



Experimental study on the thermochemistry of 3-nitrobenzophenone, 4-nitrobenzophenone and 3,3'-dinitrobenzophenone

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ABSTRACT

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of combustion, $\Delta_c H_m^\circ$, for the 3- and 4-nitrobenzophenones and for the 3,3'-dinitrobenzophenone, in the crystalline state, were determined, at the temperature $T = 298.15$ K, using a static bomb combustion calorimeter. For these compounds, the standard molar enthalpies of sublimation, $\Delta_{cr}^\circ H_m^\circ$, at $T = 298.15$ K, were determined by Calvet microcalorimetry. For the 3- and 4-nitrobenzophenones the vapour pressures as function of temperature were measured by the Knudsen effusion technique and the standard molar enthalpies of sublimation, $\Delta_{cr}^\circ H_m^\circ$, at $T = 298.15$ K, were derived by the Clausius–Clapeyron equation. The results are as follows:

	$-\Delta_c H_m^\circ(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{cr}^\circ H_m^\circ/(\text{kJ} \cdot \text{mol}^{-1})$	
		Calvet	Knudsen
3-Nitrobenzophenone	6324.5 ± 1.4	123.3 ± 2.4	121.6 ± 0.6
4-Nitrobenzophenone	6327.8 ± 1.9	122.3 ± 2.7	122.9 ± 0.7
3,3'-Dinitrobenzophenone	6154.6 ± 2.2	147.4 ± 3.9	

These values were used to derive the standard molar enthalpies of formation of the compounds in their condensed and gaseous phases, respectively. For 3- and 4-nitrobenzophenones, the standard ($p^\circ = 0.1$ MPa) molar enthalpies, entropies and Gibbs functions of sublimation, at $T = 298.15$ K, were derived. The derived standard molar enthalpies of formation in the gaseous state are analysed in terms of structural enthalpic increments.

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1. Introduction

Some derivatives of nitrobenzophenone are widely used in the pharmaceutical industry. Tolcapom (3,4-dihydroxy-4'-methyl-5-nitrobenzophenone), an inhibitor of catechol-o-methyltransferase, is used in the treatment of Parkinson's disease in combination with carbidopa–levopoda therapy [1–3]. Nitrazepam, belong to the class of 1,4-benzodiazepines, is used in the treatment of insomnia [4] and also have anxiolytic, amnestic, anticonvulsant and skeletal muscle relaxant properties. Benzophenone derivatives containing 3-nitro-4-tert-amino group has valuable pharmacological properties. These compounds are active primarily in the induction of liver microsomal enzyme, but they also have antipyretic activity [5].

Thermochemical data of some derivatives of benzophenone were recently published by our Research Group on some methylated [6,7] and chlorinated [8] derivatives.

In this paper, we report the standard ($p^\circ = 0.1$ MPa) molar enthalpies of combustion, $\Delta_c H_m^\circ$, in oxygen at $T = 298.15$ K, determined by static-bomb calorimetry, for 3- and 4-nitrobenzophenone isomers and for 3,3'-dinitrobenzophenone.

For the three compounds the enthalpies of sublimation were measured by Calvet microcalorimetry. The Knudsen mass-loss effusion technique was used to measure the vapour pressures as a function of temperature of 3- and 4-nitrobenzophenones. From the temperature dependence of the vapour pressure, the molar enthalpies and entropies of sublimation at the mean temperature of the experimental temperature range were derived. Standard molar enthalpies, entropies and Gibbs functions of sublimation, at the temperature of 298.15 K, were calculated.

2. Experimental

2.1. Compounds and purity control

All the studied compounds which were commercially obtained from Aldrich Chemical Co. with the following assessed mass

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fractions purities: 3-nitrobenzophenone [CAS 2243-80-3] 0.97, 4-nitrobenzophenone [CAS 1144-74-7] 0.99, and 3,3'-dinitrobenzophenone [CAS 21222-05-9] 0.96, were purified by successive sublimations, under reduced pressure. Purity was checked by the consistent results obtained from the combustion experiments, as well as by the closeness to unity of the carbon dioxide recovery ratios for each compound. The average ratios of the mass of carbon dioxide recovered from combustion to that calculated from the mass of sample were: 0.99979 for 3-nitrobenzophenone, 0.99975 for 4-nitrobenzophenone, and 0.99992 for 3,3'-dinitrobenzophenone. The densities, at $T = 298.15$ K, were taken for 3- and 4-nitrobenzophenone as $1.10 \text{ g} \cdot \text{cm}^{-3}$, and for 3,3'-dinitrobenzophenone as $0.882 \text{ g} \cdot \text{cm}^{-3}$ determined from the ratio mass/volume of pellets of these compounds.

