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Standard molar enthalpies of formation of methylbenzophenones

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ABSTRACT: The standard ($p^o = 0.1$ MPa) molar enthalpies of formation of 2-, 3-, and 4-methylbenzophenone were derived from the standard molar energies of combustion, in oxygen, at $T = 298.15$ K, measured by static bomb combustion calorimetry. The Calvet high temperature vacuum sublimation technique was used to measure the enthalpies of vaporization or sublimation of the three isomers. The standard molar enthalpies of formation of the three isomers of methylbenzophenone, in the gaseous phase and at $T = 298.15$ K have been derived from the corresponding standard molar enthalpies of formation in the condensed phase and standard molar enthalpies for phase transition. The results obtained are $(27.2 \pm 3.7)\ \mathrm{kJ \cdot mol^{-1}}$, $(22.7 \pm 4.0)\ \mathrm{kJ \cdot mol^{-1}}$, and $(20.4 \pm 3.0)\ \mathrm{kJ \cdot mol^{-1}}$ for 2-methyl, 3-methyl, and 4-methylbenzophenones, respectively. Standard molar enthalpies of formation were also estimated by employing two different methodologies, one based on the Cox scheme and one other based on DFT computations. The agreement between experimental and estimated results is very good. Two possible conformations were found for the 2-methyl and 3-methylbenzophenones, one with the C═O bond pointing in the same direction of the Ph—CH_3 bond and another one with these bonds pointing in different directions. The former conformations are most stable by 5.1 and $0.9\ \mathrm{kJ \cdot mol^{-1}}$ for 2-methyl and 3-methyl isomers, respectively. Copyright © 2007 John Wiley & Sons, Ltd.
Supplementary material. Tables S1 to S3 listing the details of all the Combustion Calorimetry experiments for the three isomers of methylbenzophenone studied. This material is available free of charge in Wiley Interscience. http://www.interscience.wiley.com/jpages/0894-3230/suppmat/

KEYWORDS: thermochemistry; energy of combustion; enthalpy of formation; enthalpy of vaporization; enthalpy of sublimation; methylbenzophenones

INTRODUCTION

Benzophenone or diphenylketone (Fig. 1), which is an aromatic ketone, is an important compound on organic photochemistry and perfumery as well as in organic synthesis. For example, this compound is an important constituent of synthetic perfumes and it is a starting material for the manufacture of dyes, pesticides, and drugs.[1] It is also used as a photoinitiator of UV-curing applications in inks, adhesive and coatings, optical fiber as well as in printed circuit boards.[2] Some benzophenone derivatives are excellent optical filters and, therefore, current industrial applications involve their use as sunscreen agents for the production of skin-protectors and their addition to plastic casings, which are used to prevent damaging of scents and colors by ultraviolet radiation in products such as perfumes and soaps.[3,4]

Despite the wide range and large number of applications involving benzophenone and their derivatives, little attention has been given to the gas-phase thermochemistry of these compounds. In fact, only the parent benzophenone and the 2,4,6-triisopropyl derivative have been investigated in detail so far. In the case of benzophenone, several studies have been carried out concerning the determination of its energy of combustion, enthalpy of sublimation and enthalpy of fusion, and hence the determination of its enthalpies of formation in the crystalline and gaseous states.[5] Based on a careful analysis of the several experimental results, the standard gas-phase enthalpy of formation for benzophenone is $(49.9 \pm 3.0)\ \mathrm{kJ \cdot mol^{-1}}$.[5] In the case of 2,4,6-triisopropyl benzophenone, Inagaki *et al.* have used[6] a static bomb calorimeter to determine the enthalpy of combustion of this solid, and then the enthalpy of formation in the condensed phase; the latter value is $-(304.6 \pm 3.4)\ \mathrm{kJ \cdot mol^{-1}}$. Measuring vapor pressures, these same

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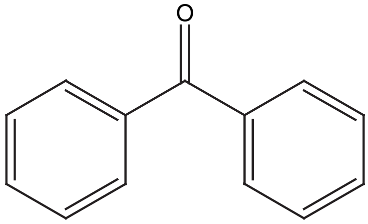

Figure 1. Benzophenone

authors determined the enthalpy of sublimation to be $(116 \pm 7)\ \mathrm{kJ \cdot mol^{-1}}$. Combining these two quantities, the standard gas-phase enthalpy of formation for 2,4,6-triisopropyl benzophenone is$-(189 \pm 8)\ \mathrm{kJ \cdot mol^{-1}}$. In the literature, it is found also a study concerning one methyl derivative, the crystalline 4-methylbenzophenone compounds, for which the standard molar enthalpy of formation in the condensed phase has been determined. In that work due to Colamina *et al.*,[7] $\Delta_f H_m^o$ (cr) was determined as being$-(77.8 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}$. This quantity has been later reviewed by Cox and Pilcher[8] as being$-(78.2 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}$. No other thermochemical data have been found for the other methylbenzophenone derivatives.

