

Thermodynamic exercises for the kinetically controlled hydrogenation of carvone

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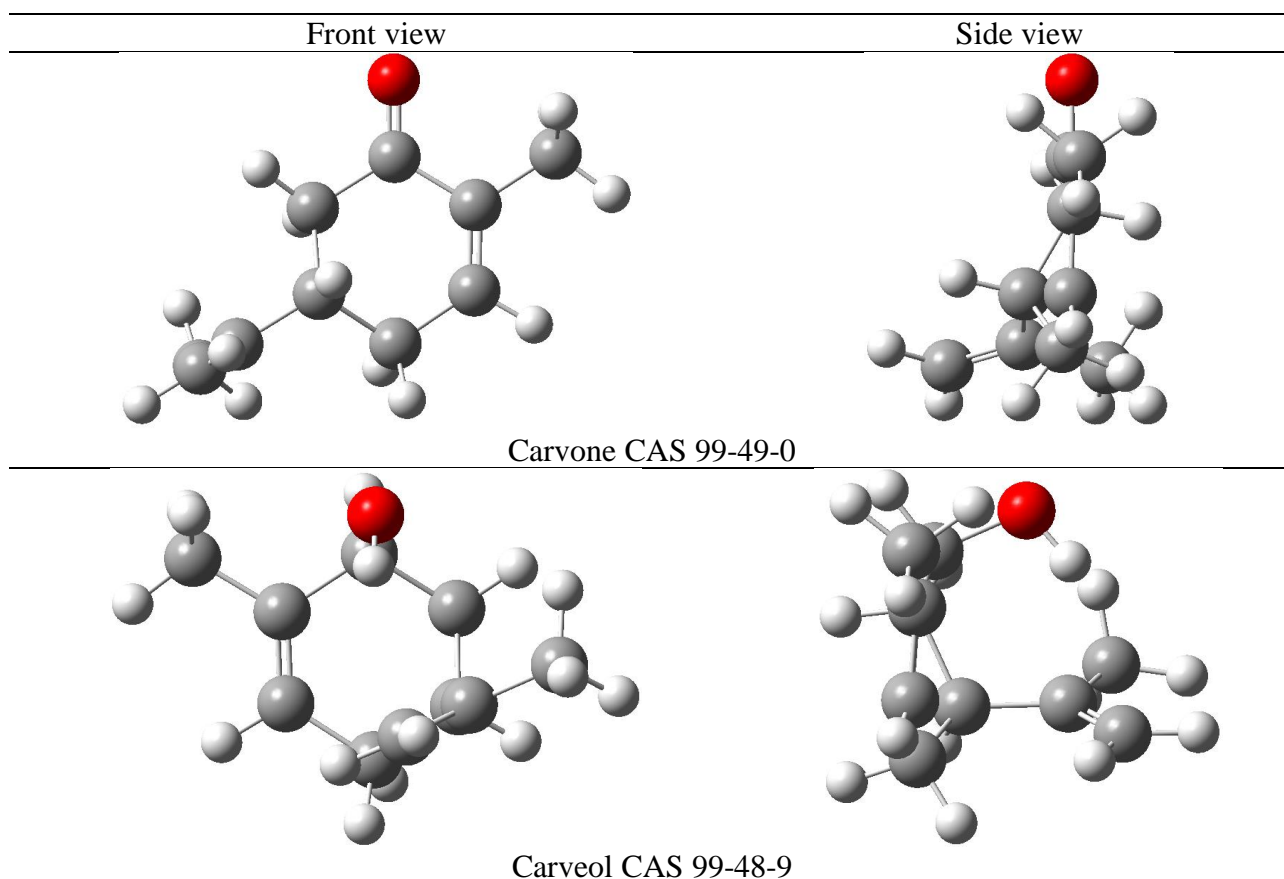
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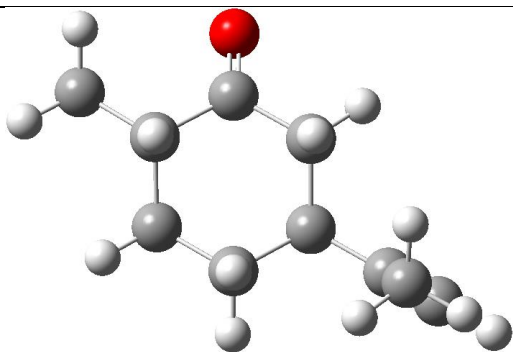
Table S1. Provenance and purity of the materials

Material ^a	CAS	Origin	GC purity (mass fraction) ^a
(-)-carvone (liq)	6485-40-1	TCI	0.9991

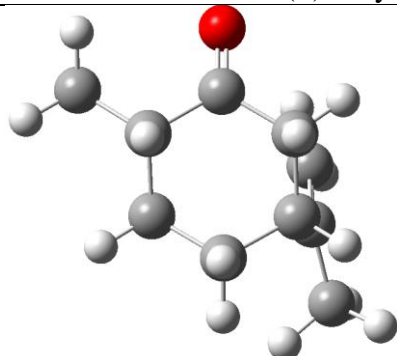
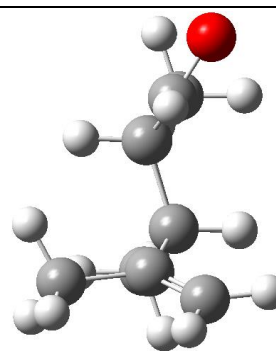
^a The final purity after purification, determined by GC.

Sample for combustion calorimetry was purified using fractional distillation. The final purity of the sample was determined by GC. The samples were analysed with a Hewlett Packard 5890 II series gas chromatograph equipped with a flame ionisation detector and an HP-5 capillary column (length, inside diameter, and film thickness of 25 m×0.32 mm×0.25 µm). The GC temperature program started at $T = 323$ K, followed by heating at a rate of $0.167 \text{ K} \cdot \text{s}^{-1}$ to $T = 573$ K. The water contents of the sample was determined by Karl Fischer titration using a Mettler Toledo DL38 Karl Fischer titrator with HYDRANALTM as the reagent. Before starting the vapour pressure measurements, the sample was preconditioned in the transpiration saturator (see below for details).

