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Vapor Pressures and Enthalpies of Sublimation of D-Glucose, D-Xylose, Cellobiose, and Levoglucosan

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The vapor pressures of α-D-glucose (or dextrose), D-xylose, D-cellobiose (or 4-β-D-glucopyranosyl-D-glucopyranose), and levoglucosan (or 1,6-anhydro-β-D-glucopyranose) have been measured using the Knudsen effusion technique, in the range of temperatures from 344 to 488 K. The measurements were all made in the solid sublimation regime, and enthalpies of sublimation were calculated from the Clausius−Clapeyron equation. The vapor pressures may be correlated by $\ln(P/\text{Pa}) = A - B/(T/\text{K})$, where $A = 53.16$, $B = 23\,382$ (±600) for D-glucose (395−406 K), $A = 46.29$ and $B = 19\,006$ (±375) for D-xylose (370−395 K), and $A = 70.30$ and $B = 36\,264$ (±5220) for cellobiose (474−488 K). Levoglucosan displayed a solid phase transition at approximately 386 K, and its vapor pressure was affected accordingly. For this material, $A = 38.96$ and $B = 15\,049$ (±123) in the temperature range 344−386 K and $A = 31.19$ and $B = 12\,066$ (±709) in the temperature range 386−405 K.

Introduction

This paper presents the results of measurements of the vapor pressures of two sugars (D-glucose and D-xylose) and two related compounds (cellobiose and levoglucosan). The work was originally motivated by the lack of vapor pressure data on cellulose pyrolysis tars, which have a character related to the glucosan (or anhydro-glucose) units that make up the cellulose. According to the literature, pyrolysis of cellulose (which is a long chain of 1,4 linked β-D-glucopyranose units) can yield tars containing glucose itself (in both α and β forms), cellobiose (the disaccharide form of the anhydroglucose), 1,6-anhydro-β-D-glucopyranose (also called levoglucosan), 1,6-anhydro-β-D-glucofuranose, and many other oligo- and polysaccharides and their condensation and dehydration products (e.g., Halpern and Patai, 1969; Shafizadeh and Fu, 1973; Halpern et al., 1973; Shafizadeh et al., 1979; Shafizadeh, 1975; Kilzer and Broido, 1965; Ponder et al., 1992). The yield of levoglucosan may be very high in vacuum or atmospheric pressure pyrolysis of cellulose. We have separately reported on the vapor pressures of actual cellulose pyrolysis tars and levoglucosan (Oja and Suuberg, 1997; Suuberg et al., 1996). The present study is, however, only concerned with the behavior of pure compounds.

Measurements of vapor pressures of low-volatility materials, such as sugars, would require high temperatures to obtain conveniently measurable pressures. High temperatures cannot, however, be employed because of the concern about thermal decomposition during measurement. This restriction requires use of a sensitive, indirect vapor pressure measurement technique. In the present program of study, this led to use of the effusion method. Use of this technique for measurements of vapor pressures of polycyclic aromatic hydrocarbons and their derivatives has recently been described (Oja and Suuberg, 1998).

Because of the low temperatures employed in this work, the samples are typically solids, and the measurements involve sublimation vapor pressures. In sublimation work, it is typical to find that the Clausius−Clapeyron equation, with a constant enthalpy of sublimation, $\Delta_{\text{sub}}H$, fits vapor pressure data reasonably well, i.e.

$$d[\ln P°]/d[1/T] = -\Delta_{\text{sub}}H/R \tag{1}$$

where $P°$ is the saturation vapor pressure, T is the absolute temperature, and R is the gas constant. This is found to generally be an excellent approximation throughout the work described below.