The methyl derivatives have been the subject of other research studies concerning mainly their polymorphism.[9] These compounds present quite different physical properties when melted and then cooled to a specific temperature which are important for the understanding of organic crystals. In this area, Kutzke *et al.* have determined the crystallographic structures of stable and metastable forms of 4-methylbenzophenone; a monoclinic and a trigonal structure have been identified.[9]

In this work, we present the experimental determination of the standard ($p^o = 0.1$ MPa) molar enthalpies of formation, both in the condensed and gaseous state, at the temperature 298.15 K, of 2-, 3-, and 4-methylbenzophenone, derived from combustion calorimetry and high temperature Calvet calorimetry. Those parameters, for the gaseous state, were also calculated by computational thermochemistry and with the Cox scheme[10] and compared with the experimental-derived results. The applicability of the Cox scheme to substituted benzophenones is discussed.

EXPERIMENTAL DETAILS

Materials and purity control

The 2-methylbenzophenone [CAS 131-58-8], 3-methylbenzophenone [CAS 643-65-2 and 4-methylbenzophenone [CAS 134-84-9] studied in this work were obtained commercially from Aldrich Chemical Co. with mass fractions purities of, respectively, 0.9910, 0.9930, and 0.9970. The liquids 2-methylbenzophenone and 3-methylbenzophenone were purified by successive fractional distillations, under reduced pressure, at $T = 473$ K. The crystalline 4-methylbenzophenone was purified by successive sublimations under reduced pressure at $T = 338$ K. The purity of the compounds was checked by GLC and from the average ratios of the mass of carbon dioxide recovered from combustion to that calculated from the mass of sample as: 1.00034 for 2-methylbenzophenone, 0.99981 for 3-methylbenzophenone, and 1.00028 for 4-methylbenzophenone. The densities, at $T = 298.15$ K, were taken for 2-methylbenzophenone as $1.083\ \mathrm{g \cdot cm^{-3}}$,[11] for 3-methylbenzophenone as $1.095\ \mathrm{g \,.\, cm^{-3}}$ and for 4-methylbenzophenone as $0.886\ \mathrm{g \cdot cm^{-3}}$, this one determined from the ratio mass/volume of pellets of this compound.

Combustion calorimetry

The combustion experiments were performed with an isoperibol calorimetric system. The bomb calorimeter, subsidiary apparatus and technique have been described previously in the literature.[12,13]

Combustion of certificated benzoic acid NBS Standard Reference Material, Sample 39i, was used for calibration of the bomb. Its massic energy of combustion is $-(26\,434 \pm 3)\ \mathrm{J \cdot g^{-1}}$, under certificate conditions.[14] The calibration results were corrected to give the energy equivalent ε(calor) corresponding to the average mass of water added to the calorimeter: 3116.3 g. From six calibration experiments, $\varepsilon(\text{calor}) = (16\,005.0 \pm 1.7)\ \mathrm{J \cdot K^{-1}}$, where the uncertainty quoted is the standard deviation of the mean.

In all combustion experiments, $1.00\ \mathrm{cm^3}$ of water was introduced into the bomb, a twin-valve static combustion bomb Type 1108, Parr Instrument Company, made of Carpenter 20Cb3 stainless steel, with an internal volume of $0.342\ \mathrm{cm^3}$. The bomb was purged twice to remove air, before being charged with 3.04 MPa of oxygen.

For all experiments, the calorimeter temperatures were measured to $\pm(1 \cdot 10^{-4})$ K, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett Packard HP 2804A), interfaced to a PC. The ignition of the samples was made at $T = (298.150 \pm 0.001)$ K, at least 100 readings, at time intervals of 10 s, after the start of the experiment, by the discharge of a 1400 μF capacitor through the platinum ignition wire. After ignition, 100 readings were taken for the main and after periods.

The crystalline sample of 4-methylbenzophenone was ignited in the pellet form, whereas the liquid samples of 2- and 3-methylbenzophenone were contained in sealed polyester bags made of Melinex® (0.025 mm of thickness) with massic energy of combustion $\Delta_c u^0 = -(22\,902 \pm 5)\ \mathrm{J \cdot g^{-1}}$.[15] The mass of Melinex® used in each experiment was corrected for the mass fraction of water ($w = 0.0032$) and the mass of carbon dioxide produced from its combustion was calculated using the factor previously reported.[15] For the cotton thread fuse of empirical formula $\mathrm{CH_{1.686}O_{0.843}}$, the

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massic energy of combustion was assigned to $-\Delta_c u^o = 16\,240\ \mathrm{J \cdot g^{-1}}$.[16] The massic energies of combustion of Melinex® and of the cotton thread fuse have been confirmed in our laboratory.