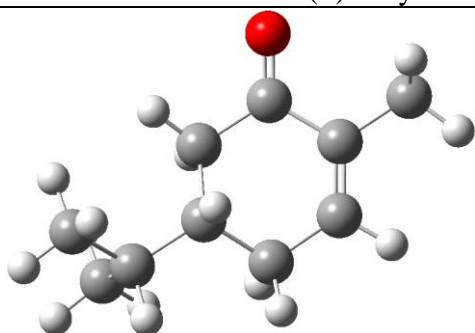
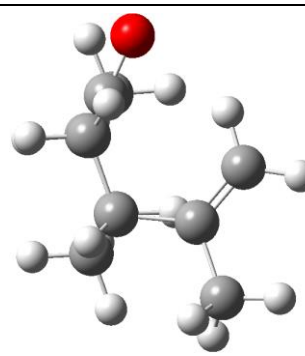




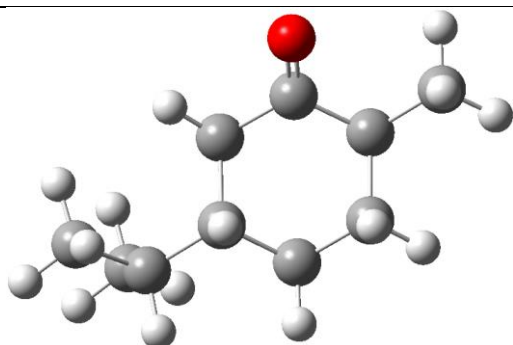
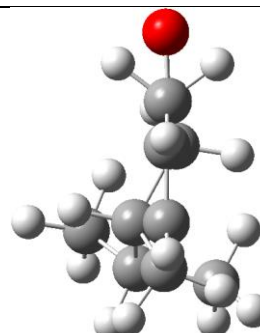
trans-(±)-dihydrocarvone CAS 5524-05-0



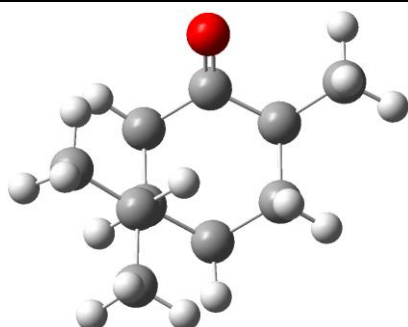
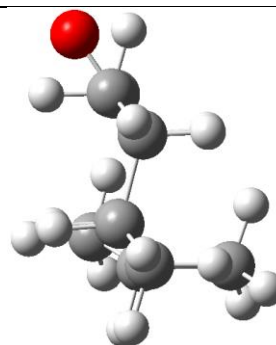
cis-(±)-dihydrocarvone CAS 3792-53-8



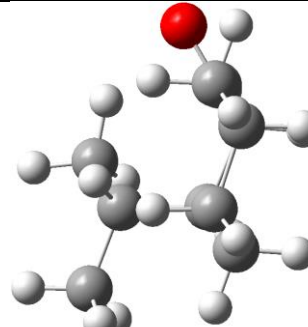
Carvotanacetone CAS 499-71-8

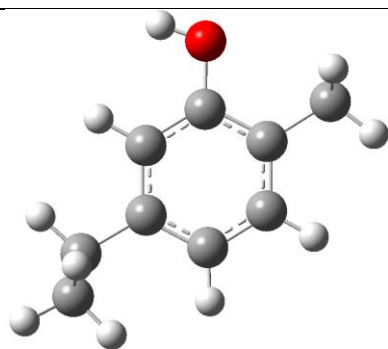


Trans-(±)- tetrahydrocarvone CAS 499-70-7

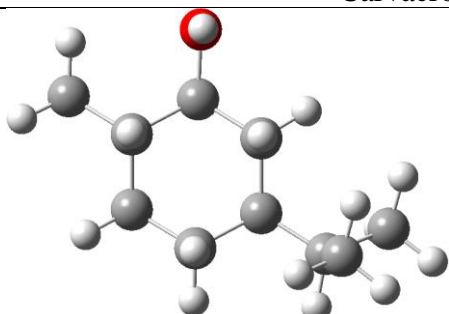
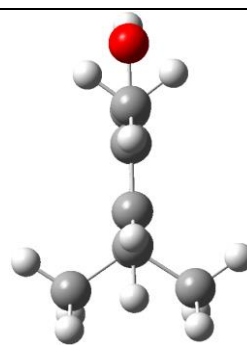


Cis-(±)-tetrahydrocarvone CAS 57875-63-5

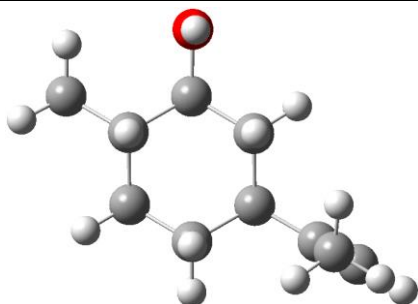
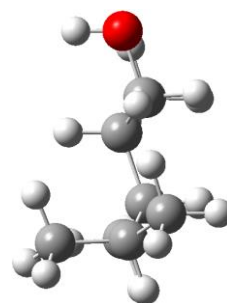




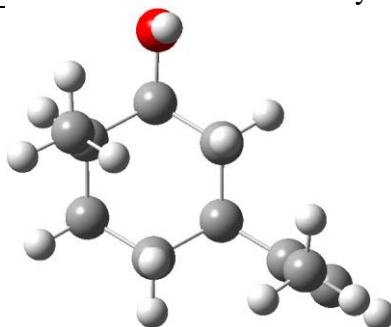
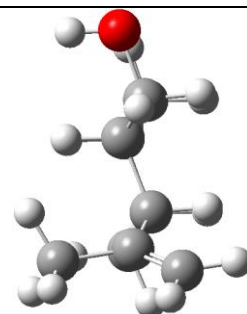
Carvacrol CAS 1499-75-2



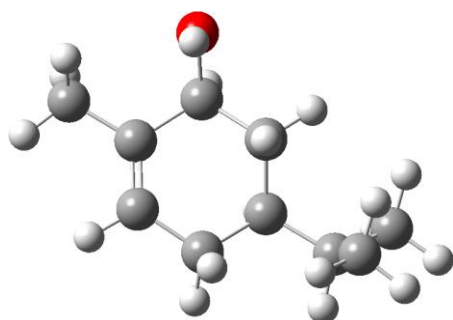
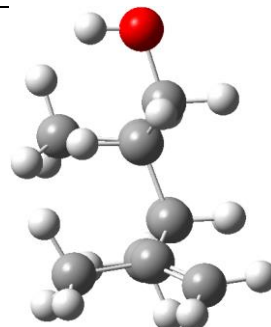
Carvomenthol CAS 1499-69-4



trans-dihydrocarveol CAS 1619-01-2



cis-dihydrocarveol CAS 1619-01-2



Carvotanacetol CAS 1536-30-1

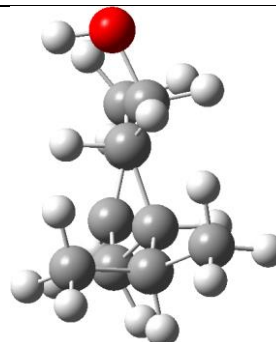


Fig. S1. Structures of the most stable conformers of carvone derivatives as calculated using the G4 method.

Absolute vapour pressures

Table S2.

The vapour pressures p , and standard vaporisation enthalpies and entropies obtained by the approximation of boiling points at different pressures available in the literature [1–3].

