



Thermochemistry of substituted benzenes: acetophenones with methyl, ethyl, cyano and acetoxy substituents

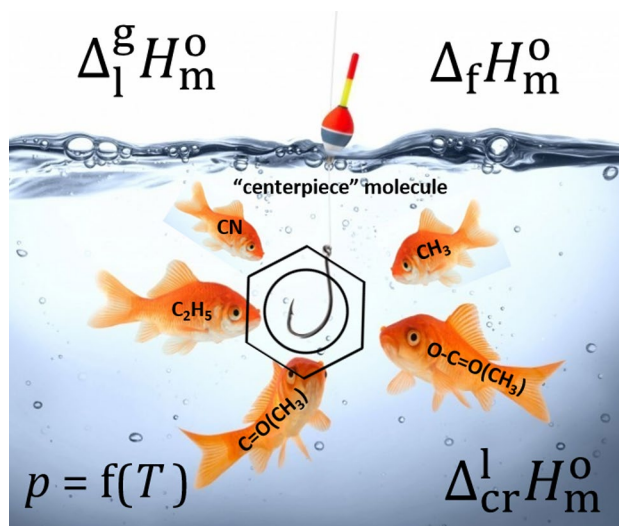
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Abstract

The enthalpies of vaporization/sublimation of 2-, 3- and 4-methyl-acetophenones and 2-, 3-, 4-cyano-acetophenones were derived from the vapor pressure temperature dependence measured with help of the gas saturation method. Enthalpies of fusion of 4-methyl-acetophenone and 2-, 3- and 4-cyano-acetophenone were measured by using DSC. The literature thermochemical data for methyl-, ethyl, cyano- and acetoxy-substituted acetophenones and new results were evaluated using structure–property correlations. The G* quantum chemical methods were validated for reliable estimation of the enthalpies of formation of substituted acetophenones in the gaseous state. The evaluated thermodynamic data were used to design the “centerpiece” method for the assessment of enthalpies of formation and enthalpies of vaporization of substituted benzenes.

Graphical abstract



Keywords Acetophenones · Group additivity · Quantum chemical calculations · Enthalpy of formation · Enthalpies of phase transitions

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Introduction

Structure–property relationships belong to the basic principles of chemistry. Substituted benzenes are a remarkable model system for structure–property manifestation. The type and position of substituents on benzene ring significantly influence the physicochemical properties of the compound

and the appropriate chemical, physical or biological effects. The quantification of these relationships in series of substituted benzenes has been a long-standing goal of our laboratory [1–3]. The aim of the present study is therefore to continue this research on series of acetophenones substituted with the methyl, ethyl, cyano and acetoxy groups.

The fundamental properties of these substituted benzenes: vapor pressures, enthalpies of formation, $\Delta_f H_m^\circ$ (g, liq or cr), and phase transitions enthalpies: $\Delta_{cr}^g H_m^\circ$ (sublimation), $\Delta_1^g H_m^\circ$ (vaporization) and $\Delta_{cr}^l H_m^\circ$ (fusion) derived in this work, as well as those from the literature and were validated and checked for internal consistency. The consistent enthalpic data sets for disubstituted benzenes were analyzed with help of a “centerpiece” approach [1–3] in order to quantify the energetics of substituent interactions on the benzene ring.

Experimental

Materials

The structural formulas of acetophenones substituted with the methyl, ethyl, cyano and acetoxy groups studied in this work are given in Fig. 1.

In this study, we used commercial samples of 95–99% purities as stated by manufacturer, see Table S1). The liquid compounds were additionally purified by vacuum distillation. The solids were re-sublimed at reduced pressure.

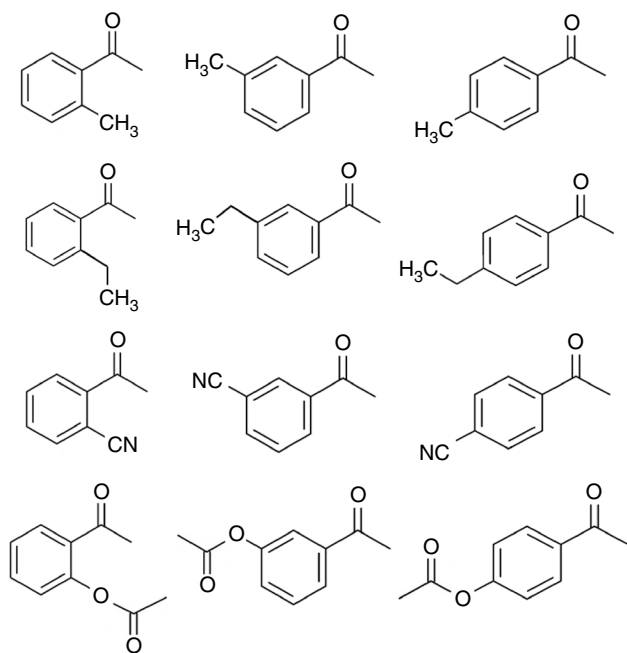


Fig. 1 Substituted acetophenones discussed in this work: 2-, 3- and 4-methyl-acetophenone, 2-, 3- and 4-ethyl-acetophenone, 2-, 3- and 4-cyano-acetophenone, 2-, 3- and 4-acetoxy-acetophenone

Purities of samples were measured by a GC equipped with a capillary column. Only residual amounts of impurities (no more than 0.05%) were detected in the compounds examined by transpiration.

Experimental and computational methods

The vapor pressures of substituted acetophenones were determined by using the gas saturation method with a self-made setup [4, 5]. The glass beads covered with the sample were placed in the saturator. The system was exposed to the nitrogen stream at a precisely defined flow rate. Before leaving the saturator, the liquid–gas (or solid–gas) equilibrium was reached. The material transported out of the saturator within a certain time was trapped and quantified with help of gas chromatography. The vapor pressure, p_i , at each saturation temperature, T_i , was derived from the amount of sample collected in the cold trap using the ideal gas law:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i; \text{ with } V = (n_{N_2} + n_i) \cdot R \cdot T_a / P_a \quad (1)$$

with m_i = mass of the condensed sample; R = ideal gas constant; T_a = ambient temperature; V = gas-phase volume consisting of n_i mole of compound in the nitrogen stream (of molar mass M_i) and n_{N_2} moles of nitrogen; and P_a is atmospheric pressure.

The vapor pressures obtained from the gas saturation method are considered reliable within (1 to 3)% [4, 5]. The temperature dependence of vapor pressure was used for evaluation of sublimation/vaporization enthalpies. The error in sublimation/vaporization enthalpies is believed to be within \pm (0.3–0.5) kJ mol^{−1} [4, 5].

Enthalpies of fusion of 4-methyl-acetophenone and 2-, 3- and 4-cyano-acetophenone were measured by using the Mettler Toledo DSC 823e equipped with Huber TC125MT. Details are published elsewhere [6]. The calibration of the DSC was carried out with indium. The deviation of the melting temperature, T_m , from that of the reference compound was not greater than 0.3 K. The enthalpy of fusion, agreed with the reference value better than 0.2 kJ mol^{−1}. In order to obtain sufficient contact between the bottom of the pan and the sample, the pan was heated in the first DSC run at a rate of 10 K·min^{−1} to a temperature that was \sim 30 K above the known T_m and then at the same rate cooled to room temperature. The choice of heat rate is caused by the fact that this rate is a yardstick for many organic substances to carry our DSC measurements. The DSC measurements were repeated 3–4 times. All measurements were taken under nitrogen flow.

The quantum chemical calculations were carried out with the Gaussian 09 [7]. The preliminary search for the stable conformers was carried out initially using MM3 [8] and then by b3lyp/6-31 g(d,p) [9]. The energies E_0 and enthalpies

H_{298} of the most stable conformers were estimated with the high-level composite methods G3MP2 [10] and G4 [11]. The standard enthalpies of formation in the gas state of the compound of interest were calculated using H_{298} taken from the output of the Gaussian 09 file. Details of the calculation procedure have been given elsewhere [12].

