THERMAL BEHAVIOUR OF THE MONOCLINIC ALLOTROPES γ-SULFUR AND α-SELENIUM AND SOME STRUCTURALLY RELATED SULFUR–SELENIUM COMPOUNDS

R. LAITINEN and L. NIINISTÖ

Department of Chemistry, Helsinki University of Technology, Otaniemi, SF-02150 Espoo 15, Finland

The thermal behaviour of γ-sulfur, monoclinic α-Se, S_6Se_2, S_5Se_3, S_4Se_4 and S_3Se_5 has been studied by hot-stage microscopy and differential scanning calorimetry. X-ray diffraction results show that S_6Se_2 and S_5Se_3 are isostructural with S_γ, but S_4Se_4 and S_3Se_5 are isostructural with monoclinic α-Se. The melting of S_γ is accompanied by rapid crystallization of S_β, which often occurs almost simultaneously with melting. The melting of S_6Se_2, S_5Se_3, S_4Se_4 and S_3Se_5 is irreversible as the compounds decompose on melting. For monoclinic α-Se no phase transformation to monoclinic β-Se was observed at 110—120°, but it changes to hexagonal α-Se when the temperature is over 120°.

The existence of several crystalline modifications of cyclo-octasulfur has been reported [1]. Of these, the only thermodynamically-stable polymorphs are ortho-rhombic α-sulfur, stable at NTP, and monoclinic β-sulfur, stable only in the narrow temperature range between 95.4° and its melting point [2]. The stability ranges and other thermal properties of α- and β-sulfur have also been established by modern thermoanalytical methods [3, 4].

The third well-known polymorph of cyclo-octasulfur is monoclinic γ-sulfur, which has recently been structurally characterized by X-ray diffraction methods [5]. Although γ-sulfur itself is not thermodynamically stable relative to the α- and β-forms, it has been reported that this structure type is found in sulfur crystals containing approximately 10−45% selenium [6−9]. When the selenium content increases to 50% and above, the prevailing structure is that of monoclinic α-selenium. The nature of these sulfur-selenium crystals was not realized, however, until Hawes [10] showed that definite ring compounds of type $S_{8-n}Se_n$ may be crystallized from melts and solutions containing both these chalcogens.

The present investigation was undertaken in order to detect, by the DSC method, possible polymorphic transformations and other thermally induced changes occurring in γ-sulfur, in monoclinic α-selenium, and in some of the structurally related compounds of the composition $S_{8-n}Se_n$. Obviously, due to its instability and difficulties involved in preparing larger quantities of γ-sulfur, no such study of the pure phase has been done. It also seems that the thermal behaviour of monoclinic α-selenium has not been studied by modern instrumental methods, in spite of the controversy regarding the existence of a phase transition to the

7*

β-form which is reported to occur at $110-120°$ [11], but which was not supported by X-ray study [12]. For the sulfur–selenium compounds, information on the thermal behaviour is even scarcer in the literature, where only the melting points are given for some of the compounds.

Experimental

Monoclinic γ-sulfur was obtained in the form of light yellow needles by de-composition of ammonium polysulfide in ethanolic solution [6]. S_6Se_2, S_5Se_3, S_4Se_4 and S_3Se_5 were prepared by crystallization from melts consisting of α-sulfur and hexagonal selenium in appropriate molar ratios. The melting was performed in a sealed ampoule under reduced pressure at $500°$. After heating for 1 hr the ampoules were rapidly quenched to room temperature and the compounds were extracted with benzene. By recrystallization from an ether – carbon disul-fide mixture $(3/1; V/V)$ at $-20°$ the compounds were obtained as orange-red needles. Monoclinic α-selenium was crystallized by slow evaporation of a carbon disulfide solution containing selenium.

α-Sulfur used in syntheses was purified by the method of Bacon and Fanelli [13], followed by vacuum distillation and prolonged heating at $90°$ to destroy the polymeric material. Metallic selenium (BDH) and the solvents (Merck) were analytical reagent grade chemicals. High-purity selenium (99.98%, Koch-Light) was used in some experiments in order to ascertain the results obtained.