$T/$ K^a	$p/$ Pa	$\Delta_l^g H_m^o/a$ $kJ \cdot mol^{-1}$	$\Delta_l^g S_m^o/$ $J \cdot K^{-1} \cdot mol^{-1}$
(-)-carvone [6485-40-1];			
$\Delta_l^g H_m^o(298.15 K) = (60.2 \pm 1.7) kJ \cdot mol^{-1}$			
$\Delta_l^g S_m^o(298.15 K) = (127.3 \pm 1.7) J \cdot K^{-1} \cdot mol^{-1}$			
$\Delta_l^g G_m^o(298.15 K) = (22.3 \pm 0.2) kJ \cdot mol^{-1}$			
$\ln(p/p_{ref}) = \frac{289.4}{R} - \frac{80022.0}{RT} - \frac{66.4}{R} \ln \frac{T}{298.15}; p_{ref} = 1 Pa$			
320	67	58.8	122.9
351	400	56.7	115.7
359	800	56.2	116.4
361	667	56.1	113.6
361	800	56.1	115.1
364	800	55.9	113.3
365	1067	55.8	115.1
366	1067	55.7	114.5
368	933	55.6	112.2
369	1333	55.5	114.6
370	1200	55.5	113.1
371	1333	55.4	113.4
371	1200	55.4	112.5
373	1333	55.3	112.5
377	1467	55.0	110.8
379	1867	54.9	111.6
379	1867	54.8	111.5
382	1867	54.7	110.0
383	1867	54.6	109.4
388	2666	54.3	109.7
430	13332	51.5	103.1
503	101325	46.6	92.8
504	101325	46.6	92.5
504	101325	46.6	92.5
504	101725	46.6	92.5
504	101325	46.6	92.5
cis-(±)-dihydrocarvone [3792-53-8];			
$\Delta_l^g H_m^o(298.15 K) = (56.8 \pm 1.6) kJ \cdot mol^{-1}$			
$\Delta_l^g S_m^o(298.15 K) = (122.8 \pm 2.8) J \cdot K^{-1} \cdot mol^{-1}$			
$\Delta_l^g G_m^o(298.15 K) = (20.2 \pm 0.3) kJ \cdot mol^{-1}$			
$\ln(p/p_{ref}) = \frac{284.8}{R} - \frac{76575.7}{RT} - \frac{66.3}{R} \ln \frac{T}{298.15}; p_{ref} = 1 Pa$			
322	133	55.2	116.5
323	133	55.2	115.7
369	2133	52.1	109.2
370	2133	52.1	109.0
370	2666	52.0	110.5
371	2666	52.0	110.0

485	91326	44.4	90.8
487	91326	44.3	90.2
493	101325	43.9	89.1
493	99992	43.9	89.0
494	100391	43.8	88.7
495	101325	43.8	88.5

trans-(±)-dihydrocarvone [5524-05-0];

$$\Delta_f^g H_m^o(298.15 \text{ K}) = (57.2 \pm 1.7) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f^g S_m^o(298.15 \text{ K}) = (123.0 \pm 2.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_f^g G_m^o(298.15 \text{ K}) = (20.5 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{285.0}{R} - \frac{76987.9}{RT} - \frac{66.3}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

343	533	54.2	114.6
344	533	54.2	114.0
358	1067	53.3	111.0
360	1067	53.1	109.8
361	1067	53.1	109.2
363	1333	52.9	109.9
364	1333	52.9	109.3
371	2133	52.4	109.2
372	2133	52.3	108.7
380	2933	51.8	107.0
381	2933	51.7	106.4
493	101325	44.3	90.0
495	101325	44.2	89.3

cis-(±)-tetrahydrocarvone [57875-63-5];

$$\Delta_f^g H_m^o(298.15 \text{ K}) = (58.4 \pm 1.6) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f^g S_m^o(298.15 \text{ K}) = (125.9 \pm 1.9) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_f^g G_m^o(298.15 \text{ K}) = (20.9 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{290.6}{R} - \frac{78982.7}{RT} - \frac{68.9}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

335	267	55.9	117.6
337	267	55.8	116.2
346	533	55.1	115.9
348	533	55.0	114.5
362	1333	54.0	113.4
363	1333	54.0	112.8
367	1467	53.7	111.5
367	1467	53.7	111.2
370	1600	53.5	110.2
372	2066	53.4	111.2
375	2666	53.1	111.6
383	3866	52.6	110.3
384	3866	52.5	109.7
403	6666	51.2	104.6
412	9333	50.6	103.1
418	11332	50.2	101.9
493	101325	45.0	91.6
493	99325	45.0	91.3
494	101325	45.0	91.3
495	101325	44.9	90.8
496	101325	44.8	90.4

trans-(±)- tetrahydrocarvone (carvomenthone) [499-70-7];

$$\Delta_1^g H_m^o(298.15 \text{ K}) = (58.0 \pm 1.7) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^g S_m^o(298.15 \text{ K}) = (124.8 \pm 1.8) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^g G_m^o(298.15 \text{ K}) = (20.8 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{289.5}{R} - \frac{78585.7}{RT} - \frac{68.9}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

335	333	55.5	118.3
337	333	55.4	116.9
362	1333	53.6	112.3
363	1333	53.6	111.7
367	1467	53.3	110.4
367	1467	53.3	110.1
370	1600	53.1	109.1
373	2000	52.9	109.3
377	2133	52.6	107.6
382	2666	52.3	106.7
403	6666	50.8	103.6
418	11999	49.8	101.5
492	93992	44.7	90.5
492	93992	44.7	90.3
493	101325	44.7	90.8
493	101325	44.6	90.6
494	101325	44.6	90.5

carvotanacetone [499-71-8];

$$\Delta_1^g H_m^o(298.15 \text{ K}) = (59.3 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^g S_m^o(298.15 \text{ K}) = (126.6 \pm 2.5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^g G_m^o(298.15 \text{ K}) = (21.6 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{290.5}{R} - \frac{79640.3}{RT} - \frac{68.2}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

317	67	58.0	122.2
319	67	57.9	120.6
341	267	56.4	116.1
343	400	56.2	118.1
353	667	55.6	115.7
361	800	55.0	112.3
370	1600	54.4	112.7
371	1333	54.3	110.6
371	1600	54.3	112.1
378	2266	53.9	111.0
379	2266	53.8	110.4
379	2866	53.8	112.4
401	6666	52.3	107.9
403	6666	52.2	106.9
427	13332	50.5	101.6
428	13332	50.5	101.1
499	99192	45.6	91.3
501	94259	45.5	90.4
501	101325	45.5	90.9

carvonementhol [499-69-4];

$$\Delta_1^g H_m^o(298.15 \text{ K}) = (69.9 \pm 3.3) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^g S_m^o(298.15 \text{ K}) = (156.7 \pm 1.7) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^g G_m^o(298.15 \text{ K}) = (23.2 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{385.2}{R} - \frac{109522.7}{RT} - \frac{132.8}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