Results and discussion

Vapor pressures of substituted acetophenones

The vapor pressures, p_i , measured for methyl- and cyano-acetophenones by the gas saturation method were approximated using the equation:

$$R \times \ln(p_i/p_{\text{ref}}) = a + \frac{b}{T} + \Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\text{o}} \times \ln\left(\frac{T}{T_0}\right) \quad (2)$$

In this equation: R = universal gas constant; $p_{\text{ref}} = 1\text{Pa}$; a and b are adjustable parameters; $\Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\text{o}}$ = difference between heat capacities $C_{\text{p,m}}^{\text{o}}$ (g) or $C_{\text{p,m}}^{\text{o}}$ (liq or cr) phases, respectively; and T_0 = arbitrarily 298.15 K. Values $\Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\text{o}}$ are given in Table S2. They were estimated using a procedure suggested by Chickos and Acree [13] based on the standard molar heat capacities $C_{\text{p,m}}^{\text{o}}$ (cr) or $C_{\text{p,m}}^{\text{o}}$ (liq). The absolute vapor pressures for methyl- and cyano-acetophenones are given in Table 1.

Absolute vapor pressure values of 2-methyl-acetophenone, 3-methyl-acetophenone, 2-cyano-acetophenone, 3-cyano-acetophenone and 4-cyano-acetophenone were not found in the literature. The temperature dependences of available vapor pressures for 4-methyl-acetophenone are shown in Fig. S1. The agreement of our new transpiration results with those from the Knudsen method [16] is poor. It should be noted, however, that the Knudsen method is normally used for measurements of very low pressures (usually below 1 Pa) over the solid samples. As a consequence, the disagreement observed could be attributed to the limitations specific for the Knudsen method. Vapor pressures derived from the coefficients of Antoine equation given by Stephenson and Malanowski [17] are also questionable as neither the method nor the purity of the sample are available.

The very limited data on vapor pressures of ethyl-substituted acetophenones prompted us to collect experimental boiling temperatures at different pressures compiled by SciFinder [18]. The accuracy of these data is questionable as it comes from the distillation of a compound after its synthesis and not from special physicochemical studies. However, the numerous data on boiling temperatures at standard pressure, as well as at reduced pressures (see Table S3), provide at least a reliable level of the experimental vapor pressures

and a reliable trend of the dependence of the vapor pressure with temperature. For example, in Fig. S2 for 2-ethylacetophenone, the boiling points at different pressures compiled by SciFinder are in fair agreement with the available data set from Stephenson and Malanowski [17]. In this work, we have systematically collected the data available for 2-, 3- and 4-ethylacetophenones in the SciFinder [18] for comparison (see Table S3). The comparisons of these results with those available from the literature are shown in Figs. S2–S4 (supporting information). From these comparisons, it was concluded that data from the static method of Khorovskaya et al. [19] for 3-ethyl- and 4-ethylacetophenone are most likely in error.

Vaporization/sublimation thermodynamics of substituted acetophenones

The experimental vapor pressures were used to estimate the enthalpies of vaporization/sublimation of substituted acetophenones according to equations:

$$\Delta_1^{\text{g}} H_{\text{m}}^{\text{o}}(T) = -b + \Delta_1^{\text{g}} C_{\text{p,m}}^{\text{o}} \times T \quad (3)$$

$$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}}(T) = -b + \Delta_{\text{cr}}^{\text{g}} C_{\text{p,m}}^{\text{o}} \times T \quad (4)$$

The vaporization/sublimation entropies at temperatures T were estimated from the experimental p – T dependences:

$$\Delta_1^{\text{g}} S_{\text{m}}^{\text{o}}(T) = \Delta_1^{\text{g}} H_{\text{m}}^{\text{o}}/T + R \times \ln(p_i/p^{\text{o}}) \quad (5)$$

$$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^{\text{o}}(T) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}}/T + R \times \ln(p_i/p^{\text{o}}) \quad (6)$$

with $p^{\text{o}} = 0.1\text{MPa}$. Values of $\Delta_{\text{l,cr}}^{\text{g}} H_{\text{m}}^{\text{o}}(T)$ and $\Delta_{\text{l,cr}}^{\text{g}} S_{\text{m}}^{\text{o}}(T)$ are collected in Table 1. The algorithm for calculating the uncertainties in the enthalpies of vaporization/sublimation can be found elsewhere [14, 15]. These combined uncertainties include uncertainties in vapor pressure, uncertainties inherent in the experimental conditions of the gas saturation method and uncertainties due to adjustment to $T = 298.15\text{K}$. The standard molar enthalpies of vaporization/sublimation of substituted acetophenones at $T = 298.15\text{K}$, estimated using Eqs. 3 and 4 are given in Table 2.

Our new result for 2-methyl-acetophenone $\Delta_1^{\text{g}} H_{\text{m}}^{\text{o}}(298.15\text{K}) = 59.3 \pm 0.4\text{kJ mol}^{-1}$ agrees well with the value $\Delta_1^{\text{g}} H_{\text{m}}^{\text{o}}(298.15\text{K}) = 58.9 \pm 0.9\text{kJ mol}^{-1}$, directly measured by Calvet calorimetry [20]. The enthalpy of vaporization for 4-methyl-acetophenone, $\Delta_1^{\text{g}} H_{\text{m}}^{\text{o}}(298.15\text{K}) = 60.7 \pm 1.0\text{kJ mol}^{-1}$, measured directly by Calvet calorimetry [20], and the values obtained in this work from the vapor pressures temperature dependences [16, 17] are in very good accordance (see Table 2). The enthalpy of sublimation $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}}(298.15\text{K}) = 97.1 \pm 0.6\text{kJ mol}^{-1}$ of 3-cyano-acetophenone measured in this work by the gas saturation method is in fair accordance with the is $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}}$

Table 1 Absolute vapor pressures p_i , standard ($p^0=0.1$ MPa) molar vaporization/sublimation enthalpies $\Delta_{l,cr}^g H_m^o$ and standard molar vaporization/sublimation entropies $\Delta_{l,cr}^g S_m^o$ measured for substituted acetophenones

T/K^a	m/mg^b	$V(N_2)^c / dm^3$	T_a/K^d	Flow/ $dm^3 \cdot h^{-1}$	p/Pa^e	$u(p_i)/Pa^f$	$\Delta_{l,cr}^g H_m^o(T)/$ $kJ \cdot mol^{-1}$	$\Delta_{l,cr}^g S_m^o(T)/$ $J \cdot K^{-1} \cdot mol^{-1}$
2-methyl-acetophenone: $\Delta_1^g H_m^o(298.15 K) = (59.3 \pm 0.4) kJ \cdot mol^{-1}$								
$\ln(p_i/p_{ref}) = \frac{299.7}{R} - \frac{80827.5}{RT} - \frac{72.2}{R} \ln \frac{T}{298.15}; p_{ref} = 1 Pa$								
293.3	0.31	0.275	294.4	1.10	20.84	0.55	59.65	132.9
298.3	0.48	0.275	294.6	1.10	31.84	0.82	59.29	131.8
303.1	0.71	0.275	294.5	1.10	47.29	1.21	58.94	130.8
308.1	2.14	0.602	294.6	1.20	64.87	1.65	58.58	129.1
312.8	2.08	0.401	294.8	1.20	94.91	2.40	58.25	128.4
295.2	0.38	0.286	293.4	1.07	24.22	0.63	59.52	132.4
290.2	0.38	0.447	294.3	1.07	15.74	0.42	59.87	133.5
285.6	0.41	0.699	294.5	1.05	10.81	0.30	60.21	134.9
300.0	2.03	1.017	294.6	2.77	36.52	0.94	59.16	131.4
306.2	1.96	0.621	294.6	1.06	57.71	1.47	58.72	129.8
312.7	2.01	0.390	294.8	1.06	93.95	2.37	58.25	128.3
319.6	2.14	0.266	295.2	1.06	146.79	3.69	57.75	126.5
326.2	3.43	0.266	295.9	1.06	235.90	5.92	57.27	125.3
332.7	5.24	0.266	295.3	1.06	359.44	9.01	56.81	123.9
285.5	0.32	1.032	295.0	5.75	2.69	0.17	60.74	131.7
3-methyl-acetophenone: $\Delta_1^g H_m^o(298.15 K) = (59.8 \pm 0.4) kJ \cdot mol^{-1}$								
$\ln(p_i/p_{ref}) = \frac{296.4}{R} - \frac{81354.1}{RT} - \frac{72.2}{R} \ln \frac{T}{298.15}; p_{ref} = 1 Pa$								
290.4	0.34	0.718	295.0	8.68	2.69	0.24	60.39	130.3
295.2	0.50	0.683	297.1	13.45	2.73	0.36	60.04	129.3
298.1	0.33	0.353	294.0	17.21	1.06	0.46	59.83	128.7
300.6	0.78	0.683	298.4	21.11	2.73	0.55	59.65	128.1
303.2	0.91	0.683	299.3	24.65	2.73	0.64	59.46	127.1
303.2	0.37	0.280	294.9	24.38	1.12	0.64	59.46	127.0
308.1	0.50	0.252	299.0	36.56	1.01	0.94	59.11	126.1
312.7	1.92	0.689	296.9	51.25	1.12	1.31	58.78	125.0
319.5	2.07	0.466	298.8	82.21	1.12	2.08	58.29	123.4
326.5	2.10	0.298	296.4	129.37	1.12	3.26	57.78	121.7
333.2	3.18	0.280	296.2	208.70	1.12	5.23	57.30	120.6
334.0	3.33	0.280	296.4	218.52	1.12	5.48	57.24	120.5
4-methyl-acetophenone: $\Delta_1^g H_m^o(298.15 K) = (61.6 \pm 0.3) kJ \cdot mol^{-1}$								
$\ln(p_i/p_{ref}) = \frac{299.8}{R} - \frac{83131.5}{RT} - \frac{72.2}{R} \ln \frac{T}{298.15}; p_{ref} = 1 Pa$								
302.6	1.41	1.413	294.5	1.07	18.30	0.48	61.28	131.0
303.6	0.46	0.441	294.5	1.06	19.19	0.50	61.22	130.5
304.6	1.57	1.388	296.0	2.97	20.79	0.54	61.14	130.2
306.6	1.83	1.383	296.2	1.06	24.35	0.63	61.00	129.8
308.5	1.52	0.968	297.2	2.90	29.00	0.75	60.86	129.5
309.5	1.56	0.942	295.8	2.97	30.45	0.79	60.79	129.1
312.5	1.53	0.730	295.4	1.83	38.44	0.99	60.57	128.4
316.5	1.61	0.562	294.6	1.05	52.22	1.33	60.28	127.7
318.4	2.23	0.674	293.9	1.06	60.24	1.53	60.14	127.2
320.4	1.52	0.404	295.2	1.05	68.70	1.74	60.00	126.7
323.4	3.27	0.727	295.6	1.06	82.33	2.08	59.78	125.8
324.4	1.45	0.298	294.4	0.99	88.76	2.24	59.71	125.6
329.3	1.75	0.249	294.4	0.99	128.01	3.23	59.36	124.9
334.3	2.54	0.264	295.7	1.05	176.54	4.44	59.00	123.8
339.3	4.28	0.330	296.7	0.99	237.67	5.97	58.63	122.6
344.3	5.78	0.330	297.9	0.99	322.09	8.08	58.28	121.6

