



Thermodynamic properties of 4-*tert*-butyl-diphenyl oxide



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ABSTRACT

The main thermodynamic functions (changes of the entropy, enthalpy, and Gibbs free energy) and functions of formation at $T = 298.15$ K of 4-*tert*-butyl-diphenyl oxide in condensed and ideal gas states were computed on the basis of experimental results obtained. The heat capacities of 4-*tert*-butyl-diphenyl oxide was measured by vacuum adiabatic calorimetry over the temperature range (8 to 371) K. The temperature, the enthalpy and the entropy of fusion were determined. The energy of combustion of the sample was determined by static-bomb combustion calorimetry. The saturation vapor pressures of the substance were measured by dynamic transpiration method over the temperature and pressure intervals (298 to 325) K and (0.05 to 1.2) Pa. The enthalpy of sublimation at $T = 298.15$ K was derived. The contribution of O-(2C_b) group (where C_b is the carbon atom in a benzene ring) into the absolute entropies of diphenyl oxide derivatives was assessed.

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1. Introduction

The diphenyl oxide derivatives belong to the family of the bicyclic aromatic compounds that find ever increasing application in technology and medicine [1–3].

Compounds with such molecular structure tend to form liquid crystals [4]. In other words, a certain temperature range they combine the properties of liquids (fluidity, the ability to form droplets) and those of crystalline materials (anisotropy). The anisotropy of their physical properties in combination with low viscosity makes it possible to easily and effectively orient (reorient) molecules by means of moderate magnitude perturbing factors (electric and magnetic fields, mechanical stress), which enables considerable variation of the structure and properties of the material. Therefore, liquid crystals are indispensable electro-optically-active systems that find extensive use in the industry of liquid crystal displays and other electronic devices [5,6].

In addition, the diphenyl oxide derivatives are biologically active substances. Nitro derivatives of diphenyl ether possess herbicidal properties and are used as components of plant protection chemicals [3].

The literature data on the thermodynamic properties of the diphenyl oxide derivatives are scanty. The diphenyl oxide itself is the most studied compound of the family. Reported are its enthalpy of combustion, low-temperature heat capacity, the

thermodynamic characteristics of phase transitions – the melting point, boiling point, enthalpy of sublimation and evaporation, and the critical parameters [7–9]. In addition, experimental values for the enthalpies of formation in the solid state [10] and low-temperature heat capacities [11] are available for 4,4'-dinitrobutyldiphenyl oxide. This work is devoted to experimental determination of the properties of another diphenyl oxide derivative that is 4-*tert*-butyl-diphenyl oxide. Literature data concerning the thermodynamic properties of this substance are absent.

2. Experimental

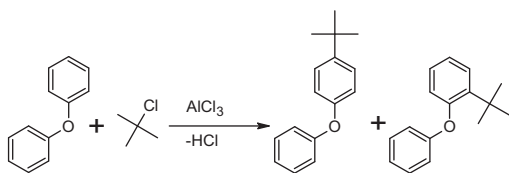
2.1. Synthesis of sample

The sample of the 4-*tert*-butyl-diphenyl oxide [(CH₃)₃CC₆H₄–O–C₆H₅, 4-TBDPhO] was synthesized and purified at the Department of the Technology of Organic and Petro-Chemical Synthesis of Samara State Technical University.

The 4-TBDPhO sample was prepared by alkylation of diphenyl oxide with the liquid 2-chloro-2-methylpropane. The synthesis was performed in *n*-hexane using AlCl₃ as the catalyst. The ratio of isomers of 2-TBDPhO and 4-TBDPhO in the reaction mixture was approximately 1:25. The reaction mixture was treated with 15% HCl in order to destroy the catalyst and the goal 4-TBDPhO was purified by fractional distillation under reduced pressure of $p = 0.8$ kPa. The fraction containing (0.98 to 0.99) mole of the 4-TBDPhO was obtained. Then this fraction was purified by means of fivefold re-crystallization from ethanol.

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The purity of the 4-TBDPhO sample was determined by chromatography (g.l.c.), and by calorimetric method of the fractional melting (table 1).

2.2. Adiabatic calorimetry

The heat capacity, triple-point temperature and enthalpy of fusion of the 4-TBDPhO was measured in a fully automated vacuum adiabatic calorimeter combined with a computer-measuring system (Termis, Moscow). Detailed description of the device configuration and calorimetric technique are in [12,13]. The calorimetric cell consists of a cylinder titan container ($V \approx 1 \text{ cm}^3$), inserted into a copper sleeve with a heater ($R \approx 300 \Omega$), and an adiabatic shell. The temperature of the calorimeter was measured by a (rhodium + iron) resistance thermometer ($R_0 \sim 50 \Omega$), which was calibrated in ITS-90 [14] over the temperature range from (5 to 373) K. The temperature difference between the container and adiabatic shell was measured by an eleven-junction (copper + 0.1 wt% iron)–Chromel differential thermocouple. The adiabatic state of the calorimeter was maintained by digital control using the computer-measuring system with an accuracy of $\pm 3 \cdot 10^{-3}$ K. The error of measurements of the temperature of the container was $\pm 2 \cdot 10^{-2}$ K. High vacuum inside the calorimetric cell was kept by means of cry-sorption provided with an efficient charcoal getter. The heat capacity of the substance was measured in the process of heating the sample. The mass of the sample was determined with a precision of $\pm 5 \cdot 10^{-2}$ mg on a Mettler balance. The method of calorimetric determinations was checked by the measurement of the heat capacity of extra purity copper having the mass fraction 0.99995 and *n*-heptane chromatographically pure. The relative combined expanded uncertainties of the heat capacity measurements, $U_{c,r}(C_{p,m})$ were 0.02 over the temperature range from (7 to 20) K, 0.007 from (20 to 40) K, 0.004 from (40 to 80) K and 0.002 above 80 K.