Experimental Section

The vapor pressures have been measured using a molecular effusion/thermogravimetry (TGA) technique. The particular implementation of the Knudsen effusion technique used here has been recently described in another publication, which also presented its modification for use in a nonisothermal mode (Oja and Suuberg, 1997). In the Knudsen method (e.g., Hollahan, 1962), the substance of interest effuses through a small pinhole, of known area, in an otherwise sealed container or cell. The measurement of vapor pressure involves determining the rate of mass loss from the effusion cell. Measurements here were made under isothermal conditions. The temperature was measured with a precision of ±0.1 K, by a thermocouple in contact with an aluminum capsule that almost completely surrounds the effusion cell. The mass loss rate was continuously recorded using a Cahn 2000 recording electrobalance. The back-pressure in the TGA system was maintained at 10^{-5} Pa, which has been noted to be sufficient so as to provide accuracy in the 10^{-4} Pa range of vapor pressures. Further details of the technique are provided elsewhere (Oja and Suuberg, 1997).

Materials Examined. Vapor pressures were measured for two sugars, cellobiose and levoglucosan. Some results for levoglucosan have been reported elsewhere (Oja and Suuberg, 1997) but are shown here in a more complete form. The compounds selected for study were all purchased in the highest available purities from commercial suppliers,

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as noted below. All compounds were therefore used "as-received", except for one important feature of the preparations. At least 5 wt % of each compound was vaporized before measurements were begun. This ensured that if any very volatile impurities were present, they would be removed. It is important to note that all of the materials are hygroscopic to some degree, so this step was also important for final drying of the sample, prior to beginning actual measurements.

The general thermal behavior of each compound was examined using differential scanning calorimetry. Reported melting points were verified for all of the compounds (see below). All showed the broad ranges typical of sugars, and the indicated values are only approximate. All of the DSC results also pointed to the thermally labile nature of the materials. There were typically secondary peaks in the DSC scans, indicating further alteration of the materials, after the first phase transition above room temperature. The actual nature of the peaks varied quite markedly from material to material, but it seemed prudent to avoid approaching these temperatures in the measurements.

The following summarizes the samples that were examined:

Levoglucosan ($C_6H_{10}O_5$, FW = 162.4, phase transition at 386 K, CAS Reg. No. (supplied by author) 498-07-7). Levolglucosan of 99% purity was obtained from the Aldrich Chemical Company, Inc. This material is commonly sold under the name 1,6-anhydro-β-D-glucose, as opposed to the more commonly accepted 1,6-anhydro-β-D-glucopyranose. On the basis of the information provided by the supplier, the material examined here is believed to contain only the glucopyranose form and does not include the furanose form, as is sometimes included in the generic use of "levoglucosan". Measurements were conducted in the temperature range from 344 K to 413 K. The 386 K "phase transition" cited above has actually been attributed to a plastic crystalline phase transition, whereas true melting appears to occur only at around 453 K (Shafizadeh, 1971). The Knudsen cell used for measurements on this compound had an orifice diameter of 0.637 mm and a Clausing factor of 0.9617.

α-D-Glucose ($C_6H_{12}O_6$, FW = 180.2, approximate mp = 425 K, CAS Reg. No. (supplied by author) 492-62-6). α-D-Glucose (or D-(+)-glucose, or dextrose) of 99.5% purity was obtained from the Sigma Chemical Company, Inc. Measurements were conducted at temperatures in the range from 395 K to 406 K. The onset temperature for decomposition of this compound has been reported to be 473 K (Raemy and Schweizer, 1983), and the present experiments were performed much below this temperature. The Knudsen cell used for these measurements had an orifice diameter of 0.9982 mm and a Clausing factor of 0.9752.

D-Xylose ($C_5H_{10}O_5$, FW = 150.1, approximate mp = 426 K, CAS Reg. No. (supplied by author) 58-86-6). D-Xylose of 99% purity was obtained from the Aldrich Chemical Company, Inc. Measurements were performed between 370 K and 395 K. D-Xylose is not a major product of cellulose pyrolysis but was examined here to provide data on a six-membered ring sugar that contains four hydroxyl groups (compared to five in D-glucose and three in levoglucosan). The onset temperature for thermal decomposition of this compound has been reported to be 468 K (Raemy and Schweizer, 1983). Again, the experiments were performed far below this temperature. The Knudsen cell used for this compound had an orifice diameter of 0.9855 mm and a Clausing factor of 0.9749.

