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Thermodynamic properties of 5-(1-adamantyl)tetrazole

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ABSTRACT

Temperature dependence of the heat capacity of 5-(1-adamantyl)tetrazole was studied between (5 and 370) K in a vacuum adiabatic calorimeter. From obtained data the thermodynamic properties of the compound in the condensed state were evaluated over the range of (0–370) K. The crystal structure of 5-(1-adamantyl)tetrazole was determined from the X-ray diffraction analysis. The saturated vapor pressure for crystalline 5-(1-adamantyl)tetrazole in the temperature ranges from (394 to 419) K was measured by the Knudsen effusion method, and its enthalpy of sublimation was obtained using these results. The standard enthalpy of formation for crystalline 5-(1-adamantyl)tetrazole at 298.15 K was determined in a static bomb combustion calorimeter. From these data, the standard enthalpy of formation for gaseous 5-(1-adamantyl)tetrazole was evaluated. The enthalpy of formation calculated using quantum chemical methods is in an excellent agreement with the experimental value. The thermodynamic properties of 5-(1-adamantyl)tetrazole in the ideal-gas state were calculated in the temperature range from (0 to 1000) K. The calculated entropy of gaseous 5-(1-adamantyl)tetrazole is in a good agreement with the one obtained from the experimental data.

1. Introduction

Adamantyltetrazoles are consisting of two cyclic systems, carbocyclic adamantane and heterocyclic tetrazole. Combination of two extremely different moieties defines unique properties of the above-mentioned compounds. In particular, due to lipophility and bulkiness of the adamantyl fragment and strong coordination ability of tetrazole-5-thiol fragment towards the metal ions, 1-(1-adamantyl)tetrazole-5-thiol has the ability to stabilize semiconductor CdS nanoparticles under solution-phase and solventless synthesis of tetrazole capped ones [1]. *N*-(1-adamantyl) tetrazoles and their derivatives show high antiviral activity against the rimantadine-resistant strain of influenza A virus [2] whereas 2-adamantylmethyltetrazoles are potent and selective inhibitors of human 11β-hydroxysteroid dehydrogenase type 1 [3]. Surprisingly, despite the potential interest, thermodynamic data for adamantyltetrazoles have not been reported. We decided to fill this gap and carried out thermodynamic and structural studies of 5-(1-adamantyl)tetrazole (CAS 60798-89-2), the simplest derivative from above family of substances. Having easy replaced hydrogen atom at the tetrazole ring 5-(1-adamantyl)tetrazole is a valuable substrate for further functionalization in order to prepare various tetrazole–adamantane derivatives, including pharmaceutically active substances [4]. Thermodynamic data reported can be useful for prediction and optimization of functionalization processes. It should be noted that this work is a continuation of our systematic studies in the field of thermodynamics of adamantane derivatives [5–9].

2. Experimental

2.1. Synthesis

A mixture of 1-cyanoadamantane (10.0 g, 62 mmol), sodium azide (7.8 g, 120 mmol), triethylamine hydrochloride (16.4 g, 120 mmol) and toluene (140 mL) was refluxed for 48 h under stirring. The reaction mixture was cooled to room temperature and diluted with water (200 mL). The resulting emulsion was broken by adding methanol and sodium chloride. The aqueous phase was acidified to pH 1 using concentrated hydrochloric acid and the product was extracted with diethyl ether (3 × 100 mL). The combined extracts were dried with anhydrous sodium sulfate, and evaporated to give 5-(1-adamantyl)tetrazole (9.90 g, 78%) as colorless crystals. The temperature of fusion for the sample recrystallized from (acetonitrile + diethyl ether) mixture determined by a capillary tube was 251 ± 1 °C. ^{1}H and ^{13}C NMR spectra were

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measured on Bruker Avance-500 spectrometer. ^{1}H NMR (500 MHz, DMSO-d$_6$); δ, 1.74 (m, 6H); 1.97 (m, 6H); 2.05 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d$_6$): 27.3 (CH_2), 32.0 (C), 35.7 (CH_2), 40.4 (CH), 162.8 (C). Analysis calculated for $C_{11}H_{16}N_4$: C, 64.68; H, 7.89; N, 27.43; found: C, 64.40; H, 7.70; N, 27.28.

The sample purity 99.92% was detected using the gas chromatograph–mass spectrometer Shimizu GCMS-QP2010Plus. A glass column (EquityTM-5 stationary phase) of 30 m length, 0.25 mm diameter and phase film thickness of 0.25 m was used. Helium at a 1 cm^3 min^{-1} rate was used as a carrier gas. Column temperature was increased from 333.15 K to 553.15 K at a rate of 5 K min^{-1}, kept at 553.15 K over 4 min and decreased to 373.15 K at a rate of 30 K min^{-1}.

2.2. Single crystal X-ray diffraction study

The single crystals of 5-(1-adamantyl)tetrazole suitable for X-ray diffraction study were obtained by recrystallization from ethanol. X-ray data were collected at 100 K on a SMART APEX II diffractometer using graphite monochromated Mo–Kα radiation (λ = 0.71073 Å). The reflection data were corrected on absorption. The structure was solved by direct methods with the program SIR2004 [10] and refined on F^2 by full-matrix least squares technique with SHELXL-2013 [11]. All non-hydrogen atoms were refined in an anisotropic approximation. The position of an H atom of the N—H group was found from a difference Fourier map and refined independently in an isotropic approximation. All the remaining H atoms were placed in the calculated positions and refined using a “riding” model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Molecular graphics was performed with the programs ORTEP-3 for Windows [12] and PLATON [13].

