Thermochimica Acta, 9 (1974) 255–259

THERMAL ANALYSIS OF ELEMENTAL SULPHUR

B. R. CURRELL AND A. J. WILLIAMS
The Polytechnic of North London, Holloway, London, N7 8DB (England)
(Received 3 December 1973)

ABSTRACT

Differential scanning calorimetry has been applied to a study of elemental sulphur. Thermal curves have been interpreted on the basis of allotropic conversions and melting points. A method has been developed for the quantitative estimation of S_α and S_β.

INTRODUCTION

In recent years the fall in the price of elemental sulphur has made it economically attractive to consider its use as a construction material. Various applications have been proposed, e.g., road striping, sulphur/aggregate concretes and foams. In many of the proposed applications elemental sulphur embrittlement due to crystallization is one of the main factors inhibiting future development. Very little fundamental information is available on the rates of crystallization and allotropic conversions in elemental sulphur and also about the methods of inhibiting these processes. The objective of this work was to develop, using differential scanning calorimetry (DSC), methods for the quantitative determination of S_α and S_β in samples containing sulphur. These methods are to be used later for the study of the rates of crystallization of sulphur materials.

The only form of sulphur thermodynamically stable at normal temperatures is the orthorhombic (S_α); other main allotropes are monoclinic (S_β) and polymeric sulphur (S_ω). S_α and S_β consist of S_8 rings, S_ω of long chains up to 10^6 atoms long. S_λ refers to the sulphur melt below 159°C (the floor temperature of S_ω) which consists mainly of S_8 molecules, while S_μ refers to the equilibrium mixture of S_ω and free S_8 molecules which is obtained from 159°C.

DISCUSSION AND RESULTS

The differential thermal analysis (DTA) of flowers of sulphur has been investigated by Miller[1], endotherms at 111, 116, 122 and 173°C were reported. These were assigned to melting point depression of monoclinic (111°C), fusion of orthorhombic

(S_λ) (122°C) and polymerization of the monomer (173°C), while the peak at 116°C was thought to be "a form of melting point depression of S_α". A sample of sulphur rapidly quenched from 200°C to liquid nitrogen temperature (−196°C) was reported to have the following assigned endotherms: 82°C, the T_g of polymeric sulphur; 108°C, fusion of S_β; 118°C, fusion of S_λ; and 173°C, polymerization. No information was given as to the composition of the flowers or quenched sulphur in terms of monomer and polymer or any indication that the transition, $S_\alpha \rightarrow S_\beta$, can be observed by DTA. The thermal analysis of sulphur has now been examined in greater detail; results and conclusions differing in important respects to those of Miller have been reached.

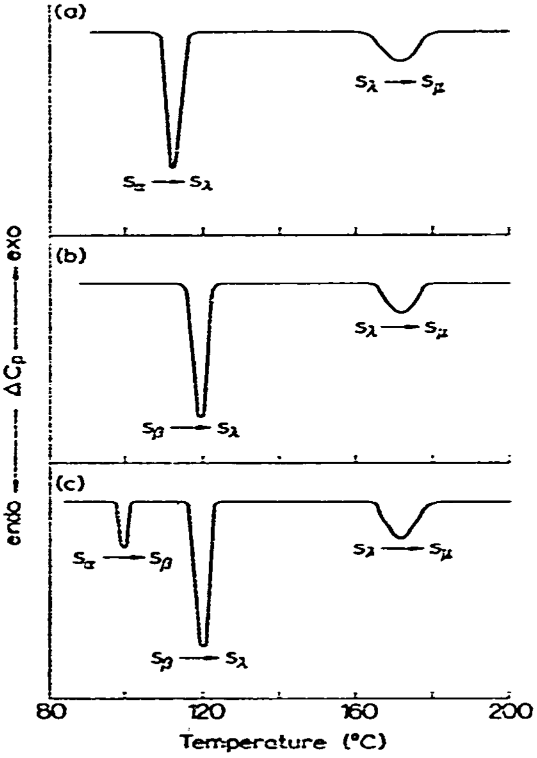

Fig. 1. DTA curves of; (a) single crystal of 6N sulphur (S_α); (b) pure S_β; and (c) microcrystalline S_α.

