



## Experimental and theoretical study of thermodynamic properties of levoglucosan



Gennady J. Kabo<sup>a</sup>, Yauheni U. Paulechka<sup>a,\*</sup>, Olga V. Voitkevich<sup>a</sup>, Andrey V. Blokhin<sup>a</sup>, Elena N. Stepurko<sup>a</sup>, Sviataslau V. Kohut<sup>a</sup>, Yakov V. Voznyi<sup>b</sup>

<sup>a</sup>Chemistry Faculty and Research Institute for Physical Chemical Problems, Belarusian State University, Leningradskaya 14, 220030 Minsk, Belarus

<sup>b</sup>N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation

### ARTICLE INFO

#### Article history:

Received 4 November 2014

Received in revised form 6 January 2015

Accepted 9 January 2015

Available online 2 February 2015

#### Keywords:

Levoglucosan

Heat capacity

Saturated vapor pressure

Enthalpy of formation

Statistical thermodynamics

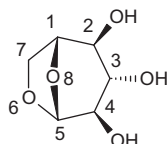
### ABSTRACT

The heat capacity of levoglucosan was measured over the temperature range (5 to 370) K by adiabatic calorimetry. The temperatures and enthalpies of a solid-phase transition and fusion for the compound were found by DSC. The obtained results allowed us to calculate thermodynamic properties of crystalline levoglucosan in the temperature range (0 to 384) K. The enthalpy of sublimation for the low-temperature crystal phase was found from the temperature-dependent saturated vapor pressures determined by the Knudsen effusion method. The thermodynamic properties of gaseous levoglucosan were calculated by methods of statistical thermodynamics using the molecular parameters from quantum chemical calculations. The enthalpy of formation of the crystalline compound was found from the experiments in a combustion calorimeter. The gas-phase enthalpy of formation was also obtained at the G4 level of theory. The thermodynamic analysis of equilibria of levoglucosan formation from cellulose, starch, and glucose was conducted.

© 2015 Elsevier Ltd. All rights reserved.

### 1. Introduction

Levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose, (1R,2S,3S,4R,5R)-6,8-dioxabicyclo[3.2.1]octane-2,3,4-triol, CASRN 498-07-7)



is an intermediate formed during thermal decomposition of cellulose and cellulosic materials. It is also the raw material for producing biodegradable polymers, antibiotics, and other agents [1,2]. Levoglucosan is formed during catalytic thermal processing of carbohydrate components of plant biomass [3]. The comprehensive study of the thermodynamic properties for this substance is needed to optimize the processes of synthesis and conversion of levoglucosan.

To our best knowledge, the heat capacity of levoglucosan has not been reported. A number of authors (table 1) used differential scanning calorimetry (DSC) for detection of phase transitions and measurement of their characteristics for the compound. A solid-phase transition into the plastic crystal phase crl and fusion were found.

Oja and Suuberg [6] measured the saturated vapor pressure of levoglucosan in the range of  $T = (344 \text{ to } 405) \text{ K}$  by the Knudsen effusion method. The standard molar enthalpies of sublimation were  $\Delta_{\text{crl}}^{\text{g}}H_{\text{m}}(362.7 \text{ K}) = (125.1 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$  for the rigid crystal and  $\Delta_{\text{crl}}^{\text{g}}H_{\text{m}}(395.8 \text{ K}) = (100.3 \pm 5.9) \text{ kJ} \cdot \text{mol}^{-1}$  for the plastic crystal. Rocha *et al.* [7] used the same method for the measurements in the temperature range (361 to 379) K. The standard molar enthalpy of sublimation for the rigid crystal was  $\Delta_{\text{crl}}^{\text{g}}H_{\text{m}}(370.1 \text{ K}) = (131.1 \pm 3.4) \text{ kJ} \cdot \text{mol}^{-1}$  for the rigid crystal. Booth *et al.* [8] measured the saturated vapor pressure close to the ambient temperature. The obtained value  $\Delta_{\text{crl}}^{\text{g}}H_{\text{m}}(307.8 \text{ K}) = (6.9 \pm 9) \text{ kJ} \cdot \text{mol}^{-1}$  is inconsistent with those published by other authors. Epstein *et al.* [9] used the static method to obtain the temperature dependence of vapor pressure over the liquid compound. From the measurements in the range of  $T = (468 \text{ to } 528) \text{ K}$ , the enthalpy of vaporization was found to be  $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(504.5 \text{ K}) = (9.23 \pm 3.5) \text{ kJ} \cdot \text{mol}^{-1}$ . A notable disagreement for the enthalpy of sublimation obtained by various

\* Corresponding author. Tel.: +375 17 209 51 97.

