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

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Table S1

Provenance and purity of samples under study

Compound	Source	Initial purity	Final purity
2-methylacetophenone	Sigma-Aldrich	0.98	0.9997 [a]
3-methylacetophenone	Sigma-Aldrich	0.98	0.9997 [a]
4-methylacetophenone	Acros	0.95	0.9987 [a]
2-cyanoacetophenone	Fluorochem	0.99	0.9998 [b]
3-cyanoacetophenone	TCI	0.98	0.9995 [b]
4-cyanoacetophenone	Sigma-Aldrich	0.99	0.9999 [b]

[a] Purification was performed by the fractional distillation under reduced pressure. [b] Purification was performed by the fractional sublimation under reduced pressure. Mass fraction purity was determined by the gas chromatography. Not significant mass fraction of water at the level of 10-20 ppm was measured by the Karl Fisher titration. The final purities are given on the water-free basis.

Table S2

Molar heat capacities $C^{o}_{p,m}$(cr, liq) and differences $\Delta^{g}_{cr,l}C^{o}_{p,m}$ of substituted acetophenones in J·K^{-1}·mol^{-1} at T = 298.15 K

compound	$C^{o}_{p,m}$(cr) [a]	$\Delta^{g}_{cr}C^{o}_{p,m}$ [b]	$C^{o}_{p,m}$(liq) [a]	$\Delta^{g}_{l}C^{o}_{p,m}$ [b]
methylacetophenone	194.7	-30.0	237.0	-72.2
ethylacetophenone	221.6	-34.0	268.9	-80.5
cyanoacetophenone	199.7	-30.7	252.0	-76.1
acethoxyacetophenone	236.9	-36.3	300.9	-88.8

[a] Estimated according by using group-additivity method [1].

[b] Estimated by using empirical equations suggested by Chickos and Acree [2].

Table S3
Compilation of boiling points at reduced pressures from the distillation data available in the literature [3].

2-Et-acetophenone		3-Et-acetophenone		4-Et-acetophenone	
T/K	*p*/Pa	*T*/K	*p*/Pa	*T*/K	*p*/Pa
357.2	800	386.2	1867	367.2	533
372.2	1733	387.2	2000	371.2	667
377.2	2266	389.2	1867	385.2	1466
377.2	2133	391.2	2000	387.2	1333
381.2	2400	416.2	5308	398.2	2666
381.2	2666	517.2	101325	403.2	3066
388.2	3333			423.2	6533
389.2	4000			518.2	101325
391.2	3866				