A single crystal of 6N sulphur, i.e., orthorhombic S_α, gives (Fig. 1a) endotherms at 112°C (melting of S_α) and 173°C (formation of polymeric sulphur). No evidence of the enantiotropic transition, $S_\alpha \rightarrow S_\beta$, was observed for single crystals even when heated under isothermal conditions for 1 h at 100°C. Presumably, the presence of a seed is essential for the $S_\alpha \rightarrow S_\beta$ conversion to occur, the endotherm for it (at 100°) is seen in the curve (Fig. 1c) of microcrystalline S_α.

Monoclinic S_β is obtained in a metastable condition by rapidly cooling a sample of 6N sulphur to ambient temperature from the melt at 120°C. This shows

(Fig. 1b) endotherms at 119 °C (S_β melting) and at ca. 170 °C due to formation of polymeric sulphur. Note that this polymerisation endotherm is obtained whatever the allotropic pedigree of the specimen.

On storage at ambient temperature for a number of hours, S_β reverts to the thermodynamically stable form S_α. Figure 1c is the curve of microcrystalline S_α formed by allowing S_β to stand at ambient temperatures. An endotherm at 100 °C is obtained and is assigned to the phase change, $S_\alpha \rightarrow S_\beta$; the endotherm at 119 °C being due to the fusion of S_β.

The assignment of peaks due to melting was confirmed in each case by visual observation. The assignment of the $S_\alpha \rightarrow S_\beta$ endotherm depends on: (a) visual observation that it does not involve melting, and (b) the fact that rapid cooling of a melt of the product gives metastable S_β. In addition, assignment of all peaks, both fusion and allotropic transitions, is confirmed by measurement of the relevant ΔH values from the peak areas; these were found to agree with those available in the literature[2,3].

(i) fusion of S_α; $\Delta H = 66.04\ \mathrm{J\ g^{-1}}$;

(ii) fusion of S_β; $\Delta H = 53.42\ \mathrm{J\ g^{-1}}$;

(iii) enantiotropic transition, $S_\alpha \rightarrow S_\beta$; $\Delta H = 12.54\ \mathrm{J\ g^{-1}}$.

The curves for the flowers and CS_2 insoluble sulphur are given in Fig. 2. Three endotherms were obtained (Fig. 2a) for flowers of sulphur, attributed to:

(i) $S_\alpha \rightarrow S_\beta$ phase change (100 °C);

(ii) S_ω (polymer) melting (104 °C);

(iii) S_β melting (108 °C).

In all of the samples of flowers of sulphur analysed, up to 30% were found to be insoluble in carbon disulphide. This insoluble portion was shown by laser Raman spectroscopy to be polymeric sulphur. Evidence that S_ω is melting (endotherm at 104 °C) and not reverting to S_α is afforded from the curves of pure S_ω polymer (Fig. 2b). This curve shows an endotherm at 115 °C, visual observation of which indicated the sample was melting to give a viscous product, as compared to S_α and S_β, the fusion products of which are not viscous. This evidence does not exclude the possibility that depolymerization and melting are occurring simultaneously. However, the absence of an endotherm, on further heating to 170 °C, suggests that depolymerization to S_8 does not occur readily. Hence, contrary to Miller's report, the presence of polymeric sulphur in flowers of sulphur and the phase change, $S_\alpha \rightarrow S_\beta$, are observable by thermal analysis. In addition, the fusion of S_α as observed by DSC is now reported to occur at a lower temperature than the fusion of S_β. Table 1 summarizes the curve data of various allotropic forms of sulphur.