2.2. Combustion calorimetry

The combustion experiments were performed with an isoperibol calorimetric system already described in the literature [9,10].

Combustion of NBS Reference Material 39j Thermochemical Standard benzoic acid was used for calibration of this bomb. Its massic energy of combustion is $-(26,434 \pm 3) \text{ J} \cdot \text{g}^{-1}$, under certificate conditions [11]. The calibration results were corrected to give the energy equivalent of the calorimeter, $\varepsilon_{\text{calor}}$, corresponding to the average mass of 3119.6 g of water added to the calorimeter. For 3- and 4-nitrobenzophenones, $\varepsilon_{\text{calor}}$ was found to be $(15915.8 \pm 0.8) \text{ J} \cdot \text{K}^{-1}$ and for 3,3'-dinitrobenzophenone $\varepsilon_{\text{calor}} = (15905.7 \pm 1.0) \text{ J} \cdot \text{K}^{-1}$.

The combustion experiments were carried out in oxygen at the pressure of 3.04 MPa with 1.00 cm^3 of water added to the bomb, a twin-valve static combustion bomb Type 1105, Parr Instrument Company, made of stainless steel, with an internal volume of 0.340 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 $\pm(1 \cdot 10^{-4}) \text{ K}$, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett Packard HP 2804A), interfaced to a PC. Data acquisition and control of the calorimeter were performed using the program LABTERMO [12]. At least 100 readings of the temperature, at time intervals of 10 s, were taken before the ignition of the samples which was made at $T = (298.150 \pm 0.001) \text{ K}$ by the discharge of a $1400 \mu\text{F}$ capacitor through the platinum ignition wire ($\phi = 0.05 \text{ mm}$, Goodfellows). After ignition, 100 readings were taken for each the main and after periods.

The crystalline samples were ignited in the pellet form. For the cotton thread fuse used, empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$, $\Delta_c u^\circ = -16,240 \text{ J} \cdot \text{g}^{-1}$ [13]. In the experiments with a small residue of carbon soot formation inside the crucible, during the combustion, the necessary energetic correction for its formation was based on $\Delta_c u^\circ = -33 \text{ J} \cdot \text{g}^{-1}$ [14]. The electrical energy for ignition was determined from the change in potential difference across the capacitor when discharged through the platinum ignition wire. The corrections for nitric acid formation were based on $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$ [15], for the molar energy of formation of $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3(\text{aq})$ from N_2 , O_2 , and $\text{H}_2\text{O}(\text{l})$. All the necessary weighings were made in a Mettler AE 240 microbalance, with sensitivity $\pm(1 \cdot 10^{-6}) \text{ g}$; corrections from apparent mass to true mass were made. An estimated pressure coefficient of specific energy, $(\partial u/\partial p)_T = -0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$ at $T = 298.15 \text{ K}$, a typical value for most organic compounds [16], was assumed. For each compound, the massic energy of combustion, $\Delta_c u^\circ$, was calculated by the procedure given by Hubbard *et al.* [17]. The amounts of the compounds used in each experiment were determined from the total mass of carbon dioxide (Mettler Toledo AT 201 balance, sensitivity $\pm(1 \cdot 10^{-5}) \text{ g}$, produced during the experiments, taking into account that formed from the combustion of

the cotton-thread fuse and that lost due to eventual carbon formation.

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2007 [18].

