Electronic Supplementary materials

Experimental and computational thermochemistry: how strong is the intramolecular hydrogen bond in alkyl 2-hydroxybenzoates (salicylates)?

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Table S1 Provenance and Purity of the Materials

Material	CAS	Origin	GC purity (mass fraction)
methyl-2-hydroxybenzoate	119-36-8	Acros, 99%	0.9999
ethyl-2-hydroxybenzoate	118-61-6	Acros, 99+%	0.9995
n-propyl-2-hydroxybenzoate	607-90-9	Acros, 99+%	0.9991
n-butyl-2-hydroxybenzoate	2052-14-4	TCI, 99%	0.9996

Combustion calorimetry: enthalpy of formation determination

The standard molar energy of combustion was measured with a self-made high-precision isoperibolic calorimeter with a static bomb and a stirred water bath. The liquid sample was transferred (in the glove box) with a syringe into the polyethylene bulb (Fa. NeoLab, Heidelberg, Germany). The neck of the bulb was compressed with special tweezers and sealed by heating the neck near a glowing wire. The bulb with the liquid sample was placed in the crucible and burnt in oxygen at a pressure of 3.04 MPa. The bomb was not preliminary purged with oxygen. Test experiments with and without purging with O_2 showed results consistent within the experimental uncertainty. The detailed procedure has been described previously [9, 10]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but neither was detected. The energy equivalent of the calorimeter $\varepsilon_{calor} = (14904.0 \pm 0.5)\ J \cdot K^{-1}$ was determined with a standard reference sample of benzoic acid (sample SRM 39*j*, NIST). Correction for nitric acid formation was based on titration with 0.1 $mol \cdot dm^{-3}$ NaOH (aq). Conventional procedures [11] were used for reduction of the data to standard conditions. Auxiliary data required for the reduction are collected in Table S2.

Table S2 Auxiliary quantities: formula, density ρ(293 K), massic heat capacity c_p(298.15 K), and expansion coefficients $(\delta V/\delta T)_p$ of the materials used in the present study [a]

Materials	Formula	Water	ρ(293 K)	c_p(298.15 K)[b]	$(\delta V/\delta T)_p$ [c]
		ppm	$g \cdot cm^{-3}$	$J \cdot K^{-1}\ g^{-1}$	$10^{-3} \cdot cm^3 \cdot K^{-1} \cdot g^{-1}$
methyl 2-hydroxybenzoate	$C_8H_8O_3$	134.1	1.179 [1]	1.61	1.0
ethyl 2-hydroxybenzoate	$C_9H_{10}O_3$	103.6	1.125 [2]	1.70	1.0
n-propyl 2-hydroxybenzoate	$C_{10}H_{12}O_3$	112.4	1.10 [3]	1.66	1.0
n-butyl 2-hydroxybenzoate	$C_{11}H_{14}O_3$	98.6	1.025 [4]	1.71	1.0
polyethylene	$CH_{1.93}$		0.92	2.53	0.1
cotton	$CH_{1.774}O_{0.887}$		1.50	1.67	0.1

[a] Data for the densities, ρ(293 K), and the specific heat capacities, c_p (298.15 K), of auxiliary materials are from our previous work [5]. The specific energy of combustion $\Delta_c u^o$(cotton) = -16945.2 $J \cdot g^{-1}$; $u(\Delta_c u^o)$ = 4.2 $J \cdot g^{-1}$. The specific energy of combustion $\Delta_c u^o$(polyethylene) = -46357.3 $J \cdot g^{-1}$; $u(\Delta_c u^o)$ = 3.5 $J \cdot g^{-1}$. The standard uncertainties are reported for the specific energies of combustion.

[c] Calculated from the molar heat capacity at 298.15 K (see Table S3).

[d] Estimated.

Transpiration method

Absolute vapour pressures were measured using the transpiration method [12, 13]. The main idea of this method is to saturate the gas stream flowing over the sample and to determine the amount of compound transferred by the gas within a given time. Approximately 0.5 to 0.8 g of the sample is mixed with glass beads (diameter 1 mm) and placed in the thermostatted U-shaped saturator. The glass beads are needed to enlarge the contact area between gas and sample. A stream of nitrogen at a well-defined flow rate was passed through the saturator at constant temperature (± 0.1 K) maintained by Julabo FP51-SL refrigerated circulator, and the transported material was collected in a cold trap. The amount of condensed substance was usually determined by GC using a suitable n-alkane as an internal standard. The saturation vapour pressure p_i at each temperature T_i was calculated from the amount of condensate collected within a definite period of time:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i \, ; \qquad V = (n_{N2} + n_i) \cdot R \cdot T_a / P_a \qquad \text{(S1)}$$