E-mail address: [paulechka@gmail.com](mailto:paulechka@gmail.com) (Y.U. Paulechka).

authors [6,7] makes it reasonable to carry out additional vapor pressure measurements for levoglucosan.

The specific energy of combustion for the compound  $\Delta_c u(298.15\text{ K}) = -17.51\text{ kJ} \cdot \text{g}^{-1}$  corresponding to  $\Delta_c H_m^0 = -28\,39\text{ kJ} \cdot \text{mol}^{-1}$  was determined by Karrer *et al.* in 1921 [11]. According to Rocha *et al.* [7],  $\Delta_c H_m^0$  of the studied compound is equal to  $-(2831.1 \pm 1.9)\text{ kJ} \cdot \text{mol}^{-1}$ .

In this work, we report the results of measurements of the heat capacity in the range of  $T = (5\text{ to }370)\text{ K}$ , the saturated vapor pressure in the range of  $T = (354\text{ to }384)\text{ K}$ , and the enthalpy of combustion for levoglucosan. Based on these data, thermodynamic functions of the compound in the crystal state and thermodynamic parameters of its sublimation were found. The molecular parameters and frequencies of normal vibrations of levoglucosan molecules obtained from quantum-chemical calculations were used to calculate thermodynamic properties of this compound in the ideal-gas state by the methods of statistical thermodynamics. The thermodynamic parameters of the levoglucosan synthesis from microcrystalline cellulose, starch, and glucose were discussed.

## 2. Experimental

### 2.1. Preparation and characterization of the sample

The sample of levoglucosan (table 2) was synthesized from phenyl  $\beta$ -D-glucoside by cyclization under alkaline conditions [12,13]. The sample was recrystallized from (ethanol + diethyl ether) mixture and sublimed in vacuum at  $T = (420\text{ to }450)\text{ K}$ .

Purity of the sample was determined with the Fisher Scientific Trace GC Ultra gas chromatograph equipped with the single quadrupole detecting system DSQ-II. The microcapillary column VF-17MS of 30 m length, 0.25 mm diameter and 0.25 mm stationary film thickness was used. The rate of the helium carrier gas was  $1\text{ cm}^3 \cdot \text{min}^{-1}$ . During the run the temperature changed from (333 to 473) K at a rate of  $5\text{ K} \cdot \text{min}^{-1}$  and from (473 to 553) K at rate of  $20\text{ K} \cdot \text{min}^{-1}$ . Chromatographic analysis of the sample dissolved in acetone revealed no impurities. Then, the hydrogen atoms of hydroxy groups were quantitatively substituted by trimethylsilyl groups using *N*-methyl-*N*-trimethylsilyltrifluoroacetamide. Chromatographic analysis of the derivatized sample demonstrated that the initial compound contained the impurity of  $\beta$ -D-galactofuranose. The sample mass fraction purity of 0.9962 was determined from peak areas assuming that sensitivities of the detector towards both the title compound and the impurity were equal.

Prior to the measurements, the sample was kept over  $\text{P}_2\text{O}_5$  at  $T = 290\text{ K}$  for  $> 72\text{ h}$ .

### 2.2. Calorimetry

The heat capacity of levoglucosan in the temperature range of (5 to 370) K was measured in a TAU-10 adiabatic calorimeter

**TABLE 1**  
Phase transition characteristics of levoglucosan determined by DSC.<sup>a</sup>

Transition	$T_{\text{trs}}/\text{K}$	$\Delta_{\text{trs}}H/\text{kJ} \cdot \text{mol}^{-1}$	Reference
crII–crI	386	24.9	[4,5]
	386		[6]
	$384.9 \pm 0.6$	$23.2 \pm 0.8$	[7]
	$384 \pm 1$	$25.0 \pm 0.4$	This work
crI–l	453	3.3	[4,5]
	$455.4 \pm 0.2$	$3.3 \pm 0.4$	[7]
	$454 \pm 1$	$2.9 \pm 0.2$	This work

<sup>a</sup> The reported uncertainties were calculated with 0.95 level of confidence ( $k \approx 2$ ) and characterize data repeatability.