2.3. Microcalorimetry Calvet

The standard molar enthalpies of sublimation of the three studied compounds were measured using the vacuum sublimation drop-microcalorimetric technique [19,20]. The apparatus and technique have been described [20]. Samples of about (3 to 8) mg of the compounds, 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 a convenient temperature T , and were removed from the hot zone by vacuum sublimation. 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 $\pm 10 \mu\text{g}$, into each of the twin calorimeter cells. The observed enthalpies of sublimation, $\Delta_{\text{cr},298.15\text{K}}^{g,T} H_m$, were corrected to $T = 298.15 \text{ K}$ using values of $\Delta_{298.15\text{K}}^T H_m^\circ(\text{g})$ estimated by a group method, based on data of Stull *et al.* [21], where T is the temperature of the hot reaction vessel.

For these measurements, the microcalorimeter was calibrated *in situ* using the reported standard molar enthalpy of sublimation of naphthalene [22] for the experiments with crystalline 3- and 4-nitrobenzophenones and for the 3,3'-dinitrobenzophenone experiments the calorimeter was calibrated with 1,3,5-triphenylbenzene [22].

2.4. Vapour pressures measurements

The vapour pressures of the crystals of 3- and 4-nitrobenzophenones were measured, at several temperatures, by the mass-loss Knudsen-effusion technique. This apparatus allows the simultaneous operation of nine aluminium effusion cells and has been tested by measuring vapour pressures between 0.1 Pa and 1 Pa, over temperature ranges of ca. 20 K, of benzoic acid, phenanthrene, anthracene, benzanthrone and 1,3,5-triphenylbenzene [23]. Both the measured vapour pressures and the derived enthalpies of sublimation of the test substances are in excellent agreement with the literature results for those compounds. The nine effusion cells are contained in cylindrical holes inside three aluminium blocks, three cells per block. Each block is kept at a constant temperature, different from the other two blocks.

For each compound, the measurements were extended through a chosen temperature interval corresponding to measured vapour pressures in the range (0.1 to 1.0) Pa. In each effusion experiment the loss of mass, Δm , of the samples, during a convenient effusion time period, t , is determined by weighing the effusion cells to $\pm 0.01 \text{ mg}$ before and after the effusion period in a system evacuated to a pressure near $(1 \cdot 10^{-4}) \text{ Pa}$. At the temperature T of the experiment, the vapour pressure p is calculated by the equation

$$p = (\Delta m / A_0 w_0 t) (2\pi RT / M)^{1/2}, \quad (1)$$

where M is the molar mass of the effusing vapour, R is the gas constant, A_0 is the area of the effusion hole and w_0 is the respective Clausing factor calculated by equation (2) where l is the thickness of the effusion hole and r its radius:

$$w_0 = \{1 + (3l/8r)\}^{-1}. \quad (2)$$

The areas and Clausing factors of the effusion orifices, made in platinum foil of 0.0125 mm thickness, are presented in the Supporting information, table S1.

3. Experimental results

Table 1 presents the results for a typical combustion experiment of each compound: $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, the mass assigned for $\epsilon(\text{calor})$, ΔU_{Σ} is the correction to the standard state and the remaining terms are as previously described [17]. For the static bomb measurements, as the samples were ignited at $T = (298.150 \pm 0.001) \text{ K}$,

$$\Delta U(\text{IBP}) = -\{\epsilon(\text{calor}) + cp(\text{H}_2\text{O}, \text{l}) \cdot \Delta m(\text{H}_2\text{O}) + \epsilon_f\} \Delta T_{\text{ad}} + \Delta U(\text{ign}), \quad (3)$$

where $\Delta(\text{IBP})$ is the energy associated to the isotherm bomb process, ϵ_f is the energy of the bomb contents after ignition, $\Delta U(\text{ign})$ is the ignition energy and ΔT_{ad} is the adiabatic temperature rise.

Detailed values of each combustion experiment performed for each studied compound are given in tables S2, S3 and S4 of the Supporting information.

The individual values of $\Delta_c u^\circ$ together with the mean value, $\langle \Delta_c u^\circ \rangle$, and its standard deviation, are given, for each compound, in table 2. Here, $\Delta_c u^\circ$ refers to the idealized combustion reaction yielding $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$.