The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. The corrections for nitric acid formation were based on $-59.7\ \mathrm{kJ \cdot mol^{-1}}$[17] for the molar energy of formation of $0.1\ \mathrm{mol \cdot dm^{-3}}$ HNO_3(aq) from N_2, O_2, and H_2O(l). In the experiments with carbon residue soot formation during the combustion, the necessary energetic correction for its formation was based on $\Delta_c u^o = -33\ \mathrm{J \cdot g^{-1}}$.[16] All the necessary weighing was made in a Mettler Toledo AT201 microbalance, sensitivity $\pm(1 \cdot 10^{-6})$ g, and corrections from apparent mass to mass were made.[18] An estimated pressure coefficient of specific energy: $(\partial u/\partial p)_T = -0.2\ \mathrm{J \cdot g^{-1} \cdot MPa^{-1}}$ at $T = 298.15$ K, a typical value for most organic compounds,[19] was assumed. For each compound, the massic energy of combustion, $\Delta_c u^o$, was calculated by the procedure given by Hubbard *et al.*[20] The amounts of methylbenzophenones used in each experiment were determined from the total mass of carbon dioxide produced (Mettler Toledo AT 201 balance, sensitivity $\pm(1 \cdot 10^{-4})$ g), produced during the experiments taking into account that formed from the combustion of the cotton-thread fuse, of the Melinex® and that lost due to carbon formation.

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2001;[21] using those masses, the molar mass for the isomers of methylbenzophenone is $196.2445\ \mathrm{g \cdot mol^{-1}}$.

Microcalorimetry Calvet

The standard molar enthalpies of phase transition of the methylbenzophenones isomers were measured using the vacuum sublimation drop-microcalorimetric technique,[22,23] and the same method was employed in the determination of the enthalpies of vaporization.[24] The apparatus and technique have been recently described.[23] Samples of about 4–8 mg of liquid 2- and 3-methylbenzophenone and of 3–6 mg of the crystalline 4-methylbenzophenone, contained in a small thin glass capillary tube sealed at one end, and a blank capillary with similar mass, were simultaneously dropped at room temperature into the hot reaction vessel in the Calvet high-temperature microcalorimeter (Setaram HT 1000), held at the convenient temperature *T*, and were removed from the hot zone by vacuum sublimation or vaporization. The thermal corrections for the glass capillary tubes were determined in separate experiments, and were minimized, as far as possible, by dropping tubes of nearly equal mass, to within ±10 μg, into each of the twin calorimeter cells. The observed enthalpies of sublimation or vaporization, $\Delta^{g,T}_{\mathrm{cr,1,298.15K}} H_m$, were corrected to $T = 298.15$ K using values of $\Delta^{g,T}_{\mathrm{298.15K}} H^0_m(\mathrm{g})$ estimated by a group method, that is, methylbenzophenone = methylbenzene + propapropanone + benzene − 2 methane, based on data of Stull *et al.*,[25] where *T* is the temperature of the hot reaction vessel. For these measurements, the microcalorimeter was calibrated *in situ* using the reported standard molar enthalpies of sublimation of naphthalene $(72.6 \pm 0.6)\ \mathrm{kJ \cdot mol^{-1}}$ [26] for crystalline 4-methylbenzophenone and of vaporization of *n*-undecane $(56.58 \pm 0.57)\ \mathrm{kJ \cdot mol^{-1}}$,[26] for the liquids 2-methylbenzophenone and 3-methylbenzophenone.

Theoretical calculations

Density functional theory computations have been performed with the B3LYP method – Becke's three-parameter hybrid functional using the non-local correlation due to Lee *et al.*,[27,28] – and two different basis sets. The 6-31G(d) basis set was used for the optimization of the geometry of all compounds studied here and to calculate the vibrational frequencies. The latter set of calculations enable to correct the energies calculated with a larger basis set, 6-311 + G(2d,2p), for $T = 298.15$ K by inclusion of vibrational, rotational, translational, and *pV* thermal corrections. All these calculations have been performed by means of the Gaussian 98 computer code.[29] This computational approach seems to be adequate for the present purposes. In fact, computed gas-phase structural parameters for the 4-methylbenzophenone are identical to those obtained experimentally for the same compound in the solid phase,[9] with maximum deviation in bond lengths and angles smaller than 0.03 Å and 1.0°, respectively. A large difference is found between the tilt angle between the phenyl rings. In the gas-phase, the tilt angle is of ~50° while in the solid the tilt angle is larger than 58°.