where V is the volume of the gas phase consisting of the n_{N2} moles of the carrier gas and n_i mole of gaseous compound under study (with the molar mass M_i) at the atmospheric pressure P_a and the ambient temperature T_a. The volume of the carrier gas V_{N2} was determined by the digital flow rate sensor from integration with a microcontroller. We used the Honeywell S&C - HAFBLF0200C2AX5 digital flow rate sensor with uncertainty at the level of 2.5 %. The flow rate of the nitrogen stream was also controlled by using a soap bubble flow meter (HP soap film flowmeter (model 0101-0113)) and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The volume of the carrier gas V_{N2} was read from the digital flow sensor. The amount of the compound under investigation n_i in the carrier gas was estimated at each temperature using the ideal gas law.

Before starting the vapour pressure measurements, the sample was first pre-conditioned at 310-320 K (within about one hour) in order to remove possible traces of water. The saturator was then kept at 310-315 K (to remove possible traces of volatile compounds). To ensure that preconditioning was completed at the selected temperature, three samples were taken sequentially during sample rinsing and analyzed by GC. A constant vapour pressure at this temperature indicated that the transpiration experiments could begin. GC analysis of the transported material did not reveal any additional contamination. The absence of impurities and decomposition products was re-checked by GC analysis of the saturator content at the end of the entire series of experiments.

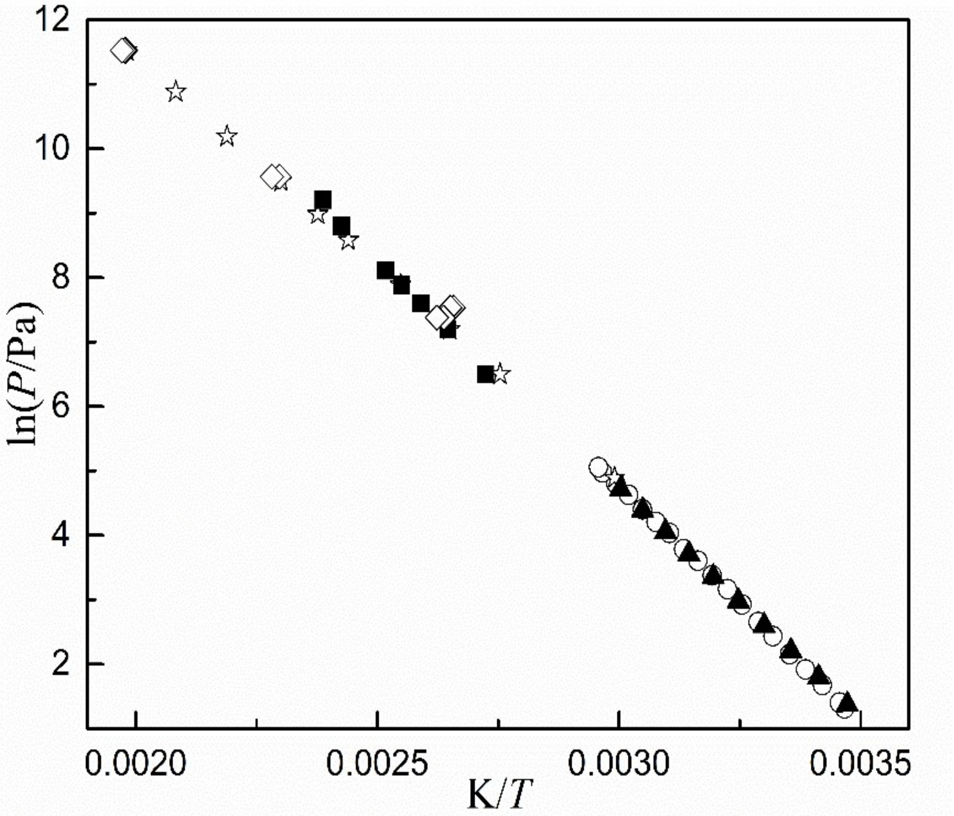

Fig. S1 The temperature dependence of vapour pressures over the liquid sample of ethyl 2-hydroxybenzoate:

○ - this work; ▲-Ref. [14]; ☆- Ref. [15]; ■ - Ref. [16]; ◇ - Ref. [17].