Table 3 lists the derived standard molar energies and enthalpies of combustion and the standard molar enthalpies of formation for 3-nitrobenzophenone, 4-nitrobenzophenone and 3,3'-dinitrobenzophenone, in the solid phase, at $T = 298.15 \text{ K}$. In accordance with normal thermochemical practice [24,25], the uncertainties assigned to the standard molar enthalpies of formation 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 obtain $\Delta_f H_m^\circ(\text{cr})$ from $\Delta_c H_m^\circ(\text{cr})$ the standard molar enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$, at $T = 298.15 \text{ K}$, $-(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$ [14], and $-(285.830 \pm 0.040) \text{ kJ} \cdot \text{mol}^{-1}$ [14], respectively, were used.

Measurements of the standard molar enthalpies of sublimation of the three studied compounds by Calvet microcalorimetry, as well as the uncertainties given by their standard deviations of the mean, are given in table 4. The uncertainties associated to the standard molar enthalpies of sublimation, at $T = 298.15 \text{ K}$, are twice the standard deviation of the mean and include the uncertainties associated with the calibration process. The observed enthalpies of sublimation, were corrected to $T = 298.15 \text{ K}$ using $\Delta_{298.15\text{K}}^\circ H_m^\circ(\text{g})$ estimated by a group method, i.e., nitrobenzophenone = 2 benzene + acetone + nitromethane – 3 methane, and

TABLE 2

Individual values of the standard ($p^\circ = 0.1 \text{ MPa}$) massic energies of combustion, $\Delta_c u^\circ$, of the studied compounds, at $T = 298.15 \text{ K}$.

3-Nitrobenzophenone	4-Nitrobenzophenone	3,3'-Dinitrobenzophenone
$\Delta_c u^\circ/(\text{J} \cdot \text{g}^{-1})$		
27837.37	27859.64	22625.15
27827.38	27843.35	22621.54
27827.43	27832.66	22628.78
27839.43	27846.16	22612.58
27825.88	27849.28	22613.46
27828.35	27845.64	22634.47
27837.23		
$\langle \Delta_c u^\circ \rangle/(\text{J} \cdot \text{g}^{-1})$		
27831.9 ± 2.2	27846.1 ± 3.6	22622.7 ± 3.5

TABLE 3

Derived standard ($p^\circ = 0.1 \text{ MPa}$) molar energies of combustion, $\Delta_c U_m^\circ$, standard molar enthalpies of combustion, $\Delta_c H_m^\circ$, and standard molar enthalpies of formation, $\Delta_f H_m^\circ$, for the compounds, at $T = 298.15 \text{ K}$.

Compound	$-\Delta_c U_m^\circ(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$-\Delta_c H_m^\circ(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$	$-\Delta_f H_m^\circ(\text{cr})/(\text{kJ} \cdot \text{mol}^{-1})$
3-Nitrobenzophenone	6323.9 ± 1.4	6324.5 ± 1.4	77.4 ± 2.2
4-Nitrobenzophenone	6327.2 ± 1.9	6327.8 ± 1.9	74.1 ± 2.5
3,3'-Dinitrobenzophenone	6158.3 ± 2.2	6154.6 ± 2.2	104.4 ± 2.8

3,3'-dinitrobenzophenone = 2 benzene + acetone – 2 methane + 2 nitromethane – 2 ethane.

The experimental results obtained from each effusion cell for 3- and 4-nitrobenzophenones, are presented in table 5.

The integrated form of the Clausius–Clapeyron equation, $\ln(p/Pa) = a - b \cdot (T/K)^{-1}$, where a is a constant and $b = \Delta_{\text{cr}}^\circ H_m^\circ(\langle T \rangle)/R$, was used to derive the standard molar enthalpies of sublimation at the mean temperature of the experimental temperature range. Table 6 presents for each hole used and for the global treatment of all the (p, T) points obtained for each studied compound, the detailed parameters of the Clausius–Clapeyron equation together with the calculated standard deviations and the standard molar enthalpies of sublimation at the mean temperature of the experiments $T = \langle T \rangle$. For both compounds, the calculated enthalpies of sublimation obtained from each individual hole are in agreement within experimental error.

