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Standard molar enthalpies of formation of monochloroacetophenone isomers

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ABSTRACT

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of the liquids 2′-, 3′-, and 4′-chloroacetophenones were derived from the standard molar energies of combustion, in oxygen, to yield $CO_2(g)$ and $HCl \cdot 600H_2O(l)$, at $T = 298.15$ K, measured by rotating-bomb combustion calorimetry. The Calvet microcalorimetry was used to measure the enthalpies of vaporization of the three compounds. These two thermodynamic parameters yielded the standard molar enthalpies of formation of the chloroacetophenone isomers, in the gaseous phase, at $T = 298.15$ K.

Compound	$\Delta_c u^\circ/(\mathrm{J \cdot g^{-1}})$	$\Delta_f H^\circ_m(\mathrm{g})/(\mathrm{kJ \cdot mol^{-1}})$
2′-Chloroacetophenone	-25939.6 ± 2.7	-99.4 ± 2.1
3′-Chloroacetophenone	-25862.5 ± 2.7	-107.4 ± 2.4
4′-Chloroacetophenone	-25802.7 ± 2.7	-117.6 ± 2.5

An empirical scheme, developed by Cox, was used to estimate the gas-phase enthalpies of formation and the obtained values were compared with the experimental ones.

1. Introduction

Accurate and reliable experimental values of the standard molar enthalpies of formation, in the gaseous phase, are needed in order to interpret the structure-energetic relationships in organic molecules.

In the past few years, we have dedicated some attention to monochloride substituted benzenes and a systematic thermochemical study is being carry on in our research laboratory with measurements on aniline [1], nitrophenol [2], nitroaniline [3,4], anisole [5], and nitrobenzene [6].

In the present work, we report the standard molar enthalpies of formation of monochloroacetophenone isomers in the gaseous state, obtained by the experimental determination of their standard molar energies of combustion, measured by rotating-bomb calorimetry, and of the enthalpies of vaporization, measured by high-temperature Calvet microcalorimetry.

Acetophenone is widely used for the production of resins from treatment of acetophenone with formaldehyde and a base; modified acetophenone–formaldehyde resins are found in coating, inks, as well as adhesives. Acetophenone is a raw material for the synthesis of some pharmaceuticals [7,8], being also used to create fragrances that resemble almond, cherry, honeysuckle, jasmine, and strawberry and occurs naturally in many foods including apple, apricot, banana, and beef [9]. Acetophenone is also a popular test substance for asymmetric transfer hydrogenation experiments [10].

2. Experimental

2.1. Compounds and purity control

The three compounds studied, commercially obtained from Aldrich Chemical Co., with the following assessed mass fractions purities: 2′-chloroacetophenone [CAS 2142-68-9] 0.97, 3′-chloroacetophenone [CAS 99-02-5] 0.98, and 4′-chloroacetophenone [CAS 99-91-2] 0.97, were purified by repeated fractional distillation under reduced pressure. The final purity of all compounds was checked by gas chromatography (Agilent 4890D), with verified purity by mass fraction: 2′-chloroacetophenone, 0.9991; 3′-chloroacetophenone, 0.9998; and 4′-chloroacetophenone, 0.9994.

The specific densities, used to calculate the mass from apparent mass in air were, $\rho = 1.190\ \mathrm{g \cdot cm^{-3}}$ [11] for 2′-chloroacetophenone, $\rho = 1.191\ \mathrm{g \cdot cm^{-3}}$ [11] for 3′-chloroacetophenone, and $\rho = 1.192\ \mathrm{g \cdot cm^{-3}}$ [11] for 4′-chloroacetophenone.

The relative atomic masses used for the elements were those recommended by the IUPAC Commission in 2007 [12] yielding the following molar mass, $154.5936\ \mathrm{g \cdot mol^{-1}}$.

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The benzoic acid used in the calibration of the rotating-bomb calorimeter was the NBS Standard Reference Material, sample 39j [13] while *n*-undecane [14] (Aldrich, mass fraction purity >0.99) was used to calibrate the high-temperature Calvet microcalorimeter.

2.2. Combustion calorimetry measurements

The combustion experiments were performed with an isoperibol rotating-bomb calorimeter, developed by Sunner [15] at the University of Lund, Sweden. The apparatus and the technique have been described in detail [3,16,17]. The combustion experiments took place in a stainless steel platinum lined bomb with the internal fittings machined from platinum, whose internal volume is $0.258\ \mathrm{dm^3}$. In each experiment, the bomb is suspended from the lid of the calorimeter can, to which 5222.5 g of water, previously weighed in a Perspex vessel, is added.

Calorimeter temperatures were measured to $\pm(1\cdot10^{-4})$ 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 [18].

For all experiments, the ignition temperature was chosen so that the final temperature would be close to T = 298.15 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. The rotating mechanism allows the simultaneous axial and end-over-end rotation of the bomb, which permits that the solution placed in the bomb wash completely all internal surfaces of the bomb, yielding a homogenous final solution. By adopting this procedure, Good *et al.* [19] 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 calorimetric system was calibrated, in the conventional way, without bomb rotation, with benzoic acid (NBS Standard Reference Material 39j), having a massic energy of combustion under bomb conditions of $-(26434\pm3)\ \mathrm{J\cdot g^{-1}}$ [13]. Six calibration experiments were made in oxygen, at the pressure of 3.04 MPa, with $1.00\ \mathrm{cm^3}$ of deionised water added to the bomb, according to the procedure recommend by Coops *et al.* [20], leading to the value of the energy equivalent of the calorimeter: $\varepsilon(\mathrm{calor}) = (25157.4\pm1.1)\ \mathrm{J\cdot K^{-1}}$, where the uncertainty quoted is the standard deviation of the mean. For each experiment, a correction to the energy equivalent was made for the deviation of the mass of water used to the reference mass of 5222.5 g.