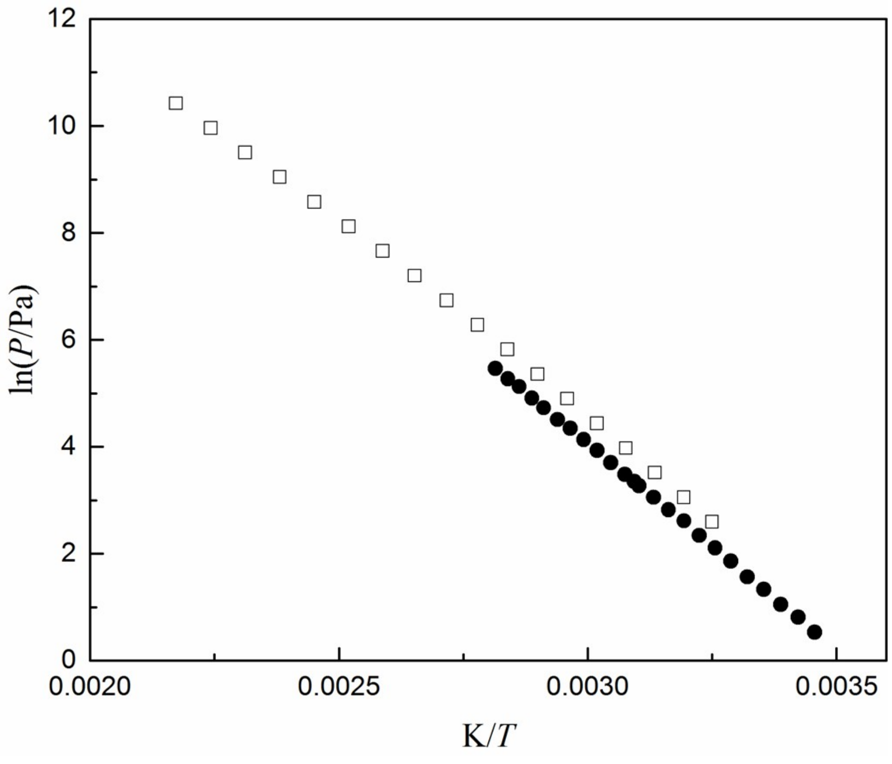

Fig. S2 The temperature dependence of vapour pressures over the liquid sample of *n*-propyl 2-hydroxybenzoate:

● -this work; □- Ref. [18].

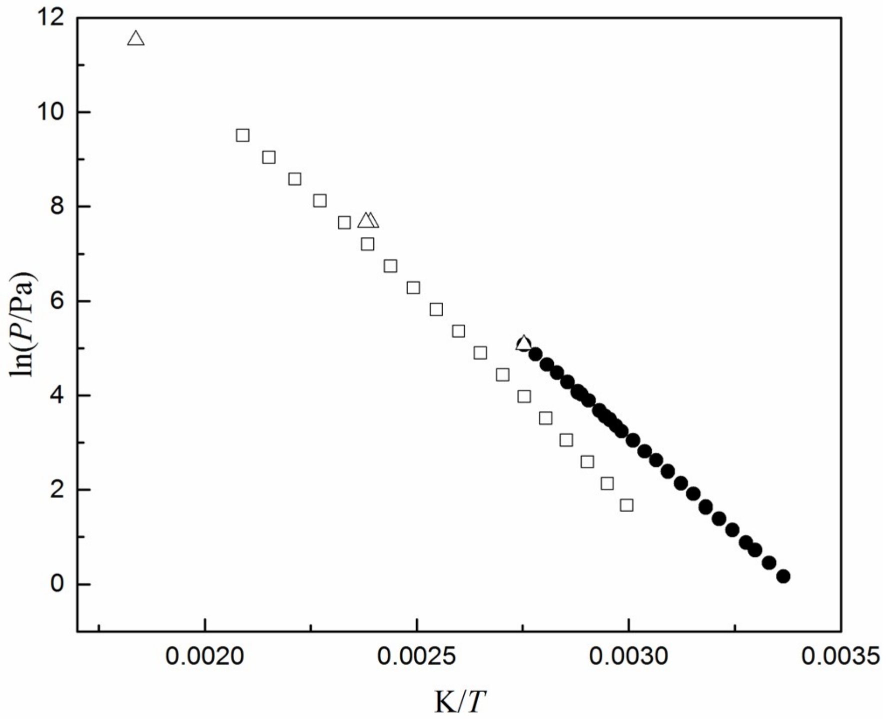

Fig. S3 The temperature dependence of vapour pressures over the liquid sample of *n*-butyl 2-hydroxybenzoate:

● - this work; Δ - Ref. [17]; □ – Ref. [18]

Adjustment of vaporisation enthalpies to the reference temperature *T* = 298.18 K