The entropies of sublimation, at equilibrium conditions, were calculated as

$$\Delta_{\text{cr}}^\circ S_m\{\langle T \rangle, p(T = \langle T \rangle)\} = \Delta_{\text{cr}}^\circ H_m^\circ(\langle T \rangle)/\langle T \rangle. \quad (4)$$

TABLE 1

Results of typical combustion experiments at $T = 298.15 \text{ K}$ ($p^\circ = 0.1 \text{ MPa}$).

	3-Nitrobenzophenone	4-Nitrobenzophenone	3,3'-Dinitrobenzophenone
$m(\text{cpd})/\text{g}$	0.73472	0.73332	0.65177
$m'(\text{fuse})/\text{g}$	0.00350	0.00364	0.00238
$\Delta T_{\text{ad}}/\text{K}$	1.29046	1.28900	0.93170
$\epsilon_f/\text{J} \cdot \text{K}^{-1}$	15.67	15.69	14.97
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.0	0.0	0.0
$-\Delta U(\text{IBP})/\text{J}$	20557.71	20534.53	14832.29
$\Delta U(\text{fuse})/\text{J}$	56.84	59.11	38.65
$\Delta U(\text{HNO}_3)/\text{J}$	32.66	29.91	36.36
$\Delta U(\text{ign})/\text{J}$	1.21	1.16	1.00
$\Delta U_{\Sigma}/\text{J}$	15.54	15.48	13.24
$-\Delta_c u^\circ/\text{J} \cdot \text{g}^{-1}$	27837.37	27859.64	22621.54

$m(\text{cpd})$ is the mass of compound burnt in each experiment; $m'(\text{fuse})$ is the mass of fuse (cotton) used in each experiment; ΔT_{ad} is the corrected temperature rise; ϵ_f is the energy equivalent of contents in the final state; $\Delta m(\text{H}_2\text{O})$ is the deviation of mass of water added to the calorimeter from the mass assigned for $\epsilon(\text{calor})$; $\Delta U(\text{IBP})$ is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U(\text{fuse})$ is the energy of combustion of the fuse (cotton); $\Delta U(\text{HNO}_3)$ is the energy correction for the nitric acid formation; $\Delta U(\text{ign})$ is the electrical energy for ignition; ΔU_{Σ} is the standard state correction; $\Delta_c u^\circ$ is the standard massic energy of combustion.

^a $\Delta U(\text{IBP})$ already includes the $\Delta U(\text{ign})$.

TABLE 4Standard ($p^\circ = 0.1$ MPa) molar enthalpies of sublimation, $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ$, at $T = 298.15$ K determined by Calvet microcalorimetry.

Compound	Number of experiments	T K	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ$ kJ · mol ⁻¹	$\Delta_{298.15\text{K}}^{\text{g}} H_{\text{m}}^\circ(\text{g})$ kJ · mol ⁻¹	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(298.15\text{K})$ kJ · mol ⁻¹
3-Nitrobenzophenone	6	401	146.9 ± 0.6	23.6	123.3 ± 2.4
4-Nitrobenzophenone	8	417	150.5 ± 0.5	28.2	122.3 ± 2.7
3,3'-Dinitrobenzophenone	7	498	206.9 ± 1.1	59.5	147.4 ± 3.9

TABLE 5

Knudsen effusion results for the 3- and 4-nitrobenzophenone.

