Calorimetric study of 2′-methylacetophenone and 4′-methylacetophenone

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ABSTRACT

Values of the condensed phase standard ($p = 0.1$ MPa) molar enthalpy of formation for 2′- and 4′-methylacetophenones were derived from the standard molar energies of combustion, in oxygen, at $T = 298.15$ K, measured by static bomb combustion calorimetry. The values of the standard molar enthalpy of vaporization, at $T = 298.15$ K, were measured by Calvet microcalorimetry. Combining these two values, the following enthalpies of formation in the gas phase, at $T = 298.15$ K, were then derived: 2′-methylacetophenone, $-(115.7 \pm 2.4)$ kJ · mol^{-1}, and 4′-methylacetophenone, $-(122.6 \pm 2.4)$ kJ · mol^{-1}. Substituent effects are discussed in terms of stability and compared with other similar compounds. The value of the standard molar enthalpy of formation for 3′-methylacetophenone was estimated from isomerization schemes.

1. Introduction

Ortho substituted methylacetophenones have long been subject of several studies. In many chemical and biochemical process, the reactions of intramolecular transfer of protonated hydrogen play an important role. Small [1] studied the photoenolization of 2′-methylacetophenone to clarify the process of hydrogen abstraction from the γ position. Also, some studies based on acid–base properties in solution of methyl-substituted acetophenones were made in order to elucidate the steric effects of *ortho* substituents on their basicities [2]. Keto-enol isomerisation of gas-phase 2′-methylacetophenone has been the subject of a study made by Giroldo and Riveros [3]. They studied the thermal dissociation of some substituted acetophenones, characterizing both the fragment ion produced in the dissociation and the molecular ion undergoing dissociation and identified the structures of molecular ions.

4′-Methylacetophenone is used for blossom notes in mimosa and for the production of hawthorn type perfumes, especially in soap perfumes [4]. This compound was also used in studies of the Bayeyer–Villiger reaction, one of the most important reactions that converts available ketones to esters or lactones used for the synthesis of dyes and pharmaceutical intermediates [5]. Also, 4′-methylacetophenone has been used in the synthesis of a functionalized terpolymer that has applications ranging from electronic devices to biological materials [6].

In this work, values of the standard molar enthalpy of formation in the gas phase of 2′-methylacetophenone and 4′-methylaceto-phenone were obtained from calorimetrically energies of combustion measured by static bomb combustion calorimetry and molar enthalpies of vaporization determined by Calvet microcalorimetry. Those parameters, for the gaseous state, are interpreted in terms of the energetic increments for the methylation of acetophenone and compared with methylated benzoic acids and benzophenones. No peculiarities in the interaction energy among methyl groups and functional groups in the *ortho*-, *para*-, and *meta*-positions of acetophenones, in comparison with those of benzoic acids or benzophenones, were detected. The estimation of the standard molar enthalpy of formation of gaseous 3′-methylacetophenone was made.

2. Experimental

2.1. Materials and purity control

The compounds studied, 2′-methylacetophenone [CAS 577-16-2], and 4′-methylacetophenone [CAS 122-00-9] were obtained commercially from Aldrich Chemical Co. with mass fraction purity values of 0.98 and 0.95, respectively. The samples were purified by repeated distillation under reduced pressure before the experimental measurements. The purity of the compounds was checked by gas–liquid chromatography (GLC, HP-1890A) and from the average ratios of the mass of carbon dioxide recovered from the combustion to that calculated from the mass of sample as: 0.99970 for 2′-methylacetophenone and 0.99992 for 4′-methylacetophenone. Table 1 lists the purities of the original samples as well as the final purities of the samples studied here.

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Chemical name	CAS	Provenance	Initial mole fraction purity	Purification method	Final mass fraction purity	Analysis method
2′-Methylacetophenone (l)	577-16-2	Sigma- Aldrich Co	0.98	Distillation	0.99970	CO_2 recovery
4′-Methylacetophenone (l)	122-00-9	Sigma- Aldrich Co	0.95	Distillation	0.99992	CO_2 recovery

2.2. Methods

2.2.1. Combustion calorimetry

The combustion experiments were performed with a static bomb combustion calorimeter, using a twin valve bomb, type 1108 of Parr Instrument Company. The apparatus and technique have been described previously [7,8] so only a brief description is made here.

For calibration of the bomb, we have used certificated benzoic acid, NBS Standard Reference Material, Sample 39j whose massic energy of combustion is $-(26434 \pm 3)\,J \cdot g^{-1}$ under certificate conditions [9]. The calibration results were corrected to give the energy equivalent ε_{calor} corresponding to the average mass of water added to the calorimeter: 3119.6 g. On the basis of six calibration experiments, $\varepsilon_{calor} = (15906.6 \pm 1.9)\,J \cdot K^{-1}$, where the uncertainty quoted is the standard deviation of the mean.