**TABLE 2**  
Description of the sample used.

Chemical name	Source	Purification method	Final mass fraction purity	Analysis method <sup>a</sup>
Levoglucosan	Synthesis	Crystallization, sublimation	0.9962	GCMS <sup>b</sup>

<sup>a</sup> Determined with a gas chromatograph-mass spectrometer (GCMS).

<sup>b</sup> After sample derivatization.

(Termis, Moscow) [14]. The detailed description of the calorimeter construction and the experimental procedures was published earlier [15]. The temperature was measured with an Fe/Rh resistance thermometer ( $R_0 = 50\ \Omega$ ) calibrated on ITS-90 by VNIIFTRI (Moscow). The relative uncertainty of the heat capacity measurements was  $4 \cdot 10^{-3} C_p$  over the temperature range of (20 to 370) K and did not exceed  $2 \cdot 10^{-2} C_p$  at  $T < 10\text{ K}$  [15]. Depending on temperature, heat capacity of the sample contributed (0.33 to 0.55) of total heat capacity of the system. The experimental heat capacities were smoothed with the polynomial equations. For all the polynomials, the rms deviations of experimental points from the smoothing curves did not exceed half of the uncertainty in the corresponding temperature range.

DSC analysis was carried out with a Netzsch STA 449 Jupiter instrument. The temperature and heat calibration of the calorimeter was conducted using the parameters of fusion for metals, as recommended by the manufacturer. Performance of the instrument was checked in experiments with benzoic acid (K-2 grade, mass fraction purity of 0.99993) whose temperature of fusion and enthalpy of fusion are close to the similar properties for a solid-phase transition of levoglucosan. A  $10\text{ K} \cdot \text{min}^{-1}$  scanning rate was applied both in calibration and measurement runs. The peak onset temperatures were considered as the phase transition temperatures.

The samples of levoglucosan of about 3 mg mass were placed in an alumina crucible. The measurements were performed under nitrogen atmosphere. Only the first run was used for determination of temperatures and enthalpies of phase transitions. Cooling of the sample after this run resulted in its supercooling and formation of phases metastable at room temperature.

The combustion energy of the levoglucosan sample was determined in a combustion calorimeter equipped with a stainless-steel bomb of a  $95.6\text{ cm}^3$  volume [16]. The energy equivalent of the calorimeter  $\epsilon_{\text{calor}} = (9834.9 \pm 2.4)\text{ J} \cdot \text{K}^{-1}$  was determined from 13 experiments on combustion of the K-2 grade benzoic acid. The initial oxygen pressure in the bomb was 3.09 MPa at  $T = 298.15\text{ K}$ . For the adjustment of the data to standard conditions, conventional procedures [17] were used. The samples were burned in bags made of  $80\ \mu\text{m}$  polyethylene film. The polyethylene was assumed to have formula  $(\text{CH}_2)_n$ . The combustion energy of the material  $\Delta_c u^0 = -(46337.6 \pm 9.6)\text{ J} \cdot \text{g}^{-1}$  was determined from the results of eight experiments. The cotton thread of the empirical formula  $(\text{CH}_{1.8}\text{O}_{0.9})_n$  had the combustion energy  $\Delta_c u^0 = -(169\,452 \pm 8.4)\text{ J} \cdot \text{g}^{-1}$  [18]. The auxiliary quantities required for the data treatment are presented in table S1.

All the reported uncertainties correspond to the 0.95 confidence interval for normal distribution ( $k \approx 2$ ).

### 2.3. Integral Knudsen effusion method

The saturated vapor pressure,  $p_s$ , over solid levoglucosan was measured by the integral Knudsen effusion method. The apparatus and the experimental technique were described previously [19]. The typical uncertainty of the experimental procedure used is  $0.05p_s$ . The temperature was kept constant within  $\pm 0.02\text{ K}$  and

Download English Version:

<https://daneshyari.com/en/article/6660541>

Download Persian Version:

<https://daneshyari.com/article/6660541>

[Daneshyari.com](https://daneshyari.com)