T/K	t/s	Orifices	m/mg			p/Pa		
			Small	Medium	Large	Small	Medium	Large
3-Nitrobenzophenone								
349.27	22,310	A3–B6–C9	6.18	9.76	14.44	0.160	0.162	0.161
351.21	22,310	A2–B5–C8	7.66	11.79	16.96	0.198	0.194	0.194
353.12	22,310	A1–B4–C7	9.50	14.89	21.22	0.244	0.248	0.245
355.13	15,640	A1–B4–C7	8.36	13.22	19.06	0.308	0.315	0.315
357.21	15,640	A2–B5–C8	10.65	16.90	24.14	0.395	0.399	0.396
359.26	15,640	A3–B6–C9	13.58	21.07	31.39	0.508	0.506	0.506
361.26	10,809	A3–B6–C9	11.31	17.59	26.11	0.614	0.613	0.610
363.20	10,809	A2–B5–C8	14.23	21.99	31.30	0.771	0.758	0.749
365.12	10,809	A1–B4–C7	17.52	26.76	38.60	0.946	0.936	0.935
4-Nitrobenzophenone								
359.27	22,391	A3–B6–C9	6.88	10.40	15.73	0.180	0.174	0.177
361.19	22,391	A2–B5–C8	8.21	12.98	18.26	0.214	0.215	0.210
363.12	22,391	A1–B4–C7	9.96	15.97	22.70	0.259	0.269	0.265
365.29	16,213	A3–B6–C9	9.40	14.73	21.96	0.342	0.344	0.344
367.20	16,213	A2–B5–C8	11.75	18.28	26.19	0.427	0.422	0.420
369.12	16,213	A1–B4–C7	14.46	21.84	31.38	0.523	0.512	0.509
371.29	10,828	A3–B6–C9	11.95	18.50	27.26	0.657	0.652	0.645
373.18	10,828	A2–B5–C8	14.43	21.99	31.73	0.791	0.767	0.769
375.10	10,828	A1–B4–C7	17.58	26.99	38.43	0.960	0.955	0.941

TABLE 6Experimental results for 3- and 4-nitrobenzophenone, where a and b are from Clausius–Clapeyron equation $\ln(p/\text{Pa}) = a - b/(T/\text{K})$ and $b = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ / (R)$; $R = 8.31451 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

Hole number	a	b	$\frac{\langle T \rangle}{\text{K}}$	$\frac{p(\langle T \rangle)}{\text{Pa}}$	$\frac{\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^{\circ} \{(\langle T \rangle, p(\langle T \rangle))\}}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$
3-Nitrobenzophenone						
1	39.51 ± 0.31	14445 ± 111	357.20	0.394	119.3 ± 0.6	334.0 ± 1.7
2	39.08 ± 0.38	14291 ± 134				
3	39.02 ± 0.37	14302 ± 134				
Global results	39.23 ± 0.19	14346 ± 70				
4-Nitrobenzophenone						
1	38.79 ± 0.49	14564 ± 182	367.19	0.416	120.2 ± 0.7	327.4 ± 1.9
2	38.40 ± 0.29	14423 ± 105				
3	38.28 ± 0.37	14379 ± 136				
Global results	38.49 ± 0.22	14455 ± 82				

The equilibrium pressure at the mean temperature range $p(T = \langle T \rangle)$ and the entropies of sublimation, at equilibrium conditions are also presented in table 6. The plots of $\ln p = f(1/T)$ for the two compounds studied experimentally are presented in figure 1.

Table 7 lists the (p, T) values calculated from the (p, T) equations for the crystalline compounds within the experimental range of pressures used: (0.1 to 1) Pa. Sublimation enthalpies, at the temperature 298.15 K, were derived from the sublimation enthalpies calculated at the mean temperature $\langle T \rangle$ of the experiments, by the equation

$$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(T = 298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^\circ(\langle T \rangle) + \Delta_{\text{cr}}^{\text{g}} C_{p,m}^\circ(298.15 \text{ K} - \langle T \rangle). \quad (5)$$

The value of $\Delta_{\text{cr}}^{\text{g}} C_{p,m}^\circ$ was calculated as $-39.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for both 3- and 4-nitrobenzophenones using equation (6) proposed by Chickos *et al.* [26],

$$\Delta_{\text{cr}}^{\text{g}} C_{p,m}^\circ = -\{0.75 + 0.15 C_{p,m}^\circ(\text{cr})\}. \quad (6)$$

The value of $C_{p,m}^\circ(\text{cr}) = 255.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was derived from data of Domalski and Hearing [27] using the following additivity approach:

$$\{[9[\text{C}_\text{B} - (\text{H})(\text{C}_\text{B})_2] + 2[\text{C}_\text{B} - (\text{CO})(\text{C}_\text{B})_2] + [\text{CO} - (\text{C}_\text{B})_2] + [\text{C}_\text{B} - (\text{NO}_2)(\text{C}_\text{B})_2]\}, \quad (7)$$

where $C_{p,m}^\circ[\text{C}_\text{B} - (\text{H})(\text{C}_\text{B})_2, \text{cr}] = 20.13 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $C_{p,m}^\circ[\text{C}_\text{B} - (\text{CO})(\text{C}_\text{B})_2, \text{cr}] = -42.89 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $C_{p,m}^\circ[\text{CO} - (\text{C}_\text{B})_2, \text{cr}] = 109.33$ and $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $C_{p,m}^\circ[\text{C}_\text{B} - (\text{NO}_2)(\text{C}_\text{B})_2, \text{cr}] = 50.90 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