γ-Sulfur and the sulfur–selenium compounds were characterized by mass-spectrometric and X-ray diffraction techniques. The mass-spectra of S_6Se_2, S_5Se_3, S_4Se_4 and S_3Se_5 were obtained in a Perkin-Elmer 270 B spectrometer at 70 eV. The X-ray powder diffraction method was used to identify the compounds as single phases. The accurate unit cell parameters for the single crystals were determined by a least-squares refinement of the angular settings of $10-20$ reflec-tions measured on a Syntex P2$_1$ automatic diffractometer.

The melting points of the compounds were determined from single crystals by hot-stage microscopy. For comparison, melting point values were also deter-mined from bulk samples with the aid of an automatic Mettler FP1 instrument, using α-sulfur as standard, and heating at the rate of $2°/min$.

DSC analyses were performed with a Perkin-Elmer instrument type DSC-1B. Fast heating up to $90°$ was employed; thereafter the heating rate was $2°/min$. High-purity indium (99.999%) was used for calibration, and alumina as reference.

Results and discussion

The X-ray diffraction study of the sulfur–selenium compounds S_6S_2 and S_5Se_3, where $n_S > n_{Se}$, confirmed their isostructurality with γ-sulfur. It would be reason-able to assume that S_7Se also fits into this series; however, it was not included

in the present study, due to its high instability [14]. When $n_S \leq n_{Se}$, i.e. in S_4Se_4 and S_3Se_5, the sulfur–selenium compounds are isostructural with monoclinic α-selenium (cf. Table 1).

The melting points of the phases studied are given in Table 2. No melting point value could be measured for γ-sulfur in the form of bulk samples however, as it always transformed rapidly into stable forms; this was obviously due to traces of other modifications present as seeds in the original samples.

Thus, DSC runs on γ-sulfur were performed on single crystals only, and it was noticed that the shapes and positions of the DSC peaks varied somewhat on

Table 1

Unit cell parameters of the phases studied. Standard deviations are given in parentheses

Phase	a Å	b Å	c Å	β deg.	V Å³	Space group	Ref.
S_γ	8.442(30)	13.025(10)	9.356(50)	124.98(30)	843.0	$P2/c$	[6]
S_6Se_2[a]	8.569(6)	13.303(6)	9.352(5)	124.32(3)	880.5	$P2/c$	This work
S_5Se_3[b]	8.567(3)	13.333(4)	9.366(2)	124.26(2)	884.2	$P2/c$	This work
S_4Se_4[a]	8.750(5)	9.139(5)	11.360(7)	90.97(5)	908.3	$P2_1/n$	This work
S_3Se_5[b]	8.855(7)	9.131(7)	11.460(8)	90.84(6)	926.5	$P2_1/n$	This work
Mon. α-S[c]	9.054(3)	9.083(5)	11.601(6)	90.81(5)	954.0	$P2_1/n$	[15]

[a] 25°, [b] 21°, [c] 26°

Table 2

Melting points and DSC phase transitions

Phase	Melting points		DSC phase transitions			
	Single crystals °C	Bulk material, °C	Transition temperature[a]		Heat of transition,[b] kJ/mole	Transition
			Single crystals, °C	Bulk material, °C		
S_γ	108—110	—	109—112	100—105	(2.0)	Melting of S_γ
S_β	119—120	119.5	—	119—124	14.3$\pm$1.0	Melting of S_β
S_6Se_2	121—122	119.2	114—125	107—117	10.2$\pm$0.8	Melting of S_6Se_2
S_5Se_3	119—120	116.3	115—123	105—113	15.2$\pm$0.9	Melting of S_5Se_3
S_4Se_4	112—113	108.1	107—124	96—108	12.6$\pm$0.9	Melting of S_4Se_4
S_3Se_5	108—109	106.5	100—110	105—114	19.2$\pm$1.2	Melting of S_3Se_5
Mon. α-Se	—	—	—	121—157	−14.1$\pm$0.1	Mon. α-Se →Hex. α-Se
Hex. α-Se	217—218	—	—	217—227	44.9$\pm$0.8	Melting of Hex. α-Se