354	667	62.6	135.4
362	933	61.4	130.9
363	933	61.3	130.1
373	1600	60.0	126.6
373	1600	59.9	126.2
490	101325	44.5	91.1
490	101325	44.5	90.8
491	101325	44.4	90.6
491	101325	44.3	90.4
491	101325	44.3	90.4

cis-(±)-carveol [1197-06-4];

$$\Delta_1^g H_m^o(298.15 \text{ K}) = (71.0 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^g S_m^o(298.15 \text{ K}) = (156.0 \pm 4.1) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^g G_m^o(298.15 \text{ K}) = (24.4 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{381.0}{R} - \frac{109590.9}{RT} - \frac{129.6}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

338	133	65.8	139.6
339	133	65.7	138.6
349	267	64.4	135.1
374	1333	61.1	127.5
374	1333	61.1	127.5
374	1333	61.1	127.5
374	1333	61.1	127.4
374	1333	61.1	127.2
375	1333	61.0	126.7
388	2000	59.3	120.3
390	2000	59.0	118.9
423	10666	54.8	110.9
504	101325	44.3	88.0

trans-(±)-carveol [99-48-9];

$$\Delta_1^g H_m^o(298.15 \text{ K}) = (72.6 \pm 2.9) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^g S_m^o(298.15 \text{ K}) = (159.5 \pm 2.8) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^g G_m^o(298.15 \text{ K}) = (25.0 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{384.8}{R} - \frac{111196.4}{RT} - \frac{129.6}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

314	20	70.5	153.7
341	133	67.0	141.4
342	133	66.9	140.5
349	267	66.0	139.7
349	267	66.0	139.7
359	400	64.7	134.2
363	667	64.2	135.1
368	667	63.5	130.9
368	667	63.5	130.9
374	1333	62.7	131.8
374	1333	62.7	131.7
374	1333	62.7	131.5
375	1333	62.6	131.0
375	1333	62.6	130.9

375	1333	62.5	130.7
378	1333	62.2	128.7
381	1467	61.8	127.1
382	1600	61.7	127.1
383	1467	61.6	125.6
384	1600	61.4	125.6
388	2000	60.9	124.5
389	2000	60.8	123.7
402	3733	59.1	119.7
499	100125	46.5	93.2
500	100125	46.4	92.8
501	101325	46.3	92.5

trans-(±)-dihydrocarveol [619-01-2];

$$\Delta_f^g H_m^o(298.15 \text{ K}) = (71.9 \pm 3.4) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f^g S_m^o(298.15 \text{ K}) = (159.8 \pm 2.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_f^g G_m^o(298.15 \text{ K}) = (24.2 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{391.5}{R} - \frac{112436.8}{RT} - \frac{136.0}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

350	400	64.8	139.3
353	400	64.4	136.6
355	400	64.2	134.8
362	667	63.2	132.9
363	667	63.1	132.1
371	1200	62.0	130.3
376	1600	61.3	128.7
380	2000	60.8	127.5
380	2000	60.8	127.5
380	1867	60.8	126.8
380	2000	60.7	127.2
380	2000	60.7	127.2
380	1867	60.7	126.6
382	1867	60.6	125.6
497	101325	44.8	90.3
498	101325	44.8	90.1
498	101325	44.7	89.9

cis-(±)-dihydrocarveol [22567-21-1];

$$\Delta_f^g H_m^o(298.15 \text{ K}) = (70.1 \pm 3.6) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f^g S_m^o(298.15 \text{ K}) = (155.4 \pm 4.5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_f^g G_m^o(298.15 \text{ K}) = (23.8 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{387.1}{R} - \frac{110677.1}{RT} - \frac{136.0}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

353	533	62.7	134.0
355	533	62.4	132.2
371	1200	60.2	125.5
376	1733	59.5	124.6
376	1600	59.5	124.0
379	1600	59.1	121.6
380	1733	59.0	121.7
380	1733	59.0	121.4
382	2000	58.8	121.6
383	2000	58.7	120.8
498	101325	42.9	86.4

carvotanacetol [536-30-1];

$$\Delta_1^g H_m^o(298.15 \text{ K}) = (73.1 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^g S_m^o(298.15 \text{ K}) = (163.2 \pm 4.5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^g G_m^o(298.15 \text{ K}) = (24.4 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{391.0}{R} - \frac{112462.8}{RT} - \frac{132.1}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

337	133	67.9	146.6
337	133	67.9	146.6
348	320	66.5	143.3
349	320	66.4	142.4
353	400	65.8	140.6
355	400	65.6	138.8
359	533	65.0	137.7
360	533	64.9	136.8
375	1867	63.0	134.9
375	1867	62.9	134.7
378	2266	62.5	133.9
381	2133	62.2	131.5
382	2133	62.1	130.7
395	4000	60.3	125.9
396	4000	60.2	125.1
495	101325	47.1	95.2

2-methyl-2-cyclohexen-1-one [1121-18-2];

$$\Delta_1^g H_m^o(298.15 \text{ K}) = (48.2 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^g S_m^o(298.15 \text{ K}) = (110.5 \pm 1.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^g G_m^o(298.15 \text{ K}) = (15.3 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{252.6}{R} - \frac{62035.5}{RT} - \frac{46.4}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

325	1067	47.0	106.7
327	1067	46.9	105.6
329	1200	46.8	105.4
334	1733	46.5	105.6
335	1867	46.5	105.7
336	1733	46.4	104.5
336	1867	46.4	105.1
338	2133	46.4	105.1
338	1867	46.4	104.0
338	2000	46.4	104.6
339	2133	46.3	104.9
339	2133	46.3	104.9
339	2000	46.3	104.1
343	2666	46.1	104.3
345	2933	46.0	104.1
345	2666	46.0	103.3
346	2933	46.0	103.6
348	3333	45.9	103.6
354	4133	45.6	102.4
355	4133	45.6	101.9
357	4933	45.5	102.3
358	4666	45.4	101.4
359	4933	45.4	101.4
363	5999	45.2	101.1

374	10266	44.7	100.5
374	10266	44.7	100.5
375	9999	44.6	99.9
377	9999	44.5	99.0
388	16665	44.0	98.6
389	16665	44.0	98.2
451	101725	41.1	91.4
451	101325	41.1	91.3
452	101325	41.1	91.0
452	101725	41.1	91.0

2-methylcyclohex-2-en-1-ol [20461-30-7];

$$\Delta_f^g H_m^o(298.15 \text{ K}) = (60.2 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f^g S_m^o(298.15 \text{ K}) = (143.9 \pm 3.3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_f^g G_m^o(298.15 \text{ K}) = (17.2 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{350.0}{R} - \frac{93031.2}{RT} - \frac{110.3}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

298	93	60.2	143.9
299	107	60.1	143.9
321	533	57.6	136.0
322	667	57.5	137.0
343	1600	55.2	126.5
346	2400	54.9	127.6
348	2400	54.6	126.0
349	2400	54.5	125.3
349	2400	54.5	125.3
359	5333	53.4	124.5
359	5333	53.4	124.5
360	5333	53.3	123.7
360	5333	53.3	123.7
398	26664	49.1	112.5
441	101325	44.4	100.8

^a Uncertainties in this table are expressed as the expanded uncertainty (0.95 level of confidence, $k = 2$). Uncertainties of the vaporisation enthalpies include uncertainties from the fitting equation, and uncertainties from temperature adjustment to $T = 298.15 \text{ K}$. Uncertainties in the temperature adjustment of vaporisation enthalpies to the reference temperature $T = 298.15 \text{ K}$ are estimated to account with 20 % to the total adjustment.

