</sup>	15.34	15.41	15.20	15.56	15.47	15.50
$\varepsilon_f$ /J K <sup>-1</sup>	16.23	16.33	16.08	16.65	16.54	16.60
$\varepsilon(\text{calor})_{\text{corr.}}$ /J K <sup>-1</sup>	15917.4	15917.4	15917.4	15917.4	15917.4	15917.4
$\Delta m(\text{H}_2\text{O})$ /g	0.0	0.0	0.0	0.0	0.0	0.0
$-\Delta U(\text{IBP})^a$ /J	19497.82	19868.44	19272.43	23242.45	21144.66	21829.19
$\Delta U(\text{fuse})$ /J	54.24	45.63	56.52	40.92	44.50	57.65
$\Delta U(\text{HNO}_3)$ /J	10.58	9.40	10.55	10.13	0.68	1.18
$\Delta U(\text{ign})$ /J	1.11	0.93	1.05	1.05	0.96	0.89
$\Delta U(\text{Carb.})$ /J	0.00	0.00	1.98	0.00	0.00	0.00
$\Delta U_{\Sigma}$ /J	11.98	12.24	11.83	14.60	13.12	13.60
$-\Delta_c u^0$ /J g <sup>-1</sup>	28336.13	28346.51	28339.55	28336.96	28338.45	28322.48
$-\langle \Delta_c u^0 \rangle = (28336.7 \pm 3.2) \text{ J g}^{-1}$						

$$^a \Delta U(\text{IBP}) = -\{\varepsilon_{\text{calor}} + c_p(\text{H}_2\text{O}, \text{l}) \bullet \Delta m(\text{H}_2\text{O}, \text{l}) + \varepsilon_f\} \bullet \Delta T_{ad} + \Delta U(\text{ign})$$

$m^*$ (cpd) is the mass of compound burnt in each experiment;  $m^{**}$ (fuse) is the mass of fuse (cotton) used in each experiment;  $T_i$  is the initial temperature rise;  $T_f$  is the final temperature rise;  $\Delta T_{ad}$  is the corrected temperature rise;  $\varepsilon_i$  is the energy equivalent of the contents in the initial state;  $\varepsilon_f$  is the energy equivalent of the contents in the final state;  $\varepsilon(\text{calor})_{\text{corr.}}$  is the corrected energy equivalent of the calorimeter for the amount of water used;  $\Delta m(\text{H}_2\text{O})$  is the deviation of mass of water added to the calorimeter from 3119.6 g;  $\Delta U(\text{IBP})$  is the energy change for the isothermal combustion reaction under actual bomb conditions;  $\Delta U(\text{fuse})$  is the energy of combustion of the fuse (cotton);  $\Delta U(\text{Melinex})$  is the energy of combustion of Melinex;  $\Delta U(\text{HNO}_3)$  is the energy correction for the nitric acid formation;  $\Delta U(\text{ign})$  is the electrical energy for ignition;  $\Delta U_{\Sigma}$  is the standard state correction;  $\Delta_c u^0$  is the standard massic energy of combustion

