

## Equilibria between Sulfur Rings in Carbon Disulfide Solution at Elevated Temperatures

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Ralf Steudel\* and Reinhard Strauss

Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D-1000 Berlin 12

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Cyclooctasulfur,  $S_8$ , dissolved in  $CS_2$  reacts at 130–155 °C in sealed ampoules to give  $S_6$  and  $S_7$  whose concentrations have been determined by HPLC. The half-time of the reaction is independent of the initial  $S_8$  concentration and decreases from 232 min at 130 °C to 64 min at 155 °C. After long reaction times equilibrium concentrations are observed which are in agreement with the law of mass action. From the temperature dependence of the equilibrium constants the following reaction enthalpies (at 130–155 °C) have been calculated:



On melting cyclooctasulfur ( $S_8$ ) is slowly transformed to an equilibrium mixture of cyclic  $S_n$  molecules of which those with  $n = 6 \dots 26$  have been definitely identified while the presence of even larger rings is likely; in addition the melt always contains polymeric sulfur which in contrast to the rings is insoluble in  $CS_2$  at 20 °C and whose concentration strongly depends on the temperature [2, 3]. We have now observed that  $S_8$ , dissolved in solvents like benzene, toluene, carbon disulfide or dichlorodisulfane ( $S_2Cl_2$ ), also yields other rings ( $S_6, S_7, S_9$ ) on heating. However, since in all cases excepting carbon disulfide by-products like organo-sulfur compounds and higher chlorosulfanes, respectively, are formed we investigated only the solutions in  $CS_2$  in some detail. For that purpose solutions of  $S_8$  in sealed glass ampoules were heated for a certain time ( $t$ ) to a constant temperature between 130 and 155 °C, quenched in ice-water and the content analyzed qualitatively and quantitatively by high-performance liquid chromatography (HPLC) [3]. The initial concentrations of  $S_8$  were varied between 0.154 and 0.429 mmol per gram of solution.

It was found that under these conditions  $S_8$  is transformed into a mixture of mainly  $S_8, S_7$  and  $S_6$ ; in addition small amounts of  $S_9$  could be detected. Larger rings or polymeric sulfur have never been observed and the solutions were always completely transparent both before and after quenching. It thus was possible to evaluate certain thermodynamic and kinetic data of the equilibria



by determination of the concentrations of  $S_6, S_7$  and  $S_8$  as a function of initial concentration, temperature and reaction time. For this purpose the dependence of the individual areas  $A$  under the chromatographic peaks on the concentrations  $c$  of  $S_6, S_7$  and  $S_8$ , respectively, had first to be determined. In each case 15 solutions of different concentration were measured; the calibration functions  $A = f(c)$  were found to be linear in all cases (correlation coefficients  $r = 1.000$ ; concentration regions 0.5–508  $\mu\text{g} \cdot \text{cm}^{-3}$ ).

Fig. 1 shows, as an example, how the concentration of  $S_8$  decreases and how those of  $S_6$  and  $S_7$  increase with time at 150 °C. The half-times ( $t_{1/2}$ ) of the concentrations of the three components were found to be identical and to increase from  $64 \pm 5$  min at 150 °C and 111 min at 140 °C to 232 min at 130 °C. Within the investigated region of 150 to 430  $\mu\text{mol}$  ( $S_8$ ) per gram solution the half-time is independent of the initial  $S_8$  concentration. The reaction is definitely of first order, and the Arrhenius activation energy has been determined as 95 kJ/mol.

After long reaction times  $t = 7 \cdot t_{1/2}$  the concentrations of  $S_6, S_7$  and  $S_8$  approach temperature dependent equilibrium values which are indicated by broken lines in Fig. 1 and listed in detail in Table I. At equilibrium the sulfur mixtures contain 91–94 mol-%  $S_8$ , 5–7%  $S_7$  and 1–2%  $S_6$ ; the concentration of  $S_9$  can be neglected within the limits of error. The measured values are in agreement with the law of mass action and the following equilibrium constants have been calculated:

	$K(1) = c_6/c_8^{3/4}$	$K(2) = c_7/c_8^{7/8}$
130 °C	0.064	0.108
140 °C	0.075	0.123
145 °C	0.083	0.132
150 °C	0.090	0.144
155 °C	0.097	0.157

From the temperature dependence of  $K(1)$  and  $K(2)$  the reaction enthalpies  $\Delta H^\circ(1) = 24 \pm 1$  and  $\Delta H^\circ(2) = 21 \pm 1$  kJ/mol (130–155 °C) have been obtained using the relationship  $d \ln K/d(1/T) = -\Delta H^\circ/R$  ( $R = 8.314 \text{ J/mol} \cdot \text{K}$ ). The values obtained are in good agreement with the vapor phase data [4] showing that the enthalpies of solution of the three molecules are of little influence. A more detailed kinetic analysis of the reaction  $S_8 \rightarrow S_7, S_6$  must await corresponding investigations of the reverse reactions  $S_7 \rightarrow S_8$  and  $S_6 \rightarrow S_8$  which are now under way.

