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Thermodynamic properties of 1,1′-biadamantane

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Abstract

A comprehensive study of thermodynamic properties of 1,1′-biadamantane in different phase states has been carried out. The heat capacity of the compound in the condensed state was measured in two adiabatic calorimeters in the temperature range from 5 to 370 K and in a single-cup scanning calorimeter from 315 to 610 K. Two solid-to-solid phase transitions at 336.3 ± 0.3 K with $\Delta_{trs}H^{\circ}_{m} = 1.154 \pm 0.019$ kJ mol^{-1} and 509.6 ± 0.5 K with $\Delta_{trs}H^{\circ}_{m} = 1.30 \pm 0.03$ kJ mol^{-1}, and fusion at $T_{fus} \sim 561$ K were revealed in this temperature interval. It was found that 1,1′-biadamantane did not form plastic crystals. The thermodynamic functions of the compound in the crystalline state were derived. The saturated vapour pressure of 1,1′-biadamantane from 393 to 443 K was determined by the Knudsen effusion method:

$$\ln\left(\frac{p}{\mathrm{Pa}}\right) = (32.82 \pm 0.37) - (13126 \pm 153)\left(\frac{K}{T}\right).$$

The sublimation enthalpy was obtained from the results of the effusion measurements: $\Delta_{sub}H^{\circ}_{m}$ (417.8 K) = 109.1 ± 1.3 kJ mol^{-1}, $\Delta_{sub}H^{\circ}_{m}$ (298.15 K) = 113.8 ± 1.4 kJ mol^{-1}. The complete set of fundamentals was compiled from experimental spectral data and results of calculations in terms of the density functional theory (B3LYP/6-31G*). The combustion enthalpy of $C_{20}H_{30}$, $\Delta_{c}H^{\circ}_{m}$ (298.15 K, cr) = $-(11801.3 \pm 7.3)$ kJ mol^{-1}, was determined by the bomb-calorimetry method and the enthalpy of formation, $\Delta_{f}H^{\circ}_{m}$ (298.15 K, cr) = $-(356.4 \pm 7.8)$ kJ mol^{-1}, was obtained. The thermodynamic properties of 1,1′-biadamantane in the ideal-gas state were calculated.

Keywords: 1,1′-Biadamantane; Heat capacity; Thermodynamics of sublimation; Formation enthalpy; Statistical thermodynamics; Thermodynamic properties

1. Introduction

Many adamantane derivatives are intermediates used in organic synthesis, in production of physiologically active substances, polymers, additives to lubricating oils and to special fuels [1]. Thermodynamic properties of adamantane [2], 1- and 2-adamantanols [3,4], 2-methyl-2-adamantanol [5], 2-adamantanone [6] and 1-bromoadamantane [7,8] have been studied in our laboratory recently. All the investigated compounds were found to form plastic crystals in various temperature ranges. Thermodynamic parameters of orientational disorder in plastic crystals of some adamantane derivatives have been determined [9].

Compounds containing several adamantane fragments are also synthesized. However, even the simplest of them, 1,1′-biadamantane ($C_{20}H_{30}$, 1,1′-bitricyclo[3.3.1.1^{3,7}]decane, Fig. 1), does not have thermodynamic properties studied in a wide temperature range. According to an X-ray diffraction analysis [10], the length of the central C–C bond in the molecule is 0.1578 nm, which exceeds the value typical for a C(sp^3)–C(sp^3) bond. Nevertheless, semi-empirical calculations (AM1 [11]) show that the barrier of rotation around this bond is rather high and amounts to 19.27 kJ mol^{-1}. It is also known [12] that condensation of adamantane molecules leads to the formation of stable polymeric compounds. That is why it would be worthwhile to obtain a thermodynamic description of the

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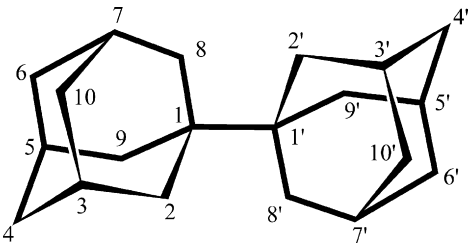

Fig. 1. The molecular structure of 1,1′-biadamantane.

condensation of adamantane into bi-, tri-, tetraadamantanes and its polymers that possess high thermostability and resistivity to various aggressive media. These polymeric materials can have other valuable properties and be used for the production of high-quality lubricating oils, additives to polymers, antirust protective covering for surfaces of machinary and its parts exploited under extreme conditions [13,14]. Thermodynamic investigation of 1,1′-biadamantane is of great interest for the development of the connection between the molecular structure and the ability to form plastic crystals.