**Table 2** Standard massic energy of combustion of 3-Hydroxymethylphenol, at  $T = 298.15$  K

Experiment	1	2	3	4	5	6
$m^*$ (cpd)/g	0.78121	0.66561	0.62566	0.64290	0.66855	0.61035
$m^{**}$ (fuse)/g	0.00261	0.00252	0.00278	0.00297	0.00279	0.00287
$T_i$ /K	298.1645	298.1500	298.1522	298.1505	298.1509	298.1502
$T_f$ /K	299.6647	299.4441	299.3786	299.4107	299.4507	299.3557
$\Delta T_{ad}$ /K	1.39230	1.18715	1.11573	1.14685	1.19166	1.08878
$\varepsilon_i$ /J K <sup>-1</sup>	15.51	15.37	15.26	15.34	15.32	15.24
$\varepsilon_f$ /J K <sup>-1</sup>	16.53	16.23	16.07	16.17	16.27	16.12
$\varepsilon(\text{calor})_{\text{corr.}}$ /J K <sup>-1</sup>	15905.7	15905.7	15905.7	15905.7	15905.7	15905.7
$\Delta m(\text{H}_2\text{O})$ /g	0.0	0.0	0.0	0.0	0.0	0.0
$-\Delta U(\text{IBP})^a$ /J	22167.57	18900.61	17763.47	18258.89	18972.61	17334.41
$\Delta U(\text{fuse})$ /J	42.39	40.92	45.15	48.23	45.31	46.61
$\Delta U(\text{HNO}_3)$ /J	11.83	10.03	9.40	10.26	1.84	0.88
$\Delta U(\text{ign})$ /J	1.19	1.11	0.96	1.11	0.98	0.95
$\Delta U_{\Sigma}$ /J	13.88	11.60	10.82	11.16	11.64	10.52
$-\Delta_c u^0$ /J g <sup>-1</sup>	28288.80	28301.95	28287.09	28292.49	28290.81	28305.73
$-\langle \Delta_c u^0 \rangle = (28294.5 \pm 3.1) \text{ J g}^{-1}$						

$$^a \Delta U(\text{IBP}) = -\{\varepsilon_{\text{calor}} + c_p(\text{H}_2\text{O}, \text{l}) \bullet \Delta m(\text{H}_2\text{O}, \text{l}) + \varepsilon_f\} \bullet \Delta T_{ad} + \Delta U(\text{ign})$$

mass of water added to the calorimeter and the mass assigned to  $\varepsilon(\text{calor})$ : 3119.6 g,  $\Delta U_{\Sigma}$  is the energy correction to the standard state and the remaining terms are as

previously defined [34, 35]. The values of the internal energy associated with the isothermal bomb process,  $\Delta U(\text{IBP})$ , were calculated using the expression (3):

**Table 3** Standard massic energy of combustion of 4-Hydroxymethylphenol, at  $T = 298.15$  K

Experiment	1	2	3	4	5	6
$m^*(\text{cpd})/\text{g}$	0.54536	0.82492	0.60543	0.66582	0.51058	0.40827
$m^{**}(\text{fuse})/\text{g}$	0.00248	0.00277	0.00259	0.00280	0.00338	0.00279
$m^{***}(\text{Melinex})$	0.04148	0.04177	0.04092	0.04246	0.04317	0.04371
$T_i/\text{K}$	298.1507	298.1538	298.1518	298.1509	298.1501	298.1509
$T_f/\text{K}$	299.3018	299.7758	299.3971	299.5022	299.2386	299.0729
$\Delta T_{\text{ad}}/\text{K}$	1.03165	1.52949	1.13704	1.24742	0.97325	0.79010
$\varepsilon_i/\text{J K}^{-1}$	15.26	15.56	15.33	15.36	15.22	15.08
$\varepsilon_f/\text{J K}^{-1}$	16.08	16.74	16.21	16.33	15.94	15.70
$\varepsilon(\text{calor})_{\text{corr.}}/\text{J K}^{-1}$	15917.4	15917.4	15917.4	15917.4	15917.4	15917.4
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.0	0.0	0.0	0.0	0.0	0.0
$-\Delta U(\text{IBP})^a/\text{J}$	16436.97	24370.33	18116.23	19875.18	15506.27	12587.87
$\Delta U(\text{fuse})/\text{J}$	40.28	44.98	42.06	45.47	54.89	45.31
$\Delta U(\text{Melinex})$	949.88	956.51	937.09	972.50	988.72	1001.06
$\Delta U(\text{HNO}_3)/\text{J}$	0.33	5.56	3.62	3.46	5.00	0.95
$\Delta U(\text{ign})/\text{J}$	0.82	0.84	0.95	0.89	0.85	0.89
$\Delta U(\text{Carb.})/\text{J}$	0.00	0.00	0.00	0.00	0.00	19.14
$\Delta U_{\Sigma}/\text{J}$	10.11	15.64	11.25	12.46	9.53	7.64
$-\Delta_c u^0/\text{J g}^{-1}$	28304.92	28302.91	28281.07	28297.87	28297.49	28295.12
$-\langle \Delta_c u^0 \rangle = (28296.6 \pm 3.4) \text{ J g}^{-1}$						