The vaporisation enthalpies, which are derived from the experimental vapor pressure-temperature dependencies according to the Clausius–Clapeyron relation, are referenced to the average temperature, T_{av}, of the examined interval. For engineering calculations, these enthalpies should be adjusted to the reference temperature *T* = 298.15 K. The enthalpies of vaporisation are derived using the following equation:

$$\Delta_l^g H_m^o(T) = -b + \Delta_l^g C_{p,m}^o \times T \qquad \text{(S2)}$$

The $\Delta_l^g C_{p,m}^o$-values used in Eq. (S2) are usually derived according to empirical equations developed by Chickos and Acree [8].

$$\Delta_l^g C_{p,m}^o(298.15\ K) = -0.26 \times C_{p,m}^o(liq, 298.15\ K) - 10.58 \qquad \text{(S3)}$$

where $C_{p,m}^o$(liq, 298.15 K) values (see Table S3) are of experimental origin or they can be also estimated according to the group-additivity procedure [7].

Table S3 Compilation of data on molar heat capacities $C_{p,m}^o$(liq) and heat capacity differences $\Delta_l^g C_{p,m}^o$ (in J·K^{-1}·mol^{-1}) at *T* = 298.15 K

Compounds	$C_{p,m}^o(liq)$	$-\Delta_l^g C_{p,m}^o$
methyl 2-hydroxybenzoate	244.3 [1]	72.0 [6]
ethyl 2-hydroxybenzoate	283.1 [2]	84.2 [b]
n-propyl 2-hydroxybenzoate	300 [a]	88.6 [b]
n-butyl 2-hydroxybenzoate	332 [a]	96.9 [b]
n-pentyl 2-hydroxybenzoate	371.9 [a]	107.3
iso-pentyl 2-hydroxybenzoate	365.4 [a]	105.6

[a] Calculated according to group-additivity procedure developed by Chickos *et al.* [7] based on the heat capacity of methyl 2-hydroxybenzoate

[b] Calculated according to empirical procedure developed by Chickos *et al.*[8].

Table S4 Absolute vapour pressures *p*, and standard vaporisation enthalpies and entropies obtained by the transpiration method.

