# Supplementary Materials

# Energetic and Structural Studies of Two Biomass-Derived Compounds: 6- and 7-hydroxy-1-indanones

**Ana L. R. Silva,* and Maria D. M. C. Ribeiro da Silva**

Research Center in Chemistry-CIQUP, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal; mdsilva@fc.up.pt

* Correspondence: analuisa.rs@fc.up.pt

**This supplementary information includes:**

- data of all the combustion calorimetry experiments of 6-hydroxy-1-indanone and 7-hydroxy-1-indanone (**Tables S1 and S2**);

- the values of standard molar heat capacities in the gaseous phase for the compounds studied (**Table S3 and S4**);

- Conformational analysis of the hydroxy-1-indanones studied and their corresponding total electronic energy plus the internal thermal energy (**Table S5**);

- G3(MP2)//B3LYP results for 6HI and 7HI conformers (**Table S6**);

- G3(MP2)//B3LYP calculated absolute enthalpies, at $T$ = 298.15 K, and experimental gas-phase values for all the atoms/molecules used (**Table S7**).

**Acronyms used throughout this supplementary data:**

**6HI** for 6- hydroxy-1-indanone
**7HI** for 7-hydroxy-1-indanone

**Combustion Calorimetry:**

The calibration experiments were made in an oxygen atmosphere at $p$ = 3.04 MPa, with 1.00 cm$^3$ of deionized water added to the bomb; the energy equivalent of the calorimeter was determined from the combustion of benzoic acid (NIST SRM 39j) having a massic energy of combustion, under standard bomb conditions, of –(26434 ± 3) J.g$^{-1}$. From six calibration experiments $\varepsilon_{\mathrm{cal}}$ = (16002.6 ± 1.7) J K$^{-1}$, for an average mass of water added to the calorimeter of 3119.6 g; the mentioned uncertainty is the standard deviation of the mean.

Samples of both compounds were burnt in pellet form, with a small amount of nhexadecane, as auxiliary of combustion, under oxygen at $p$ = 3.04 MPa, with 1.00 cm$^3$ of deionised water added to the bomb;

The calorimeter temperatures were measured to ±(1×10$^{-4}$) K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett-Packard HP 2804 A), interfaced to a PC; the ignition occurs at $T$ = (298.150 ± 0.001) K;

n-Hexadecane (Aldrich, mass fraction > 0.999), stored under nitrogen was used as auxiliary combustion. The massic energy of combustion of the sample used, was determined in our laboratory as $\Delta_c u^\circ = -(47136.7 \pm 2.3)$ J.g$^{-1}$;

The cotton thread fuse (empirical formula: $CH_{1.686}O_{0.843}$) had a standard massic energy of combustion [S1], $\Delta_c u^\circ = -16240$ J.g$^{-1}$;

The ignition energy was determined from the change in potential difference on discharge of a 1400 F condenser across a platinum wire;

Pressure coefficient of specific energy $(\partial u/\partial p)_T = -0.2$ J.g$^{-1}$.MPa$^{-1}$ (typical value for organic compounds [S2]);

The nitric acid formed in the calorimetric experiments was determined using Devarda's alloy method [S3] and the energy correction for the formation of 0.1 mol.dm$^{-3}$ $HNO_3$(aq) [S4] from $N_2$ (g), $O_2$ (g) and $H_2O$ (l) was based on −59.7 kJ.mol$^{-1}$;

Corrections for carbon formation relied on the standard massic energy of combustion of carbon [S5], $\Delta_c u^\circ = -32.76$ kJ.g$^{-1}$.

Specific density of the studied compounds at $T = 298.15$ K:

$\rho = 1.305$ g cm$^{-3}$ for **6HI** and **7HI** [S6];

For both isomers, the value of the massic heat capacity, at $T = 298.15$ K, was calculated as 1.251 J.K$^{-1}$.g$^{-1}$ using Kopp's rule [S7].