Table 1 (continued)

T/K^a	m/mg^b	$V(N_2)^c / dm^3$	T_a/K^d	Flow/ $dm^3 \cdot h^{-1}$	p/Pa^e	$u(p_i)/Pa^f$	$\Delta_{i,cr}^g H_m^o(T)/$ $kJ \cdot mol^{-1}$	$\Delta_{i,cr}^g S_m^o(T)/$ $J \cdot K^{-1} \cdot mol^{-1}$
349.3	7.62	0.330	297.8	0.99	423.64	10.62	57.91	120.4
354.2	10.05	0.330	297.9	0.99	558.24	13.98	57.56	119.4
2-cyano-acetophenone: $\Delta_{i,cr}^g H_m^o(298.15 K) = (72.9 \pm 0.4) \cdot kJ \cdot mol^{-1}$								
$\ln(p_i/p_{ref}) = \frac{309.8}{R} - \frac{95544.7}{RT} - \frac{76.1}{R} \ln \frac{T}{298.15}; p_{ref} = 1 Pa$								
322.9	0.18	1.186	295.8	2.74	2.63	0.07	70.97	132.1
325.3	0.18	1.004	297.6	2.87	3.13	0.08	70.79	131.3
325.3	0.18	1.004	297.3	2.87	3.08	0.08	70.79	131.2
328.2	0.19	0.852	298.3	2.84	3.90	0.10	70.57	130.6
329.2	0.19	0.770	296.4	2.43	4.23	0.11	70.50	130.4
330.0	0.19	0.730	295.6	2.74	4.41	0.12	70.43	130.1
332.1	0.18	0.601	297.0	1.03	5.20	0.16	70.27	129.6
333.2	0.19	0.555	296.4	1.08	5.77	0.17	70.19	129.5
336.1	0.17	0.412	297.4	1.03	7.06	0.20	69.97	128.7
339.9	0.20	0.358	297.3	1.08	9.64	0.27	69.68	128.1
341.1	0.16	0.258	297.7	1.03	10.45	0.29	69.59	127.8
346.0	0.67	0.770	297.6	1.08	14.92	0.40	69.21	126.8
352.9	0.63	0.466	298.5	1.08	22.99	0.60	68.69	125.0
360.1	0.69	0.323	298.3	1.08	36.57	0.94	68.14	123.4
366.9	0.90	0.269	297.9	1.08	57.34	1.46	67.62	122.2
372.4	1.25	0.269	297.2	1.08	78.82	2.00	67.21	121.1
3-cyano-acetophenone: $\Delta_{i,cr}^g H_m^o(298.15 K) = (72.9 \pm 0.4) \cdot kJ \cdot mol^{-1}$								
$\ln(p_i/p_{ref}) = \frac{332.1}{R} - \frac{106212.7}{RT} - \frac{30.7}{R} \ln \frac{T}{298.15}; p_{ref} = 1 Pa$								
318.4	0.13	3.559	299.8	2.85	0.64	0.02	96.44	203.5
323.8	0.13	1.898	298.8	2.85	1.20	0.03	96.27	203.1
328.3	0.28	2.395	299.7	3.59	2.03	0.06	96.13	203.0
330.4	0.13	0.898	300.6	3.59	2.56	0.07	96.07	202.8
332.5	0.14	0.759	296.1	2.85	3.03	0.08	96.01	202.2
333.2	0.18	0.958	300.0	3.59	3.26	0.09	95.98	202.2
336.3	0.14	0.513	300.7	1.14	4.63	0.12	95.89	202.2
338.2	0.30	0.898	299.5	3.59	5.64	0.17	95.83	202.1
341.4	0.13	0.304	300.3	1.14	7.50	0.21	95.73	201.5
348.2	0.24	0.285	300.4	1.14	14.54	0.39	95.52	200.9
350.7	0.30	0.280	299.7	1.12	18.70	0.49	95.45	200.8
354.8	0.45	0.285	300.5	1.14	27.41	0.71	95.32	200.4
360.3	0.73	0.280	300.0	1.12	44.76	1.14	95.15	200.0
362.3	0.40	0.133	300.8	1.14	51.48	1.31	95.09	199.5
4-cyano-acetophenone: $\Delta_{i,cr}^g H_m^o(298.15 K) = (87.7 \pm 0.7) \cdot kJ \cdot mol^{-1}$								
$\ln(p_i/p_{ref}) = \frac{313.7}{R} - \frac{96872.9}{RT} - \frac{30.7}{R} \ln \frac{T}{298.15}; p_{ref} = 1 Pa$								
303.2	0.14	5.398	296.6	3.00	0.46	0.02	87.57	186.6
306.3	0.14	3.599	296.8	3.00	0.64	0.02	87.47	186.2
308.2	0.16	3.249	295.2	3.00	0.82	0.03	87.41	186.3
312.2	0.14	1.849	297.0	3.00	1.25	0.04	87.29	185.8
313.2	0.10	1.230	296.0	3.08	1.37	0.04	87.26	185.6
316.2	0.14	1.200	297.2	3.00	1.95	0.05	87.17	185.5
318.1	0.12	0.854	297.2	3.01	2.30	0.06	87.11	185.1
318.2	0.12	0.923	295.8	3.08	2.29	0.06	87.11	185.0
320.2	0.14	0.800	296.6	3.00	2.95	0.08	87.04	185.2
323.1	0.17	0.753	297.4	3.01	3.91	0.10	86.96	184.8
327.1	0.16	0.476	297.8	1.10	5.76	0.17	86.83	184.3

Table 1 (continued)