2.3. Adiabatic calorimetry

Heat capacity of 5-(1-adamantyl)tetrazole under saturated vapor pressure (C_s) in the temperature range of (5–370) K was determined in a TAU-10 adiabatic calorimeter (Termis, Moscow). The instrument and the experimental procedures were described in [14]. The uncertainty in the heat capacity measurements was $\pm 4 \times 10^{-3}$ C_s over the temperature range of (20–370) K and did not exceed $\pm 2 \times 10^{-2}$ C_s at $T < 20$ K [14]. Because of air and moisture insensitivity, the sample was loaded into a calorimetric vessel in air. The sample mass corrected for buoyancy was 0.6048 g.

2.4. Knudsen effusion method

Saturated vapor pressure p_{sat} for crystalline 5-(1-adamantyl)tetrazole in the interval of (394–419) K was measured by the integral Knudsen effusion method. The description of the apparatus and experimental procedures was published earlier [15]. The uncertainty of the measurements was established to be ±5% [15]. The temperature was kept constant within ±0.02 K and controlled with the use of a platinum resistance thermometer placed in a thermostating block. The residual pressure in the system was <1 mPa.

The measurements were performed with a cylindrical cell made of stainless steel with a height of 12.0 mm and an internal diameter of 10.8 mm. Three (0.10 ± 0.01) mm thick nickel membranes with the orifice diameters (0.612 ± 0.009) mm, (1.051 ± 0.018) mm, and d = (1.156 ± 0.021) mm were used. The mass loss in each experiment was from (1.8 to 6.5) mg.

The vapor pressures were calculated according to the equation [16]:

$$p_{\text{sat}} = \left(\frac{1}{\alpha\gamma S_{\text{sub}}} + \frac{1}{kS_{\text{or}}}\right)\frac{\Delta m}{\tau}\sqrt{\frac{2\pi RT}{M}} \qquad (1)$$

where Δm is the mass loss during the vacuum exposition time τ, S_{or} is the cross-section area of the orifice; k is the transmission coefficient; S_{sub} is the geometrical surface area of the sample; $\alpha\gamma$ is the product of the condensation coefficient and the roughness coefficient for the sample surface; R is the gas constant (R = 8.314462 J K^{-1} mol^{-1}); T is the temperature in the effusion experiment; M is the vapor molar mass.

The gas phase of the compound under study was assumed to consist of monomers.

The k transmission coefficient was calculated according to the Kennard formula [17]. The $\alpha\gamma$ value was found from the least-squares fit of the vapor pressure values obtained with different effusion orifices.

2.5. Bomb combustion calorimetry

The energy of combustion of crystalline 5-(1-adamantyl)tetrazole was measured in a home-made combustion calorimeter with an isothermal air bath and a static bomb of 95.6 cm^3 volume. Its design and the measurement procedure were described in detail earlier [9]. The calibration of the calorimeter was carried out with the reference benzoic acid (K-2 grade, mass-fraction purity of 0.99993). The energy equivalent was found in a series of 13 experiments to be 9834.9 ± 2.4 J K^{-1}. The samples were weighted on a Mettler Toledo AG 245 balance with an uncertainty of $\pm 2 \times 10^{-5}$ g. The samples pressed into pellets were burnt in a Pt crucible in oxygen atmosphere at an initial oxygen pressure of 3.04 MPa. Corrections for nitric acid formation were based on titration with 0.1 mol dm^{-3} NaOH (aq). The adjustment to the standard conditions was performed using the conventional procedures [18,19] assuming what the molar energy of formation of 0.1 mol dm^3 HNO_3 from N_2, O_2, and liquid H_2O is equal to −59.7 kJ mol^{-1} [20].

The enthalpy of formation of the compound was calculated using the standard enthalpies of formation of gaseous carbon dioxide, $\Delta_f H_m^\circ(\text{CO}_2, \text{g}) = (-393.51 \pm 0.13)\text{kJmol}^{-1}$, and liquid water, $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{liq}) = (-393.51 \pm 0.13)\text{kJmol}^{-1}$ [21].

The recommended molar mass of 5-(1-adamantyl)tetrazole is (204,270 . . . 204,286) g mol^{-1} [22]. Since the molar mass cannot be calculated as the mean of the bounds according to the IUPAC recommendations (2013) [22], we assumed 204.28 g mol^{-1} to be the molar mass of 5-(1-adamantyl)tetrazole. The maximum error introduced to the molar enthalpy of formation by this assumption does not exceed ±0.3 kJ mol^{-1} and can be neglected compared to the experimental uncertainty.

The density of crystalline 5-(1-adamantyl)tetrazole 1.47 ± 0.09 g cm^{-3} at 19 °C was measured in a pycnometer using the saturated solution of the substance as the working fluid. The volume of the pycnometer was determined from a calibration with bi-distilled water using the recommended density of water from [23].

2.6. Calculations

Quantum-chemical calculations were performed in the Gaussian 09 Revision B suite of programs [24]. The molecular and spectral data required for statistical thermodynamics calculations were obtained at the B3LYP/6–311 + G(d,p) theory level. The relative tautomers energies of 5-(1-adamantyl)tetrazole and the enthalpies of the molecules studied in this work were determined using the G3MP2 composite quantum-chemical method [25]. Methodology for calculating thermodynamic properties of a compound in the ideal-gas state by means of statistical thermodynamics is rigorously described in Ref. [26,27].