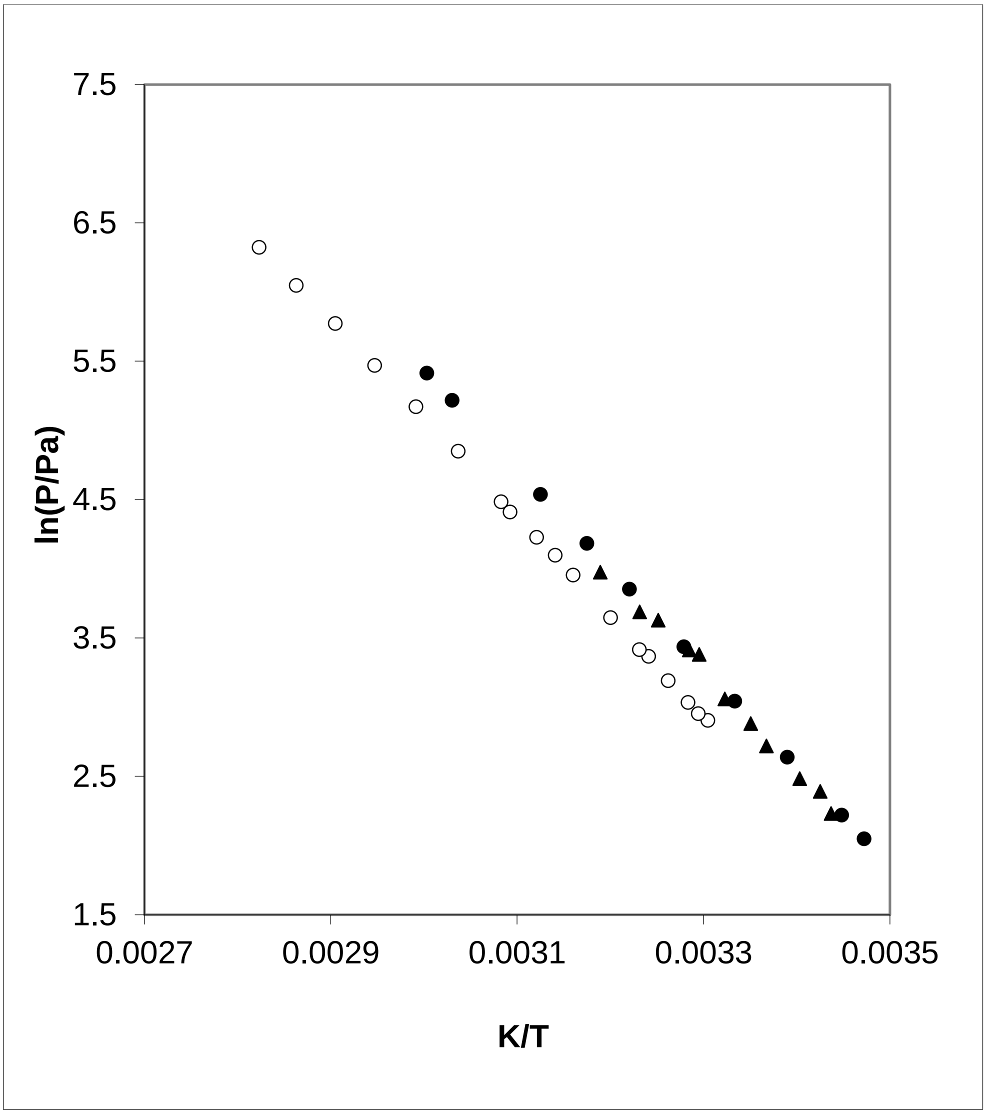

Fig. S1. Temperature dependence of available vapor pressures for 4-methylacetophenone:

○ - this work, transpiration; ▲ – Knudsen method [4]; ● – method is not available [5].