The liquid samples of chloroacetophenone isomers were burnt enclosed in polyester bags made from Melinex (0.025 mm thickness) using the technique described by Skinner and Snelson [21]. The combustion experiments were made in oxygen at the pressure of 3.04 Pa, in the presence of an aqueous solution of As_2O_3, in order to reduce to hydrochloric acid all the free chloride produced during the combustion. At the end of each experiment, the remaining quantity of aqueous As_2O_3 was determined by titration with a standardized iodine solution and the nitric acid formed was analysed by the Devarda's alloy method [22]. The energy of oxidation of aqueous As_2O_3 to As_2O_5, $\Delta U(As_2O_3)$, was calculated as described by Hu *et al.* [23], using the enthalpies of oxidation of $As_2O_3(aq)$ by Cl_2 [24] and the thermal effects of mixing $As_2O_5(aq)$ with strong acids [25]. The amount of $H_2PtCl_6(aq)$ was determined from the loss of mass of platinum of the crucible and the energy correction was based on $\Delta_f H^\circ_m(H_2PtCl_6,aq) = -(676.1\pm0.1)\ \mathrm{kJ\cdot mol^{-1}}$ [26].

The ignition energy was measured by the change in the potential difference on the discharge of a capacitor (1281 μF) across a platinum wire (ϕ = 0.05 mm, Goodfellow, mass fraction 0.9999).

For the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^\circ = -16240\ \mathrm{J\cdot g^{-1}}$ [20] and for dry Melinex, $\Delta_c u^\circ = -(22902\pm5)\ \mathrm{J\cdot g^{-1}}$ [21]; these values have been previously confirmed in our Laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032). Corrections for the nitric acid formed were based on $\Delta_f U^\circ_m(HNO_3, aq, 0.1\ \mathrm{mol\cdot dm^{-3}}) = -59.7\ \mathrm{kJ\cdot mol^{-1}}$ [26], from 1/2 $N_2(g)$, 5/4$O_2(g)$, and 1/2$H_2O(l)$.

An estimated pressure coefficient of massic 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 [27], was used for all isomers of chloroacetophenone.

The standard massic energy of combustion, $\Delta_c u^\circ$, for each compound, was calculated by a similar procedure implemented by Hu *et al.* [23] for chlorine containing compounds, based on the method developed by Hubbard *et al.* [28].

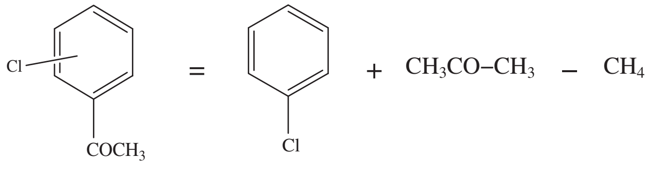
The 4-chlorobenzoic acid has been recommended as a test substance for bomb combustion calorimetry of organic chlorine compounds [14,23]. Hence, the accuracy of the calorimeter has been checked in our laboratory by measuring the energy of combustion of 4-chlorobenzoic acid, in the pellet form, under oxygen at 3.04 MPa, in the presence of an aqueous solution of As_2O_3 in the bomb. The results obtained for the energy of combustion of 4-chlorobenzoic acid, $\Delta_c U^\circ_m = -(3064.5\pm1.2)\ \mathrm{kJ\cdot mol^{-1}}$ [29] and $\Delta_c U^\circ_m = -(3063.92\pm0.91)\ \mathrm{kJ\cdot mol^{-1}}$ [3] are in very good agreement with the recommended value $\Delta_c U^\circ_m = -(3063.48\pm0.23)\ \mathrm{kJ\cdot mol^{-1}}$ [14]. Values of $\Delta_c U^\circ_m$ refer to the reaction with $HCl\cdot600H_2O(l)$ as the chlorine containing product in the final state.

2.3. Calvet microcalorimetry measurements

The standard molar enthalpies of vaporization of the 2′-, 3′-, and 4′-chloroacetophenone were measured using a similar technique of the drop-method described for the sublimation of solid compounds by Skinner *et al.* [30], previously tested in our laboratory for liquid vaporization [31]. The measuring procedure and the detailed description of the apparatus have been reported [32], as well as the experimental results obtained during testing by measuring reference compounds (benzoic acid, phenanthrene, anthracene, and ferrocene).

Samples of about (5 to 8) mg of the liquid compounds were placed into a small glass capillary tube sealed at one end, and together with the blank reference capillary, were simultaneously dropped at room temperature into the hot calorimetric cells in the high-temperature Calvet microcalorimeter (Setaram HT 1000), held at a predefined temperature and then removed from the hot zone by vacuum 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 near equal mass into each of the twin calorimeter cells [32].

The observed enthalpies of vaporization, $\Delta^{g,T}_{l,298.15\,\mathrm{K}}H^\circ_m$, at the experimental temperature T of the hot reaction vessel, were corrected to T = 298.15 K using values of $\Delta^{T}_{298.15\,\mathrm{K}}H^\circ_m(g)$ estimated



SCHEME 1. Group scheme for $\Delta^{T}_{298.15\,\mathrm{K}}H^\circ_m(g)$ estimation.