Transpiration method: Vapour pressure measurements

Absolute vapour pressures were measured using the transpiration method [4,5]. 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 ($\pm 0.1 \text{ K}$) 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:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i; \quad V = (n_{N_2} + n_i) \cdot R \cdot T_a / P_a \quad (\text{S1})$$

where V is the volume of the gas phase consisting of the n_{N_2} 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_{N_2} 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_{N_2} 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.

The procedure for calculating the expanded uncertainties (0.95 level of confidence) of the vaporisation enthalpies from the transpiration method includes uncertainties from the experimental transpiration conditions, uncertainties in the vapor pressure and uncertainties in the temperature adjustment to $T = 298.15$ K, as described elsewhere [6,7].

The uncertainties of the $\Delta_l^g H_m^o(298.15 \text{ K})$ -values derived from the vapor pressures reported in the literature include uncertainties from the fitting equation and uncertainties from temperature adjustment to the reference temperature. Uncertainties in the temperature adjustment of vaporisation enthalpies to $T = 298.15$ K are estimated to account with 20% to the total adjustment.

The experimental absolute vapour pressures measured in this work are given in Table S3.

Table S3

Absolute vapour pressures p , and standard molar vaporisation enthalpies and entropies determined using 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
(-)-carvone [6485-40-1]								
$\Delta_l^g H_m^o(298.15 \text{ K}) = (61.7 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$								
$\Delta_l^g S_m^o(298.15 \text{ K}) = (130.8 \pm 0.7) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$								
$\Delta_l^g G_m^o(298.15 \text{ K}) = (22.7 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$								
$\ln(p/p_{\text{ref}}) = \frac{293.0}{R} - \frac{81547.1}{RT} - \frac{66.4}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$								
279.6	0.93	7.850	292.4	4.71	1.95	0.05	63.0	135.1
282.8	0.91	5.694	292.4	4.68	2.62	0.07	62.8	134.3
286.4	0.88	3.987	291.8	4.69	3.60	0.10	62.5	133.3
293.2	0.66	1.590	293.1	1.06	6.80	0.20	62.1	132.0
298.1	1.04	1.610	293.3	1.05	10.57	0.29	61.8	131.0
303.0	1.02	1.050	293.2	1.05	15.76	0.42	61.4	130.0
308.0	0.93	0.665	293.5	1.05	22.79	0.59	61.1	128.7
313.1	1.14	0.543	293.0	1.05	33.97	0.87	60.8	127.6
318.0	1.05	0.345	291.0	1.09	48.99	1.25	60.4	126.7
323.0	1.15	0.270	291.6	1.08	68.44	1.74	60.1	125.5
328.0	1.07	0.180	291.7	1.08	95.53	2.41	59.8	124.4
333.0	1.03	0.126	291.9	1.08	131.35	3.31	59.4	123.4

^a Saturation temperature measured with the standard uncertainty ($u(T) = 0.1 \text{ K}$).

^b Mass of transferred sample condensed at $T = 243 \text{ K}$.

^c Volume of nitrogen ($u(V) = 0.005 \text{ dm}^3$) used to transfer m ($u(m) = 0.0001 \text{ g}$) 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 $u(p_i/\text{Pa}) = 0.005 + 0.025(p_i/\text{Pa})$ for pressures below 5 Pa and with $u(p_i/\text{Pa}) = 0.025 + 0.025(p_i/\text{Pa})$ 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/sublimation enthalpy $U(\Delta_l^g H_m^o)$ is the expanded uncertainty (0.95 level of confidence) calculated according to procedure described elsewhere [6,7]. Uncertainties include uncertainties from the experimental conditions and the fitting equation, vapour pressures, and uncertainties from adjustment of vaporisation enthalpies to the reference temperature $T = 298.15 \text{ K}$.

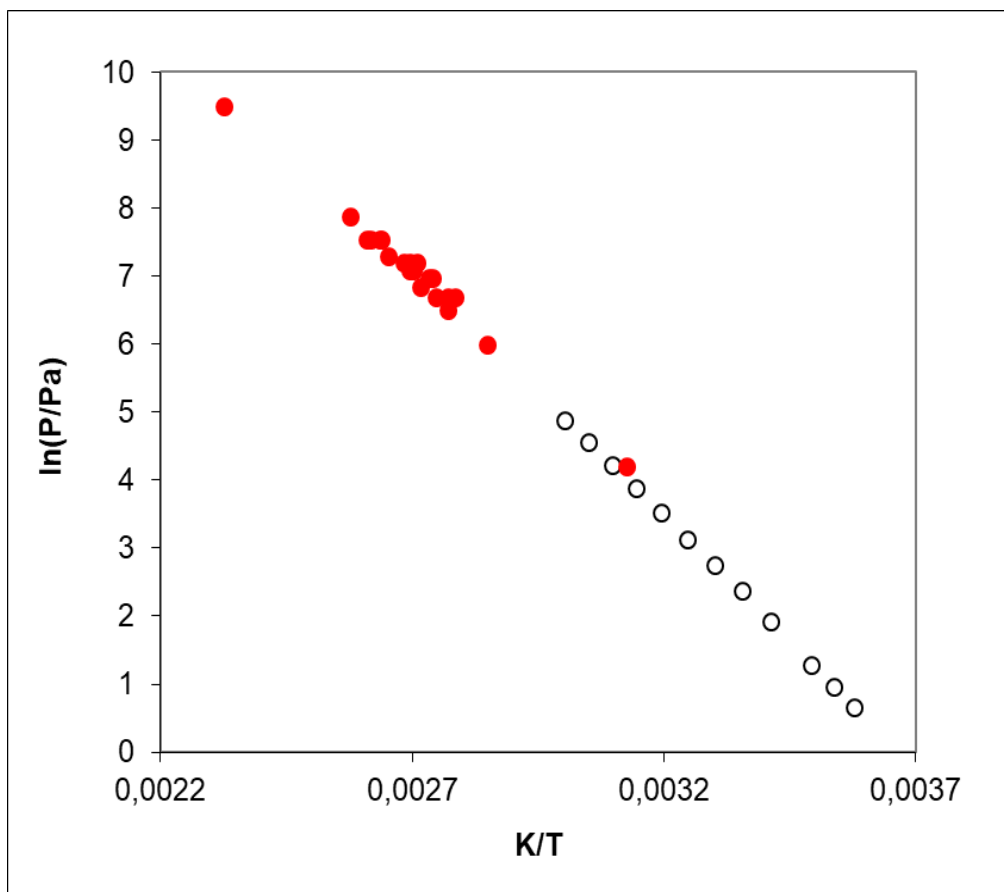


Fig. S2. Vapour pressure - temperature dependence for (-)-carvone:

● - experimental boiling temperatures at different pressures (Table S2); ○ – transpiration method, this work (Table S3).