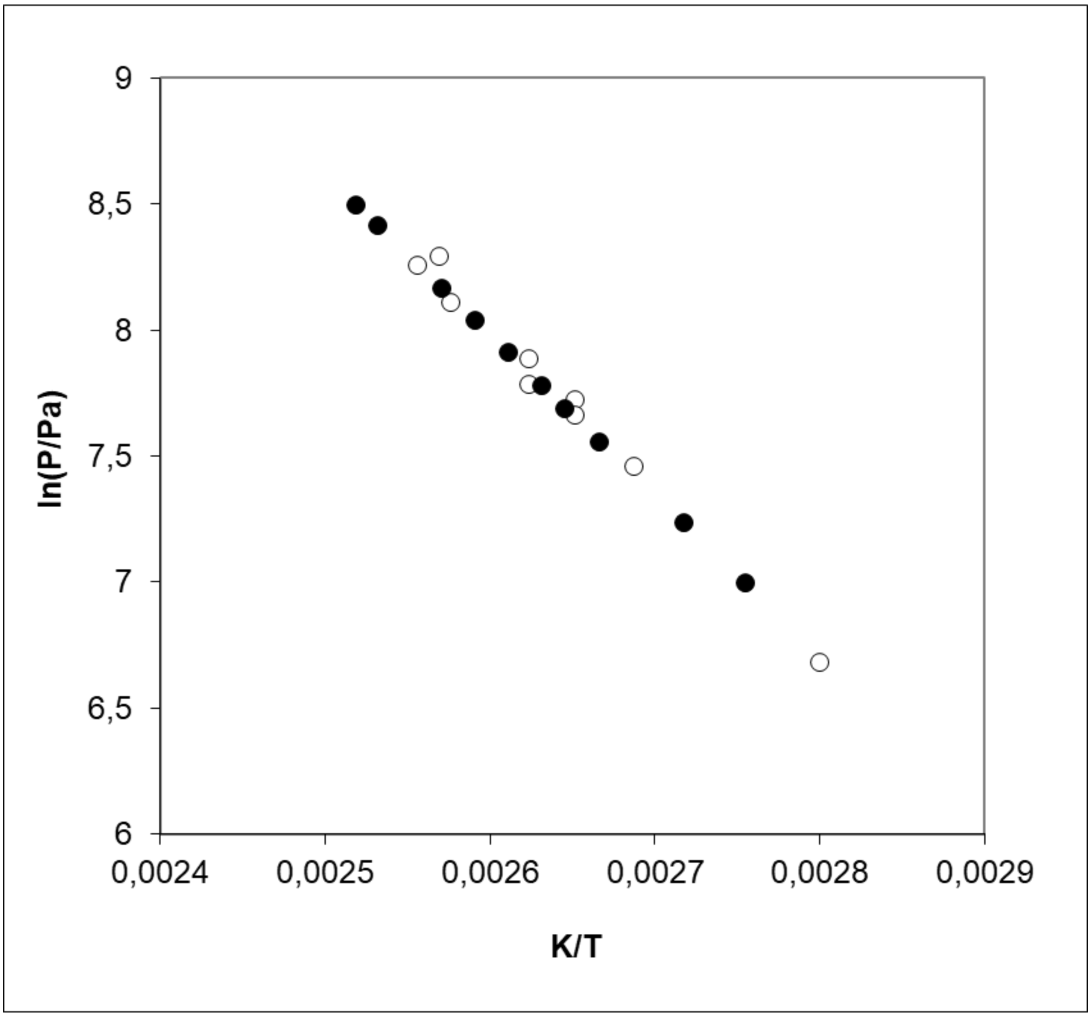

Fig. S2. Temperature dependence of available vapor pressures for 2-ethylacetophenone:
○ - boiling temperatures at reduced pressures [3]; ● - [5]

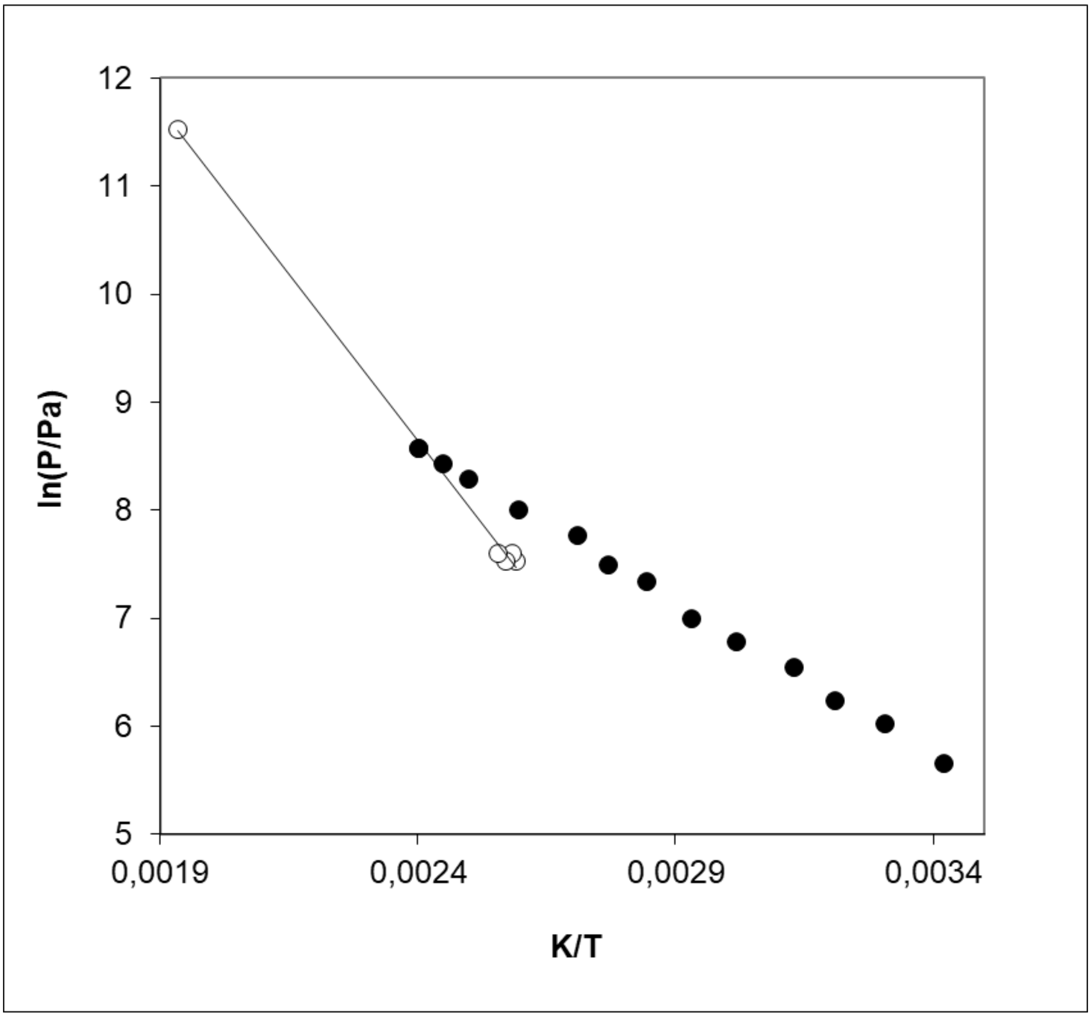

Fig. S3. Temperature dependence of available vapor pressures for 3-ethylacetophenone: ○- boiling temperatures at reduced pressures [3]; ● – [6]