RESULTS

Results for a typical combustion experiment of each compound are given in Table 1, where $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3116.3 g, the mass assigned to ε(calor), and ΔU_Σ is the energy correction to the standard state. The remaining quantities are as previously defined.[20] The samples were ignited at $T = (298.150 \pm 0.001)$ K, with

$$\Delta U(\mathrm{IPB}) = -\{\varepsilon_{\mathrm{cal}} + \Delta m(\mathrm{H_2O}) c_p(\mathrm{H_2O}, 1) + \varepsilon_f\}\Delta T_{\mathrm{ad}} + \Delta U(\mathrm{ign}), \qquad (1)$$

where ΔT_{ad} is the adiabatic temperature raise.

The individual values of $-\Delta_c u^o$ together with the mean value, $\langle \Delta_c u^o \rangle$, and its standard deviation, are given, for each compound, in Table 2. Here, $\Delta_c u^o$ refers to the idealized combustion reaction yielding CO_2(g) and H_2O(l).

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Table 1. Results of a typical combustion experiment at $T = 298.15$ K

	2-methylbenzophenone	3-methylbenzophenone	4-methylbenzophenone
$m(CO_2, \text{total})$/g	2.68862	1.78470	2.29693
m'(cpd)/g	0.81213	0.52736	0.72898
m''(fuse)/g	0.00297	0.00240	0.00510
m'''(Melinex)/g	0.05854	0.05463	—
ΔT_{ad}/K	1.93804	1.28187	1.66194
ϵ_f / $(J \cdot K^{-1})$	16.77	16.00	16.17
$\Delta m(H_2O)$/g	0.0	0.0	0.0
$-\Delta U$(IBP)/J[a]	31 050.3	20 535.66	26 625.4
ΔU(Melinex)/J	1340.76	1251.21	—
ΔU(fuse)/J	48.23	38.98	82.82
$\Delta U(HNO_3)$/J	1.12	0.99	3.90
ΔU(ign)/J	0.53	1.18	0.82
ΔU_Σ/J	19.10	12.07	15.70
$-\Delta_c u^0/J \cdot g^{-1}$	36 497.96	36 469.22	36 383.69

[a] ΔU(IBP) already includes the ΔU(ign).

Table 2. Individual values of the massic energy of combustion $-\Delta_c u^0$ of the compounds at $T = 298.15$ K

2-methylbenzophenone	3-methylbenzophenone	4-methylbenzophenone
	$-\Delta_c u^0/J \cdot g^{-1}$	
36 497.96	36 471.37	36 388.58
36 510.82	36 463.02	36 379.77
36 492.84	36 477.61	36 383.69
36 507.24	36 469.22	36 382.98
36 510.56	36 448.12	36 390.38
35 499.76	36 442.85	36 393.82
36 509.74	36 442.79	36 393.87
	$-\Delta_c u^0/J \cdot g^{-1}$	
36 504.1 ± 2.7	36 459.3 ± 5.5	36 387.6 ± 2.1

Table 3 lists the derived standard molar energies and enthalpies of combustion and standard molar enthalpies of formation for the methylbenzophenones in the condensed phase, at $T = 298.15$ K. In accordance with normal thermochemical practice,[30,31] the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of auxiliary quantities used. To derive $\Delta_f H_m^o$ (cr, 1) from $\Delta_c H_m^o$(cr, 1), the standard molar enthalpies of formation of $CO_2(g)$ and $H_2O(l)$, at $T = 298.15$ K, $-(393.51 \pm 0.13)$ $kJ \cdot mol^{-1}$ [32] and $-(285.830 \pm 0.004)$ $kJ \cdot mol^{-1}$ [32], respectively, were used.