Adjustment of vaporisation enthalpies to the reference temperature $T = 298.18\text{ K}$

The standard molar enthalpies of vaporisation at temperatures T were derived from the temperature dependence of the vapor pressures, approximated by Eq. (S2) using the following equation:

$$\Delta_l^g H_m^o(T) = -b + \Delta_l^g C_{p,m}^o \times T \quad (\text{S3})$$

where b is one of the adjustable parameters of Eq. (S2).

The $\Delta_l^g C_{p,m}^o$ -values used in Eq. (S3) are usually derived according to empirical equations developed by Acree and Chickos [8]:

$$\Delta_l^g C_{p,m}^o(298.15\text{ K}) = -0.26 \times C_{p,m}^o(\text{liq}, 298.15\text{ K}) - 10.58 \quad (\text{S4})$$

where $C_{p,m}^o(\text{liq}, 298.15\text{ K})$ values are of experimental origin or they can be also estimated according to the group-additivity procedure by Chickos *et al.* [9]. The empirical coefficients in Eqs. (S4) and (S5) were originally derived from experimental data available for various organic compounds, but carvone derivatives did not participated in the parameterization of these equations.

The vapor pressures available in the literature over the liquid phase of carvone derivatives were available at high temperatures and even at temperatures close to the boiling point. For this type of vapor pressure data, the influence of differences in isobaric heat capacities $\Delta_l^g C_{p,m}^o$ is significant.

The validity of the $\Delta_l^g C_{p,m}^o$ -values can be independently checked with help of the Clarke and Glew equation [10]:

$$R \times \ln(p_i/p^o) = -\frac{\Delta_l^g G_m^o(\theta)}{\theta} + \Delta_l^g H_m^o(\theta) \left(\frac{1}{\theta} - \frac{1}{T} \right) - \Delta_l^g C_{p,m}^o(\theta) \left(\frac{\theta}{T} - 1 + \ln \left(\frac{T}{\theta} \right) \right) \quad (\text{S5}),$$

where p_i is the vapour pressure at the temperature T , p° is an arbitrary reference pressure ($p^\circ = 1$ Pa in this work), θ is an arbitrary reference temperature (in this work we use $\theta = 298.15$ K), R is the molar gas constant, $\Delta_l^g G_m^\circ(\theta)$ is the difference in the standard molar Gibbs energy between the gaseous and the liquid phases, $\Delta_l^g H_m^\circ(\theta)$ is the standard molar vaporisation enthalpy, and $\Delta_l^g C_{p,m}^\circ(\theta)$ is the difference in the molar heat capacity at constant pressure between the gaseous and the liquid phase. An advantage of the Clarke and Glew equation is that the fitting coefficients (in contrast to Eq. (S2)) are directly related to the thermodynamic functions of vaporisation. In our experience, however, a prerequisite for the application of Clarke and Glew's equation is good quality and consistency of the experimental data. In addition, the vapour pressures used for the fitting should cover the temperature range of at least 100 K. These prerequisites are fulfilled only in few highly accurate static and ebulliometric measurements reported for the cyclic ketones [11–15] and cyclic alcohols [11]. These experimental vapour pressures were approximated using Eq. (S5) and the $\Delta_l^g C_{p,m}^\circ$ -values were derived and analyzed. It has turned out that the $\Delta_l^g C_{p,m}^\circ$ -values calculated using the conventional method of Acree and Chickos [8] are systematically and significantly different when the procedure is applied to cyclic ketones and alcohols. This observation has prompted the recalculations of the empirical coefficients in Eq. (S4) using the $\Delta_l^g C_{p,m}^\circ$ -values evaluated according to Eq. (S5) from reliable vapor pressures: for cyclic ketones [11–15]:

$$\Delta_l^g C_{p,m}^\circ(298.15 \text{ K}) = -0.26 \times C_{p,m}^\circ(\text{liq}, 298.15 \text{ K}) + 5.6 \quad (\text{S6}),$$

for cyclic alcohols [11]:

$$\Delta_l^g C_{p,m}^\circ(298.15 \text{ K}) = -0.26 \times C_{p,m}^\circ(\text{liq}, 298.15 \text{ K}) - 51.0 \quad (\text{S7}),$$

These equations were used in this work for the temperature adjustments of vaporisation enthalpies of carvone derivatives to the reference temperature $T = 298.15$ K (see Table S4).

Table S4

Compilation of data on molar heat capacities $C_{p,m}^\circ(\text{liq or cr})$ and heat capacity differences $\Delta_{l,\text{cr}}^g C_{p,m}^\circ$ (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) at $T = 298.15$ K

Compounds	$C_{p,m}^\circ(\text{liq})^a$	$-\Delta_l^g C_{p,m}^\circ^b$
(-)-carvone, 2244-16-8	276.8 ^c	66.4 [Eq. 6]
(±)-dihydrocarvone	276.6	66.3 [Eq. 6]
carvotanacetone, 499-71-8	284.0	68.2 [Eq. 6]
(±)-trans-tetrahydrocarvone (carvomenthone), 499-70-7	286.4	68.9 [Eq. 6]
(±)-cis-tetrahydrocarvone, 57875-63-5	286.4	68.9 [Eq. 6]
(±)-cis-carveol, 1197-06-4	302.3	129.6 [Eq. 7]
(±)-trans-carveol, 9948-9	302.3	129.6 [Eq. 7]
dihydrocarveol, 619-01-2	327.2	136.0 [Eq. 7]
carvotanacetol, 536-30-1	312.1	132.1 [Eq. 7]
carvomenthol, 499-69-4	314.5	132.8 [Eq. 7]
carvacrol, 499-75-2	322.4 [16]	
2-methyl-cyclohexanone, 583-60-8	204.6 [17]	47.6 [Eq. 6]
2-methyl-2-cyclohexen-1-one, 1121-18-2	199.9	46.4 [Eq. 6]
2-methylcyclohex-2-en-1-ol, 20461-30-7	228.0	110.3 [Eq. 6]

^a Calculated according to the group-additivity procedure developed by Chickos et al. [9].

^b Calculated according to the empirical procedures developed by Acree and Chickos [8] and modified in this work (see text above).