2.3. Combustion calorimetry

The energy of combustion was determined by means of a static bomb isoperibolic macrocalorimeter. The principle description of the method is given elsewhere [15]. The temperature rise was measured with a copper resistance thermometer and a bridge circuit. The standard uncertainty of the temperature measurements was $5 \cdot 10^{-5}$ K. The energy equivalent of the calorimeter, w , was determined by combustion of thermochemical standard benzoic acid (sample K-1, supplied by the Russian Research Institute of Metrology) and was equal to $(53949.4 \pm 7.0) \text{ J} \cdot \Omega^{-1}$. The energy of combustion of benzoic acid, $\Delta_b U$, was equal

$-(26432.5 \pm 1.9) \text{ J} \cdot \text{g}^{-1}$ under certified conditions at $T = 298.15 \text{ K}$. The correction for small deviations from these conditions was calculated according to Jessup's formula [16] and made $\Delta_b U = -(26431.4 \pm 1.9) \text{ J} \cdot \text{g}^{-1}$.

Before combustion experiments, the 4-TBDPhO was pressed into pellets and placed into a small platinum cup. The bomb, with 1 cm^3 of added water, was charged with purified oxygen to a pressure of 3.04 MPa. The initial temperature did not differ from 298.15 K by more than $\pm 2 \cdot 10^{-2}$ K. Provision for ignition was made by means of a platinum wire heated by the discharge of a capacitor. After each experiment, the combustion products were analyzed for carbon dioxide by the Rossini method [16]. Soot formation was not observed in any combustion experiment. Qualitative tests for CO with indicator tubes ("CO-0,2" TU 12.29.14-70, Donetsk plant of mine-rescue equipment, Ukraine) were negative within the limits of their sensitivity $\pm 1 \cdot 10^{-6}$ g. The data of calorimetric experiments are presented in table 2. The combined standard uncertainties of the mean values of the energy equivalent of the calorimeter, w , and the standard energy of combustion, $\langle -\Delta_c u^\circ \rangle$, corresponds to the 95% confidence interval for normal distribution ($k = 1.96$).

2.4. Transpiration method

Vapour pressures and enthalpies of vaporization of 4-TBDPhO were determined using the transpiration method [21,22]. About 0.7 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with diameter of 1 mm provide a surface, which is large enough for (vapor + solid) equilibration. At constant temperature ($\pm 0.1 \text{ K}$), gas stream of helium was passed through the U-tube and the transported amount of studied substance was collected in a cooling trap. The amount of condensed substance was determined by chromatography analysis using an external standard – *n*-octadecane.

The saturated vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a definite period of time, and the small value of the residual vapor pressure at the temperature of condensation was added. The latter was calculated from a linear correlation between $\ln(p_i^{\text{sat}})$ and T^{-1} obtained by iteration. Assuming that Dalton's law of partial pressures applied to the gas stream saturated with the substance, values of p_i^{sat} were calculated:

$$p_i^{\text{sat}} = \frac{m_i \cdot R \cdot T_a}{V \cdot M_i}; \quad V = V_{\text{He}} + V_i; \quad (V_{\text{He}} \gg V_i), \quad (1)$$

where $R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i is volume contribution of the sample to the gaseous phase; V_{He} is the volume of transporting gas and T_a is the temperature of the soap bubble meter. The volume of transporting gas, V_{He} , was determined from the flow rate and time measurements. The relative combined expanded uncertainty of the vapor pressures derived from the transpiration method was $U_{c,r}(p) = 0.03$.

3. Results

3.1. Heat capacity and parameters of fusion

The heat capacity of 4-TBDPhO was measured at the saturated vapor pressures, $C_{\text{sat},m}$, over the temperature range from (8 to 371) K using liquid helium and nitrogen as refrigerants. The difference $(C_{p,m} - C_{\text{sat},m}) = T(\delta V/\delta T)_p(\delta P/\delta T)_{\text{sat}}$, estimated for the liquid phase at $T = 300 \text{ K}$, was less than uncertainties of experimental $C_{\text{sat},m}$ values and therefore it was not taken into account for the whole temperature interval studied. The mass of sample was equal

TABLE 1
Provenance and purity of the 4-*tert*-butyl-diphenyloxide sample.

Source	Initial mass fraction purity	Purification method	Analysis method	Final fraction purity by mass or mole
Synthesis	0.98 to 0.99	Fivefold re-crystallization from ethanol	g.l.c. fractional melting	0.9993 mass 0.9970 \pm 0.0003 mol

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