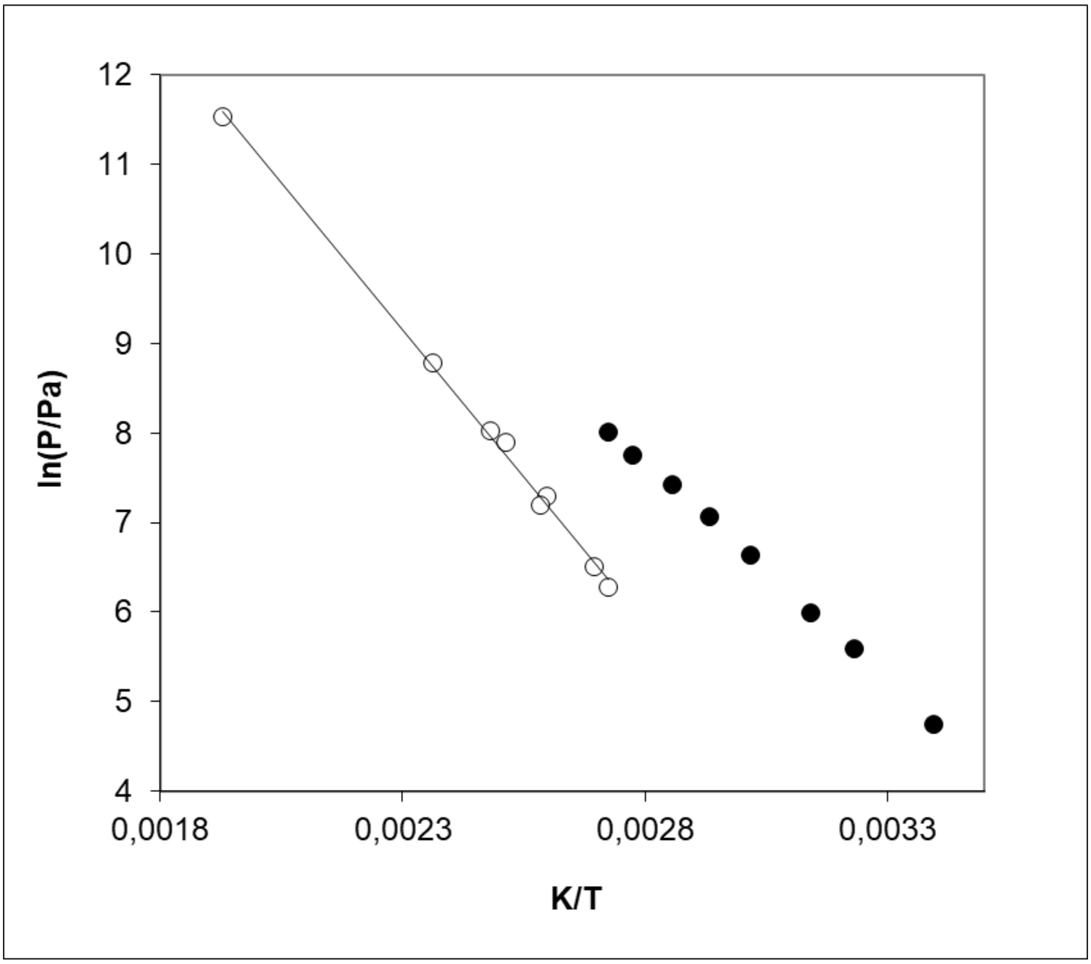

Fig. S4. Temperature dependence of available vapor pressures for 4-ethylacetophenone:

○- boiling temperatures at reduced pressures [3]; ● - [6]

