



Standard molar enthalpy of formation of methoxyacetophenone isomers



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ABSTRACT

Values of the standard ($p^\circ = 0.1$ MPa) molar enthalpy of formation of 2'-, 3'- and 4'-methoxyacetophenones were derived from their standard molar energy 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 sublimation/vaporization of the compounds studied. The standard molar enthalpies of formation of the three compounds, in the gaseous phase, at $T = 298.15$ K, have been derived from the corresponding standard molar enthalpies of formation in the condensed phase and the standard molar enthalpies for the phase transition. The results obtained are $-(232.0 \pm 2.5)$, $-(237.7 \pm 2.7)$ and $-(241.1 \pm 2.1)$ $\text{kJ} \cdot \text{mol}^{-1}$ for 2'-, 3'- and 4'-methoxyacetophenone, respectively. Standard molar enthalpies of formation were also estimated from different methodologies: the Cox scheme as well as two different computational approaches using density functional theory-based B3LYP and the multilevel G3 methodologies.

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1. Introduction

The methoxyl group (OCH_3) is one of the commonest substituents found in natural products. It is present in most classes of alkaloids, in anthraquinones and in flavones and related compounds. Many mould metabolic compounds and a few antibiotics (e.g., chloramphenicol, erythromycin and carbomycin) contain the methoxyl group. The methoxyl group is an electron donor in many reactions, and the feature of its opposing inductive and mesomeric effects has been of great use in studying reaction mechanisms [1].

The influence of substituents on the structure and reactivity of organic compounds is one of the most widely studied problems in physical organic chemistry. Fundamental research works on benzene derivatives have been one of the subjects of our Research Group. Those studies aim the understanding of the effect of different substituents on the structure/energetics of benzene derivatives. Recently, some of us investigated the thermochemistry of some anisoles and acetophenones considering substituents such as methyl [2], nitro [3,4], hydroxyl [5,6], amide [7] and different halogens [8–10,11,12]. Accurate experimental thermochemical

measurements of benzene derivatives are important for the calibration of computational thermochemistry approaches due to the large number of studies involving different substituents and ring positions.

In this work, we report the experimental determination of the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, both in the condensed and gaseous state, at $T = 298.15$ K, of 2'-, 3'- and 4'-methoxyacetophenones, derived from combustion calorimetry and high temperature Calvet microcalorimetry.

In addition, the empirical Cox scheme and other accurate techniques based on the quantum chemical principles have also been used both to estimate the standard molar enthalpies of formation in the gaseous state and to help explain and rationalize the relative stability of the studied isomeric molecules.

2. Experimental details

2.1. Materials and purity control

The 2'-, 3'- and 4'-methoxyacetophenones studied in this work were obtained commercially from Aldrich Chemical Co. with mass fractions purities of, respectively, 0.99, 0.97 and 0.99. 2'-methoxyacetophenone and 3'-methoxyacetophenone were purified by

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vacuum distillation and 4'-methoxyacetophenone was purified by repeated sublimation under reduced pressure until the combustion results were consistent. The purity of the three compounds has been checked by (gas + liquid) chromatography, performed on an Agilent 4890D Gas Chromatography equipped with an HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane (15 · 0.530 mm i.d. · 1.5 µm film thickness), and using nitrogen as carrier gas, as being ≥ 0.9995 mass fraction. Further details of the origin and purification of the samples are presented in [table 1](#). The final purity of each sample was confirmed during the combustion experiments by closeness to unity of the carbon dioxide recovery ratios. The literature values of the specific densities used were $\rho = 1.09 \text{ g} \cdot \text{cm}^{-3}$ [13] for 2'-methoxyacetophenone, $\rho = 1.094 \text{ g} \cdot \text{cm}^{-3}$ [13] for 3'-methoxyacetophenone and $\rho = 1.0818 \text{ g} \cdot \text{cm}^{-3}$ for 4'-methoxyacetophenone [14]. The relative atomic masses used for the elements were those recommended by the IUPAC Commission in 2011 [15].

