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The heat capacities and thermodynamic functions of some derivatives of ferrocene

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Abstract

The heat capacities of benzoylferrocene (BOF), $C_5H_5FeC_5H_4COC_6H_5$, and benzylferrocene (BF), $C_5H_5FeC_5H_4CH_2C_6H_5$, have been measured by the low-temperature adiabatic calorimetry in the temperature range from 6 K to 372 K. The purity benzylferrocene and thermodynamic properties – the triple point temperature and the enthalpy of fusion have been obtained. The ideal gas thermodynamic functions (changes of the entropy, enthalpy, and Gibbs free energy) of BOF and BF were derived at $T = 298.15$ K using the heat capacities and previously determined data on the saturation vapours pressures and the enthalpies of sublimation. The ideal gas enthalpy of formation and absolute entropy of BOF at $T = 298.15$ K have been obtained from quantum chemical calculations, where as the thermodynamic properties of BF have been estimated by empirical method of group equations. A good agreement between experimental and theoretical values provides an additional check of the reliability of the experimental data.

Keywords: Ferrocene derivatives; Adiabatic calorimetry; Heat capacity; Vapour pressure; Thermodynamic functions; Difference and DFT calculation methods

1. Introduction

The derivatives of ferrocene are sandwich type organometallic compounds. Due to favorable conjunction of the chemical and physical properties (low toxicity, high thermal stability, and volatility), the iron cyclopentadienyl derivatives have found ever-increasing application in many fields of technology and medicine as heat resistant polymers, electronic materials, regulators of fuel combustion, and anti-cancer and blood-creating drugs [1]. The literature data on the thermophysical properties of the ferrocene derivatives (FD) are scanty, that delays working out the scientific basis of their manufacture and application. There are experimental data on the enthalpies of combustion and formation, the heat capacities and the main thermodynamic functions determined by adiabatic calorimetry for eight aliphatic derivatives of ferrocene [2,3]. DSC method was used for studying the heat capacities of four acetyl- and benzoyl-derivatives of ferrocene [4]. The saturated vapour pressures for three FD were measured by a transpiration method [5]. There are numerous data on the melting temperatures of BOF and BF determined by a simple capillary method [6–10]. Dispersions of these data are within limits from 1 K to 6 K. This paper deals with determination of many thermodynamic properties of benzoylferrocene and benzylferrocene based on the adiabatic calorimetry, quantum chemistry, and empirical additive methods. The heat capacities of BOF and BF were studied by adiabatic calorimetry for the first time.

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2. Experimental

2.1. Preparation of the compounds

Benzoylferrocene was prepared by acylation of ferrocene with benzoyl chloride in a dry solution of methylene chloride. The reaction was proceeded in the presence of aluminum chloride as a catalyst [11]. The reagents were taken in the equimolar quantities that allowed minimizing the impurities of the ferrocene and dibenzoylferrocene in the final products. $PhCO^+$-cation – acylation agent of the complex salt, $PhCO^+AlCl_4^-$, was formed by the interaction of benzoyl chloride with aluminum chloride. The content of impurities was shown, to diminish in the sample of BOF when more active, before hand prepared complex salt was used for benzoylating the ferrocene. Synthesized benzoylferrocene was isolated from reaction products by the column chromatography method (CCM) on Al_2O_3, the residue of ferrocene and BOF being eluated with the petroleum ether (PE), and a mixture of PE and benzene (1:1), respectively.

Benzylferrocene was synthesized by reduction of benzoylferrocene with metallic Na in the ethanol solution [11]. To increase the BOF conversion and decrease the impurity content in BF, the fine-crumbled sodium was added into reaction mixture by small portions during intensive boiling and stirring the alcohol solution of BOF. The reaction was kept on till the full BOF disappearance that was accompanied by changing the colour of the solution from dark red to bright yellow. The end of the reaction was checked by a thin layer chromatography (TLC) on Silufol plates. The sample of BF was purified by CCM on silica gel.