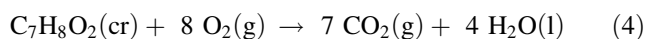
$$^a \Delta U(\text{IBP}) = -\{\varepsilon_{\text{calor}} + c_p(\text{H}_2\text{O}, \text{l}) \cdot \Delta m(\text{H}_2\text{O}, \text{l}) + \varepsilon_f\} \cdot \Delta T_{\text{ad}} + \Delta U(\text{ign})$$

**Table 4** Derived standard molar energies of combustion,  $\Delta_c U_m^0$ , standard molar enthalpies of combustion,  $\Delta_c H_m^0$  and standard molar enthalpies of formation,  $\Delta_f H_m^0$ , in the condensed phase, for the hydroxymethylphenol isomers at  $T = 298.15$  K, with  $p^0 = 0.1$  MPa

Compound	$-\Delta_c U_m^0(\text{cr})/\text{kJ mol}^{-1}$	$-\Delta_c H_m^0(\text{cr})/\text{kJ mol}^{-1}$	$-\Delta_f H_m^0(\text{cr})/\text{kJ mol}^{-1}$
2-Hydroxymethylphenol (cr)	$3517.7 \pm 1.1$	$3520.2 \pm 1.1$	$377.7 \pm 1.4$
3-Hydroxymethylphenol (cr)	$3512.4 \pm 1.1$	$3514.9 \pm 1.1$	$383.0 \pm 1.4$
4-Hydroxymethylphenol (cr)	$3512.7 \pm 1.1$	$3515.2 \pm 1.1$	$382.7 \pm 1.4$

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

where  $\Delta T_{\text{ad}}$  is the calorimeter temperature change corrected for the heat exchange and the work of stirring (adiabatic temperature rise),  $\varepsilon(\text{calor})_{\text{corr.}} = \varepsilon_{\text{calor}} + c_p(\text{H}_2\text{O}, \text{l}) \times \Delta m(\text{H}_2\text{O}, \text{l})$ . The values of  $\Delta_c u^0$  referred to the combustion reactions described by Eq. 4:



and lead to the corresponding standard molar enthalpies of formation in the condensed phase, at  $T = 298.15$  K, presented in Table 4 using  $\Delta_f H_m^0(\text{CO}_2, \text{g}) = -(393.51 \pm 0.13) \text{ kJ mol}^{-1}$  [37] and  $\Delta_f H_m^0(\text{H}_2\text{O}, \text{l}) = -(285.830 \pm 0.040) \text{ kJ mol}^{-1}$  [37]. The uncertainties assigned to the standard molar energies  $\Delta_c U_m^0(\text{cr})$  and enthalpies of combustion,  $\Delta_c H_m^0$ , are twice the overall standard deviation of the mean and include the uncertainties in calibration and in

the values of auxiliary quantities used, in conformity with the normal thermochemical practice [38, 39].

The integrated form of the Clausius–Clapeyron equation,  $\ln(p/\text{Pa}) = a - b \times (K/T)$ , where  $a$  is a constant and  $b = \Delta_{\text{cr}}^{\text{g}} H_m^0(\langle T \rangle)/R$ , was used to derive the standard molar enthalpies of sublimation at the mean temperature  $\langle T \rangle$  of the experimental temperature range. Table 5 presents, for each compound and for each effusion orifice used, the experimental results obtained for the hydroxymethylphenol isomers, together with the residuals of the Clausius–Clapeyron equation, derived from least squares adjustment.