The equilibria between sulfur rings in solvents can be related to the recently discovered equilibrium between  $S_6, S_7$  and  $S_8$  which is established in organic solvents at 20 °C within a few minutes [5]. Possible mechanisms for these reactions have been discussed elsewhere [3].

\* Reprint requests to Prof. Dr. R. Steudel.  
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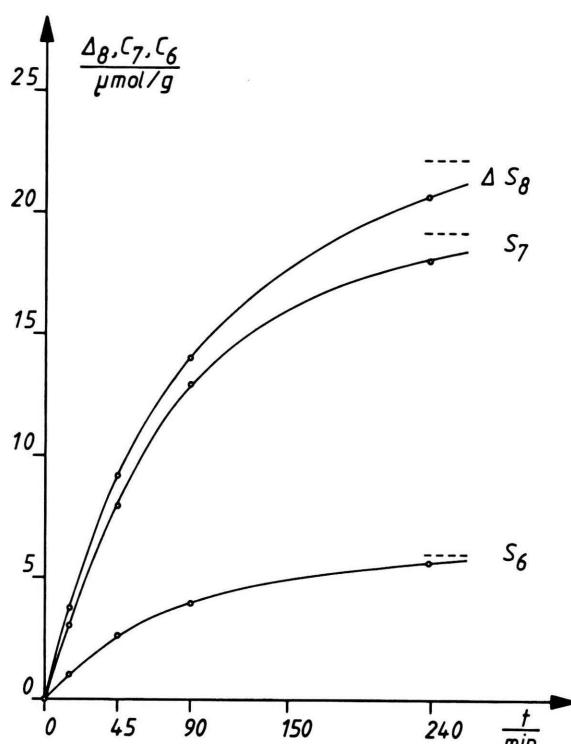


Fig. 1. Change of the concentrations of  $S_6$ ,  $S_7$  and  $S_8$  when  $S_8$  dissolved in  $CS_2$  is heated to  $150\text{ }^\circ\text{C}$ .  $\Delta S_8$  is the amount of  $S_8$  which has reacted to give  $S_6$ ,  $S_7$  and traces of  $S_9$ . The final equilibrium values are indicated by short broken lines.

## Experimental

Sublimed sulfur ( $S_8$ ) was recrystallized from  $CS_2$  p.a. which also was used for the chromatography without further purification. The glass ampoules (Duran) had a capacity of  $11\text{ cm}^3$  and were heated in an electronically controlled Haake liquid thermostat (model F3-S). The ampoules were sealed after repeated freezing and evacuation to remove all air.

The liquid chromatograph (Varian, model 5020) was equipped with a microprocessor control and connected to a UV detector (Waters, model 440) working at  $254\text{ nm}$  and a Varian data system (model CDS 111). Radial-Pak C 18 columns ( $10\text{ cm}$  length,  $8\text{ mm}$  inner diameter,  $10\text{ }\mu\text{m}$  particle size) from Waters were used (radially compressed by 140 to 170 bar in an RCM 100 module by Waters). The eluent was a methanol/cyclohexane mixture (90/10 v/v).

Table I. Equilibrium concentrations ( $c_n$ ) of  $S_6$ ,  $S_7$  and  $S_8$  in  $CS_2$  solution at different temperatures and initial  $S_8$  concentrations ( $c_0$ ).

T [°C]	$c_0$ [ $\mu\text{mol/g}$ ]	$n$	$c_n$ [ $\mu\text{mol/g}$ ]	mol-%
130	292	6	4.3	1.5
		7	14.7	5.0
		8	274	93.5
140	297	6	5.1	1.7
		7	16.9	5.6
		8	278	92.7
145	296	6	5.6	1.9
		7	18.0	6.0
		8	276	92.1
150	154	6	3.7	2.4
		7	10.8	7.0
		8	139	90.6
150	290	6	6.0	2.0
		7	19.2	6.5
		8	268	91.4
150	429	6	7.8	1.8
		7	26.4	6.1
		8	400	92.1
155	295	6	6.5	2.2
		7	21.3	7.1
		8	273	90.8

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