Carbohydrate Research, 41 (1975) 351–354

Note

Solid-state transition and thermodynamic properties of crystalline thiolevoglucosan

FRED SHAFIZADEH, RONALD A SUSOTT, AND CRAIG R MCINTYRE
Wood Chemistry Laboratory, Department of Chemistry and School of Forestry, University of Montana, Missoula, Montana 59801 (*U S A*)

(Received December 26th, 1974, accepted for publication, January 16th, 1974)

Physical changes that precede pyrolytic reactions[1], particularly the solid-state transition of 1,6-anhydro-β-D-glucopyranose (levoglucosan) and its stereoisomers to a plastic, crystalline form, have been reported in several communications from this laboratory[2–5] Compounds that show the plastic-phase transition are characterized by a low entropy of fusion (<21 J mol^{-1} deg^{-1}) preceded by a major change of entropy during the first-order transition Wide-line, n m r studies of levoglucosan showed that the transition results in a randomization of the molecular orientation, whereas the crystal coherence is maintained until melting occurs at a higher temperature[5]. At the transition temperature, some of the hydrogen bonds involved in the polycrystalline structure break, allowing the individual molecules the freedom to reorient about their center of gravity and to show the self-diffusion phenomenon[4,5] The transition affects the heat capacity, hardness, X-ray diffraction, vapor pressure, and infrared (i r.) spectrum of the material[4].

Only 1,6-anhydro sugars have shown a plastic-crystal phase, because of their globular shape, which is required for molecular reorientations without serious disruption of the crystalline lattice[6] The same type of transition has now been observed in an analog of levoglucosan, namely, 1,6-anhydro-1(or 6)-thio-β-D-glucopyranose (thiolevoglucosan), supporting this conclusion

A comparison of the differential thermal analysis (d t a) curves of levoglucosan and thiolevoglucosan is shown in Fig 1 The thiolevoglucosan curve, having a major endotherm at 89–99° followed by a weaker, melting endotherm at 179–182°, closely resembles the curve for levoglucosan, which shows a strong transition at 111–120° as the latter is transformed into a plastic, crystalline phase, and an endotherm due to melting at 181–184°

The temperature (*T*), enthalpies (ΔH), and entropies (ΔS) obtained from differential scanning calorimetry (d s c.) for the transition (*t*) and fusion (*f*) of the two compounds are given in Table I The heat capacity of thiolevoglucosan was also measured, before and after the transition, in the same way. The results shown

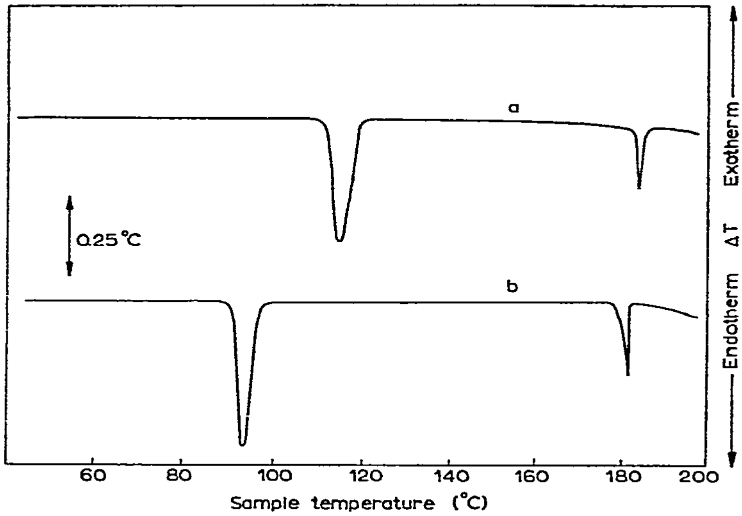

Fig 1 D t a curves for levoglucosan (a) and thiolevoglucosan (b)