Table 1. Vapor Pressure Data Summary

T/K	P/Pa	T/K	P/Pa
	Levoglucosan		
344.96	0.00939	385.64	0.950
349.24	0.0161	390.58	1.35
352.37	0.0238	391.93	1.44
354.03	0.0290	391.98	1.47
360.52	0.0630	396.56	2.07
364.25	0.0950	396.56	2.07
365.11	0.105	398.25	2.53
367.79	0.136	400.74	2.87
370.82	0.196	401.41	3.15
378.99	0.479	404.98	4.15
	D-Xylose		
370.73	0.00700	385.28	0.0472
375.88	0.0136	390.43	0.0939
380.65	0.0267	395.41	0.168
	Cellobiose		
474.23	0.00211	484.19	0.0104
478.01	0.00413	488.02	0.0186
480.65	0.00506		
	D-Glucose		
395.55	0.00260	401.47	0.00606
397.29	0.00337	404.12	0.00912
399.67	0.00471	405.78	0.0116

Cellobiose ($C_{12}H_{22}O_{11}$, FW = 342.3, apparent mp = 513 K, CAS Reg. No. (supplied by author) 528-50-7). D-Cellobiose (or 4-β-D-glucopyranosyl-D-glucopyranose) of 99% purity was obtained from the Aldrich Chemical Company, Inc. Measurements were performed between 474 K and 488 K. The Knudsen cell used for this compound had an orifice diameter of 0.9982 mm and a Clausing factor of 0.9752.

In one study, thermal decomposition of this compound has been reported to begin at about 503 K (Raemy and Schweizer, 1983). On the other hand, Scheer (1983) has reported a measurable rate of dehydration in the temperature range of interest in the present study but did not give actual values of the absolute rate. It is believed that the actual rate of decomposition or dehydration in the range of temperatures of interest here is very low. Nevertheless, we performed a number of experiments to confirm this. In one experiment, the DSC signature of the cellobiose was examined before and after heating at the experimental conditions. No change was observed in these DSC results. In addition, the ^{1}H NMR, ^{13}C NMR, and FTIR spectra of the sample were examined after heating under the experimental conditions. No changes could be discerned in the sample on the basis of these measurements, and there was certainly no significant formation of any other components in the sample. Thus while we believe that very slow dehydration of cellobiose might be possible under our experimental conditions, it is not occurring at any significant rate, relative to the time scale of our measurements. Further evidence to support this conclusion will be offered below.

Results and Discussion

The raw data for all of the compounds studied are displayed in Table 1. A graphical comparison of the results on all four materials is shown in Figure 1. For all of the measurements performed here, the results have been correlated using the integrated form of the Clausius−Clapeyron equation, with a constant enthalpy of vaporization:

$$\ln (P/\mathrm{Pa}) = A - B/(T/\mathrm{K}) \tag{2}$$

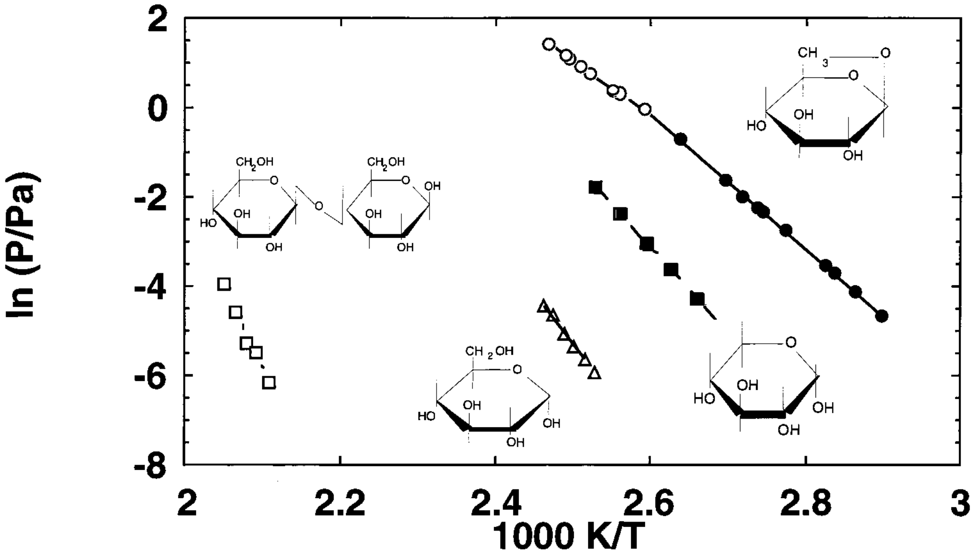

Figure 1. Comparison of the vapor pressures of levoglucosan (circles), D-xylose (closed squares), D-glucose (triangles), and cellobiose (open squares). In the case of levoglucosan, the closed circles indicate data obtained below the first phase transition at 386 K, and the open circles indicate data obtained above this transition temperature (see Figure 2).

Table 2. Summary of Results

compound	temperature range/K	*A*	*B*	$\Delta_{sub}H$/ kJ·mol^{-1}
levoglucosan	344–386	38.96	15 049 (±123)[a]	125.1 (±1.0)
	386–405	31.19	12 066 (±709	100.3 (±5.9)
D-xylose	370–395	46.29	19 006 (±375)	158.0 (±3.1)
D-glucose	395–406	53.16	23 382 (±600)	194.4 (±5.0)
cellobiose	474–488	70.30	36 264 (±5220)	301.5 (±43.9)

[a] Uncertainty calculated at a 95% confidence level.

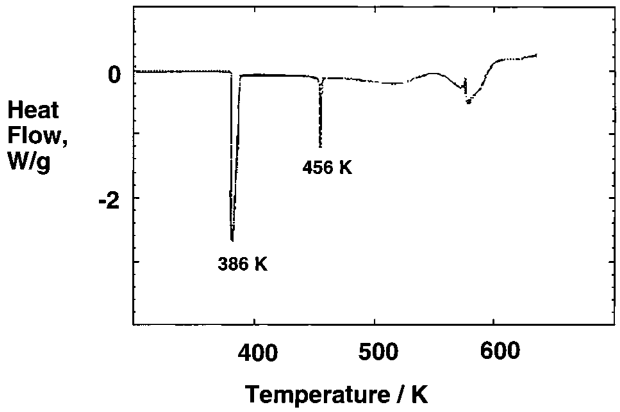

Figure 2. Differential scanning calorimetry results obtained on levoglucosan at a heating rate of 5 K/min.

where *A* and *B* are constants, and it is recognized that $B = \Delta_{sub}H/R$, where $R = 8.314$ J/mol·K. Table 2 summarizes the values of *A* and *B* for all of the compounds studied and the temperature range over which the data were obtained.

There is a very large variation in the vapor pressures of these materials. This would be expected from the differences in molecular weight and hydroxyl content. The latter is expected to play a key role through hydrogen-bonding interactions. While there is a high degree of uncertainty in the calculated enthalpy of sublimation for cellobiose, it also clearly has one of the highest values of any of the high molecular weight materials that we have studied in this laboratory. No other data could be found in the literature for similar compounds, in which hydrogen bonding plays a significant role. An illustration of the significance of hydrogen bonding is offered by a comparison with the results for coronene, an aromatic hydrocarbon of similar molecular weight (300, as opposed to 342 for cellobiose), which has been previously examined by the same technique. Coronene has been observed in a comparable temperature range to exhibit a sublimation enthalpy of around 133 kJ/mol (as opposed to 301.5 kJ/mol for cellobiose), and it exhibits a much higher vapor pressure (by almost 2 orders of magnitude near 475 K, see Oja and Suuberg (1998)).

It is also useful to note the large value of the sublimation enthalpy, with respect to the concern about possible dehydration of cellobiose, discussed above. In the temperature range of interest in this study, the activation energy of dehydrative decomposition has been reported to be 136 kJ/mol (Scheer, 1983). This is far smaller than the value of enthalpy of sublimation, reported in Table 2 (301.5 kJ/mol), which again suggests that the two processes are not linked and that dehydration plays no role in the measurements.