T/ K[a]	m/ mg[b]	$V(N_2)$[c] / dm^3	T_a/ K[d]	Flow/ dm^3·h^{-1}	p/ Pa[e]	$u(p)$/ Pa[f]	$\Delta_l^g H_m^o$/ kJ·mol^{-1}	$\Delta_l^g S_m^o$/ J·K^{-1}·mol^{-1}
ethyl 2-hydroxybenzoate; $\Delta_l^g H_m^o$(298.15 K) = (62.1±0.3) kJ·mol^{-1}								
$\ln(p/p_{ref}) = \frac{310.5}{R} - \frac{87191.8}{RT} - \frac{84.2}{R}\ln\frac{T}{298.15}$; p_{ref} = 1 Pa								
288.5	2.41	9.653	295.9	6.03	3.72	0.10	62.9	133.3
289.4	2.49	9.131	295.9	5.89	4.08	0.11	62.8	133.1
292.4	2.71	7.601	295.9	5.92	5.31	0.16	62.6	132.2
295.4	2.49	5.400	295.9	5.89	6.87	0.20	62.3	131.3
298.3	2.29	3.953	295.9	5.93	8.60	0.24	62.1	130.3
301.4	2.28	2.975	295.9	5.95	11.39	0.31	61.8	129.6
304.2	2.26	2.357	295.9	1.96	14.21	0.38	61.6	128.8
307.3	2.42	1.924	295.9	1.96	18.62	0.49	61.3	128.2
310.2	2.41	1.557	295.9	1.99	22.95	0.60	61.1	127.3
313.3	4.14	2.081	295.9	1.84	29.48	0.76	60.8	126.6
316.2	2.35	0.985	295.9	1.97	35.37	0.91	60.6	125.5
319.2	2.16	0.725	295.9	1.98	44.23	1.13	60.3	124.8
322.2	2.41	0.664	295.9	1.05	53.73	1.37	60.1	123.9
325.1	2.67	0.586	295.9	1.03	67.44	1.71	59.8	123.3
328.1	2.44	0.437	295.9	1.05	82.62	2.09	59.6	122.6
331.2	2.53	0.374	295.9	1.02	100.02	2.53	59.3	121.7
334.1	2.46	0.298	295.9	1.05	122.20	3.08	59.1	121.0
337.2	2.79	0.285	295.9	1.07	144.58	3.64	58.8	120.0
338.2	2.78	0.263	295.9	1.05	156.03	3.93	58.7	119.9
n-propyl 2-hydroxybenzoate; $\Delta_l^g H_m^o$(298.15 K) = (65.9±0.3) kJ·mol^{-1}								
$\ln(p/p_{ref}) = \frac{320.6}{R} - \frac{92297.0}{RT} - \frac{88.6}{R}\ln\frac{T}{298.15}$; p_{ref} = 1 Pa								
289.4	3.81	30.54	294.0	3.27	1.70	0.05	66.7	139.1
292.2	3.42	21.00	299.0	2.00	2.25	0.06	66.4	138.4
295.2	1.82	8.674	294.0	4.34	2.85	0.08	66.1	137.1
298.2	2.45	8.819	294.0	4.34	3.79	0.10	65.9	136.3
301.2	3.06	8.674	294.0	4.34	4.79	0.12	65.6	135.2
304.2	3.40	7.228	296.4	4.34	6.43	0.19	65.3	134.6
307.2	5.21	8.674	296.4	4.34	8.23	0.23	65.1	133.7
310.2	3.01	3.976	296.4	4.34	10.37	0.28	64.8	132.7
313.2	3.26	3.273	296.4	3.27	13.63	0.37	64.6	132.1
316.3	4.03	3.273	296.4	3.27	16.83	0.45	64.3	131.0
319.3	4.19	2.727	299.0	3.27	21.20	0.56	64.0	130.2
322.3	3.81	2.000	299.0	2.00	26.27	0.68	63.7	129.3
323.3	3.92	1.890	297.2	2.84	28.44	0.74	63.7	129.0
325.3	3.93	1.667	299.0	2.00	32.53	0.84	63.5	128.4
328.3	3.91	1.333	299.0	2.00	40.42	1.04	63.2	127.6
331.3	4.30	1.167	299.0	2.00	50.87	1.30	62.9	127.0
334.3	4.26	0.933	297.2	2.00	62.48	1.59	62.7	126.2
337.3	4.31	0.767	297.2	2.00	76.97	1.95	62.4	125.5
340.2	3.31	0.500	297.2	2.00	90.81	2.30	62.2	124.5
343.5	5.72	0.692	297.2	2.77	113.22	2.86	61.9	123.7
346.3	5.28	0.533	297.2	2.00	135.59	3.41	61.6	123.1
349.4	9.08	0.738	297.2	2.77	168.29	4.23	61.3	122.5

352.2	7.10	0.500	297.2	2.00	194.38	4.88	61.1	121.6
355.3	8.59	0.500	297.2	2.00	235.09	5.90	60.8	120.9

n-butyl 2-hydroxybenzoate; $\Delta_l^g H_m^o$(298.15 K) = (69.7±0.3) kJ·mol^{-1}

$$\ln{(p/p_{ref})} = \frac{332.8}{R} - \frac{98621.9}{RT} - \frac{96.9}{R}ln\frac{T}{298.15}\;;\ p_{\mathrm{ref}} = 1\ \mathrm{Pa}$$

297.2	4.15	44.86	297.8	3.43	1.18	0.03	69.8	140.7
300.2	6.06	49.24	297.4	3.40	1.57	0.04	69.5	139.7
303.2	5.16	32.00	297.5	3.20	2.06	0.06	69.2	138.7
305.2	5.15	27.14	296.6	2.86	2.41	0.07	69.1	137.9
308.2	3.50	14.15	298.4	3.40	3.16	0.08	68.8	137.0
311.2	1.77	5.660	297.4	3.40	3.99	0.10	68.5	135.8
311.2	3.90	12.45	297.7	3.40	4.00	0.10	68.5	135.9
314.3	1.97	4.811	297.4	3.40	5.20	0.16	68.2	134.9
314.3	3.83	9.623	297.5	3.40	5.08	0.15	68.2	134.7
317.2	4.56	8.573	298.2	3.43	6.79	0.19	67.9	134.3
320.2	4.53	6.792	297.4	3.40	8.49	0.24	67.6	133.2
323.4	0.58	0.674	298.4	1.99	10.98	0.30	67.3	132.3
323.4	4.32	5.067	297.0	3.20	10.83	0.30	67.3	132.2
326.3	5.49	5.067	297.0	3.20	13.78	0.37	67.0	131.5
329.2	3.13	2.400	298.0	3.20	16.66	0.44	66.7	130.4
332.2	7.26	4.373	297.0	3.20	21.10	0.55	66.4	129.6
335.2	3.74	1.867	298.0	3.20	25.55	0.66	66.1	128.6
336.7	4.75	2.105	297.0	3.16	28.65	0.74	66.0	128.2
338.3	5.08	1.981	296.2	3.40	32.49	0.84	65.8	127.9
338.4	1.27	0.497	298.4	1.99	32.71	0.84	65.8	127.9
339.7	4.39	1.579	297.0	3.16	35.31	0.91	65.7	127.4
341.2	4.46	1.440	298.4	3.20	39.55	1.01	65.6	127.0
344.2	4.09	1.067	298.4	3.20	48.95	1.25	65.3	126.3
346.2	4.63	1.053	297.0	3.16	55.84	1.42	65.1	125.7
347.2	4.15	0.907	298.4	3.20	58.39	1.48	65.0	125.3
347.2	3.98	0.849	296.2	3.40	59.37	1.51	65.0	125.4
350.2	4.53	0.800	298.4	3.20	72.34	1.83	64.7	124.6
353.2	5.52	0.800	298.4	3.20	88.10	2.23	64.4	123.9
356.2	6.71	0.816	298.2	3.16	104.87	2.65	64.1	123.0
359.7	3.85	0.377	298.2	1.46	130.00	3.27	63.8	122.1
363.2	4.74	0.377	298.2	1.46	159.91	4.02	63.4	121.1