T/K^a	m/mg^b	$V(N_2)^c /dm^3$	T_a/K^d	Flow/ $dm^3 \cdot h^{-1}$	p/Pa^e	$u(p_i)/Pa^f$	$\Delta_{l,cr}^g H_m^o(T)/$ $kJ \cdot mol^{-1}$	$\Delta_{l,cr}^g S_m^o(T)/$ $J \cdot K^{-1} \cdot mol^{-1}$
328.0	0.14	0.367	294.0	1.10	6.25	0.18	86.80	184.2
329.2	0.13	0.311	299.6	1.10	6.94	0.20	86.77	184.0
331.1	0.63	1.281	296.2	3.08	8.37	0.23	86.71	183.9
4-cyano-acetophenone: $\Delta_1^g H_m^o(298.15 K) = (72.1 \pm 0.4) kJ \cdot mol^{-1}$								
$\ln(p_i/p_{ref}) = \frac{31081}{R} - \frac{94819.2}{RT} - \frac{76.1}{R} \ln \frac{T}{298.15}; p_{ref} = 1 Pa$								
333.2	0.16	0.330	299.6	1.10	8.41	0.24	69.47	130.5
334.1	0.56	1.053	295.2	1.02	9.01	0.25	69.40	130.3
337.2	0.64	0.951	296.8	1.02	11.41	0.31	69.16	129.7
338.2	0.23	0.321	299.6	1.10	12.19	0.33	69.09	129.4
340.1	0.60	0.713	296.6	1.02	14.28	0.38	68.94	129.1
343.2	0.33	0.330	300.4	1.10	17.29	0.46	68.71	128.2
344.1	0.61	0.560	296.8	1.02	18.52	0.49	68.64	128.0
346.2	0.65	0.510	297.0	1.02	21.57	0.56	68.48	127.6
349.1	0.62	0.408	297.0	1.02	26.00	0.67	68.26	126.9
354.2	0.62	0.289	297.2	1.02	36.63	0.94	67.87	125.9
359.2	0.75	0.255	296.6	1.02	49.89	1.27	67.49	124.7
364.3	1.03	0.255	297.3	1.02	69.03	1.75	67.10	123.7
369.2	1.41	0.255	297.4	1.02	94.27	2.38	66.73	122.8

^aTemperature of saturation, ($u(T) = 0.1 K$)

^bMass of sample collected in the cold trap at $T = 243 K$

^cVolume of carrier gas ($u(V) = 0.005 dm^3$) used to transfer m ($u(m) = 0.0001 g$) of the sample

^d T_a is the ambient temperature during the determination of the gas flow

^eAbsolute vapor pressure at temperature T , calculated from the m and the residual vapor pressure at the temperature of the cold trap calculated by an iteration procedure

^fUncertainties of absolute vapor pressures: $u(p_i/Pa) = 0.025 + 0.025(p_i/Pa)$ for pressures from 5 to 3000 Pa and $u(p_i/Pa) = 0.005 + 0.025(p_i/Pa)$ for pressures below 5 Pa. The standard uncertainties of enthalpies of vaporization/sublimation are calculated as described elsewhere [14, 15]

(298.15 K) = $94.7 \pm 1.5 kJ \cdot mol^{-1}$ measured by a Calvet calorimeter [22].

Vapor pressures over liquid and crystalline samples of 2-acetoxy-, 3-acetoxy- and 4-acetoxy-acetophenones, were systematically studied by combination of the static and Knudsen method just recently [22]. We approximated these experimental vapor pressures by Eq. (1) and estimated (see Table 2) the phase transition enthalpies according to Eqs. (3) and (4) with $\Delta_{cr,l}^g C_{p,m}^o$ -values from Table S2. Table 2 obviously shows that the liquid–gas and the crystal–gas phase transitions for all three isomers are very consistent and these values were taken for thermochemical calculations in the current study.

Validation of experimental vaporization enthalpies

The limited amount of vaporization enthalpies available for substituted acetophenones and the inconsistency in vapor pressures observed for ethylacetophenones have required additional validation of our results.

Validation using normal boiling temperatures

Empirical correlations within series of similarly shaped series of compounds, e.g., correlation of vaporization enthalpies with boiling points, T_b , is a valuable option to establish the consistency of available experimental results [23]. The available literature data on T_b for substituted acetophenones [18, 24] were correlated with the $\Delta_1^g H_m^o(298.15 K)$ -values evaluated in Table 3.

For the set of compounds collected in Table 3, the following linear correlation was estimated (in $kJ \cdot mol^{-1}$):

$$\Delta_1^g H_m^o(298.15 K) = -47.6 + 0.2199 \times T_b \text{ with } (R^2 = 0.966) \quad (7)$$

Table 3 shows that the results derived from this correlation with the boiling temperatures agree well (within the uncertainties) with results measured with the gas saturation method. Thus, such close agreement indicates a successful way to validate the experimental $\Delta_1^g H_m^o(298.15 K)$ data derived (see Table 1) using the gas saturation method. According to Table 3, the differences between estimated according to Eq. 7 and experimental values are mostly below

Table 2 Data on enthalpies of vaporization $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}$ and enthalpies of sublimation $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}$ of substituted acetophenones

Compound, CAS	Method ^a	<i>T</i> - range K	$\Delta_{\text{l,cr}}^{\text{g}}H_{\text{m}}^{\circ}(T_{\text{av}})$ kJ·mol ⁻¹	$\Delta_{\text{l,cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K})^{\text{b}}$ kJ·mol ⁻¹	Refs.
2-methyl-acetophenone (liq) 577-16-2	C	339	65.7 ± 0.2	58.9 ± 0.9	[20]
	T	293.3–332.7	58.6 ± 0.3	59.3 ± 0.4	This work
	<i>T</i> _b			59.5 ± 1.5	Table 3
	<i>J</i> _x			58.8 ± 0.7	Table 4
				59.2 ± 0.3	Average ^c
3-methyl-acetophenone (liq) 585-74-0	T	285.5–334.0	59.0 ± 0.3	59.8 ± 0.4	This work
	<i>T</i> _b			60.8 ± 1.5	
	<i>J</i> _x			60.2 ± 0.7	
				59.9 ± 0.3	Average ^c
4-methyl-acetophenone (liq) 122-00-9	K	291.0–313.6	59.3 ± 1.7	59.5 ± 1.8	[16]
	n/a	288–333	59.5 ±	60.4 ± 1.6	[17]
	C	339	67.5 ± 0.3	60.7 ± 1.0	[20]
	T	302.6–354.2	59.6 ± 0.2	61.6 ± 0.3	This work
	<i>T</i> _b			62.2 ± 1.5	Table 3
	<i>J</i> _x			61.6 ± 0.7	Table 4
					61.5 ± 0.3
2-ethylacetophenone (liq) 2142-64-5	n/a	363–397	52.8 ± 1.0	59.4 ± 1.2	[17]
	SF	357.2–391.2	54.5 ± 2.1	60.6 ± 2.2	Table S2
	<i>T</i> _b			63.4 ± 1.5	Table 3
	<i>J</i> _x			63.3 ± 0.7	Table 4
				62.3 ± 0.5	Average ^c
3-ethylacetophenone (liq) 22,699-70-3	S	292.3–416.2	23.7 ± 0.5	(27.7 ± 0.6)	[19]
	SF	386.2–514.2	52.1 ± 1.5	63.9 ± 1.7	Table S2
	<i>T</i> _b			65.5 ± 1.5	Table 3
	<i>J</i> _x			64.7 ± 0.7	Table 4
				64.7 ± 0.6	Average ^c
4-ethyl-acetophenone (liq) 937-30-4	S	294.6–367.2	40.4 ± 0.3	(42.9 ± 0.4)	[19]
	SF	367.2–518.2	54.7 ± 0.8	65.7 ± 1.1	Table S2
	<i>T</i> _b			66.3 ± 1.5	Table 3
	<i>J</i> _x			66.8 ± 0.7	Table 4
				66.4 ± 0.6	Average ^c
2-cyano-acetophenone (liq) 91,054-33-0	T	322.9–372.4	69.3 ± 0.3	72.9 ± 0.4	This work
				86.6 ± 0.5	Table 5
2-cyano-acetophenone (cr)					
3-cyano-acetophenone (cr) 6136-68-1	C	360.1	105.5 ± 0.5	94.7 ± 1.5	[19]
	T	318.4–362.3	95.8 ± 0.4	97.1 ± 0.6	This work
				96.8 ± 0.6	Average ^c
3-cyano-acetophenone (liq)				74.5 ± 1.6	Table 5
4-cyano-acetophenone (cr)	T	303.2–331.1	87.1 ± 0.4	87.7 ± 0.7	This work
4-cyano-acetophenone (liq) 1443-80-7	T	333.2–369.2	68.2 ± 0.2	72.1 ± 0.4	This work
				71.8 ± 1.6	Table 5
				72.0 ± 0.5	Average ^c
2-acetoxy-acetophenone (cr) 7250-94-4	S	313.0–356.5	103.1 ± 0.1	104.4 ± 0.5	[22]
	K	298.0–321.3	104.3 ± 0.4	104.7 ± 0.8	[22]
				104.5 ± 0.4	Average ^c
2-acetoxy-acetophenone (liq)	S	344.7–398.0	68.6 ± 0.1	75.0 ± 0.4	[22]
				75.5 ± 1.4	Table 5
				75.1 ± 0.4	Average ^c
3-acetoxy-acetophenone (cr II)	K	297.7–307.7	100.4 ± 1.1	100.5 ± 1.9	[22]
3-acetoxy-acetophenone (liq)	S	305.1–368.5	75.6 ± 0.1	78.9 ± 0.3	[22]