The samples of BOF and BF were purified by repeated sublimation in vacuum at the temperatures ~349 K and ~383 K, respectively. Purification of the substances under study was carried out until removing the impurities which were analyzed by TLC. According to the differentional scanning calorimetry (DSC), the mole fractions of the main substances in BOF and BF samples were: 0.9960 and 0.9970, respectively. The mole fraction of BF determined by calorimetric melting study was 0.9947.

2.2. Heat capacity measurements

A fully automated setup for the heat capacity measurement includes a modified adiabatic calorimeter, a data acquisition and control system, AK-9.02, and a personal computer, PC. The construction of the calorimeter and experimental procedure were analogous to [12]. The calorimeter cell consists of a titanium cylindrical container (volume ~ 1 cm^3), a copper-sleeve for holding the container, and an adiabatic shield. The calorimeter heater ($R \sim 300\ \Omega$) was wounded on the external surface of the sleeve. A miniature (rhodium + iron) resistance thermometer ($R_0 \sim 100\ \Omega$) calibrated on ITS-90 was mounted on the inner surface of the adiabatic shield for decreasing the heat capacity of the empty container. The accuracy of the temperature measurement was $\pm 5 \cdot 10^{-3}$ K. The calorimeter cell was modified as compared with [12]. Eleven-junction thermocouple, (Cu + 0.1%Fe) alloy against Chromel, was used instead of four-junction one in [12]. To eliminate the temperature gradient in the shield, the additional three-junction thermocouple and the heater were employed. The additional heater ($R \sim 133\ \Omega$) was mounted on the upper part of the shield, to which electrical wires of the thermometer and the main heater were connected. The additional differential thermocouple was placed between the upper and middle parts of the shield.

The automatic procedure of the heat capacity measurement is performed by AK-9.02 system running under PC control [12]. The program realizes a step-wise heating method and maintains adiabatic conditions in the calorimeter. Additional heater of the shield allows making up a lack of the second adiabatic shield that usually employs in the precision adiabatic calorimeters, but cannot be placed in our miniature calorimeter. The modified adiabatic shield was more sensitive than that in [12], as the adiabatic conditions of the experiment were controlled with better stability (~0.5 mK instead of ~3 mK [12].) for the whole temperature interval. Due to small size, the cryostat with the calorimeter was placed into the transport Dewar vessels with refrigerants (liquid helium or nitrogen). The high vacuum inside the cryostat was kept by means of cryosorption provided with an efficient charcoal getter. The calorimeter was tested with high pure copper OSCH 11-4 having the mass fraction of 0.99995. Obtained $C_{p,\mathrm{m}}$ values of copper came to an agreement with the precise heat capacity data [13,14] within 6% between the temperatures 6 K and 30 K, ~1% from 30 K to 60 K, and 0.3–0.2% above 60 K.

Benzoylferrocene and benzylferrocene were the crystal powders of the red and bright yellow colors, respectively. For measuring the heat capacities, they were pressed into tablets and divided to several pieces for filling the calorimeter container. The latter was sealed vacuum-tight by means of bronze brass lid and indium gasket, then pumped out, and filled with the helium heat-exchange gas up to $p \approx 24$ kPa.

The heat capacities of BOF and BF were measured in 370 and 335 experiments over the temperature ranges from 6 K to 372 K using liquid helium and nitrogen as refrigerants. The temperature increments in the heating period (h.p.) of the calorimetric experiments were from 0.1 K to 2.0 K. The equilibrium times after h.p. were from 60 s to 800 s, depending on the temperature interval of the normal (undisturbed) heat capacity measurements in helium and nitrogen fields. This time was previously ascertained by calibration of the modified calorimetric cell using standard copper specimen. The molar heat capacities of the ferrocene derivatives, $C_{p,\mathrm{m}}$, were about 0.20 to 0.55 of the total heat capacity of the calorimeter with the substance. The $C_{p,\mathrm{m}}$ values obtained repeatedly at the same temperature (from 80 K to 85 K) by using helium or nitrogen refrigerants agreed within instrumental errors – from 0.1 % to