[a] Saturation temperature measured with the standard uncertainty ($u(T)$ = 0.1 K).

[b] Mass of transferred sample condensed at T = 243 K.

[c] Volume of nitrogen ($u(V)$ = 0.005 dm^3) used to transfer m ($u(m)$ = 0.0001 g) of the sample. Uncertainties are given as standard uncertainties.

[d] T_a is the temperature of the soap bubble meter used for measurement of the gas flow.

[e] Vapour pressure at temperature T, calculated from the m and the residual vapour pressure at the condensation temperature calculated by an iteration procedure.

[f] Standard uncertainties were calculated with $u(p_i/\mathrm{Pa})$ = 0.005 +0.025(p_i/Pa) for pressures below 5 Pa, and $u(p_i/\mathrm{Pa})$ = 0.025 + 0.025(p_i/Pa) for pressures from 5 to 3000 Pa. The standard uncertainties for T, V, p, m, are standard uncertainties with 0.683 confidence level. Uncertainty of the vaporisation enthalpies $U(\Delta_l^g H_m^o)$ are the expanded uncertainty (0.95 level of confidence) calculated according to procedure described elsewhere [19]. Uncertainties include uncertainties from the experimental conditions and the fitting equation, vapour pressures, and uncertainties from adjustment of vaporisation enthalpies to the reference temperature T = 298.15 K.

Table S5 The vapour pressures p, and standard vaporisation enthalpies and entropies obtained by the approximation of boiling points at different pressures available in the literature [17].

T/ K[a]	p/ Pa	$\Delta_l^g H_m^o$/[a] kJ·mol^{-1}	$\Delta_l^g S_m^o$/ J·K^{-1}·mol^{-1}
ethyl 2-hydroxybenzoate; $\Delta_l^g H_m^o$(298.15 K) = (62.1±2.7) kJ·mol^{-1}			
$\ln(p/p_{ref}) = \frac{312.4}{R} - \frac{87235.7}{RT} - \frac{84.2}{R}\ln\frac{T}{298.15}$; p_{ref} = 1 Pa			
376.2	1867	55.6	114.6
377.2	1867	55.5	114.0
379.2	1600	55.3	111.5
381.2	1600	55.1	110.3
435.2	14265	50.6	100.1
438.2	14265	50.3	98.7
505.2	101325	44.7	88.6
505.7	101325	44.7	88.4
507.2	101325	44.5	87.9
n-butyl 2-hydroxybenzoate; $\Delta_l^g H_m^o$(298.15 K) = (72.9±3.5) kJ·mol^{-1}			
$\ln(p/p_{ref}) = \frac{340.4}{R} - \frac{101750.6}{RT} - \frac{96.9}{R}\ln\frac{T}{298.15}$; p_{ref} = 1 Pa			
544.2	101324.7	49.02	90.2
418.2	2133.2	61.23	114.4
420.2	2133.2	61.04	113.3
363.2	159.9	66.56	129.7

[a] Uncertainty of the vaporisation enthalpy is expressed as twice the standard uncertainties. They include uncertainties from the fitting equation, and uncertainties from temperature adjustment to T = 298.15 K. Uncertainties in the temperature adjustment of vaporisation enthalpies to the reference temperature T= 298.15 K are estimated to account with 20 % to the total adjustment.