**Table S1.** Standard ($p^{o}$ = 0.1 MPa) mass energy of combustion of crystalline **6HI**, at $T$ = 298.15 K.

| | | | | | | |
|---|---|---|---|---|---|---|
| $m(CO_2$, total) /g | 1.19849 | 1.26901 | 1.26883 | 1.47623 | 1.57394 | 1.36481 |
| $m$(cpd) /g | 0.29270 | 0.33901 | 0.28455 | 0.43000 | 0.42348 | 0.37995 |
| $m$(fuse) /g | 0.00241 | 0.00298 | 0.00259 | 0.00269 | 0.00257 | 0.00244 |
| $m$(n-hexadec.) /g | 0.13252 | 0.11509 | 0.16206 | 0.10402 | 0.14088 | 0.11099 |
| $T_i$ /K | 298.1507 | 298.1583 | 298.1504 | 298.1506 | 298.1511 | 298.1584 |
| $T_f$ /K | 299.1597 | 299.2012 | 299.2272 | 299.3179 | 299.4124 | 299.2596 |
| $\Delta T_{ad}$ /K | 0.92660 | 0.96091 | 0.99929 | 1.09238 | 1.18980 | 1.02233 |
| $_f$ /(J·K$^{-1}$) | 15.97 | 15.99 | 16.12 | 16.15 | 16.34 | 16.07 |
| $\Delta m(H_2O)$ /g | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $-\Delta U$(IBP) /J | 14841.61 | 15391.22 | 16006.59 | 17497.87 | 19058.74 | 16375.66 |
| $\Delta U(HNO_3)$ /J | 0.85 | 0.52 | 0.78 | 0.54 | 0.90 | 0.40 |
| $\Delta U$(ign) /J | 1.20 | 1.20 | 0.76 | 0.69 | 0.59 | 0.71 |
| $\Delta U_{\Sigma}$ /J | 6.93 | 7.65 | 7.17 | 9.39 | 9.78 | 8.43 |
| $\Delta U$(carb.) /J | – | – | – | 10.23 | 3.96 | – |
| $-\Delta U$(n-hexadec.) /J | 6246.75 | 5425.08 | 7639.01 | 4903.10 | 6640.83 | 5231.58 |
| $-\Delta U$(fuse) /J | 39.14 | 48.40 | 42.06 | 43.69 | 41.74 | 39.63 |
| $-\Delta_c u^{o}$ /(J·g$^{-1}$) | 29203.76 | 29230.91 | 29230.61 | 29189.26 | 29209.05 | 29202.84 |

% $CO_2$ = (100.09 ± 0.04) [b]

$-\langle\Delta_c u^{o}\rangle$ = (29211.1 ± 6.8) J·g$^{-1}$ [b]

$m(CO_2$. total) is the total mass of $CO_2$ recovered in the experiment; $m$(cpd) is the mass of compound burnt in each experiment; $m$(fuse) is the mass of fuse (cotton) used in each experiment; $m$(n-hexadec.) is the mass of n-hexadecane 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; $_f$ is the energy equivalent of contents in the final state; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3119.6 g; $\Delta U$(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions and includes $\Delta U$(ign); $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; $\Delta U$(ign) is the electrical energy for ignition; $\Delta U$ is the standard state correction; $\Delta U$(carb.) is the correction energy for carbon soot formation; $\Delta U$(n-hexadec.) is the energy of combustion of the n-hexadecane; $\Delta U$(fuse) is the energy of combustion of the fuse (cotton); $\Delta_c u^\circ$ is the standard massic energy of combustion. [a] Mean value and standard deviation of the mean.