2.2. 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 [16,17]. Combustion of certificated benzoic acid NBS Standard Reference Material, Sample 39j, was used for calibration of the bomb. Its massic energy of combustion is $(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ under certificate conditions [18]. The calibration results were corrected to give the energy equivalent, $e_{(\text{calor})}$, corresponding to the average mass of water added to the calorimeter: 3119.6 g. From six calibration experiments, $e_{(\text{calor})} = (15905.0 \pm 0.8) \text{ J} \cdot \text{K}^{-1}$, where the uncertainty quoted is the standard deviation of the mean. In all combustion experiments, 1.00 cm^3 of water was introduced into 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. The liquid samples of the 2'- and 3'-methoxyacetophenone isomers were contained in sealed polyester bags made of Melinex (0.025 mm of thickness) with massic energy of combustion $\Delta_c u^0 = -(22902 \pm 5) \text{ J} \cdot \text{g}^{-1}$ [19], a value which was confirmed in our Laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water ($w = 0.0032$). The crystalline samples of 4'-methoxyacetophenone were ignited in the pellet form. For the cotton thread fuse of empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$, the massic energy of combustion was assigned to $-\Delta_c u^0 = 16240 \text{ J} \cdot \text{g}^{-1}$ [20].

For all experiments, the calorimeter temperatures were measured to $T = \pm(1 \cdot 10^{-4}) \text{ K}$, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett Packard HP 2804A), interfaced to a PC. At least 100 readings of the temperature, at time intervals of 10 s, were made before the ignition of the samples which were made at $T = (298.150 \pm 0.001) \text{ K}$ by the discharge of a 1400 µF capacitor through the platinum ignition wire. The electrical energy for ignition was determined from the change in potential difference across the capacitor when discharged through the platinum ignition wire. After ignition, 100 readings were taken for each the main and remaining time periods. Data acquisition and control of the calorimeter were performed using the program LABTERMO

[21]. The corrections for nitric acid formation were based on $59.7 \text{ kJ} \cdot \text{mol}^{-1}$ [22], 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 $\text{H}_2\text{O} (\text{l})$. 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 [23], was assumed. For each compound, the massic energy of combustion, $\Delta_c u^0$, was calculated by the procedure given by Hubbard et al. [24] and corrections from apparent mass to true mass were made. The amount of compound used in each experiment was determined from the total mass of carbon dioxide produced during the combustion experiments taking into account that formed from the combustion of the cotton-thread fuse and from Melinex. The carbon dioxide was collected in absorption tubes filled with Ascarite (sodium hydroxide-coated silica) previously weighed and the quantity of nitric acid was determined by titration with NaOH (aq).

2.3. Microcalorimetry Calvet

The standard molar enthalpies of phase transition of the 2'-, 3'- and 4'-methoxyacetophenones were determined by high temperature Calvet microcalorimetry, using for liquids a technique similar to that described for sublimation of solids, the so called "vacuum sublimation drop-microcalorimetric technique" [25]. The apparatus and technique have been recently described [26]. Samples, about (3 to 6) mg of each compound, 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 1000D), held at a convenient temperature T , and were removed from the hot zone by vacuum sublimation/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 $\pm 10 \mu\text{g}$, into each of the twin calorimeter cells. The observed enthalpies of phase transition $\Delta_{\text{cr,l},298.15\text{K}}^{\text{g,T}} H_m^0$, were corrected to $T = 298.15 \text{ K}$ using the equation,

$$\Delta_{\text{cr,l}}^{\text{g}} H_m^0(298.15\text{K}) = \Delta_{\text{cr,l},298.15\text{K}}^{\text{g,T}} H_m^0 - \int_{298.15\text{K}}^T C_{p,m}^0(\text{g}) dT. \quad (1)$$

For these measurements, the microcalorimeter was calibrated *in situ* using the reported standard molar enthalpies of sublimation of naphthalene ($72.6 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$ [27] for the experiments with crystalline 4'-methoxyacetophenone and the standard molar enthalpy of vaporization of *n*-undecane ($56.58 \pm 0.57 \text{ kJ} \cdot \text{mol}^{-1}$ [27] for the experiments with the liquids 2'- and 3'-methoxyacetophenones.

2.4. Computational methods

Two different computational techniques have been adopted to obtain quantum chemical energies for the title systems; Density Functional Theoretical calculations using the Becke 3-parameter hybrid exchange [28] and the non-local Lee–Yang–Parr [29] correlation density functional (B3LYP) together with the 6-31G(d) [30] basis set, were used both to obtain the most stable conformations of the title molecules and to further characterize such conformations as true minima through the construction and diagonalization

TABLE 1
Purification details of the methoxyacetophenone isomers.

Chemical name	CAS	Provenance	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
2'-Methoxyacetophenone	579-74-8	Sigma–Aldrich®	0.99	Distillation	0.9997	CO ₂ recovery
3'-Methoxyacetophenone	586-37-8	Sigma–Aldrich®	0.97	Distillation	1.0002	CO ₂ recovery
4'-Methoxyacetophenone.	100-06-1	Sigma–Aldrich®	0.99	Sublimation	0.9999	CO ₂ recovery

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