Table 2 (continued)

Compound, CAS	Method ^a	T- range K	$\Delta_{l,cr}^g H_m^o(T_{av})$ kJ·mol ⁻¹	$\Delta_{l,cr}^g H_m^o(298.15\text{ K})^b$ kJ·mol ⁻¹	Refs.
2454-35-5				77.2 ± 3.9 78.8 ± 1.0	Table 5 Average ^c
4-acetoxy-acetophenone (cr II)	K	298.1–309.3	99.4 ± 0.5	99.6 ± 1.5	[22]
4-acetoxy-acetophenone (cr I)	S	315.0–323.9	98.5 ± 0.6	99.3 ± 2.0	[22]
4-acetoxy-acetophenone (liq)	S	328.9–378.3	74.3 ± 0.1	79.1 ± 0.4	[22]
13,031-43-1				79.6 ± 3.1 79.1 ± 1.0	Table 5 Average ^c

Values given in bold are recommended for thermochemical calculations

^aMethods: T=transpiration; K=Knudsen effusion method; C=Calvet calorimetry; n/a—not available; S=static method; SF=from experimental boiling temperatures reported at different pressures compiled by SciFinder [18] (see text); T_b —estimation based on the use of normal boiling temperatures; J_x —correlation gas chromatography

^bVapor pressures were treated using Eq. (1) and Eqs. (3) and (4) with help of heat capacity differences from Table S2 to evaluate the enthalpies of vaporization/sublimation at 298.15 K in the same way [14, 15] as our own results in Table 1

^cWeighted average value with the standard uncertainty. Values given in brackets were excluded by averaging

Table 3 Vaporization enthalpies $\Delta_1^g H_m^o(298.15\text{ K})$ of substituted acetophenones taken for correlation with their T_b normal boiling temperatures ^a

CAS	Compound	T_b^b K	$\Delta_1^g H_m^o(298.15\text{ K})_{exp}$ kJ·mol ⁻¹	$\Delta_1^g H_m^o(298.15\text{ K})_{calc}^c$ kJ·mol ⁻¹	Δ^d kJ·mol ⁻¹
108-88-3	toluene	384	38.1 ± 0.2 [25]	36.8	1.3
100-41-4	ethylbenzene	409	42.3 ± 0.2 [25]	42.4	-0.1
98-86-2	acetophenone	475	55.4 ± 0.3 [26]	56.9	-1.5
577-16-2	2-methyl-acetophenone	487	59.2 ± 0.2 ^e	59.5	-0.3
585-74-0	3-methyl-acetophenone	493	59.8 ± 0.2 ^e	60.8	-1.0
122-00-9	4-methyl-acetophenone	499	61.4 ± 0.2 ^e	62.2	-0.8
2142-64-5	2-ethyl-acetophenone	505	–	63.4	
22,699-70-3	3-ethyl-acetophenone	514	–	65.5	
937-30-4	4-ethyl-acetophenone	518	–	66.3	
93-55-0	1-phenyl-1-propanone	491	60.9 ± 0.8 [27]	60.3	0.6
103-79-7	1-phenyl-2-propanone	490	57.7 ± 0.3 [28]	60.1	-2.4
15,764-15-5	2,3,5-tri-methyl-acetophenone	521	70.9 ± 0.7 [29]	66.9	4.0

^aUncertainty in this table are expressed as standard uncertainties

^bNormal boiling temperatures are from [18, 24]

^cEstimated with help of Eq. 7

^dDifference between experimental and calculated by Eq. 7 values

^eMeasured with the gas saturation method (see Table 1)

2 kJ·mol⁻¹. Hence, the uncertainties of ± 1.5 kJ·mol⁻¹ can be ascribed to estimates obtained with Eq. (7). We used Eq. (7) to estimate the questionable vaporization enthalpies of isomeric ethylacetophenones (see Table 3). The latter values were denoted by a symbol T_b and shown in Table 2 for comparison with results derived by other methods.

Validation with Kovats's retention indices

Correlating the experimental $\Delta_1^g H_m^o(298.15\text{ K})$ -values of parent substances with their Kovats's indices, J_x [30], is another way for establishing data consistency [23, 31]. The Kovats's retention indices for substituted benzenes [31] were correlated with the $\Delta_1^g H_m^o(298.15\text{ K})$ -values evaluated in Table 2. The results are shown in Table 4.

Table 4 Results of correlation of $\Delta_1^{\text{g}}H_m^{\circ}(298.15\text{ K})$ of substituted acetophenones with Kovats's indices (J_x)^a

CAS	Compound	J_x ^b	$\Delta_1^{\text{g}}H_m^{\circ}(298.15\text{ K})_{\text{exp}}$ kJ·mol ⁻¹	$\Delta_1^{\text{g}}H_m^{\circ}(298.15\text{ K})_{\text{calc}}$ ^c kJ·mol ⁻¹	Δ^{d} kJ·mol ⁻¹
71-43-2	benzene	670	33.9 ± 0.2 [25]	33.3	0.6
108-88-3	toluene	750	38.1 ± 0.2 [25]	38.0	0.1
100-41-4	ethylbenzene	840	42.3 ± 0.2 [25]	43.2	-0.9
	acetophenone	1050	55.4 ± 0.3 [26]	55.4	0.0
577-16-2	2-methyl-acetophenone	1108	59.3 ± 0.4 ^e	58.8	0.4
585-74-0	3-methyl-acetophenone	1132	59.8 ± 0.4 ^e	60.2	-0.4
122-00-9	4-methyl-acetophenone	1156	61.6 ± 0.3 ^e	61.6	-0.2
2142-64-5	2-ethyl-acetophenone	1186	-	63.3	
22,699-70-3	3-ethyl-acetophenone	1210	-	64.7	
937-30-4	4-ethyl-acetophenone	1245	-	66.8	
93-55-0	1-phenyl-1-propanone	1140	60.9 ± 0.8 [27]	60.6	0.3
103-79-7	1-phenyl-2-propanone	1091	57.7 ± 0.3 [28]	57.8	-0.1
15,764-15-5	2,3,5-tri-methyl-acetophenone	1312	70.9 ± 0.7 [29]	70.7	0.2

^aUncertainties are expressed as the standard uncertainty^bKovats's indices, J_x , on standard nonpolar columns from [32]^cEstimated using Eq. 8^dDifference between experimental and calculated by Eq. 8 values^eTaken from Table 1

The experimental $\Delta_1^{\text{g}}H_m^{\circ}(298.15\text{ K})$ -values show a linear correlation with Kovats's indices in a series of n-alcohols, n-alkanes, aliphatic ethers, alkylbenzenes, etc. [33]. Also, the $\Delta_1^{\text{g}}H_m^{\circ}(298.15\text{ K})$ -values of substituted benzenes (collected in Table 4) show a linear correlation with J_x -values:

$$\Delta_1^{\text{g}}H_m^{\circ}(298.15\text{ K})/(\text{kJ} \cdot \text{mol}^{-1}) = -5.7 + 0.0582 \times J_x \text{ with } (R^2 = 0.989) \quad (8)$$

The $\Delta_1^{\text{g}}H_m^{\circ}(298.15\text{ K})$ -values derived from the correlation with the Kovats's indices (see Table 4) agree perfectly with values obtained by the gas saturation method. This agreement can be regarded as a complementary validation of our new experimental data given in Table 1. According to Table 4, the differences between Eq. 8 estimates and the experimental values are mainly below 1 kJ·mol⁻¹. Therefore, the uncertainties of ±0.7 kJ·mol⁻¹ can be ascribed to estimates using Eq. (8). We also used Eq. (8) to calculate the questionable enthalpies of vaporization of the isomeric ethylacetophenones (see Table 4). The latter values were denoted by a symbol J_x and shown in Table 2 for comparison with results derived by other methods.