**Table S2.** Standard ($p^\circ$ = 0.1 MPa) mass energy of combustion of crystalline 7HI, at $T$ = 298.15 K.

| | | | | | | |
|---|---|---|---|---|---|---|
| $m(CO_2$, total) /g | 1.19166 | 1.29231 | 1.43019 | 1.70668 | 1.25306 | 1.46551 |
| $m$(cpd) /g | 0.31994 | 0.35721 | 0.39439 | 0.48449 | 0.33607 | 0.35971 |
| $m$(fuse) /g | 0.00246 | 0.00244 | 0.00276 | 0.00220 | 0.00298 | 0.00290 |
| $m$(n-hexadec.) /g | 0.10688 | 0.10802 | 0.11943 | 0.13117 | 0.11249 | 0.16053 |
| $T_i$ /K | 298.1505 | 298.1509 | 298.1509 | 298.1506 | 298.1508 | 298.1511 |
| $T_f$ /K | 299.1339 | 299.2027 | 299.3015 | 299.4955 | 299.1817 | 299.3610 |
| $\Delta T_{ad}$ /K | 0.89996 | 0.97109 | 1.07336 | 1.27201 | 0.94699 | 1.13122 |
| $_f$ /(J·K$^{-1}$) | 15.90 | 16.00 | 16.15 | 16.43 | 15.98 | 16.29 |
| $\Delta m(H_2O)$ /g | 3.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| −$\Delta U$(IBP) /J | 14426.27 | 15554.29 | 17192.69 | 20375.17 | 15168.24 | 18119.68 |
| $\Delta U(HNO_3)$ /J | 0.64 | 0.46 | 0.92 | 0.92 | 0.55 | 0.74 |
| $\Delta U$(ign) /J | 1.04 | 1.21 | 1.20 | 1.20 | 1.20 | 1.21 |
| $\Delta U_\Sigma$ /J | 7.16 | 7.93 | 8.86 | 10.92 | 7.58 | 8.71 |
| $\Delta U$(carb.) /J | – | 22.44 | – | – | – | – |
| −$\Delta U$(n-hexadec.) /J | 5038.08 | 5091.88 | 5629.44 | 6183.04 | 5302.38 | 7566.80 |
| −$\Delta U$(fuse) /J | 39.95 | 39.63 | 44.82 | 35.73 | 48.40 | 47.10 |
| −$\Delta_c u^\circ$ /(J·g$^{-1}$) | 29194.34 | 29217.64 | 29180.88 | 29194.73 | 29188.34 | 29179.97 |

| |
|---|
| % $CO_2$ = (100.01 ± 0.04) $^{b}$ |
| $-\langle \Delta_c u^\circ \rangle$ = (29192.6 ± 5.6) $J \cdot g^{-1}$ $^{b}$ |

$m(CO_2$. total) is the total mass of $CO_2$ recovered in the experiment; $m$(cpd) is the mass of compound burnt in each experiment; $m$(fuse) is the mass of fuse (cotton) used in each experiment; $m$(n-hexadec.) is the mass of n-hexadecane 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; $_f$ is the energy equivalent of contents in the final state; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3119.6 g; $\Delta U$(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions and includes $\Delta U$(ign); $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; $\Delta U$(ign) is the electrical energy for ignition; $\Delta U$ is the standard state correction; $\Delta U$(carb.) is the correction energy for carbon soot formation; $\Delta U$(n-hexadec.) is the energy of combustion of the n-hexadecane; $\Delta U$(fuse) is the energy of combustion of the fuse (cotton); $\Delta_c u^\circ$ is the standard massic energy of combustion.[a] Mean value and standard deviation of the mean.

**Table S3.** Standard ($p^{o}$ = 0.1 MPa) molar heat capacities in the gaseous phase for **6HI.**

| $T$ / K | $C^{\circ}_{p,\mathrm{m}}$(g) / J.k$^{-1}$.mol$^{-1}$ |
|---|---|
| 200 | 109.24 |
| 250 | 134.39 |
| 298.15 | 158.69 |
| 300 | 159.62 |
| 350 | 183.90 |
| 400 | 206.51 |
| 450 | 227.12 |
| 500 | 245.65 |
| 550 | 262.23 |
| 600 | 277.05 |