The standard molar enthalpy of formation in the crystalline state of 4-methylbenzophenone determined in the present work is, within the associated uncertainties, identically to that obtained previously.[7,8]

Measurements of the standard molar enthalpies of sublimation/vaporization of methylbenzophenones, by microcalorimetry, as well the respective uncertainties, taken as twice the standard deviations of the mean and include the uncertainties in calibration, are given in Table 4. The derived standard molar enthalpies of formation in the condensed phase, and the standard molar enthalpies of phase transition yield the standard molar enthalpies of formation in the gaseous phase of the

Table 3. Derived standard molar energies, $\Delta_c U_m^o$, standard molar enthalpies of combustion, $\Delta_c H_m^o$, and standard molar enthalpies of formation, $\Delta_f H_m^o$, for the compounds at $T = 298.15$ K with $p^0 = 0.1$ MPa

	$-\Delta_c U_m^o$(cr,1) $(kJ \cdot mol^{-1})$	$-\Delta_c H_m^o$(cr,1) $(kJ \cdot mol^{-1})$	$-\Delta_f H_m^o$(cr,1) $(kJ \cdot mol^{-1})$
2-methylbenzophenone (l)	7163.9 ± 2.7	7170.1 ± 2.7	54.0 ± 3.3
3-methylbenzophenone (l)	7155.0 ± 3.3	7161.2 ± 3.3	62.9 ± 3.8
4-methylbenzophenone (cr)	7141.0 ± 2.1	7147.2 ± 2.1	76.9 ± 2.8

Table 4. Microcalorimetric standard ($p^0 = 0.1$ MPa) molar enthalpies of sublimation or vaporization, $\Delta^{g}_{cr,1}H^{o}(298.15\,K)$, at $T = 298.15$ K[a]

	Number of experiments	T (K)	$\Delta^{g,T}_{cr,1,298K}H^{o}_{m}$ ($kJ \cdot mol^{-1}$)	$\Delta^{T}_{298.15K}H^{0}_{m}(g)$ ($kJ \cdot mol^{-1}$)	$\Delta^{g}_{cr,1}H^{0}_{m}(298.15\,K)$ ($kJ \cdot mol^{-1}$)
2-methylbenzophenone (l)	6	523	141.8 ± 1.7	60.6	81.2 ± 1.7
3-methylbenzophenone (l)	5	523	146.2 ± 1.2	60.6	85.6 ± 1.2
4-methylbenzophenone (cr)	5	401	120.8 ± 1.0	23.5	97.3 ± 1.0

[a] $\Delta^{g,T}_{cr,1,298K}H_{m}$ is the measured enthalpy for the transformation from the condensed state, at $T = 298.15$ K to the gaseous state at temperature T; $\Delta^{T}_{298.15K}H^{0}_{m}(g)$ is the difference of enthalpies of the gaseous compound between the temperatures T and 298.15 K.

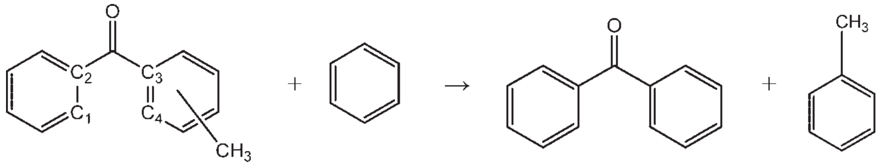
three isomers of methylbenzophenone which are summarized in Table 5. Although these values can be considered equal within the associated uncertainties, they seem to diminish from the *ortho*-methyl to the *meta*-methyl, and from this one to the *para*-methyl.

Cox suggested[10] a method to estimate the standard molar enthalpies of formation of gaseous benzene derivatives, by assuming that each group, when substituted into a benzene ring, produces a characteristic increment in $\Delta_f H^{o}_{m}(g)$ and that each *ortho*-pair of substituents leads to an enthalpy increment of $4\,kJ \cdot mol^{-1}$, with another additional correction of $4\,kJ \cdot mol^{-1}$ for every set of three substituents in three consecutive carbon atoms of the aromatic ring. From the literature values, $\Delta_f H^{o}_{m}$ ($C_6H_5CH_3$, g) = (50.5 ± 0.5) $kJ \cdot mol^{-1}$ [33] and $\Delta_f H^{o}_{m}$ (C_6H_6, g) = (82.6 ± 0.7) $kJ \cdot mol^{-1}$ [33] the enthalpic increment for the monomethylation of benzene is $-(32.1 \pm 0.9)$ $kJ \cdot mol^{-1}$, so, from the enthalpy of formation of benzophenone, $\Delta_f H^{o}_{m}$ (C_6H_6, g) = (49.9 ± 3.0) $kJ \cdot mol^{-1}$,[5] accordingly to the Cox scheme, the estimated value for the standard molar enthalpy of formation, in the gaseous state, of 2-methylbenzophenone is (21.8 ± 2.6) $kJ \cdot mol^{-1}$, whereas the estimated value for both the 3-methylbenzophenone and the 4-methylbenzophenone isomers is (17.8 ± 2.6) $kJ \cdot mol^{-1}$, *c.f.* Table 6.