^c For comparison: $C_{p,m}^\circ(\text{liq}, 298.15 \text{ K}) = 279.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [18] for (+)-carvone measured by Tian-Calvet calorimetry

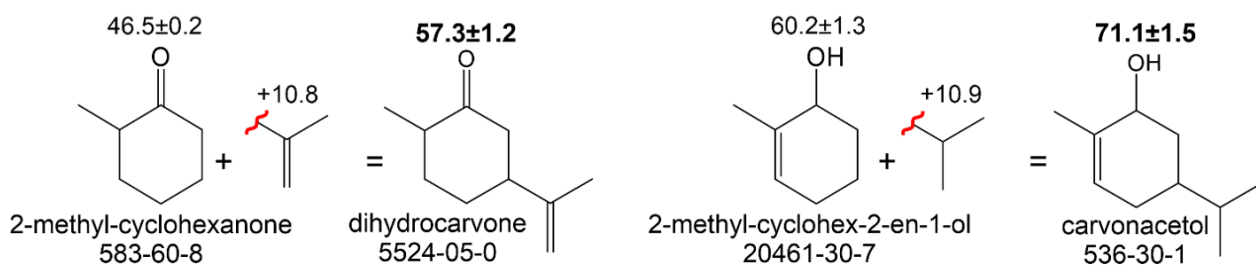


Fig. S3 Calculation the enthalpy of vaporisation, $\Delta_1^g H_m^o(298.15 \text{ K})$, of dihydrocarvone using the 2-methyl-cyclohexanone as the “centerpiece” (left). Calculation the enthalpy of vaporisation, $\Delta_1^g H_m^o(298.15 \text{ K})$, of carvonacetol using the 2-methyl-cyclohex-2-en-1-ol as the “centerpiece” (right). All values in $\text{kJ} \cdot \text{mol}^{-1}$. The experimental values of vaporisation enthalpies of the “centerpieces” are given in Tables S2 and S5.

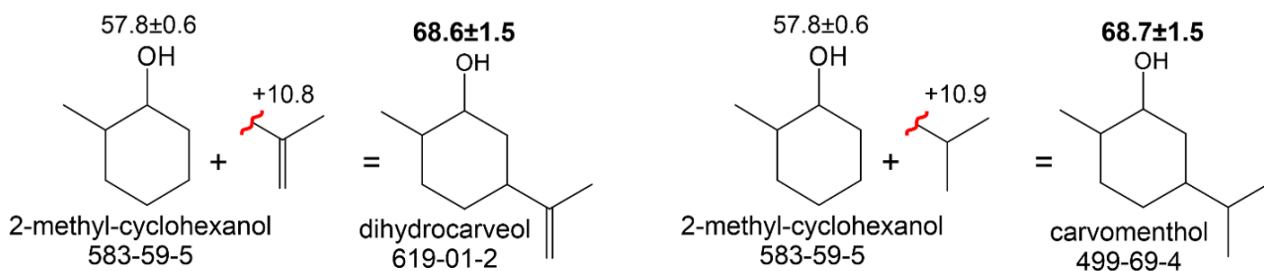


Fig. S4 Calculation the enthalpy of vaporisation, $\Delta_1^g H_m^o(298.15 \text{ K})$, of dihydrocarveol using the 2-methyl-cyclohexanol as the “centerpiece” (left). Calculation the enthalpy of vaporisation, $\Delta_1^g H_m^o(298.15 \text{ K})$, of carvomenthol using the 2-methyl-cyclohexanol as the “centerpiece” (right). All values in $\text{kJ} \cdot \text{mol}^{-1}$. The experimental values of vaporisation enthalpies of the “centerpieces” are given in Table S5.

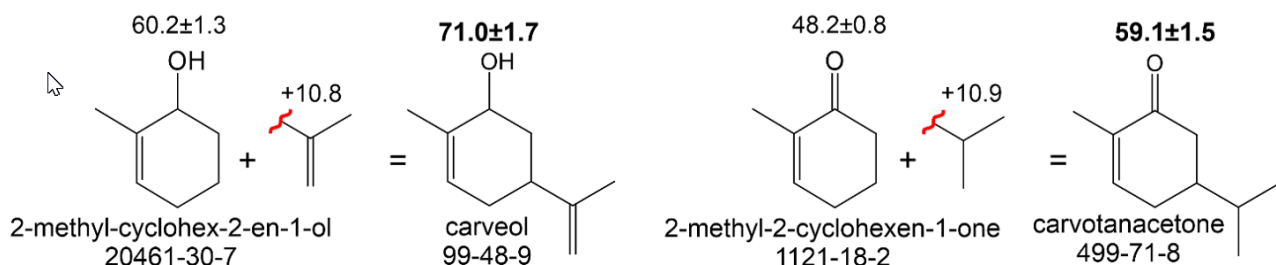


Fig. S5 Calculation the enthalpy of vaporisation, $\Delta_1^g H_m^o(298.15 \text{ K})$, of carveol using the 2-methyl-2-cyclohex-2-en-1-ol as the “centerpiece” (left). Calculation the enthalpy of vaporisation, $\Delta_1^g H_m^o(298.15 \text{ K})$, of carvotanacetone using the 2-methyl-2-cyclohexen-1-one as the “centerpiece” (right). All values in $\text{kJ} \cdot \text{mol}^{-1}$. The experimental values of vaporisation enthalpies of the “centerpieces” are given in Tables S2 and S5.

Table S5

The enthalpies of vaporisation, $\Delta_1^g H_m^o$, and enthalpies of formation, $\Delta_f H_m^o(\text{liq})$, of the auxiliary reference compounds at $T = 298.15 \text{ K}$ ($p^o = 0.1 \text{ MPa}$) in $\text{kJ}\cdot\text{mol}^{-1}$

CAS	Compounds	$\Delta_1^g H_m^o$	$\Delta_f H_m^o$ [19]
110-82-7	cyclohexane	33.1±0.2 [20]	-156.4±0.8
696-29-7	<i>iso</i> -propyl-cyclohexane	44.0±0.2 [20]	
583-59-5	2-methyl-cyclohexanol	57.8±0.6 [21]	
108-94-1	cyclohexanone	45.1±0.2 [20]	-271.2±2.1
583-60-8	2-methyl-cyclohexanone	46.5±0.2 [13]	
2157-18-8	<i>iso</i> -propenyl-cyclohexane	43.9±1.1 [22]	
110-83-8	cyclohexene		-38.5±0.8
98-83-9	α -methyl-styrene		70.5±1.2
98-82-8	<i>iso</i> -propylbenzene		-41.1±1.0
67-64-1	acetone		-248.1±0.7
67-63-0	2-propanol		-318.1±0.5
108-93-0	cyclohexanol		-348.2±2.1

Table S6

Compilation of the standard molar enthalpies of vaporisation, $\Delta_1^g H_m^o$, of the carvone derivatives using the “centerpiece” approach (in $\text{kJ}\cdot\text{mol}^{-1}$)

Compounds, CAS	$\Delta_1^g H_m^o$ ^a	$\Delta_1^g H_m^o$ ^b
	298.15 K	298.15 K
(-)-carvone, 6485-40-1	61.7±0.3	59.0±1.4
cis-(±)-dihydrocarvone, 3792-53-8	56.8±1.6	57.3±1.2
trans-(±)-dihydrocarvone, 5524-05-0	57.2±1.7	57.3±1.2
cis-(±)-tetrahydrocarvone, (CAS not found)	58.4±1.6	57.4±1.0
trans-(±)-tetrahydrocarvone (carvomenthone), 499-70-7	58.0±1.7	57.4±1.0
carvotanacetone, 499-71-8	59.3±1.5	59.1±0.9
carvomenthol, 499-69-4	69.9±3.3	68.7±1.5
(±)-cis-carveol, 1197-06-4	71.0±3.0	71.0±1.7
(±)-trans-carveol, 99-48-9	72.6±2.9	71.0±1.7
trans-dihydrocarveol, 619-01-2	71.9±3.4	68.6±1.5
cis-dihydrocarveol, 22567-21-1	70.1±3.6	68.6±1.5
carvotanacetol, 536-30-1	73.1±3.0	71.1±1.5

^a From Table 3.