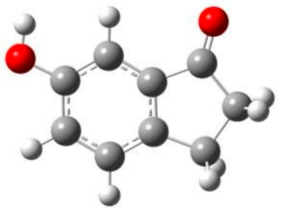
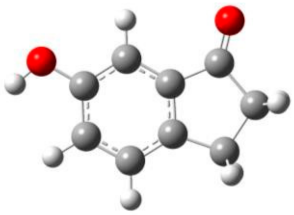
$$C^{\circ}_{p,\mathrm{m}}(\mathrm{g}) = -\,3.705\times10^{-7}\,T^{3} + 1.130\times10^{-4}\,T^{2} + 5.218\times10^{-1}\,T + 3.043$$

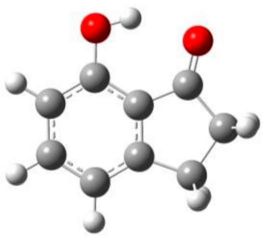
**Table S4.** Standard ($p^{o}$ = 0.1 MPa) molar heat capacities in the gaseous phase for **7HI.**

| $T$ / K | $C^{\circ}_{p,\mathrm{m}}$(g) / J.k$^{-1}$.mol$^{-1}$ |
|---|---|
| 200 | 104.50 |
| 250 | 129.66 |
| 298.15 | 154.23 |
| 300 | 155.16 |
| 350 | 179.80 |
| 400 | 202.80 |
| 450 | 223.77 |
| 500 | 242.66 |
| 550 | 259.56 |
| 600 | 274.68 |

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{g}) = -\,4.186\times10^{-7}\,T^{3} + 1.748\times10^{-4}\,T^{2} + 5.033\times10^{-1}\,T - 1.139\times10^{-1}$$

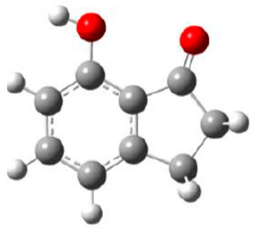
**Table S5.** Conformational analysis of the hydroxy-1-indanones studied and their corresponding total electronic energy plus the internal thermal energy, $E^{\circ}_{298.15\,\mathrm{K}}$ (1 a.u. = 2625.5 kJ mol$^{-1}$).

| **Molecular structure** | **$E^{\circ}_{298.15\,\mathrm{K}}$ / a. u.** | | **$E^{\circ}_{298.15\,\mathrm{K}}$ / a. u.** |
|---|---|---|---|
| | **6-hydroxy-1-indanone (6HI)** | | |
| <br>Conformer Ia | −497.477455 | <br>Conformer IIa | -497.476348 |
| | **7-hydroxy-1-indanone (7HI)** | | |



-497.487089

Conformer Ib



-497.474215

Conformer IIb

**Table S6.** G3(MP2)//B3LYP results for **6HI** and **7HI** conformers.

| **Compound** | **Conformer** | $H_m°$ [a] | $G_m°$ [a] | $\Delta G_{rel}(i)$ [b] | $\chi_i$ [c] |
|---|---|---|---|---|---|
| **6HI** | Ia | −497.476511 | −497.520876 | 0.00 | 0.731 |
| | IIa | −497.475404 | −497.519932 | 2.48 | 0.269 |
| **7HI** | Ib | −497.486145 | −497.529484 | 0.00 | 1.000 |
| | IIb | −497.473271 | −497.517709 | 30.92 | 0.000 |

[a] In Hartrees. [b] Value calculated according to this formula: $\Delta G_{rel}(i) = G^{\circ}_{m}(i) - G^{\circ}_{m}$ (conformer I); In kJ mol-1.

[c] Value calculated using the formula $\chi_i = \frac{e^{-\frac{\Delta G_{rel}(i)}{RT}}}{\sum_{i=1}^{n} e^{-\frac{\Delta G_{rel}(i)}{RT}}}$.