It is also difficult to find literature data against which to compare the results for glucose and xylose. In a study of polyhydric alcohols, Barone et al. (1990) have, however, reported comparable enthalpies of sublimation for *myo*-inositol and Pentaerythritol of 154.7 and 161.0 kJ/mol, respectively. The enthalpies of sublimation may be inferred for several other five or six carbon polyhydric alcohols studied by that group (from enthalpies of vaporization and enthalpies of fusion), and all of the values so obtained are quite comparable to the values obtained here for the five and six-carbon sugars.

It should be noted that the constants for levoglucosan given in Table 2 are not the same as others previously published by our group on this material (Oja and Suuberg, 1997; Suuberg et al., 1996). One main reason is that it had not been recognized in the previous work that a “plastic phase transition” mentioned above (observed at around 386 K in the DSC) was influencing the vapor pressure behavior of the material above this temperature. A sample DSC trace for levoglucosan is presented as Figure 2. The enthalpy of the phase transition around 386 K was measured to be 24.5 kJ/mol from experiments such as those in Figure 2.

In correlating the vapor pressure results for levoglucosan, the point at 385.64 K was included in both high-

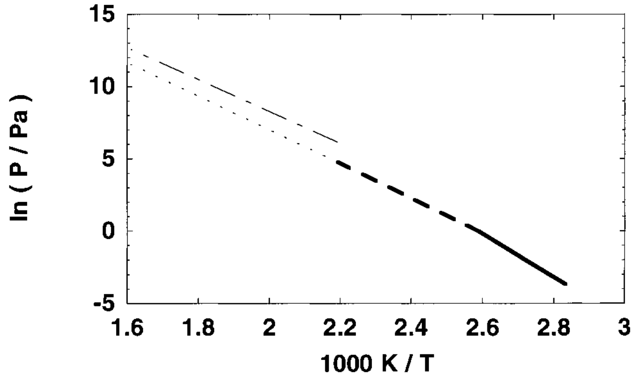

Figure 3. Comparison of the results of this study (solid and dashed heavy lines) and their extrapolation to the liquid phase (thin dotted line) with the experimental correlation of Enstein et al. (1964), shown as the dash−dot curve.

and low-temperature correlations, since it was judged to effectively be right at the transition. Comparison of the calculated enthalpies of sublimation of levoglucosan at temperatures above and below the 386 K phase transition temperature shows a difference of 24.8 kJ/mol (see Table 2). This provides an estimate of the solid phase transition enthalpy itself. It may be seen that this value is in quite good agreement with the directly measured enthalpy of the solid phase change.

No literature data could be found for direct comparison with the present results. There was only one report of vapor pressure measurements on *liquid* levoglucosan, in the temperature range from 468 to 528 K (Enstein et al., 1964). These data suggest an enthalpy of vaporization of 92.3 kJ/mol. Using the measured enthalpies of both the phase transitions, i.e., that at 386 K and the second (fusion) phase change at around 456 K, in Figure 2 with $\Delta H = 3.2$ kJ/mol, we can crudely estimate an extrapolated enthalpy of vaporization of approximately 97 kJ/mol near the melting transition. The agreement is only fair, but this is not surprising, considering the rough nature of the extrapolation. Figure 3 shows a poor comparison between the extrapolated vapor pressures from the present work and the correlation presented by Enstein et al. The reasons for this are not yet clear.

Conclusions

There appear to be very few reports of vapor pressure measurements on saccharides and related compounds in the literature, since these materials are typically considered nonvolatile and typically degrade prior to vaporizing. In pyrolysis applications, however, sufficiently high temperatures can be reached quickly enough to permit evaporation of some of these types of species. The vapor pressures obtained here confirm the very nonvolatile nature of these materials and also reveal how high their enthalpies of vaporization are. Knudsen effusion appears to be a reliable method for exploring these vapor pressures.

The present results also confirm the importance of DSC or other calorimetric measurements to accompany the vapor pressure measurements. Levoglucosan exhibits a solid phase transition that significantly affects its measured sublimation pressures.

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