TABLE I

TRANSITIONS OF THIOLEVOGLUCOSAN AND LEVOGLUCOSAN

Compound	T_t (*K*)	ΔH_t (*kJ mol*$^{-1}$)	ΔS_t (*J mol*$^{-1}$ *deg*$^{-1}$)	T_f (*K*)	ΔH_f (*kJ mol*$^{-1}$)	ΔS_f (*J mol*$^{-1}$ *deg.*$^{-1}$)
Thiolevoglucosan	366	19 8	54 1	454	2 9	6 3
Levoglucosan[4]	385	25 0	65 1	454	3 3	7 5

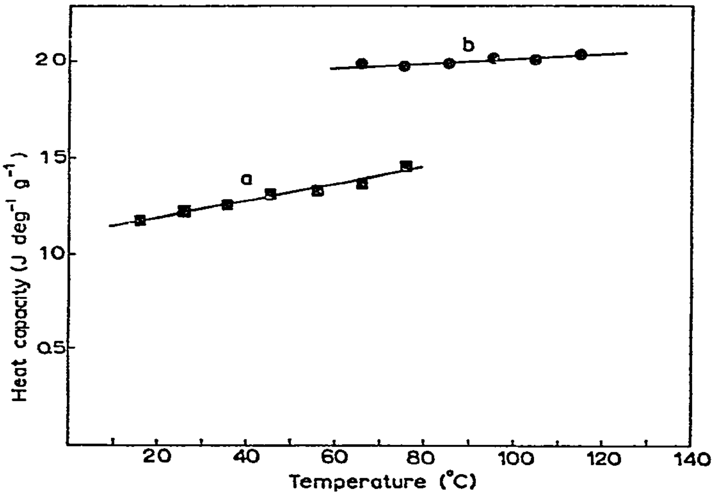

Fig 2 Heat capacity of thiolevoglucosan (a, Before the plastic-crystal transition, b, after the plastic-crystal transition)

in Fig. 2 indicate an increase of 0.54 J.deg^{-1} g^{-1} in the heat capacity of thiolevoglucosan after the transition. This change is similar to those reported for levoglucosan and other anhydro sugars[4]. However, the enthalpy and entropy of transition are considerably lower for the sulfur compound.

The lower values could be explained by differences in the crystal structures of the analogs. As the structure of levoglucosan contains molecules linked by chains of hydrogen bonds, with the anhydro oxygen-atom hydrogen-bonded to the 4-hydroxyl group[7], the substitution of sulfur for the anhydro oxygen-atom could cause a change in the bonding. The breakage of hydrogen bonds should thus be much easier in the thio derivative than in levoglucosan, as the hydrogen-bond energy is expected to be ~5 kJ mol^{-1} less for sulfur in this situation[8]. This value is in agreement with the experimental results given in Table I, showing that transition of the thio compound occurs at a temperature 19° lower, and is accompanied by 5.2 kJ mol^{-1} less change in the enthalpy. In view of these considerations, the close agreement of

