



Calorimetric study of bromoacetophenone isomers



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ABSTRACT

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of 2-, 2'-, 3'- and 4'-bromoacetophenones were derived from the standard molar energies of combustion in oxygen, to yield CO_2 (g) and $\text{HBr} \cdot 600\text{H}_2\text{O}$ (l) at $T = 298.15$ K, measured by rotating bomb combustion calorimetry. The standard molar enthalpies associated with phase transitions of the isomers studied at $T = 298.15$ K, were obtained by high temperature Calvet microcalorimetry. The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of all the bromoacetophenone isomers in the gaseous phase at $T = 298.15$ K were derived from the experimental results. The gas-phase enthalpies of formation were also estimated by the empirical scheme developed by Cox and the values obtained were compared with the experimental ones. The results are interpreted in terms of the energetic increments for the introduction of the substituents in the benzene ring.

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1. Introduction

Brominated organic compounds are important technical products used as gasoline additives [1], flame-retardants [2] and fumigants, [3], playing also a significant role as intermediates in the pharmaceutical industry. They are characterized by their long life, chemical stability and have become a serious environmental issue. Because they are difficult to decompose completely by incineration, giving rise to dioxins many researchers have devoted attention to conducting photocatalytic reactions for decomposition of halogenated compounds [4–6]. Among these compounds, α -haloacetophenone derivatives have received considerable attention mainly in pharmaceutical industries, due to their ability to act as a novel class of potent, photo reversible, and membrane permeable inhibitors of protein tyrosine phosphatases (PTPs) [7,8]. PTPs inhibitors may be promising drugs to treat some diseases such diabetes, obesity and cancer [9].

The establishment of relationships between the energetic and structural properties of compounds is relevant in explaining their behavior in terms of reactivity. Our research group, is involved in a systematic investigation of the energetic effects of the introduction of bromine atoms on the aromatic ring of some

benzene and heterocyclic derivatives such as bromonitrobenzenes [10,11], bromine substituted benzoic acids [12,13], bromoanilines [14], bromoanisoles [15], bromophenols [16,17], bromobenzonitriles [18], bromopyridines [19], bromoquinolines [20], bromonaphthalenes [21], bromo-8-hydroxyquinolines [22], bromouracil [23] and bromoindolines [24]. The aim of these studies is to provide an understanding of the effect of different substituents on the structure and energetic properties of brominated compounds, with the ultimate goal to develop predictive schemes, based on the transferability of group enthalpic contributions. In this context, should be possible to estimate thermochemical parameters for other compounds whose experimental study is not possible due to the difficulties in their synthesis and/or in obtaining them pure enough to be studied. Obviously, the availability of reliable data for the thermodynamic properties of the compounds on which group contributions can be based is essential.

This work reports the standard molar enthalpies of formation of the bromoacetophenone isomers, in the gaseous phase, at $T = 298.15$ K derived from measurements of the standard molar enthalpies of combustion in oxygen by rotating-bomb calorimetry and from the standard molar enthalpies associated with the phase transitions as measured by Calvet microcalorimetry.

The derived values of the standard molar enthalpies of formation of the compounds in the gaseous state are analysed

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and compared in terms of enthalpic increments due to the introduction of a bromine atom group into several benzene derivatives.

2. Experimental

2.1. Compounds and purity control

The compounds were commercially obtained from Aldrich Chemical Co., with the following assessed mass fractions/purities: 2-bromoacetophenone [CAS 70-11-1] 0.98; 2'-bromoacetophenone [CAS 2142-69-0] 0.99; 3'-bromoacetophenone [CAS 2142-63-4] 0.99 and 4'-bromoacetophenone [CAS 99-90-1] 0.98. The liquids 2'- and 3'-bromoacetophenones were purified by repeated distillation under reduced pressure and the solids 2- and 4'-bromoacetophenones were purified by successive sublimations under reduced pressure. The final purity of all compounds was checked by gas chromatography (Agilent 4890D). Table 1 lists the origin and purification details of the original samples as well as the final purities of the samples studied here.

2.2. Combustion calorimetry measurements

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of combustion of the isomers under study were measured in two different isoperibol calorimetric systems:

- For 2-, 3'- and 4'-bromoacetophenones, the system used for the calorimetric measurements is an isoperibol rotating-bomb calorimeter first constructed at the University of Lund, Sweden according to the design of Sunner [25]. A detailed description can be found in the literature [26,27]. The combustion experiments were performed in a stainless steel, platinum lined bomb, with the internal fittings machined from platinum, whose internal volume is 0.258 dm³.
- The calorimetric study of 2'-bromoacetophenone was performed in an isoperibol rotating bomb calorimeter, already described in the literature [28,29], with an internally lined tantalum bomb, with an internal volume of 0.329 dm³.