Table S6 Compilation of the enthalpies of vaporisation, $\Delta_l^g H_m^o$, of methyl 2-hydroxybenzoate[6]

Method[a]	T-range	T_{av}	$\Delta_l^g H_m^o$ T_{av}	$\Delta_l^g H_m^o$ 298.15 K[b]	Ref.
	K	K	kJ·mol^{-1}	kJ·mol^{-1}	
S	341.9-495.6	418.8	52.7±0.2	61.2±1.7	20
S	352.1-493.6	422.9	52.4±0.2	61.0±1.7	21
n/a	327.2-496.4	411.8	53.0±1.5	60.4±2.1	14
n/a	329-496	412.5	52.4±1.5	60.7±2.2	16
n/a	288-333	310.5	56.8±1.5	57.7±1.5	16
TGA	393-443	418.0	52.3±2.5	60.9±3.0	22
T	263.5-303.5	283.5	61.3±0.6	60.2±0.7	23
TGA	296-316	306.0	64.4±1.4	65.0±1.4	1
CGC	298.15			56.2±3.0	24
CGC	298.15			62.0±3.6	25
CGC	298.15			62.1±1.2	26
CGC	298.15			61.4±2.4	27
CGC	298.15			63.1±1.4	28
CGC	298.15			62.1±1.6	29
T	278.3-343.2	310.8	58.6±0.6	59.2±0.7	30
T	318.4-348.3	333.4	56.8±0.4	59.3±0.5	6
				59.9±0.2 [c]	average

[a] Methods: S = static method; TGA = thermogravimetry; CGC = correlation gas-chromatography; T = transpiration method; n/a = method was not available.

[b] Vapour pressures available in the literature were treated using Eqs. (S1) and (S2) with help of heat capacity differences from Table S3 to calculate the enthalpies of vaporisation at 298.15 K. Uncertainties of the vaporisation enthalpies $U(\Delta_l^g H_m^o)$ are the expanded uncertainties (0.95 level of confidence). They include uncertainties from the fitting equation and uncertainties from temperature adjustment to T = 298.15 K. Uncertainties in the temperature adjustment of vaporisation enthalpies to the reference temperature T= 298.15 K are estimated to account with 20% to the total adjustment

[c] Weighted mean value (uncertainties were taken as the weighting factor). Value in bold was recommended for further thermochemical calculations.

Table S7 Thermochemical data at T = 298.15 K ($p°$ = 0.1 MPa) for reference compounds (in kJ·mol^{-1}) [a]

Compound	$\Delta_l^g H_m^o$ [31]	Compound	$\Delta_l^g H_m^o$ [32]
methyl glycolate	52.5±0.2 [33]		
methyl lactate	50.2±0.4	methyl acetate	32.3±0.2
ethyl lactate	52.8±0.4	ethyl acetate	35.6±0.2
n-propyl lactate	56.1±0.5	*n*-propyl acetate	39.1±0.2
n-butyl lactate	60.2±0.5	*n*-butyl acetate	**43.6**±0.4
n-pentyl lactate	64.9±0.7	*n*-pentyl acetate	**48.6**±0.2
n-hexyl lactate	69.7±1.2	*n*-hexyl acetate	51.9±0.3
n-octyl lactate	78.6±1.6		
n-decyl lactate	89.0±2.2		

[a] The uncertainties in this table are given as two times the standard deviation.

Table S8 Correlation of vaporization enthalpies $\Delta_l^g H_m^o$(298.15 K) of alkyl salicylates with the their T_b (normal boiling temperatures)[a]

R	Compound	T_b [b] K	$\Delta_l^g H_m^o$(298.15 K)$_{exp}$ kJ·mol^{-1}	$\Delta_l^g H_m^o$(298.15 K)$_{calc}$[c] kJ·mol^{-1}	Δ[d] kJ·mol^{-1}
C_1	methyl salicylate	495.2	59.9±0.2 [Table S6]	60.0	-0.1
C_2	ethyl salicylate	507.2	62.1±0.6 [Table S4]	62.5	-0.5
C_3	*n*-propyl salicylate	519.2	65.9±0.4 [Table S4]	64.9	1.0
C_4	*n*-butyl salicylate	544.2	69.7±0.4 [Table S4]	70.0	-0.3

[a] The uncertainties in this table are given as two times the standard deviation.

[b] Normal boiling temperatures are from Ref. [17].

[c] Calculated using Eq. (10) from the main text.

[d] Difference between experimental and calculated values.