These estimated values differ from the experimental ones by less than $6\,kJ \cdot mol^{-1}$, which is very well within the limit of acceptance of $10\,kJ \cdot mol^{-1}$ indicated by Cox for his scheme.[10] The Cox scheme fails completely in the differentiation between the 3- and 4-methylbenzophenone isomers since the same value is predicted for these two isomers, which was expected since Cox did not provide any correction to differentiate substitution at aromatic ring positions 3 or 4 due to the possibility of different resonance/inductive effects depending on the substituent, which could increase or decrease the overall compound stability.

From the values of the standard molar enthalpies of formation, in the gaseous state, of the three monomethylated isomers of benzoic acids[5] registered in Table 7, it is found that the calculated increments for the *ortho*, *meta*, and *para* methylations of benzoic acid show the same tendency as the ones in benzophenone, i.e., the increasing of the relative stability of the methyl isomers from the *ortho* to the *meta* to the *para*, supporting the basis transferability principle which is inherent in the Cox scheme.

The B3LYP/6-311 + G(2d,2p)//B3LYP/6-31G(d) approach has been used to compute the enthalpy of the following reaction:



(2)

Then, using the experimental enthalpies of formation for benzophenone, methylbenzene, and benzene (values given above) and the enthalpy of reaction (2), the standard molar enthalpies of formation of the three methylbenzophenone isomers were estimated. The DFT estimated

Table 5. Derived standard ($p^0 = 0.1$ MPa) molar enthalpies of formation, $\Delta_f H^{0}_{m}$, and of vaporization or sublimation, $\Delta^{g}_{cr,1}H^{o}$, at $T = 298.15$ K

	$\Delta_f H^{0}_{m}(cr,1)$ ($kJ \cdot mol^{-1}$)	$\Delta^{g}_{cr,1}\ H^{0}_{m}(298.15\,K)$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^{0}_{m}(g)$ ($kJ \cdot mol^{-1}$)
2-methylbenzophenone (l)	54.0 ± 3.3	81.2 ± 1.7	27.2 ± 3.7
3-methylbenzophenone (l)	62.9 ± 3.8	85.6 ± 1.2	22.7 ± 4.0
4-methylbenzophenone (cr)	76.9 ± 2.8	97.3 ± 1.0	20.4 ± 3.0

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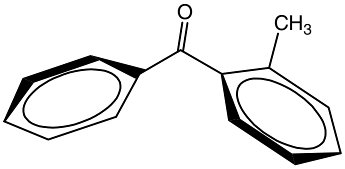
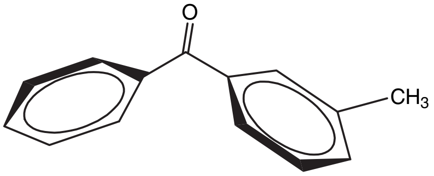
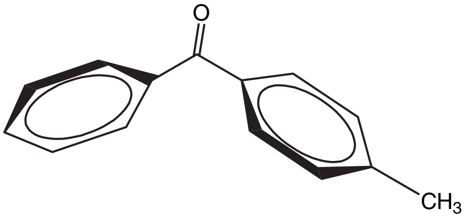
Table 6. Comparison of experimental and estimated values of standard molar enthalpies of formation in the gaseous state, $\Delta_f H_m^0$ (g), in kJ · mol^{-1}

Compound	Experimental	Estimated		Computed	
		Cox method	Δ	B3LYP	Δ
	27.2 ± 3.7	21.8 ± 2.6	5.4 ± 4.5	26.6	0.6
	22.7 ± 4.0	17.8 ± 2.6	4.9 ± 4.8	18.6	4.1
	20.4 ± 3.0	17.8 ± 2.6	2.6 ± 4.0	17.4	3.0

Δ = (Experimental value) − (Estimated/Calculated value).

Table 7. Enthalpic increments for the methylation of benzophenone and benzoic acid. Values in kJ · mol^{-1}

Compound	X = Benzophenone		X = Benzoic acid	
	$\Delta_f H_m^0$ (g)	Δ (methylation)	$\Delta_f H_m^0$ (g)	Δ (methylation)
X	49.9 ± 2.4[b]		−296.1 ± 1.5[b]	
2-CH_3-X	27.2 ± 3.7[a]	22.7 ± 4.4	−320.6 ± 1.5[b]	24.5 ± 1.8
		↓ 4.4		↓ 7.3
3-CH_3-X	22.8 ± 4.0[a]	27.1 ± 4.7	−327.9 ± 1.4[b]	31.8 ± 1.7
		↓ 2.4		↓ 2.5
4-CH_3-X	20.4 ± 3.0[a]	29.5 ± 3.8	−330.4 ± 1.5[b]	34.3 ± 1.8

[a] This work.
[b] Reference 5.