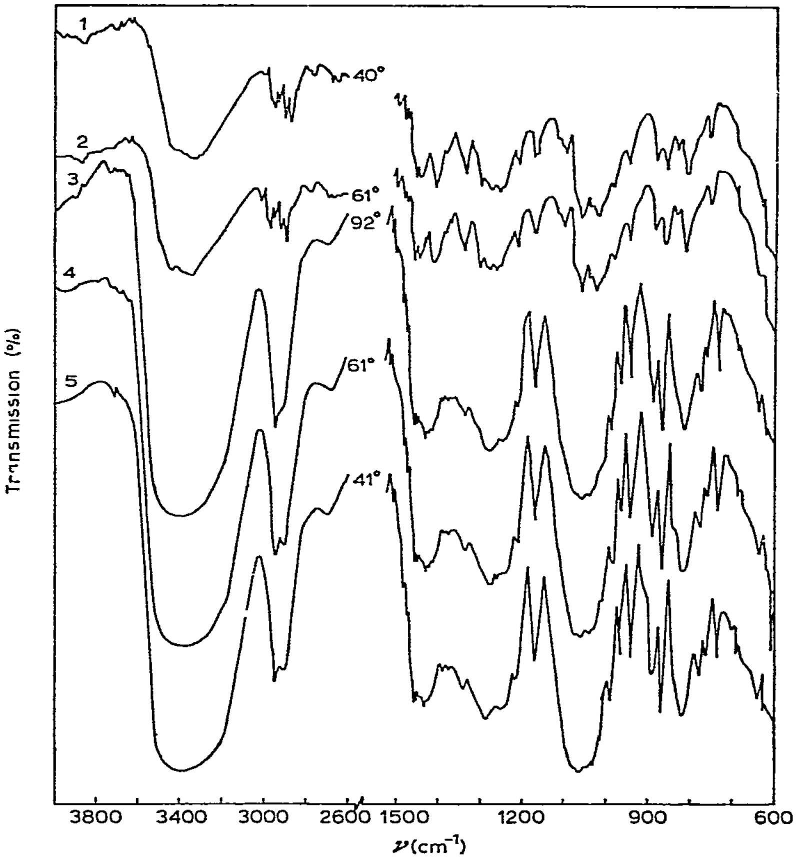

Fig. 3 The changes in the i.r. spectrum of thiolevoglucosan over the range 40–92° and the reverse

the temperatures and entropies of fusion for the two compounds suggests that the structure of their plastic-crystal phase should be very similar

The changes in the i r. spectrum of thiolevoglucosan with temperature are shown in Fig 3 Spectrum 2, recorded at 61°, does not significantly differ from the initial spectrum at room temperature Further heating to 92° (spectrum 3) produces noticeable changes in several regions of the spectrum The bands in the region of 3400 cm^{-1} become stronger and less differentiated, and shift slightly toward higher frequency The same shift also appears for the bands in the region near 2900 cm^{-1}. Cooling of the sample does not necessarily reverse the spectral changes, as shown in spectra 4 and 5 These variations are similar to those reported earlier for levoglucosan[4], and are indicative of subtle, crystalline changes

EXPERIMENTAL

Sample preparation — Thiolevoglucosan was prepared by the method of Akagi and co-workers[9].

Thermal analysis — The d t a data (see Fig 1) were obtained with a DuPont 990 Thermal Analyzer equipped with a d s c cell Samples (~1 mg) were heated under nitrogen at the rate of 15° min^{-1} in a small, aluminum pan The calorimetric data were obtained with a Perkin–Elmer DSC-1B instrument for 10-mg samples heated in sealed pans at the rate of 10° min^{-1}

I r spectra — The i r spectra were recorded with a Beckman IR-33 instrument Each sample was slurried in the minimal volume of ether, and deposited as a thin film on the surface of a NaCl plate Microscopic examination showed that the samples retained their crystallinity. This method was adopted to avoid possible changes that might be caused by the heat generated by the grinding and pressure involved in making KBr pellets

ACKNOWLEDGMENT

The authors thank the National Science Foundation for supporting this work under the RANN (Research Applied to National Needs) Program, Grant No. GI-43096

REFERENCES

1 F Shafizadeh and R A Susott, *J Org Chem*, 38 (1973) 3710–3715

2 F Shafizadeh, G D McGinnis, C W Philpot, and R A Susott, *Carbohyd Res*, 13 (1970) 184–186

3 F Shafizadeh, C W Philpot, and N Ostojic, *Carbohyd Res*, 16 (1971) 279–287

4 F Shafizadeh, G D McGinnis, R A Susott, and C W Philpot, *Carbohyd Res*, 15 (1970) 165–178

5 G W Smith and F Shafizadeh, *J Chem Soc*, *B*, (1971) 908–911

6 L A K Staveley, *Ann Rev Phys Chem*, 13 (1962) 351–368

7 Y J Park, H S Kim, and G A Jeffrey, *Acta Crystallogr*, B27 (1971) 220–227

8 I V Zuika and Yu A Benkovsku, *Russ Chem Rev* (*Engl Transl*), 42 (1973) 22–36.

9 M Akagi, S Tejima, and M Haga, *Chem Pharm Bull* (Tokyo), 11 (1963) 58–61