For each compound, the calculated enthalpies of sublimation obtained from each individual hole are in agreement within experimental uncertainty. Table 6 presents for each hole used and for the global treatment of all ( $p$ ,  $T$ ) points, for each isomer of hydroxymethylphenol, the parameters of the Clausius–Clapeyron equation together with the calculated standard deviations and the standard

**Table 5** Knudsen-effusion results for the isomers of hydroxymethylphenol for small, medium and large orifices

Oven	$T/K$	Effusion Time/s	$p/\text{Pa}$			$10^2 \Delta \ln(p/\text{Pa})$		
			Small	Medium	Large	Small	Medium	Large
<i>2-Hydroxymethylphenol</i>								
O3	304.22	28982	0.146	0.141	0.137	0.3	-0.5	-0.1
O2	306.18	28982	0.187	0.186	0.176	0.1	2.0	-0.1
O1	308.10	28982	0.241	0.231	0.227	0.9	-0.2	1.1
O3	310.22	21694	-	0.299	0.292	-	-1.0	-0.1
O2	312.19	21694	0.385	0.382	0.369	-2.5	-0.4	-0.6
O1	314.11	21694	0.503	0.483	0.469	0.8	-0.5	0.1
O3	316.21	10963	0.640	0.619	0.595	-0.2	-0.9	-1.3
O2	318.17	10963	0.801	0.795	0.757	-0.9	1.0	-0.2
O1	320.10	10963	1.026	0.991	0.962	1.4	0.5	1.2
<i>3-Hydroxymethylphenol</i>								
O3	324.20	29157	0.115	0.116	0.117	-0.8	-1.8	-1.1
O2	326.17	29157	0.153	0.156	0.152	1.2	1.9	-0.4
O1	328.12	29157	0.199	0.197	0.198	2.3	0.7	1.0
O3	330.19	23892	0.248	0.255	0.252	-2.5	0.1	-0.9
O2	332.14	23892	0.324	0.322	0.321	-0.4	-0.4	-1.0
O1	334.12	23892	0.424	0.414	0.415	1.5	0.2	0.4
O3	336.20	14573	0.524	0.529	0.525	-3.2	-0.4	-1.2
O2	338.14	14573	0.684	0.656	-	-0.4	-2.3	-
O1	340.12	14573	0.892	0.865	0.845	-0.8	2.0	-0.4
<i>4-Hydroxymethylphenol</i>								
O3	333.20	29171	0.064	0.061	0.061	-1.0	-3.1	-0.3
O2	335.21	29171	0.082	0.083	0.081	-3.0	0.6	0.3
O1	337.14	29171	0.114	0.109	0.106	3.3	1.4	1.5
O3	339.19	22081	0.145	0.142	0.136	0.2	0.9	-1.0
O2	341.25	22081	-	0.181	0.178	-	-1.8	-1.6
O1	343.19	22081	0.255	0.246	0.232	3.9	3.7	0.1
O3	345.20	11835	0.310	0.314	0.303	-2.4	2.3	0.9
O2	347.13	11835	0.410	-	0.384	0.8	-	0.0
O1	349.17	11835	0.515	0.487	-	-1.9	-3.9	-

The equilibrium vapour pressure is denoted by  $p$ , and the deviations of experimental results from those given by the Clausius–Clapeyron equation are denoted by  $\Delta \ln(p/\text{Pa})$

molar enthalpies of sublimation at the mean temperature  $\langle T \rangle$ . These results are in agreement within experimental uncertainty. The equilibrium pressures at the mean temperature,  $p(\langle T \rangle)$ , and the entropies of sublimation at equilibrium conditions,  $\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}(\langle T \rangle, p(\langle T \rangle))$ , calculated as  $\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}(\langle T \rangle, p(\langle T \rangle)) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}}(\langle T \rangle) / \langle T \rangle$ , are also presented in Table 6. Figure 1 shows the plots of  $\ln p = f(1/T)$  for the global results obtained for each compound.

Table 7 lists the  $(p, T)$  values calculated from the  $(p, T)$  equations for the three crystalline compounds within the experimental range of pressures used (0.1–1 Pa). The standard molar enthalpies of sublimation, at  $T = 298.15$  K,