The enthalpic difference between *o*-, *m*-, and *p*-methyl-substituted benzophenone isomers is presented. The standard enthalpies of formation are found to be correlated with the tilting angle between the aromatic rings.

values are also given in Table 6 and in the case of the 2-methyl and 3-methylbenzophenones, the values refer to the most stable conformation, i.e., with the methyl group pointing in the same direction of the ketone bond. The estimated enthalpies of formation for the least stable conformations for the 2-methyl and 3-methylbenzophenones, (Fig. 2), are 31.7 and 19.5 kJ · mol^{-1}, respectively. The enthalpies of formation computed for all isomers show clearly that the 4-methyl derivative is the most stable methylbenzophenone, even its enthalpy of formation is similar to those computed for the two 3-methylbenzophenone conformations, and that the 2-methylbenzophenone is the least stable isomer. The more positive enthalpies of formation for the two 2-methylbenzophenone conformations are a consequence of the destabilizing interaction between the methyl group and the oxygen lone-pairs when both C=O and Ph—CH_3 bonds are pointing in the same direction and between the methyl substituent and the other benzene ring when these bonds are pointing in different directions. This is clearly seen from the computed C_1—C_2—C_3—C_4 dihedral angles in benzophenone and in the different methylbenzophenones. In the non-substituted compound, the B3LYP optimized dihedral angle is 50.0° and a similar

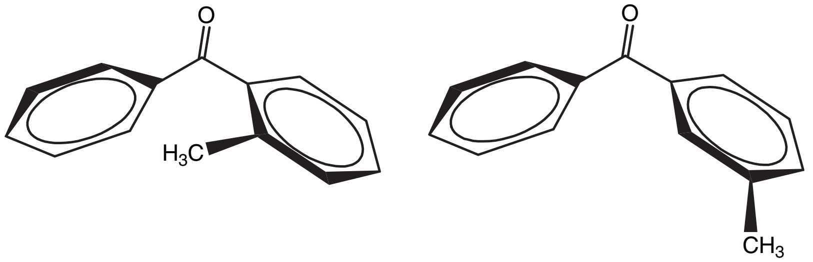


Figure 2. The two other least stable minima on the potential energy surface computed for 2-methyl and 3-methylbenzophenones

value is found for the two possible conformations (C═O and Ph—CH_3 pointing in the same or opposite directions) obtained for 3-methylbenzophenone and also for the 4-methylbenzophenone isomer. In these cases, the C_1—C_2—C_3—C_4 dihedral angles are 50.2°, 49.5°, and 50.2°, respectively. In the case of the 2-methylbenzophenone, the angle increases to 56.2° when the C═O and Ph—CH_3 bonds point in the same direction and it is even larger, 62.9°, in the case of the least 2-methylbenzophenone conformation with C═O and Ph—CH_3 bonds pointing in opposite directions.

CONCLUSIONS

The standard molar gas-phase enthalpies of formation, at $T = 298.15$ K, of 2-methyl-, 3-methyl-, and 4-methylbenzophenone have been obtained both by experimental and computational techniques. The enthalpies of formation were indirectly obtained from static bomb combustion calorimetry and Calvet microcalorimetry experiments, and their values show that the 4-methylbenzophenone is the most stable isomer. Those parameters were also estimated by the Cox scheme yielding values in reasonable agreement.

The $\Delta_f H^o_m$ values have been also estimated by DFT using the B3LYP/6-311 + G(2d,2p)//B3LYP/6–1G(d) approach and a convenient work reaction. All computed values are in excellent agreement with the experimental data herewith reported, with a maximum deviation of 4.1 kJ · mol^{-1}. The computed values also confirm that the 4-methylbenzophenone is the most stable isomer of methylbenzophenone, a fact that can be understood by the dihedral angle of the two benzenic rings of the different isomers.