Consistency of solid–liquid, solid–gas and liquid–gas phase transitions

All cyano-acetophenones and all acetoxy-acetophenones are solids at room temperatures. We have collected in Table 5 the solid phase transition data available for these compounds.

The enthalpy of fusion of 4-methyl-acetophenone, $\Delta_{\text{cr}}^{\text{l}}H_m^{\circ}(T_{\text{fus}}) = 14.3 \pm 0.1\text{ kJ} \cdot \text{mol}^{-1}$ at $T_{\text{fus}} = 251.8 \pm 0.1\text{ K}$, was measured for the first time. A typical DSC curve of 4-methyl-acetophenone is shown in Fig. S5. The only fusion temperature available for comparison, $T_{\text{fus}} = 208.7\text{ K}$ [35] is significantly lower than the value we obtained. Taking into account the absence of purity attestation for the sample measured by Timmermans [35], our result for the highly pure sample of 4-methyl-acetophenone ($99.1 \pm 0.1\%$) appears to be more reliable.

Melting temperatures, T_{fus} , and enthalpies of fusion, $\Delta_{\text{cr}}^{\text{l}}H_m^{\circ}(T_{\text{fus}})$, of 2-, 3- and 4-cyano-acetophenone were not found in the literature for comparison. The enthalpies of fusion and melting temperatures of 2-, 3- and 4-acetoxy-acetophenone (see Table 5) were taken from the literature [22]. According to common practice, the experimental, (T_{fus})-values have to be adjusted to $T = 298.15\text{ K}$ using Eq. (9) [13]:

$$\Delta_{\text{cr}}^{\text{l}}H_m^{\circ}(298.15\text{ K})/(\text{J} \cdot \text{mol}^{-1}) = \Delta_{\text{cr}}^{\text{l}}H_m^{\circ}(T_{\text{fus}}/\text{K}) - \left(\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^{\circ} - \Delta_1^{\text{g}}C_{\text{p,m}}^{\circ} \right) \times [(T_{\text{fus}}/\text{K}) - 298.15\text{ K}] \quad (9)$$

The values of $\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^{\circ}$ and $\Delta_1^{\text{g}}C_{\text{p,m}}^{\circ}$ are listed in Table S2. The enthalpies of fusion, $\Delta_{\text{cr}}^{\text{l}}H_m^{\circ}(298.15\text{ K})$, estimated with Eq. (9) are given in Table 5. These values can now be used to establish consistency of the phase transitions for cyano-acetophenones and acetoxy-acetophenones collected in Table 2 as follows. Vaporization, fusion and sublimation enthalpies are related by Eq. (10):

Table 5 Thermodynamics of phase transitions of substituted acetophenones (in $\text{kJ}\cdot\text{mol}^{-1}$)^a

Compound	T_{fus}/K	$\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}$ at T_{fus}	$\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}$ ^b	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}$ ^c 298.15 K	$\Delta_1^{\text{g}} H_{\text{m}}^{\circ}$ ^d
1	2	3	4	5	6
4-methyl-acetophenone	251.8 ± 0.1	14.3 ± 0.1 ^f	12.3 ± 0.3	73.8 ± 0.5 ^e	61.5 ± 0.3 ^c
2-cyano-acetophenone	322.4 ± 0.1	14.8 ± 0.1 ^f	13.7 ± 0.3	86.6 ± 0.9 ^e	72.9 ± 0.4 ^c
3-cyano-acetophenone	370.4 ± 0.1	25.6 ± 0.1 ^f	22.3 ± 1.0	96.8 ± 1.2	74.5 ± 1.6
4-cyano-acetophenone	331.6 ± 0.1	17.4 ± 0.1 ^f	15.9 ± 0.4	87.7 ± 1.4	71.8 ± 1.5
2-acetoxy-acetophenone	361.8 ± 0.1	32.3 ± 0.4 [22]	29.0 ± 1.1	104.5 ± 0.8	75.5 ± 1.4
3-acetoxy-acetophenone(cr II)	316.2 ± 0.3	24.2 ± 0.6 [22] ^g	23.3 ± 0.9	100.5 ± 3.8	77.2 ± 3.9
4-acetoxy-acetophenone (cr II)	324.1 ± 0.5	21.4 ± 0.5 [22] ^h	20.0 ± 0.6	99.6 ± 3.0	79.6 ± 3.1

^aUncertainties in this table are expressed as twice the standard deviations

^bThe $\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}$ at T_{fus} were adjusted to 298.15 K with Eq. 9. Uncertainties were estimated with 30% of the total adjustment [34]

^cTaken from Table 2

^dEstimated as the difference between column 5 and 4 in the current table

^eEstimated as the sum of column 6 and 4 in the current table

^fFrom this work

^gEstimated according to recommendation by Acree and Chickos [13] as the sum of phase transition $\Delta_{\text{phase II}}^1 H_{\text{m}}^{\circ} = 1.0 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$ [22] and enthalpy of fusion $\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ} = 23.2 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$ [22] at T_{fus} and adjusted to the reference temperature with help of Eq. 9

^h Estimated according to recommendation by Acree and Chickos [13] as the sum of phase transition $\Delta_{\text{phase II}}^1 H_{\text{m}}^{\circ} = 0.6 \pm 0.1 \text{ kJ}\cdot\text{mol}^{-1}$ [22] and enthalpy of fusion $\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ} = 20.8 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$ [22] at T_{fus} and adjusted to the reference temperature with help of Eq. 9

$$\Delta_1^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) - \Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}(298.15 \text{ K}) \quad (10)$$

when all enthalpies are adjusted to the common temperature $T = 298.15 \text{ K}$.

For example, the vapor pressures of 4-cyano-acetophenone were deliberately measured (see Table 1) below and above the melting temperature using the gas saturation method. The sublimation enthalpy, $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = 87.7 \pm 0.7 \text{ kJ}\cdot\text{mol}^{-1}$, and the vaporization enthalpy, $\Delta_1^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = 72.1 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$, of 4-cyano-acetophenone are given in Table 1. According to Eq. (10) and together with the fusion enthalpy, $\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}(298.15 \text{ K}) = 15.9 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$, the “theoretical” vaporization enthalpy of 4-cyano-acetophenone was estimated to be $\Delta_1^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = 87.7 - 15.9 = 71.8 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$. The latter value is in excellent agreement with the experiment, demonstrating consistency of the phase transition data for this compound. In a similar way, the consistency of the data for other cyano-acetophenones and acetoxy-acetophenones was established (see calculations in Table 5 and the final values in Table 2).

Evaluation of available vaporization enthalpies

In order to ascertain the accuracy of the vaporization thermodynamics of the alkyl-substituted acetophenones, we

applied three empirical methods ($\Delta_1^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) - T_{\text{b}}$ correlation), ($\Delta_1^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) - J_{\text{x}}$ correlation) and consistency of phase transitions. The *experimental* and “*theoretical*” vaporization enthalpies derived for each set of substituted acetophenones, are given in Table 2.

This table shows that for each substituted acetophenone agreement among available $\Delta_1^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K})$ and $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K})$ values, obtained in different ways is generally within the error bars. To improve the reliability, we calculated the weighted average (the uncertainty was used as a weighing factor) for each substituted acetophenone given in Table 2. These values are highlighted in bold and are recommended for thermochemical estimations and the general quantitative analysis of the results. For example, in our previous work [36–42], it was found that *meta*- and *para*-disubstituted benzenes have similar vaporization enthalpies values. *ortho*-disubstituted benzenes usually differ from those for *meta*- and *para*-disubstituted species. The size of the differences depends on the nature of the substituents. The general trend, however, is that the enthalpies of vaporization of the *ortho*-species are somewhat lower compared to *meta*- and *para*-substitution. The vaporization enthalpies of methyl, ethyl, cyano and acetoxy-acetophenones follow this general trend (see Table 2) and confirm the consistency of the data evaluated.