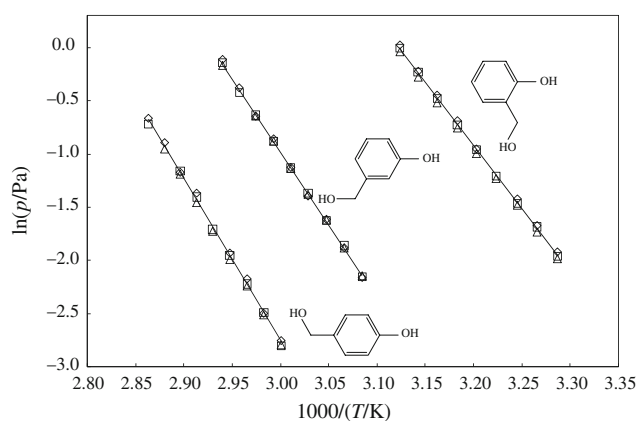
were derived from the sublimation enthalpies calculated at the mean temperature  $\langle T \rangle$  using the relation

$$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}}(\langle T \rangle) + \Delta_{\text{cr}}^{\text{g}} C_{p,\text{m}}^{\text{o}} \times (298.15 \text{ K} - \langle T \rangle), \quad (5)$$

where  $\Delta_{\text{cr}}^{\text{g}} C_{p,\text{m}}^{\text{o}} = C_{p,\text{m}}^{\text{o}}(\text{g}) - C_{p,\text{m}}^{\text{o}}(\text{cr})$ . For the isomers of hydroxymethylphenol,  $\Delta_{\text{cr}}^{\text{g}} C_{p,\text{m}}^{\text{o}}$  was estimated as  $-50 \text{ J mol}^{-1} \text{ K}^{-1}$ , in accordance with similar estimations made by other authors [40], which we have already used in previous articles for other organic compounds [41–47]. The obtained standard molar enthalpies, entropies and Gibbs energies of sublimation, at  $T = 298.15$  K, of for each

**Table 6** Experimental results for the studied compounds where,  $a$  and  $b$  are from Clausius–Clapeyron equation  $\ln(p/\text{Pa}) = a - b \times (K/T)$  and  $b = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T \rangle)/R$ ;  $R = 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$ 

Orifices	$a$	$b$	$r^2$	$\langle T \rangle/\text{K}$	$p(\langle T \rangle)/\text{Pa}$	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T \rangle)/\text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}(\langle T \rangle, p(\langle T \rangle))/\text{J K}^{-1} \text{ mol}^{-1}$
<i>2-Hydroxymethylphenol</i>							
Small	$37.11 \pm 0.27$	$11876 \pm 83$	0.9997	312.16	0.586	$98.7 \pm 0.7$	$316.2 \pm 2.2$
Medium	$37.14 \pm 0.21$	$11895 \pm 67$	0.9998	312.16	0.566	$98.9 \pm 0.6$	$316.8 \pm 1.8$
Large	$36.99 \pm 0.17$	$11854 \pm 52$	0.9999	312.16	0.550	$98.6 \pm 0.4$	$315.8 \pm 1.4$
Global results	$37.10 \pm 0.32$	$11883 \pm 101$	0.9983	312.16	0.582	$98.8 \pm 0.8$	$316.5 \pm 2.7$
<i>3-Hydroxymethylphenol</i>							
Small	$40.90 \pm 0.45$	$13958 \pm 150$	0.9992	332.16	0.504	$116.1 \pm 1.3$	$349.5 \pm 3.9$
Medium	$39.91 \pm 0.34$	$13631 \pm 112$	0.9995	332.16	0.491	$113.3 \pm 0.9$	$341.1 \pm 2.7$
Large	$39.88 \pm 0.20$	$13622 \pm 67$	0.9999	332.16	0.481	$113.3 \pm 0.6$	$341.1 \pm 1.8$
Global results	$40.26 \pm 0.22$	$13748 \pm 72$	0.9993	332.16	0.504	$114.3 \pm 0.6$	$344.1 \pm 1.8$
<i>4-Hydroxymethylphenol</i>							
Small	$43.21 \pm 0.62$	$15314 \pm 210$	0.9989	341.18	0.289	$127.3 \pm 1.7$	$373.1 \pm 5.0$
Medium	$42.85 \pm 0.70$	$15200 \pm 239$	0.9985	341.18	0.274	$126.4 \pm 2.0$	$370.5 \pm 5.9$
Large	$42.84 \pm 0.28$	$15203 \pm 96$	0.9998	341.18	0.223	$126.4 \pm 0.8$	$370.5 \pm 2.3$
Global results	$43.10 \pm 0.42$	$15283 \pm 144$	0.9980	341.18	0.288	$127.1 \pm 1.2$	$372.5 \pm 3.5$