[a] Peak width according to recommendations of ICTA [16]
[b] For S the values obtained are from single measurement given in Fig. 1; the other values are averages from four to six measurements

subsequent runs. All curves showed an endothermic peak at $109-112°$, which is mainly due to melting of S_γ and also a peak at $116-117°$, caused by melting of S_β. The crystallization of S_β from the melt was not generally clearly visible in the curves between these peaks. Under a microscope it was observed that the trans-formation into solid S_β starts immediately after the melting of S_γ, and thus the two processes in the DSC curve probably overlap; the irregular shape of the first DSC peak seems to support this. In one case, however, the two peaks were completely resolved (cf. Fig. 1). From this curve it can be calculated that the heat of melting of S_γ is 2.0 kJ/mole; the small sample size, however, renders this value rather unreliable.

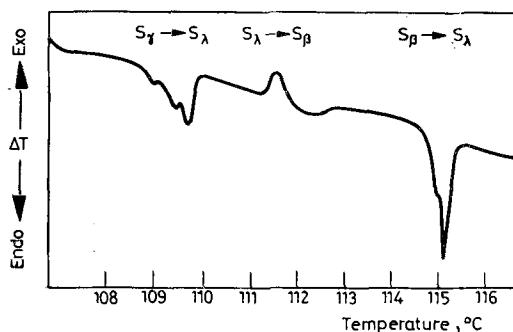Fig. 1. DSC curve of S_γ single crystal. The heating rate is $2°$/min and the sample weight is 0.5 mg
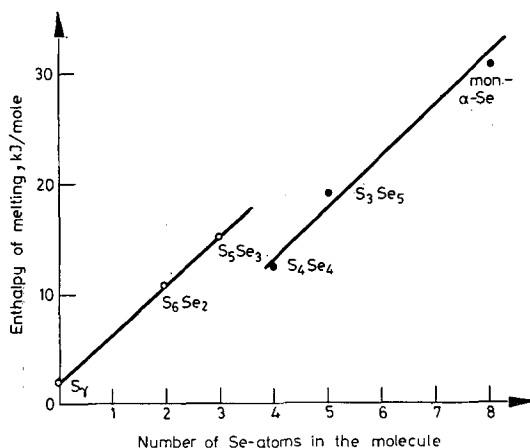

Fig. 2. Enthalpies of melting processes for $S_{8-n}Se_n$ as a function of the number of selenium atoms in the molecule. The enthalpy of melting of monoclinic α-Se has been calculated from the melting of hex. α-Se and from the transition mon. α-Se $\rightarrow$ hex. α-Se. Notation: $\circ$ S_γ-structure type, $\bullet$ mon. α-Se-structure type

For monoclinic α-selenium, the peaks occurring in the DSC runs were due to transformation into the hexagonal form above 120° and to melting of the hexagonal phase around 220° (cf. Table 2). No evidence was found for the phase transition to the β-form reported by Kudryavtsev [11], which is in agreement with the X-ray study by Abdullaev et al. [12].

Likewise, for S_6Se_2, S_5Se_3, S_4Se_4 and S_3Se_5 the curves of neither bulk samples nor single crystals revealed polymorphic transformations in the temperature range from room temperature up to the melting points.

It is interesting to note that the enthalpies of the melting processes vary almost linearly with the selenium content within each structure type (cf. Table 2 and Fig. 2). When comparing the values it should be noticed that decomposition of sulfur–selenium compounds starts upon melting. Thus, the change is not reversible and the enthalpy value obtained may not be due to melting alone.