Table 6 Thermochemical data at $T=298.15$ K ($p^\circ=0.1$ MPa) (in $\text{kJ}\cdot\text{mol}^{-1}$)^a

Compound	$\Delta_f H_m^\circ$ (l or cr)	$\Delta_{l,cr}^g H_m^\circ$ ^b	$\Delta_f H_m^\circ(\text{g})_{\text{exp}}$	$\Delta_f H_m^\circ(\text{g})_{\text{ther}}$ ^c
1	2	3	4	5
2-methyl-acetophenone (liq)	-174.6 ± 2.2 [20]	59.2 ± 0.6	-115.4 ± 2.3	-110.7 ± 2.6
3-methyl-acetophenone (liq)		59.9 ± 0.6		-120.1 ± 2.6
4-methyl-acetophenone (liq)	-183.3 ± 2.2 [20]	61.5 ± 0.6	-121.8 ± 2.3	-120.8 ± 2.6
2-cyano-acetophenone (cr)		86.6 ± 0.9		60.3 ± 2.6
3-cyano-acetophenone (cr)	-42.3 ± 1.5 [21]	96.8 ± 1.2	54.5 ± 1.9	50.4 ± 2.6
4-cyano-acetophenone (cr)		87.7 ± 1.4		50.0 ± 2.6
2-acetoxy-acetophenone (cr)		104.5 ± 0.8		-435.4 ± 2.6
3-acetoxy-acetophenone (cr II)		100.5 ± 3.8		-444.9 ± 2.6
4-acetoxy-acetophenone (cr II)		99.6 ± 3.0		-445.1 ± 2.6

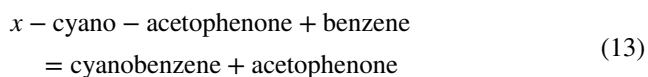
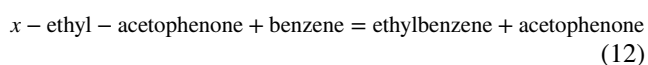
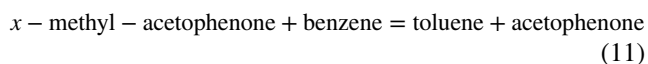
^aUncertainties in this table represent two standard deviations^bTaken from Table 2^cAveraged result from G3MP2 and G4 methods (see Table 7)

Standard molar enthalpies of formation

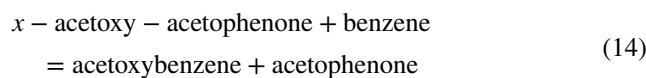
Very limited enthalpies of formation of substituted acetophenones are available in the literature. The $\Delta_f H_m^\circ(298.15)$ -values of 2-methyl- and 4-methyl-acetophenone were measured by Amaral et al. [20] by the combustion calorimetry. Later, the enthalpy of formation of 3-cyano-acetophenone was measured in the same laboratory [21]. The numerical data available in the literature are summarized in Table 6.

In order to compensate for the lack of enthalpic data, the gas-phase formation enthalpies for methyl, ethyl, cyano and acetoxy-substituted acetophenones were estimated with help of quantum chemical methods.

Structures of substituted acetophenones were optimized with MM3 [8] and B3LYP/6-31 g(d,p) methods [9]. Energies of the most stable conformers for each isomer were calculated by using the composite G3MP2 [10] and G4 methods [11]. The H_{298} enthalpies of the most stable conformers of the substituted acetophenones estimated by the composite methods were converted into the *theoretical* enthalpies of formation using the *experimental* gas-phase standard molar enthalpies of formation, $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K})$, of benzene, toluene, ethylbenzene, cyanobenzene, acetoxybenzene and acetophenone (see Table S4) using the following well-balanced reactions:

**Table 7** G3MP2 and G4 *theoretical* gas-phase enthalpies of formation at $T=298.15$ K ($p^\circ=0.1$ MPa) for methyl-, ethyl-, cyano- and acetoxy-substituted acetophenones (in $\text{kJ}\cdot\text{mol}^{-1}$)

Compound	$\Delta_f H_m^\circ(\text{g})_{\text{G3MP2}}$ ^a	$\Delta_f H_m^\circ(\text{g})_{\text{G4}}$ ^b	$\Delta_f H_m^\circ(\text{g})_{\text{theor}}$ ^c
2-methyl-acetophenone	-109.7	-111.6	-110.7 ± 2.6
3-methyl-acetophenone	-119.0	-120.9	-120.1 ± 2.6
4-methyl-acetophenone	-119.7	-121.6	-120.8 ± 2.6
2-ethyl-acetophenone	-	-130.9	-130.9 ± 3.5
3-ethyl-acetophenone	-	-141.4	-141.4 ± 3.5
4-ethyl-acetophenone	-	-141.9	-141.9 ± 3.5
2-cyano-acetophenone	60.1	60.5	60.3 ± 2.6
3-cyano-acetophenone	50.1	50.6	50.4 ± 2.6
4-cyano-acetophenone	49.7	50.2	50.0 ± 2.6
2-acetoxy-acetophenone	-433.9	-436.6	-435.4 ± 2.6
3-acetoxy-acetophenone	-443.3	-446.1	-444.9 ± 2.6
4-acetoxy-acetophenone	-443.6	-446.3	-445.1 ± 2.6

^aCalculated by the G3MP2 method with help of reactions 11–14 using experimental $\Delta_f H_m^\circ(\text{g})$ -values for the reaction participants. The expanded uncertainty assessed to be $\pm 4.0 \text{ kJ}\cdot\text{mol}^{-1}$) [10]^bCalculated by the G4 method with help of reactions 11–14 using experimental $\Delta_f H_m^\circ(\text{g})$ -values for the reaction participants. The expanded uncertainty assessed to be $\pm 3.5 \text{ kJ}\cdot\text{mol}^{-1}$) [11]^cThe weighted average value calculated using uncertainties as the weighting factor

The *theoretical* enthalpies of formation of the substituted acetophenones calculated by G3MP2 and G4 methods are summarized in Table 7. Using two methods simultaneously helps to avoid possible systematic errors caused by the calculations.

The *theoretical* values of $\Delta_f H_m^{\circ}(\text{g}, 298.15 \text{ K})$ as calculated by the G3MP2 and the G4 method are very close for each compound (see Table 7). Therefore, we calculated the weighted average value for each substituted acetophenone in Table 7 and designated it as the *theoretical* value, $\Delta_f H_m^{\circ}(\text{g}, 298.15 \text{ K})_{\text{theor}}$, for comparison with the *experimental* values, $\Delta_f H_m^{\circ}(\text{g}, 298.15 \text{ K})_{\text{exp}}$, compiled in Table 6. Comparison of column 5 with column 4 in Table 6 shows good agreement between the *theoretical* and *experimental* $\Delta_f H_m^{\circ}(\text{g}, 298.15 \text{ K})$ -values for 2-methyl-acetophenone, 4-methyl-acetophenone and 3-cyano-acetophenone. Such good agreement can be viewed as a manifestation of internal consistency of experimental results evaluated in Table 6. These new evaluated results are recommended for thermochemical calculations, *e.g.*, of the liquid-phase enthalpies of formation $\Delta_f H_m^{\circ}(\text{liq}, 298.15 \text{ K})$ according to the general equation:

$$\Delta_f H_m^{\circ}(\text{liq}, 298.15 \text{ K}) = \Delta_f H_m^{\circ}(\text{g}, 298.15 \text{ K}) - \Delta_1^{\text{g}} H_m^{\circ}(298.15 \text{ K}) \quad (15)$$

Indeed, the reliable *theoretical* enthalpies of formation $\Delta_f H_m^{\circ}(\text{g})_{\text{theor}}$ given in Table 7 have compensated for the lack of required data for Eq. (15) data. Together with the reliable enthalpies of vaporization evaluated in Table 2, these results can therefore be used to calculate the *theoretical* liquid-phase enthalpies of formation (see Table 8, column 4).

Comparison of column 5 with column 4 in Table 8 shows agreement between the *theoretical* and *experimental* $\Delta_f H_m^{\circ}(\text{liq}, 298.15 \text{ K})$ -values available for 2-methyl-acetophenone, 4-methyl-acetophenone and 3-cyano-acetophenone. These results for the enthalpies of formation in the liquid phase of substituted acetophenones can now be recommended for thermochemical calculations.