Table 8 presents, for each compound, the values, at $T = 298.15 \text{ K}$, of the standard molar enthalpies of sublimation, the standard molar entropies of sublimation calculated by equation (8), were $p^\circ = 10^5 \text{ Pa}$, and the standard molar Gibbs energies of sublimation.

$$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^\circ(T = 298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^\circ\{\langle T \rangle, p(\langle T \rangle)\} + \Delta_{\text{cr}}^{\text{g}} C_{p,m}^\circ \ln(298.15 \text{ K} / \langle T \rangle) - R \ln\{p^\circ / p(\langle T \rangle)\}. \quad (8)$$

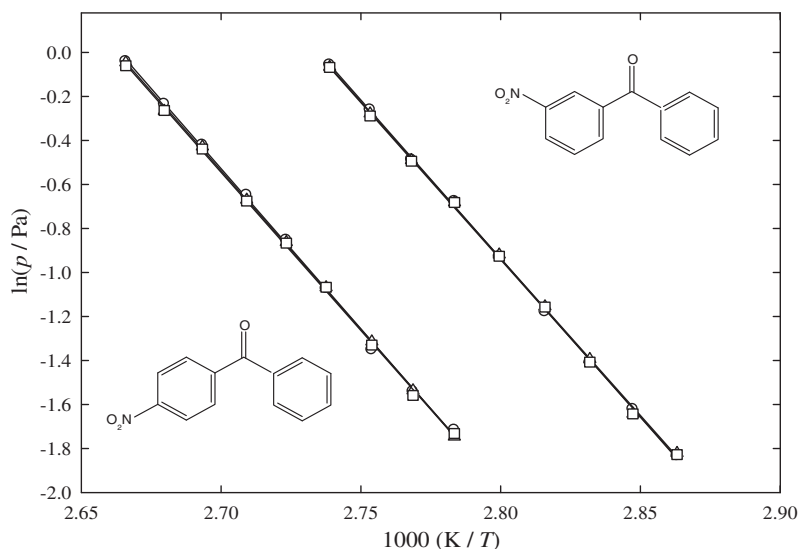


FIGURE 1. Plots of $\ln(p/\text{Pa})$ against $1/T$ for 3- and 4-nitrobenzophenones: \circ , smaller holes; Δ , medium holes; \square , larger holes.

TABLE 7

(p , T) values from the vapour pressures equations for 3- and 4-nitrobenzophenone.

p/Pa	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	T/K									
3-Nitrobenzophenone	345.4	351.3	354.8	357.3	359.3	361.0	362.4	363.6	364.7	365.7
4-Nitrobenzophenone	354.4	360.5	364.2	366.8	368.9	370.6	372.1	373.4	374.5	375.6

TABLE 8

Values of the standard ($p^\circ = 0.1 \text{ MPa}$) molar enthalpies, $\Delta_{\text{cr}}^\circ H_m^\circ$, entropies, $\Delta_{\text{cr}}^\circ S_m^\circ$, and Gibbs energies, $\Delta_{\text{cr}}^\circ G_m^\circ$, of sublimation, at $T = 298.15 \text{ K}$, for the 3- and 4-nitrobenzophenone.

Compound	$\Delta_{\text{cr}}^\circ H_m^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr}}^\circ S_m^\circ / (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr}}^\circ G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1})$
3-Nitrobenzophenone	121.6 ± 0.6	223.5 ± 1.7	55.0 ± 0.8
4-Nitrobenzophenone	122.9 ± 0.7	216.2 ± 1.9	58.4 ± 0.9

TABLE 9

Derived standard ($p^\circ = 0.1 \text{ MPa}$) molar enthalpies of formation, $\Delta_f H_m^\circ$, at $T = 298.15 \text{ K}$.