Combustion experiments were made in oxygen, at $p = 3.04$ MPa, with 1.00 cm³ of water added to the bomb. The bomb was purged twice to remove air, before being charged with oxygen. The electrical energy for ignition, $\Delta U(ign)$, was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire.

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. At least 100 readings of the temperature were taken before the ignition of the samples which were made at $T = (298.150 \pm 0.001)\,K$ by the discharge of a 1400 µF capacitor through the platinum ignition wire. After ignition, 100 readings were taken for each the main and the after periods.

The liquid samples of the two compounds were contained in sealed polyester bags made of Melinex (0.025 mm of thickness) with massic energy of combustion $\Delta_c u° = -(22902 \pm 5)\,J \cdot g^{-1}$ [10],

a value which was confirmed in our Laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water ($w = 0.0032$). For the cotton-thread fuse, empirical formula $CH_{1.686}O_{0.843}$, the value of $\Delta_c u° = -16240\,J \cdot g^{-1}$ [11], was taken for the massic energy of combustion, a value that has been confirmed in our laboratory.

The corrections for nitric acid formation were based on $-59.7\,kJ \cdot mol^{-1}z$ [12], for the molar energy of formation of $0.1\,mol \cdot dm^{-3}\,HNO_3(aq)$ from N_2, O_2, and $H_2O(l)$. 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 true mass were made. An estimated pressure coefficient of specific energy, $(\partial u / \partial p)T = -0.2\,J \cdot g^{-1} \cdot MPa^{-1}$ at $T = 298.15$ K, a typical value for most organic compounds [13], was assumed. For each compound, the massic energy of combustion, $\Delta_c u°$, was calculated by the procedure given by Hubbard *et al.* [14]. The amount of compound used in each experiment was determined from the total mass of carbon dioxide [Mettler Toledo AT 201 balance, sensitivity $\pm (1 \cdot 10^{-5})$ g], 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).

The densities, at $T = 298.15$ K, were taken for 2′-methylacetophenone as $1.026\,g \cdot cm^{-3}$ [15], and for 4′-methylacetophenone as $1.005\,g \cdot cm^{-3}$ [15]. The relative atomic masses used were those recommended by the IUPAC Commission in 2009 [16].

2.2.2. High temperature microcalorimetry

Calvet High Temperature Microcalorimeter (Setaram, HT 1000D) [17], was used for the determination of the standard molar enthalpies of vaporization of the two methylacetophenones
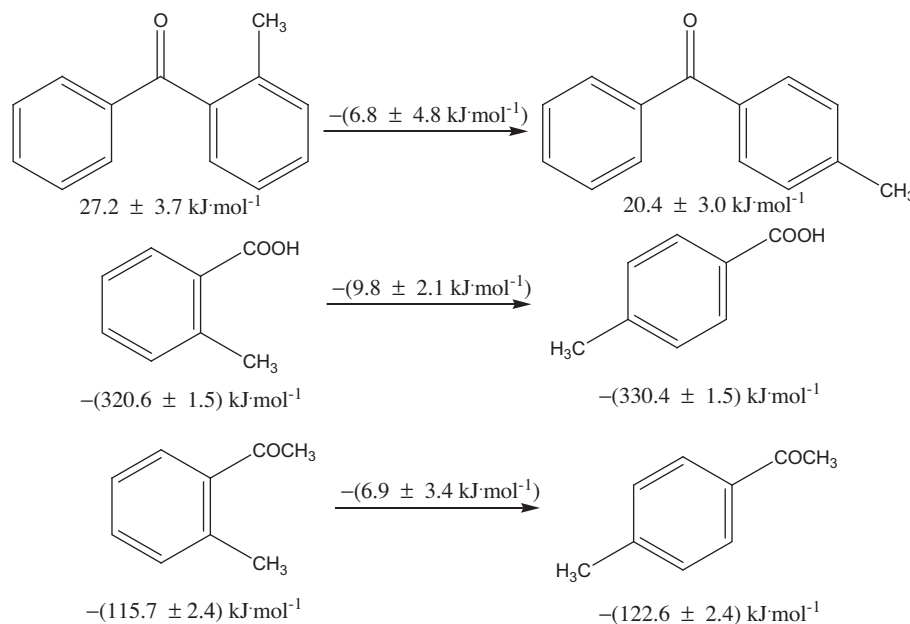
SCHEME 1. Enthalpies of isomerization of the $-CH_3$ group from *ortho* to *para* positions.