**Fig. 1** Plots of  $\ln(p/\text{Pa}) = f(1/T)$  for each isomer of hydroxymethylphenol. *Open diamond*: small orifices, *Open square*: medium orifices and *Open triangle*: large orifices

isomer, together with the calculated vapour pressure of the pure compound at the same reference temperature, are presented in Table 8. The standard molar enthalpies of formation, in the gaseous phase, at  $T = 298.15 \text{ K}$ , derived from the experimental values of the standard molar enthalpies of

formation, in the crystalline phase and from the values of the standard molar enthalpies of sublimation, are summarized in Table 9.

## Discussion

The experimental results obtained for the standard molar enthalpies of formation in the gas-phase of the three studied compounds (Table 9), clearly expose that the 2-hydroxymethylphenol is rather enthalpically more stable when compared with the other two isomeric hydroxymethylphenols.

Therefore, the insertion of a  $-\text{CH}_2\text{OH}$  group in the aromatic ring of phenol creates an enthalpic effect of stabilization higher in *ortho*- > *meta*- > *para*-position, with a difference of  $(24.8 \pm 5.3) \text{ kJ mol}^{-1}$  between the least and the more stable isomer. The stabilization effect verified for the 2-hydroxymethylphenol results from the formation of an internal hydrogen bond between the oxygen atom of the  $-\text{CH}_2\text{OH}$  group and the hydrogen atom of the hydroxyl group [1, 48].

**Table 7** The  $(p/T)$  values from the vapour pressure and temperature relation determined for 2-, 3- and 4-hydroxymethylphenol isomers

$p/\text{Pa}$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$T/\text{K}$										
2-Hydroxymethylphenol	301.58	306.98	310.23	312.58	314.42	315.95	317.25	318.38	319.39	320.30
3-Hydroxymethylphenol	323.01	328.35	331.56	333.88	335.70	337.20	338.48	339.60	340.59	341.48
4-Hydroxymethylphenol	336.61	341.83	344.96	347.21	348.98	350.44	351.68	352.77	353.73	354.59

**Table 8** Standard molar enthalpy, entropy and Gibbs energy of sublimation and vapour pressure at  $T = 298.15$  K, for 2-, 3- and 4-hydroxymethylphenol

Compound	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ} / \text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^{\circ} / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}} G_{\text{m}}^{\circ} / \text{kJ mol}^{-1}$	$p / \text{Pa}$
2-Hydroxymethylphenol	$99.5 \pm 1.5$	$218.6 \pm 2.7$	$34.3 \pm 1.7$	$(1.2 \pm 0.8) \times 10^{-1}$
3-Hydroxymethylphenol	$116.0 \pm 3.7$	$248.1 \pm 2.2$	$42.0 \pm 3.8$	$(1.1 \pm 1.0) \times 10^{-2}$
4-Hydroxymethylphenol	$129.3 \pm 4.7$	$273.2 \pm 3.8$	$47.8 \pm 4.9$	$(1.5 \pm 1.5) \times 10^{-3}$

**Table 9** Standard ( $p^{\circ} = 0.1$  MPa) molar enthalpies of formation  $\Delta_{\text{f}} H_{\text{m}}^{\circ}$  and of sublimation  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}$ , at  $T = 298.15$  K

Compound	$-\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{cr}) / \text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ} / \text{kJ mol}^{-1}$	$-\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{g}) / \text{kJ mol}^{-1}$
2-Hydroxymethylphenol	$377.7 \pm 1.4$	$99.5 \pm 1.5$	$278.2 \pm 2.1$
3-Hydroxymethylphenol	$383.0 \pm 1.4$	$116.0 \pm 3.7$	$267.0 \pm 4.0$
4-Hydroxymethylphenol	$382.7 \pm 1.4$	$129.3 \pm 4.7$	$253.4 \pm 4.9$

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