Quantitative allotropic determination of elemental sulphur

The area under the peak representing the transition, $S_\alpha \rightarrow S_\beta$, may be used to

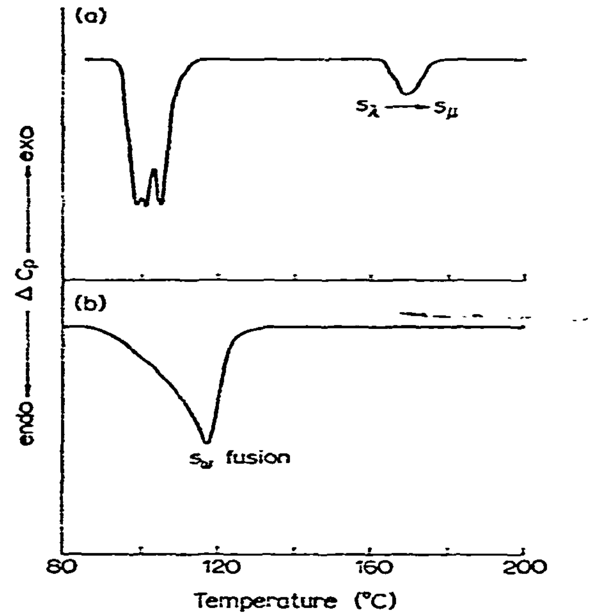

Fig. 2. DSC curves of; (a) flowers of sulphur; and (b) polymeric sulphur S_ω.

TABLE I

TRANSITION TEMPERATURE OF VARIOUS ALLOTROPES OF SULPHUR, AS INDICATED BY DSC PEAK TEMPERATURES

Allotrope	*Transition*	*Temperature (°C)*
S_π	$S_\pi \rightarrow S_\lambda$	112
S_β	$S_\beta \rightarrow S_\lambda$	119
S_ω	$S_\omega \rightarrow S_{\omega 1}$	115
S_α	$S_\alpha \rightarrow S_\beta$	100
S_λ	$S_\lambda \rightarrow S_\mu$	170
S_λ liquid S_8		
$S_{\omega 1}$ liquid polymer		
S_μ mixture monomer and polymer		

give the weight of S_α present in the sample. This area is proportional to both the weight of S_α and energy of transition ($\Delta H_t = 12.54$ J g^{-1}). Similarly, the S_β fusion peak is proportional to the weight, $S_\alpha + S_\beta$, present in the original sample and the energy of transition ($\Delta H_f = 53.42$ J g^{-1}). Note that any S_α present in the original sample is converted to S_β before fusion.

It is not possible to determine the allotropic nature of flowers of sulphur or sulphur which has been rapidly cooled from the melt above 159 °C. These samples contain both monomer and polymer and because of the broad poorly resolved endotherm obtained for monomeric sulphur in the presence of polymer, it is not possible to integrate the area for each fraction, i.e., monomer or polymer.

Ten determinations of crystalline sulphur ($S_\alpha + S_\beta$) were carried out on a mixture of sulphur and polymeric polysulphides. An average value of 64.3% with a standard deviation of 2.15 was obtained.

EXPERIMENTAL

A Perkin-Elmer DSC-1B calorimeter was used for all measurements. For the indium standard a scan rate of 4°C min^{-1}, sensitivity 8 mcal, and chart speed of 20 mm min^{-1} were used. For the sulphur samples, a scan rate 4°C min^{-1}, sensitivity 4 mcal, and chart speed 20 mm min^{-1} were employed. Sample sizes were 15–20 mg. Static air atmosphere.

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial assistance from The Sulphur Institute.

REFERENCES

1 G. W. Miller, *J. Appl. Polym. Sci.*, 15 (1971) 1985.
2 M. Barnes, in B. Meyer (ed.), *Elemental Sulphur*, Interscience, New York, 1965, p. 86.
3 E. D. West, *J. Amer. Chem. Soc.*, 81 (1959) 29.