The calibration of both calorimetric systems were performed following the procedure described by Coops *et al.* [30] by combustion of benzoic acid NIST Thermochemical Standard 39j, with a certified massic energy of combustion, under bomb conditions, of $-(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ [31]. For the system described in (i) the energy equivalent of the calorimeter was determined, as $\varepsilon_{\text{cal}} = (25157.4 \pm 1.1) \text{ J} \cdot \text{K}^{-1}$, where the uncertainty quoted is the standard deviation of the mean. For the experiments 4 to 7 of 3'-bromoacetophenone, the value, $\varepsilon_{\text{cal}} = (25146.4 \pm 1.3) \text{ J} \cdot \text{K}^{-1}$, was used; the quoted uncertainty is the standard deviation of the mean. The calibration results were corrected to give the energy equivalent of the calorimeter, ε_{cal} corresponding to the average mass of 5222.5 g of water added to the calorimeter.

The value of the energy equivalent of the calorimeter described in (ii) was found to be $\varepsilon_{\text{cal}} = (20349.2 \pm 1.0) \text{ J} \cdot \text{K}^{-1}$, as a mean of six calibration experiments, for an average mass of water added to the

calorimeter of 3965.0 g; the quoted uncertainty refers the standard deviation of the mean.

The samples of the compounds were ignited in oxygen, at a pressure $p = 3.04$ MPa, with volumes of 15.00 cm³ of an aqueous solution of As₂O₃ ($\approx 0.09 \text{ mol} \cdot \text{dm}^{-3}$), in order to reduce to hydrobromic acid all the free bromine produced during the combustion experiments. At the end of each experiment, the remaining quantity of aqueous As₂O₃ was determined by titration with a standardized iodine solution. The energy of oxidation of aqueous As₂O₃ to As₂O₅, $\Delta U(\text{As}_2\text{O}_3)$, was calculated as described by Hu *et al.* [32], using the enthalpies of oxidation of As₂O₃(aq) by Br₂ [33] and the thermal effects of mixing As₂O₅(aq) with strong acids [34]. The solids 2- and 4'-bromoacetophenones were burnt in the pellet form and the liquid samples of 3'-bromoacetophenone were burnt enclosed in previously weighed polyester bags made of Melinex (0.025 mm of thickness). The energy of combustion of the Melinex used in each experiment, $\Delta U(\text{Melinex})$, was calculated using the value of the massic energy of combustion of dry Melinex, $\Delta_c u^\circ = -(22902 \pm 5) \text{ J} \cdot \text{g}^{-1}$ [35], after making the correction for the mass fraction of water, $w = 0.0032$ [35]. The liquid 2'-bromoacetophenone was burnt enclosed in polyethylene bags, $\Delta_c u^\circ = -(46282.4 \pm 4.8) \text{ J} \cdot \text{g}^{-1}$, a value measured in our laboratory by combustion of polyethylene samples.

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 programmed to compute the adiabatic temperature change. At least 100 readings were taken for the main period and for both the fore and after periods. Data acquisition and control of the calorimeter were performed using the program LABTERMO [36,37].

For each experiment, the ignition temperature was selected so that the final temperature would be close to $T = 298.15 \text{ K}$, and the rotation of the bomb was started when the temperature rise of the main period reached about 0.63 of its total value and was continued throughout the rest of the experiment. By adopting this procedure, Good *et al.* [38] have shown that the frictional work due to the rotation of the bomb is automatically integrated in the temperature corrections for the work of water stirring and for the heat exchanged with the surrounding isothermal jacket. The rotating mechanism allows the simultaneous axial and end-over-end rotation of the bomb, allowing the solution placed in the bomb to completely wash all internal surfaces of the bomb, yielding a homogenous final solution.

The electrical energy for ignition was determined from the change in potential difference across a 1400 μF condenser discharged through a platinum wire ($\varphi = 0.05 \text{ mm}$, Goodfellow, mass fraction 0.9999).

The amount of H₂PtBr₄ (aq) was determined from the loss of mass of platinum of the crucible and the energy correction was based on $\Delta_f H_m^\circ(\text{H}_2\text{PtBr}_4, \text{aq}) = -(368.2 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$ [39].

For the cotton thread fuse of empirical formula CH_{1.686}O_{0.843}, $\Delta_c u^\circ = -16240 \text{ J} \cdot \text{g}^{-1}$ [30]. The nitric acid formed was analysed by the Devarda's alloy method [40] and corrections were based on $\Delta_f U_m^\circ(\text{HNO}_3, \text{aq}, 0.1 \text{ mol} \cdot \text{dm}^{-3}) = -59.7 \text{ kJ} \cdot \text{mol}^{-1}$ [39], from 1/2 N₂(g), 5/4 O₂(g) and 1/2 H₂O(l).

TABLE 1

Purification details of the studied bromoacetophenones.

Chemical name	CAS	Provenance	Initial mole fraction purity	Purification method	Final mass fraction purity	Analysis method
2-Bromoacetophenone (cr)	70-11-1	Sigma-Aldrich Co	0.98	Sublimation	0.9997	GC ^a
2'-Bromoacetophenone (l)	2142-69-0	Sigma-Aldrich Co	0.99	Distillation	0.9996	GC ^a
3'-Bromoacetophenone (l)	2142-63-4	Sigma-Aldrich Co	0.99	Distillation	0.9994	GC ^a
4'-Bromoacetophenone (cr)	99-90-1	Sigma-Aldrich Co	0.98	Sublimation	0.9998	GC ^a

^a Gas-liquid chromatography.

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