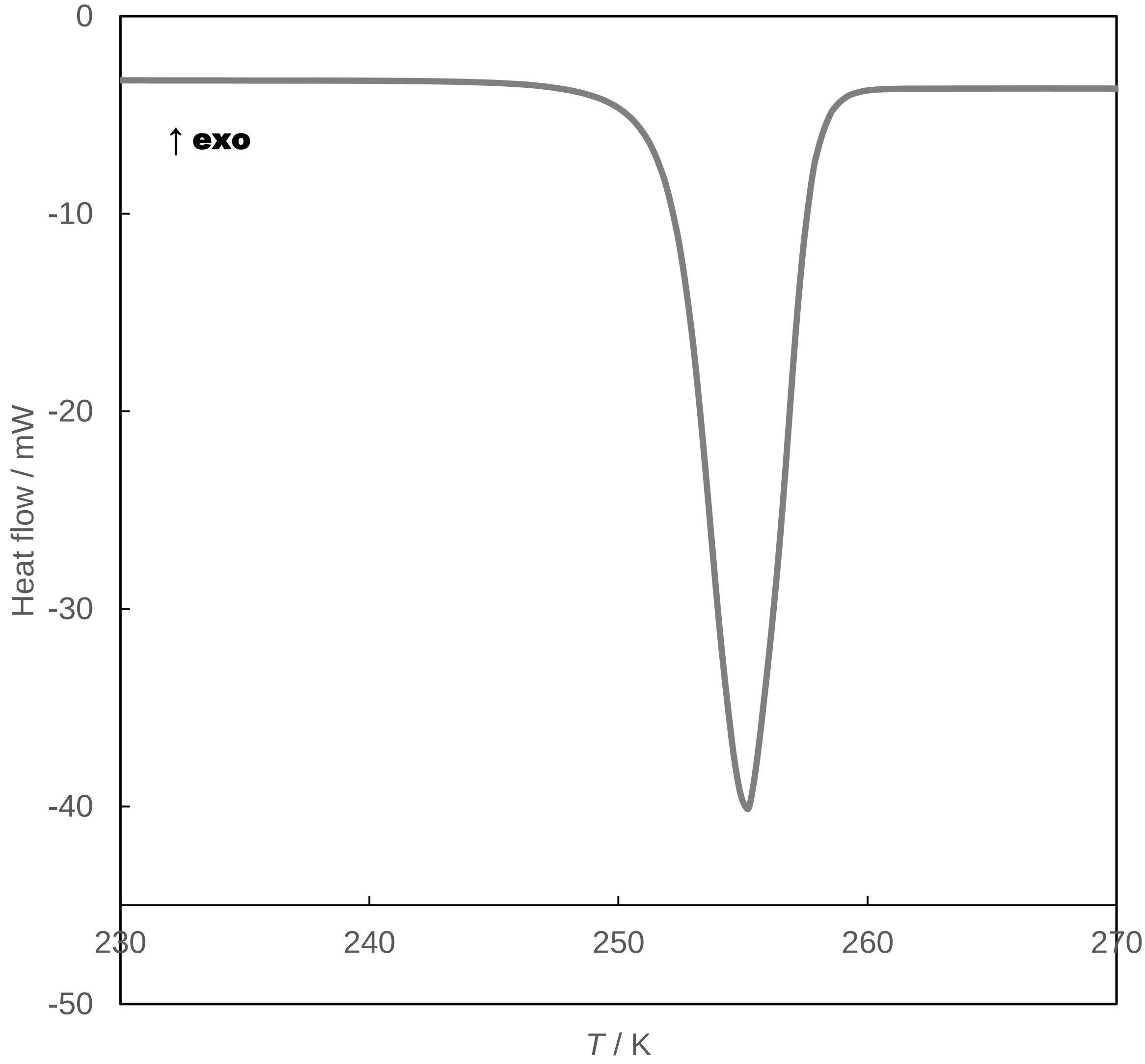

Fig. S5. Typical DSC-thermogram of 4-methylacetophenone

TABLE S4
Experimental thermochemical data at T = 298.15 K (p° = 0.1 MPa) for reference compounds (in $kJ \cdot mol^{-1}$).

	$\Delta_f H_m^o$(liq)	$\Delta_l^g H_m^o$	$\Delta_f H_m^o$(g)
benzene	49.0±0.9 [7]	33.9±0.1 [7]	82.9±0.9 [7]
methylbenzene	12.0±1.1 [7]	38.1±0.1 [7]	50.1±1.1 [7]
ethylbenzene	-12.3±0.9 [8]	42.2±0.1 [9]	29.9±0.9
cyanobenzene	164.6±0.7[10]	51.1±0.1[10]	215.7±0.7
acetophenone	-142.5±1.0 [11]	55.4±0.3 [12]	-87.1±1.0
acetoxybenzene	-334.8±0.9[13,14]	59.0±0.3 [15]	-275.8±1.0

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