**Table S7.** G3(MP2)//B3LYP absolute enthalpies (in *Hartrees**) and experimental enthalpies of formation (in kJ·mol$^{-1}$). in the gaseous state. at $T$ = 298.15 K. for the studied compounds and the auxiliary atoms/molecules used in the gas-phase working reactions.

| **Compounds studied / Auxiliary atoms and molecules** | **G3(MP2)//B3LYP absolute enthalpies** | **Experimental enthalpies of formation (298.15 K)** |
|---|---|---|
| Carbon ($^3$P) | −37.788425 | (716.7 ± 0.5) [S8] |
| Hydrogen($^2$S) | −0.499780 | (218.00 ± 0.01) [S8] |
| Oxygen($^3$P) | −74.989704 | (249.2 ± .1) [S8] |
| 6-Hydroxy-1-indanone (**6HI**) | −497.476213 | −(240.2 ± 3.1) [a] |
| 7-Hydroxy-1-indanone (**7HI**) | −497.486146 | −(265.6 ± 3.0) [a] |
| Benzene | −231.835136 | (82.6 ± 0.7) [S9] |
| 1-Indanone | −422.32525 | −(64.0 ± 3.7) [S10] |
| Phenol | −306.986464 | − (96.4 ± 0.9) [S9] |
| Ethane | −79.651018 | −(83.8 ± 0.3) [S9] |
| Cyclopentanone | −270.127404 | −(192.1 ± 1.7) [S9] |
| Naphthalene | −385.22368 | (150.3 ± 1.4) [S9] |
| 1-Hydroxynaphthalene | −460.375327 | −(30.4 ± 1.6) [S9] |

| | | |
|---|---|---|
| 2-Hydroxynaphthalene | −460.3746 | −(29.9 ± 1.7) [S9] |
| Toluene | −271.074374 | (50.1 ± 1.1)[S11] |
| 6-Methyl-1-indanone | −461.564681 | −(95.1 ± 2.8)[S12] |
| $\alpha$-Tetralone | −461.565278 | −(95.27 ± 0.77)[S13] |
| 7-Hydroxy-$\alpha$-tetralone | −536.716925 | [−271.0] [c] |

[a] This work. [b] Value estimated at the G3(MP2)//B3LYP level of theory. [c] Value estimated from the DFT calculations with the B3LYP functional and the 6-311G** basis set.

[*] 1 Hartree = 2625.5 kJ·mol$^{-1}$

## REFERENCES

[S1] Coops J, Jessup RS, van Nes K (1956) In *Experimental Thermochemistry*; Vol. 1, F.D. Rossini, Ed.; Interscience: New York, Chapter 3

[S2] Washburn EW (1933) Standard states for bomb calorimetry. J Res Nat Bur Stand 10:525-558

[S3] Vogel AI (1978) *Quantitative Inorganic Analysis*; Longman: London

[S4] Wagman DD, Evans WH, Parker VB, Schumm RH, Halow I, Bailey SM, Churney KL, Nuttall RL (1982), J Phys Chem Ref Data 11(suppl. 2)

[S5] Medvedev VA, Cox JD, Wagman DD (eds). (1989) CODATA key values for thermodynamics. New York: Hemisphere Publishing Corporation.

[S6] https://www.lookchem.com/6-Hydroxy-1-indanone/ (accessed in 01/08/19).

[S7] Hurst JE, Harrison BK (1992) Estimation of liquid and solid heat capacities using a modified Kopp's rule. Chem Eng Comm 112:21-30

[8] Chase Jr MW (1998) J Phys Chem Ref Data, Monograph 9, 1-1951

[S9] Pedley JP (1994) Thermochemical data and structures of organic compounds, Thermodynamics Research Centre. College Station, Texas.

[S10] Matos MAR, Miranda MS, Monte MJS, Santos LMNBF, Morais VMF, Chickos JS, Umnahanant P, Liebman JF (2007) J. Phys. Chem. A 2007 111:11153-11159

[S11] Roux MV, Temprado M, Chickos JS, Nagano Y (2008) Critically evaluated thermochemical properties of polycyclic aromatic hydrocarbons. J Phys Chem Ref Data 37:1855-1996

[S12] Silva ALR, Lima ACMO, Ribeiro da Silva MDMC (2018) Energetic characterization of indanone derivatives involved in biomass degradation. J Therm Anal Calorim 134:1267–1276

[S13] Verevkin SP (1998) Thermochemistry of aromatic ketones. Experimental enthalpies of formation and structural effects. Thermochim Acta 310:229-235