Table 8 Estimation of the liquid-phase enthalpies of formation $\Delta_f H_m^{\circ}(\text{liq})$ at $T=298.15 \text{ K}$ ($p^{\circ}=0.1 \text{ MPa}$) for substituted acetophenones (in $\text{kJ}\cdot\text{mol}^{-1}$)^a

Compound	$\Delta_f H_m^{\circ}(\text{g})_{\text{theor}}^{\text{b}}$	$\Delta_1^{\text{g}} H_m^{\circ}{}^{\text{c}}$	$\Delta_f H_m^{\circ}(\text{liq})_{\text{theor}}^{\text{d}}$	$\Delta_f H_m^{\circ}(\text{liq})_{\text{exp}}$
2-methyl-acetophenone	-110.7 ± 2.6	59.2 ± 0.6	-169.9 ± 2.7	-174.6 ± 2.2 [15]
3-methyl-acetophenone	-120.1 ± 2.6	59.8 ± 0.6	-179.8 ± 2.7	
4-methyl-acetophenone	-120.8 ± 2.6	61.5 ± 0.6	-182.1 ± 2.7	-183.3 ± 2.2 [15]
2-ethyl-acetophenone	-130.9 ± 3.5	62.3 ± 1.0	-193.2 ± 3.6	
3-ethyl-acetophenone	-141.4 ± 3.5	64.7 ± 1.2	-206.1 ± 3.7	
4-ethyl-acetophenone	-141.9 ± 3.5	66.4 ± 1.2	-208.3 ± 3.7	
2-cyano-acetophenone	60.3 ± 2.6	72.9 ± 0.8	-12.6 ± 2.7	
3-cyano-acetophenone	50.4 ± 2.6	74.5 ± 1.6	-24.1 ± 3.1	$-20.0 \pm 1.8^{\text{e}}$ [18]
4-cyano-acetophenone	50.0 ± 2.6	72.0 ± 0.8	-22.0 ± 2.7	
2-acetoxy-acetophenone	-435.4 ± 2.6	75.1 ± 0.8	-510.3 ± 2.7	
3-acetoxy-acetophenone	-444.9 ± 2.6	78.8 ± 0.8	-523.5 ± 2.7	
4-acetoxy-acetophenone	-445.1 ± 2.6	79.1 ± 0.8	-524.1 ± 2.7	

^aThe uncertainties are twice standard deviation

^bFrom Table 7

^cFrom Table 2

^dEstimated according to Eq. (15)

^eEstimated as sum of $\Delta_f H_m^{\circ}(\text{cr}, 298.15 \text{ K})$ from Table 6 and the $\Delta_{\text{cr}}^{\text{l}} H_m^{\circ}(298.15 \text{ K})$ from Table 5

Development of a "centerpiece" approach for substituted benzenes

The main idea of this group additivity-based approach is to select an appropriate "centerpiece" molecule (*e.g.*, benzene, acetophenone or toluene) with well-known thermochemical

Table 9 Parameters for calculation of thermodynamic properties of substituted acetophenones at 298.15 K (in $\text{kJ}\cdot\text{mol}^{-1}$)^a

Contribution	$\Delta_1^{\text{g}} H_m^{\circ}$	$\Delta_f H_m^{\circ}(\text{g})$	$\Delta_f H_m^{\circ}(\text{liq})$
benzene	33.9 [25]	82.9[25]	49.0 [25]
$\Delta H(\text{H} \rightarrow \text{COCH}_3)$	21.5	-170.0	-191.5
$\Delta H(\text{H} \rightarrow \text{CH}_3)$	4.2	-32.8	-37.0
$\Delta H(\text{H} \rightarrow \text{CH}_2\text{CH}_3)$	8.3	-53.0	-61.3
$\Delta H(\text{H} \rightarrow \text{CN})$	17.2	132.8	115.6
$\Delta H(\text{H} \rightarrow \text{OCOCH}_3)$	25.1	-358.7	-383.8
ortho $\text{CH}_3\text{-COCH}_3$	-0.4	9.2	4.9
meta $\text{CH}_3\text{-COCH}_3$	0.3	-0.2	-0.3
para $\text{CH}_3\text{-COCH}_3$	1.9	-0.9	-2.6
ortho $\text{CH}_2\text{CH}_3\text{-COCH}_3$	-1.4	9.2	10.6
meta $\text{CH}_2\text{CH}_3\text{-COCH}_3$	1.0	-1.0	-2.3
para $\text{CH}_2\text{CH}_3\text{-COCH}_3$	2.7	-1.8	-4.5
ortho CN-COCH_3	0.3	14.6	14.3
meta CN-COCH_3	1.9	4.7	2.8
para CN-COCH_3	-0.6	4.3	4.3
ortho $\text{OCOCH}_3\text{-COCH}_3$	-5.4	10.4	16.0
meta $\text{OCOCH}_3\text{-COCH}_3$	-1.7	0.9	2.8
para $\text{OCOCH}_3\text{-COCH}_3$	-1.4	0.7	2.2

^aEstimated using the values evaluated in Table 6 and the reliable experimental values from Table S4

properties. Different substituents can be appended to the “centerpiece” in various positions. The enthalpic contribution for each appended substituent is quantified as the differences between the enthalpy of the benzene and enthalpy of the substituted benzene. The consistent sets of thermochemical data on $\Delta_f H_m^\circ(298.15\text{ K})$, $\Delta_f H_m^\circ(\text{g}, 298.15\text{ K})$ and $\Delta_f H_m^\circ(\text{liq}, 298.15\text{ K})$ evaluated in this work have been used for developing a “centerpiece” group contribution approach that is particularly suitable for aromatic compounds. Using this idea, the contributions $\Delta H(\text{H} \rightarrow \text{CH}_3)$, $\Delta H(\text{H} \rightarrow \text{C}_2\text{H}_5)$, $\Delta H(\text{H} \rightarrow \text{COCH}_3)$, $\Delta H(\text{H} \rightarrow \text{CN})$ and $\Delta H(\text{H} \rightarrow \text{OCOCH}_3)$ were derived (see Table 9) using data for toluene, ethylbenzene, acetophenone, cyanobenzene, acetoxybenzene and benzene compiled in Table S4. These enthalpic contributions $\Delta H(\text{H} \rightarrow \text{R})$ can be further used to build a framework of arbitrary structured substituted benzene derivatives starting from the “centerpieces” (e.g., acetophenone in this work). In terms of energy, this framework needs to be extended to include interactions between the substituents on the benzene ring.

The enthalpic contributions for mutual pairwise interactions of substituents are specific for the *ortho*-, *meta*- and *para*-positions of substituents attached to the benzene ring. The usual method for quantifying these interactions are reaction enthalpies, $\Delta_f H_m^\circ(\text{g or liq})$, according to Eqs. 11, 12, 13, 14, written in reverse (e.g., for Eq. 11 it is written as follows: *toluene + acetophenone = x-methyl-acetophenone + benzene*). This approach also applies to the estimation of contributions to the enthalpy of vaporization. The pairwise interactions for all three thermodynamic properties derived in this way are given in Table 9.

The intensity of substituent interactions quantitatively, strongly depends on the type of *ortho*-, *meta*- or *para*-pairs. Let us consider the strength of pairwise interaction in terms of $\Delta_f H_m^\circ(\text{g})$. Table 9 shows that all *ortho*-substituted benzenes exhibit a strong destabilization at the level of 10–15 kJ mol^{-1} on their enthalpies of formation (g or liq) due to interactions of bulky groups placed in close proximity. Usually, the *meta*- and *para*-interactions of substituents are less intensively compared to *ortho*-interactions. This trend also applies to the interactions of the substituents examined in this work. The moderate stabilization or destabilization at the level from 2 to 5 kJ mol^{-1} (see Table 9) is observed for the *meta*- and *para*-isomers. The pairwise interaction in terms of $\Delta_f H_m^\circ(\text{liq})$ follow the similar trends as for the gaseous species (see Table 9).

The understanding of pairwise interactions with respect to $\Delta_f H_m^\circ$ is rather limited, since they related to the structuring of the liquid. However, for practical calculations, these contributions collected in Table 9, column 2, have to be used as empirical constants in order to get the correct enthalpies of vaporization.

Conclusions

Absolute vapor pressures and enthalpies of vaporization/sublimation of methyl- and cyano-acetophenones have been measured using the transpiration method. Data available from the literature on enthalpy of vaporization values for ethyl- and acetoxy-acetophenones were collected and analyzed. The enthalpies of fusion of 4-methyl-acetophenone, 2-, 3- and 4-cyano-acetophenones were measured using the DSC method. The available experimental data were collected from the literature. The experimental results on the liquid–gas, solid–gas and solid–liquid phase transitions were evaluated using empirical correlations based on boiling points and retention indices. The high-level quantum chemical methods were validated with help of reliable experimental results and the gas-phase enthalpies of the formation of substituted acetophenones were estimated. The set of thermodynamic data was evaluated using empirical and quantum chemical methods. These data were used to design and refine the “centerpiece” method for predicting vaporization and formation of disubstituted benzenes. The pairwise interactions of substituents on a benzene ring obtained in this work are expected to be transferable for estimation of properties of poly-substituted benzenes.

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Authors' Contributions IVA was involved in investigation, validation, formal analysis, and writing, reviewing and editing, and SPV was responsible for conceptualization, methodology, writing and preparing the original draft and supervision.

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