^b Calculated using the “centerpiece” approach (see Section 4.2.3).

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. About 0.3-0.5 g of the solid sample was pressed into a pellet, weighed with a microbalance with a resolution of 10^{-6} g, and burned in oxygen at a pressure of 3.04 MPa. In a preliminary series of combustion experiments, a considerable amount of soot was sometimes observed on the walls of the Pt crucible. To achieve complete combustion, a certain amount of polyethylene cuttings was used as an auxiliary compound. The pellet was placed in the crucible, surrounded with polyethylene cuts and ignited. The clean experiments with and without polyethylene showed results that agreed within the experimental

uncertainty. The bomb was not purged with oxygen beforehand. Test experiments with and without purging with O₂ showed results that were also consistent within the experimental uncertainty. The detailed procedure has already been described [23,24].

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 combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but neither was detected. The energy equivalent of the calorimeter $_{\text{calor}}$ was determined with a standard reference sample of benzoic acid (sample SRM 39j, N.I.S.T.). Correction for nitric acid formation was based on titration with 0.1 mol·dm⁻³ NaOH (aq). Conventional procedures [25] were used for reduction of the data to standard conditions. Auxiliary data required for the reduction are collected in Table S7.

Table S7

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 content ^b	ρ (293 K)	c_p (298.15 K) ^c	$(\delta V/\delta T)_p$ ^d
		ppm	g·cm ⁻³	J·K ⁻¹ g ⁻¹	10 ⁻³ ·cm ³ ·K ⁻¹ ·g ⁻¹
(-)-carvone	C ₁₀ H ₁₄ O	396	0.966 ^e	1.84	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 [26]. The specific energy of combustion $\Delta_c u^\circ(\text{cotton}) = -16945.2 \text{ J}\cdot\text{g}^{-1}$; $u(\Delta_c u^\circ) = 4.2 \text{ J}\cdot\text{g}^{-1}$. The specific energy of combustion $\Delta_c u^\circ(\text{polyethylene}) = -46357.3 \text{ J}\cdot\text{g}^{-1}$; $u(\Delta_c u^\circ) = 3.5 \text{ J}\cdot\text{g}^{-1}$. The standard uncertainties are reported for the specific energies of combustion.

^b The results of combustion experiments were corrected for this residual amount of water.

^c Calculated from the molar heat capacities at 298.15 K (see Table S4).

^d Estimated.

^e From Ref. [27].

The experimental standard molar enthalpy of formation in the liquid state $\Delta_f H_m^\circ(\text{liq}) = -186.8 \pm 2.3 \text{ kJ}\cdot\text{mol}^{-1}$, (see Table S8) was calculated based on the $\Delta_c H_m^\circ$ -value of the reaction according to Eq. (13) using Hess's Law and the standard molar enthalpies of formation of H₂O(l) and CO₂(g) assigned by CODATA [28]. The total uncertainties of $\Delta_c H_m^\circ$ and $\Delta_f H_m^\circ$ -values have been calculated according to the guidelines presented by Hubbard *et al.* [25] and Olofsson [29]. The uncertainty of combustion energy, $\Delta_c u^\circ(\text{liq})$, are expressed as standard deviation of the mean. According to the thermochemical practice, the uncertainties assigned to the $\Delta_f H_m^\circ(\text{liq})$ -value are twice the overall standard deviations and include the uncertainties of the calibration, the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H₂O and CO₂.

Table S8.

Compilation of combustion results at $T = 298.15 \text{ K}$ ($p^\circ = 0.1 \text{ MPa}$) obtained for (-)-carvone^a

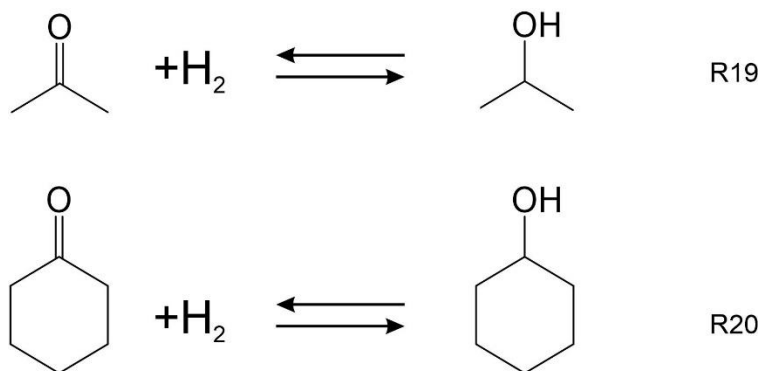
$\Delta_c u^\circ(\text{liq})$	$\Delta_c H_m^\circ(\text{liq})$	$\Delta_f H_m^\circ(\text{liq})_{\text{exp}}$
J·g ⁻¹	kJ·mol ⁻¹	kJ·mol ⁻¹
-38222.5±4.3	-5479.1±1.9	-186.8±2.3

^a Uncertainties related to the combustion experiments were estimated according to the procedure recommended by Olofsson [29]. The auxiliary information for the combustion experiments is given in Table S7.

Table S9

Calculation of the liquid phase thermodynamic properties for reactions R1 to R20 (see Table 5)

Reactions	$\Delta_r H_m^\circ$ (298 K)	$\Delta_r S_m^\circ$ (298 K)	$T \times \Delta_r S_m^\circ$ (298 K)
	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$
1	-92.7	-115.9	-34.5
2	-114.7	-130.5	-38.9
3	-70.7	-158.6	-47.3
4	-111.8	-122.5	-36.5
5	-95.6	-123.9	-36.9
6	-56.9	-166.4	-49.6
7	-110.4	-114.0	-34.0
8	-111.1	-124.6	-37.1
9	-110.3	-118.4	-35.3
10	-111.2	-120.2	-35.8
11	13.9	119.2	35.5
12	-97.9	-3.3	-1.0
13	-1.5	8.8	2.6
14	-1.6	-1.9	-0.6
15	-9.5	-2.4	-0.7
16	-180.2	-401.6	-119.7
17	-207.4	-246.4	-73.4
18	-278.1	-404.9	-120.7
19	-70.0	-150.5	-44.8
20	-77.0	-155.8	-46.4

**Fig. S6.** Reactions 19 and 20 (see Table 5) for hydrogenation of acetone and cyclohexanone**References**

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