Table S9 Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$(298.15 K), of alkyl 2-hydroxybenzoates with their Kovats indices (J_x)

R	Compound	J_x [a]	$\Delta_l^g H_m^o$(298 K)$_{exp}$ kJ·mol^{-1}	$\Delta_l^g H_m^o$(298 K)$_{calc}$[b] kJ·mol^{-1}	Δ[c] kJ·mol^{-1}
C_1	methyl salicylate	1181	59.9±0.2 [Table S6]	59.6	0.3
C_2	ethyl salicylate	1257	62.1±0.6 [Table S4]	62.4	-0.4
C_3	*n*-propyl salicylate	1357	65.9±0.4 [Table S4]	66.0	-0.1
C_4	*n*-butyl salicylate	1457	69.7±0.4 [Table S4]	69.6	0.1

[a] Kovats indices, J_x, on the standard non-polar column SE-30, program [34].

[b] Calculated using Eq. (11, main text) with the assessed expanded uncertainty of ±0.5 kJ·mol^{-1} (0.95 level of confidence, k = 2)

[c] Difference between column 4 and 5 in this table.

Table S10 Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$(298.15 K), of alkyl 2-hydroxybenzoates with their Kovats indices (J_x)

R	Compound	J_x [a]	$\Delta_l^g H_m^o$(298 K)$_{exp}$ kJ·mol^{-1}	$\Delta_l^g H_m^o$(298 K)$_{calc}$[b] kJ·mol^{-1}	Δ[c] kJ·mol^{-1}
C_1	methyl salicylate	1176.5	59.9±0.2 [Table S6]	59.6	0.3
C_2	ethyl salicylate	1249	62.1±0.6 [Table S4]	62.2	-0.2
C_3	*n*-propyl salicylate	1357	65.9±0.4 [Table S4]	66.0	-0.1
C_4	*n*-butyl salicylate	1455	69.7±0.4 [Table S4]	69.5	0.2

[a] Kovats indices, J_x, on the standard non-polar column SE-30 [35] at 373 K.

[b] Calculated using Eq. (12, main text) with the assessed expanded uncertainty of ±0.5 kJ·mol^{-1} (0.95 level of confidence, k = 2)

[c] Difference between column 4 and 5 in this table.

Table S11 Thermochemical data at T = 298.15 K ($p°$ = 0.1 MPa) for reference compounds (in kJ·mol^{-1})

Compound	$\Delta_f H^o_m$(cr,liq)	$\Delta_l^g H^o_m$	$\Delta_f H^o_m$(g)$_{\text{exp.}}$
benzene (liq)	49.0±0.9 [36]	33.9±0.1 [36]	82.9±0.9 [36]
phenol (liq)		58.0±0.6 [37]	-92.5±1.2 [37, 38]
methoxy benzene(liq)	-116.9±0.7 [37]	46.4±0.2 [37]	-70.3±0.7 [37]
methyl benzoate (liq)	-334.1±1.3 [39]	56.6±0.1 [39]	-273.5 ± 0.8 [39]
ethyl benzoate (liq)	-365.2±0.9 [39]	59.9±0.7 [39]	-305.3±1.1 [39]
n-propyl benzoate(liq)		65.6±0.6 [40]	-327.3±2.0 [a]
n-butyl benzoate (liq)		70.1±0.8 [40]	-348.3±2.0 [b]
methyl 4-hydroxybenzoate (cr)	-563.5±1.4 [6]		455.6±1.4 [6]

[a] Calculated based on the $\Delta_f H^o_m$(g) of ethyl benzoate from this table and the difference between n-propyl-benzene and ethyl-benzene with their $\Delta_f H^o_m$(g)-values from Pedley *et al.* [41].

[b] Calculated based on the $\Delta_f H^o_m$(g) of *n*-propyl benzoate from this table and the difference between *n*-butyl-benzene and *n*-propyl-benzene with their $\Delta_f H^o_m$(g)-values from Pedley *et al.* [41].

Table S12 Theoretical gas-phase enthalpies of formation $\Delta_f H^o_m$(g) at T = 298.15 K ($p°$ = 0.1 MPa) for 2-hydroxybenzoates as calculated by different methods (in kJ·mol^{-1}).[a]

Compound	G3MP2	G4	G4	G3	W1-F-12
methyl 2-hydroxybenzoate	-481.7	-478.4	-476.3 [1]	-479.7[42]	-474.2 [b]
ethyl 2-hydroxybenzoate	-516.7	-511.9	-510.2 [2]		
n-propyl 2-hydroxybenzoate	-537.4	-532.4			
n-butyl 2-hydroxybenzoate	-558.3	-553.4			

[a] Calculated according to the standard atomization procedure.

[b] Calculated in this work.

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