We have performed a comprehensive investigation of thermodynamic properties of 1,1′-biadamantane, which includes measurements of the heat capacity in the range from 5 to 580 K, of the saturated vapour pressure and the sublimation enthalpy, of the formation enthalpies of the compound in the crystalline and gaseous states. Quantum-chemical and statistical thermodynamics calculations have been carried out for obtaining the thermodynamic properties of 1,1′-biadamantane in the ideal gaseous state.

2. Experimental

2.1. Materials

1,1′-Biadamantane was synthesized by the Wurtz reaction [15] by boiling of 1-bromoadamantane in toluene over metallic sodium. Crystalline 1,1′-biadamantane obtained after removing the solvent by evaporation was purified by twice recrystallization from toluene and subsequent sublimation under vacuum conditions. The mass-fraction purity of the sample was >0.999 according to GLC ("Chrom-5" with a flame-ionization detector and a quartz capillary column (50 × 0.0002) m with a SE-30 stationary phase; helium as a carrier gas (0.15 MPa), temperatures of an evaporator and of a column are 543 and 493 K, respectively).

Benzoic acid (VNIIFTRI, Moscow, Russia; K-2 grade with mass-fraction purity >0.99993) and synthetic corundum (VNIIM, St. Petersburg, Russia; mass fraction purity >0.99995).

2.2. Apparatus and measurement procedures

2.2.1. Adiabatic calorimetry

The heat capacity of 1,1′-biadamantane between 5 and 105 K was measured in a TAU-1 vacuum adiabatic calorimeter made in VNIIFTRI (Moscow, Russia) and described in detail earlier [16–18]. The relative uncertainty of the heat-capacity measurements in the range from 40 to 105 K was ±0.4%, increased gradually with decreasing temperature from 40 K downwards but did not exceed ±2% from 5 to 10 K.

A low-temperature vacuum adiabatic calorimeter made by the Termis close corporation (Moscow, Russia) was used to obtain the heat of capacity, C_s, of the compound in the temperature range 80–370 K [19]. It was found that the uncertainty of the C_s determination over this interval did not exceed 0.4% [19]. The temperature was measured with an iron-rhodium resistance thermometer ($R_0 = 50\ \Omega$) calibrated for the ITS-90 scale by VNIIFTRI. The corrections on reducing $C_{s,m}$ to $C_{p,m}$ and on sublimation of the substance were neglected because they are several orders of magnitude lower than the experimental error (the sum of the corrections is $<10^{-4}\ C_{s,m}$ near 300 K).

2.2.2. Differential scanning calorimetry

The high-temperature heat capacity between 300 and 600 K of 1,1′-biadamantane was measured in an improved automatic one-cup scanning calorimeter [20]. The temperature scale of the device was tested by measuring the melting points of tin, lead, indium and benzoic acid. The heat-flow rate calibration [21] was carried out by the heat capacity of reference synthetic corundum (mass-fraction purity >0.99995).

In the measurements, a sample of 1,1′-biadamantane of 0.6897 g mass was placed in an aluminium ampoule. The average scanning rate was about 1 K min^{-1}, the temperature step of the heat-capacity measurements did not exceed 0.3 K. The uncertainty of the heat-capacity determination in the scanning calorimeter was ±2%.

2.2.3. The Knudsen effusion method

The saturated vapour pressure of the compound was obtained by the integral effusion Knudsen method. The device description and the measurement procedure were presented earlier [22]. The uncertainty of the vapour-pressure determination was found to amount to ±5%. Three membranes were applied to the measurements (l is a membrane thickness, d is an orifice diameter):

- membrane 1: $l = 5.0 \times 10^{-5}$ m, $d = (1.833 \pm 0.004) \times 10^{-4}$ m;
- membrane 2: $l = 8.4 \times 10^{-5}$ m, $d = (4.467 \pm 0.005) \times 10^{-4}$ m;
- membrane 3: $l = 5.0 \times 10^{-5}$ m, $d = (8.370 \pm 0.004) \times 10^{-4}$ m.

Preliminary experiments revealed that the vapour pressure of 1,1′-biadamantane at $T = 300$ K was lower than 10^{-4} Pa. The main measurements were conducted with the use of a high-temperature massive thermostat that maintained a present temperature within ±0.02 K. The weighing of a container with the substance before and after an effusion experiment was performed with an accuracy of $\pm 2 \times 10^{-5}$ g. The thermostat temperature was measured with a platinum resistance thermometer ($R_0 = 10.0447\ \Omega$).

The saturated vapour pressure of the compound was calculated according to the following generalized equation that took into account vapour undersaturation in the Knudsen cell and