*

References

1. B. MEYER, Chem. Rev., 76 (1976) 367.
2. E. O. WEST, J. Am. Chem. Soc., 81 (1959) 29.
3. G. W. MILLER, J. Appl. Polymer Sci., 15 (1971) 1985.
4. B. P. CURREL and A. J. WILLIAMS, Thermochim. Acta, 9 (1974) 255.
5. Y. WATANABE, Acta Cryst., Sect. B. 30 (1974) 1396.
6. W. MUTHMANN, Z. Kryst., 17 (1890) 336.
7. F. HALLA, E. MEHL and F. X. BOSCH, Z. Phys. Chem., 12B (1931) 377.
8. Y. M. DE HAAN and M. P. VISSER, Physica, 26 (1960) 127.
9. J. E. FERGUSSON, G. M., PRATT, G. A. RODLEY and C. J. WILKINS, J. Inorg. Nucl. Chem., 24 (1962) 157.
10. L. L. HAWES, Nature, 198 (1963) 1267.
11. A. A. KUDRYAVTSEV, The Chemistry & Technology of Selenium and Tellurium (transl. E. M. ELKIN), Collet's (Publishers) Ltd, London, 1974, p. 22.
12. G. B. ABDULLAEV, Y. G. ASADOV and K. P. MAMEDOV, The Physics of Selenium and Tellurium, ed. W. C. COOPER, Pergamon Press Inc., Oxford, 1969, p. 179.
13. R. F. BACON and R. FANELLI, Ind. Eng. Chem., 34 (1942) 1043.
14. R. COOPER and J. V. CULKA, J. Inorg. Nucl. Chem., 32 (1970) 1857.
15. P. CHERIN and P. UNGER, Acta Cryst., Sect. B, 28 (1972) 313.
16. R. C. MACKENZIE, Thermal Analysis, ed. H. G. WIEDEMANN, Birkhäuser Verlag, Basel and Stuttgart, 1972, Vol. 1, p. 609.

RÉSUMÉ — On a étudié le comportement thermique du soufre γ, du sélénium α monoclinique, de S_6Se_2, S_5Se_3, S_4Se_4 et de S_3Se_5 par microscopie avec platine chauffante et par analyse calorimétrique différentielle (DSC). Les résultats de la diffraction des rayons X montrent que S_6Se_2 et S_5Se_3 sont isostructuraux avec S_γ, tandis que S_4Se_4 et S_3Se_5 sont isostructuraux avec Se α monoclinique. La fusion de S_γ s'accompagne d'une cristallisation rapide de S_β qui a souvent lieu presque simultanément avec la fusion. La fusion de S_6Se_2, S_5Se_3, S_4Se_4 et S_3Se_5 est irréversible car ces composés se décomposent lors de la fusion. On n'a pas observé la transformation de phase $Se_\alpha \rightarrow Se_\beta$ entre 100 et 120° mais la transformation en Se_α hexagonal au-dessus de 120°.

ZUSAMMENFASSUNG — Das thermische Verhalten von γ-Schwefel, monoklinem α-Se, S_6Se_2, S_5Se_3, S_4Se_4 und S_3Se_5 wurde mittels Heißphasenmikroskopie und Differential Scanning-Kalorimetrie untersucht. Röntgendiffraktionsergebnisse zeigen, daß S_6Se_2 und S_5Se_3 mit S_γ isostrukturell sind, doch sind S_4Se_4 und S_3Se_5 mit monoklinem α-Se isostrukturell. Das Schmelzen von S_γ wird von der schnellen Kristallisation von S_β begleitet, welche oft beinahe simultan mit dem Schmelzen verläuft. Das Schmelzen von S_6Se_2, S_5Se_3, S_4Se_4 und S_3Se_5 ist irreversibel, da die Verbindungen während des Schmelzens zersetzt werden. Bei monoklinem α-Se wurde zwischen 110 und 120° keine Phasentransformation zu monoklinem β-Se beobachtet, doch wird ersteres bei Temperaturen über 120° in hexagonales α-Se umgewandelt.

Резюме—Изучено термическое поведение γ-серы, моноклинных α-Se, S_6Se_2, S_5Se_3, S_4Se_4, S_3Se_5 с помощью микроскопии в горячем состоянии и дифференциальной сканирующей калориметрии. Результаты рентгеновского дифракционного анализа показали, что S_6Se_2 и S_5Se_3 изоструктурны с $S\gamma$, в то время как S_4Se_4 и S_3Se_5 изоструктурны с моноклинным α-Se. Плавление $S\gamma$ сопровождается быстрой кристаллизацией S_β, которая часто происходит одновременно с плавлением. Плавление S_6Se_2, S_5Se_3 S_4Se_4 и S_3Se_5 является необратимым, поскольку они при этом разлагаются. При 110—120; ие неблюдалось фазового превращения α-Se до моноклинного β-Se, но при температуре выше 120° происходит переход до гексагонального α-Se.