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REFERENCES

1. Schmitt MR, Carzaniga R, Cotter HVT, O'Connell R, Hollomon D. *Manag. Sci.* 2006; **62**: 383–392.
2. Wang H, Wei J, Jiang X, Yin J. *J. Polym. Sci. Part A: Polym. Chem.* 2006; **44**: 3738–3750.
3. Forbes MA, Brannen M, King WC. *South. Med. J.* 1966; **59**: 321.
4. Gaspar LR, Campos PMBGM. *Int. J. Pharm.* 2006; **307**: 123.
5. Afeefy HY, Liebman JF, Stein SE''Neutral Thermochemical Data'' In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Linstrom PJ, Mallard WG (eds). National Institute of Standards and Technology: Gaithersburg MD, June 2005. (http://webbook.nist.gov).
6. Inagaki S, Murata S, Sakiyama M, Ito Y, Umihara Y, Hijiya T, Matsura T. *Bull. Chem. Soc. Jpn.* 1982; **55**: 2803.
7. Colamina M, Cambeiro M, Perez-Ossorio R, Latorre C. *Ber. Bunsenges. Phys. Chem.* 1959; **59**: 1–6.
8. Cox JD, Pilcher G. *Thermochemistry of Organomettalic Compounds*. Academic Press: London, 1970.
9. Kutzke H, Al-Mansour M, Klapper H. *J. Mol. Struct.* 1996, **374**: 129.
10. Cox JD. *A method of estimating the enthalpies of formation of benzene derivatives in the gas state*. NPL Report CHEM 83. June 1978.
11. Aldrich. *Chemical Handbook of Fine Chemicals and Laboratory Equipment*. The Sigma-Aldrich Chemical Co: Gillingham, UK, (2005–2006).
12. Ribeiro da Silva MAV, Ribeiro da Silva MDMC, Pilcher G. *Rev. Por. Quím.* 1984; **26**: 163–172.
13. Ribeiro da Silva MAV, Ribeiro da Silva MDMC, Pilcher G. *J. Chem. Thermodyn.* 1984; **16**: 1149–1155.
14. *Certificate of analysis standard reference material 39i benzoic acid calorimetric standard*. NBS, Washington 1995.
15. Skinner HA, Snelson A. *Trans Faraday Soc.* 1960; **6**: 1776–1783.
16. Copps J, Jessup RS, Van Nes K. In *Experimental Thermochemistry*, vol. 1, Rossini FD (ed.). Interscience: New York, 1956; Chapter 3, 27–58.
17. Wagman DD, Evans WH, Parker VB, Shum RH, Halow F, Bailey SM, Churney KL, Nuttall RL. *J. Phys. Chem. Ref. Data.* 1982; **11**(Suppl. 2).
18. Mendham J, Denney RC, Barnes JD, Thomas M. *Vogel's Textbook for Quantitative Chemical Analysis*. Prentice Hall: London 2000.
19. Washburn EN. *J. Res. Nalt. Bur. Stand. (US)* 1935; **10**: 525–558.
20. Hubbard WN, Scott DW, Waddington G. In *Experimental Thermochemistry*, vol. 1, Rossini FD (ed.). Interscience: New York, 1956; Chapter 5, 75–128.
21. Loss RD. *Pure Appl. Chem.* 2003; **75**: 1107–1122.

22. Adedeji FA, Brown DLS, Connor JA, Leung M, Paz-Andrade MI, Skinner HA. *J. Organomet. Chem.* 1975; **97**: 221–228.
23. Santos LMNB, Schröder B, Fernandes OOP, Ribeiro da Silva MAV. *Thermochim. Acta* 2004; **415**: 15–20. DOI:10.1016/j.tca.2003.07.016.
24. Ribeiro da Silva MAV, Matos MAR, Amaral LMPF. *J Chem. Thermodyn.* 1995; **27**: 565–574.
25. Stull RD, Westrum EF Jr., Sinke GC. *The Chemical Thermodynamics of Organic Compounds*. Wiley: New York, 1969.
26. Sabbah R, Xu-wu A, Chickos JS, Leitão MLP, Roux MV, Torres LA. *Thermochim. Acta* 1999; **331**: 93–204.
27. Becke AD. *J. Chem. Phys.* 1993; **98**: 5648.
28. Lee C, Yang W, Parr RG. *Phys. Rev. B* 1980; **37**: 785.
29. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith T, Petersson GA, Montgomery JA, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Cioslowski P, Stefanov BB, Nanayakkara A, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JP, Head-Gordon M, Gonzalez C, Pople JA. Gaussian 98, revision A.9. Gaussian, Pittsburgh, PA. 1998.
30. Rossini FD. In *Experimental Thermochemistry*, vol. 1, Rossini FD (ed.). Interscience: New York, 1956; Chapter 14, 297–320.
31. Olofsson G. In *Combustion Calorimetry*, Sunner S, Månsson M (eds). Combustion Calorimetry, Pergamon: Oxford, 1989; 137–159.
32. Cox JD, Wagman DD, Medvedev VA (eds). *CODATA Key Values for Thermodynamics*. Hemisphere: New York, 1989.
33. Pedley JB. *Thermochemical Data and Structures of Organic Compounds*, Vol. 1. Thermodynamics Research Center, College Station: Texas, 1994.

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