Compound	$-\Delta_f H_m^\circ(\text{cr}) / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr}}^\circ H_m^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f H_m^\circ(\text{g}) / (\text{kJ} \cdot \text{mol}^{-1})$
3-Nitrobenzophenone	77.4 ± 2.2	121.6 ± 0.6	44.2 ± 2.3
4-Nitrobenzophenone	74.1 ± 2.5	122.9 ± 0.7	48.8 ± 2.6
3,3'-Dinitrobenzophenone	104.4 ± 2.8	147.4 ± 3.9	43.0 ± 4.8

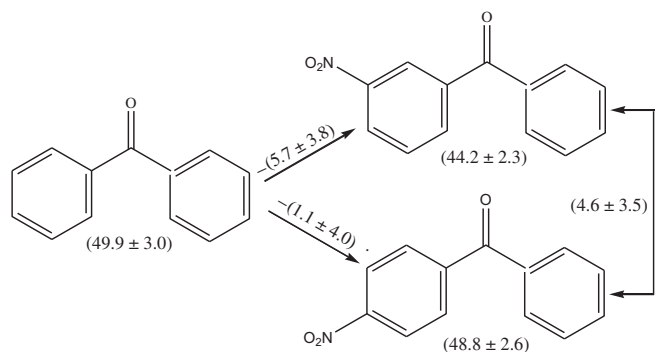
The values of the standard molar enthalpies of sublimation, at $T = 298.15 \text{ K}$, of 3- and 4-nitrobenzophenone, derived from the Knudsen effusion method (table 8) are in agreement with the ones determined by Calvet microcalorimetry (table 4).

For the studied compounds, the standard molar enthalpies of formation in the gaseous state, at $T = 298.15 \text{ K}$, obtained by the addition of the derived standard molar enthalpies of formation in the crystalline state and the standard molar enthalpies of sublimation, are summarized in table 9. For the 3- and 4-nitrobenzophenones, the Knudsen values were used for the calculation of the standard molar enthalpies of formation in the gaseous state.

4. Discussion

Considering the values of the standard molar enthalpies of formation, in the gaseous phase, of benzophenone, $\Delta_f H_m^\circ(\text{g}) = (49.9 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$ [28] and the experimental ones obtained in this work for 3- and 4-nitrobenzophenones, one can calculate the enthalpic effect due to the introduction of a $-\text{NO}_2$ group in the 3- and 4-positions of the benzophenone ring. The introduction of the $-\text{NO}_2$ group produces, within the experimental uncertainties, the same effect in both positions, a fact which is emphasized by the low enthalpy of isomerization; $\Delta_{\text{isom}} H = (4.6 \pm 3.5) \text{ kJ} \cdot \text{mol}^{-1}$ (see scheme 1).

The gas-phase enthalpy of formation of the 3,3'-dinitrobenzophenone can be estimated by adding to the value of benzophenone, twice the enthalpy increment for 3-nitro substitution, obtaining a value of $\Delta_f H_m^\circ(\text{g}) = (38.5 \pm 6.2) \text{ kJ} \cdot \text{mol}^{-1}$, which within the associated uncertainties is in agreement with our experimental result, $(43.0 \pm 4.8) \text{ kJ} \cdot \text{mol}^{-1}$, giving us confidence to propose an estimated value of $\Delta_f H_m^\circ(\text{g}) = (47.7 \pm 6.4) \text{ kJ} \cdot \text{mol}^{-1}$ for 4,4'-dinitrobenzophenone.



SCHEME 1. Enthalpic effect for the introduction of a nitro group in position 3- or 4- of benzophenone. (Values in $\text{kJ} \cdot \text{mol}^{-1}$.)

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Appendix A. Supplementary data

Supplementary data associated with this article, as orifices diameters, areas and Clausing factors of the effusion orifices of the Knudsen effusion apparatus (table S1), and detailed data on the combustion calorimetry experiments of the 3-nitrobenzophenone, 4-nitrobenzophenone and 3,3'-dinitrobenzophenone (tables S2, S3 and S4).

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2010.11.005.

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