# THE EFFECT OF S6 AND S7 ON THE POLYMERIZATION OF LIQUID SULFUR[1]

Ralf Steudel[a]

[a] Institut für Anorganische und Analytische Chemie, Technische Universität, Berlin 12, F. R. Germany

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# THE EFFECT OF S$_6$ AND S$_7$ ON THE POLYMERIZATION OF LIQUID SULFUR[1]

## RALF STEUDEL

*Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Sekr. C2, D-1000 Berlin 12, F. R. Germany*

It is shown that the partial polymerization of liquid sulfur which occurs on heating to temperatures above 159°C is initiated by free radicals originating from the homolytic dissociation of the cyclic molecules S$_6$ and S$_7$ whose first dissociation enthalpies are calculated from thermodynamic data as 124 and 127 kJ/mol, respectively.

Liquid sulfur, obtained by melting of S$_8$, is the only chemical system which partly polymerizes on heating while subsequent cooling results in a depolymerization as a consequence of the positive value of the enthalpy of polymerization.[2] Since certain amounts of polymeric sulfur (insoluble in CS$_2$ and termed S$_\mu$) are present at all temperatures, the melt is often considered to be a mixture of just S$_\lambda$ (S$_8$ molecules) and S$_\mu$. However, it has been known for a long time that the equilibrium sulfur melt at all temperatures contains several percent of what has been called $\pi$-sulfur (S$_\pi$). Recently S$_\pi$ was shown to be a mixture of the cyclic molecules S$_7$, S$_6$, and S$_x$ (with $x > 8$, up to at least 26) of which S$_7$ has the highest concentration followed by S$_6$.[3] Since the structures and other properties of many of these species are known[4] and since their reactivity is much higher than that of S$_8$[5] their influence on the chemical and physical properties of liquid sulfur should be taken into account. The enthalpies of the reactions

$$S_8 \rightleftharpoons \tfrac{8}{7}S_7 \qquad\qquad (1)$$

$$S_8 \rightleftharpoons \tfrac{4}{3}S_6 \qquad\qquad (2)$$

have been determined in the vapor phase, in the melt and in CS$_2$ solution (see Table I); the most reliable values for condensed phases seem to be those for CS$_2$ solutions measured by HPLC at 130–155°C. These data, which reflect the bond angle and torsional strain of the smaller ring molecules, are important in connection with the formation of free radicals in liquid sulfur by homolytic S—S bond dissociation. Such radicals are believed to initiate the reversible polymerization of the melt at temperatures above 159°C.[11] The enthalpy of the radical formation reaction

$$-S-S- \rightleftharpoons -S\cdot + \cdot S- \qquad\qquad (3)$$
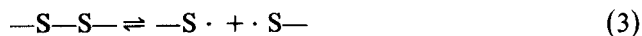
has been determined by e.s.r. spectroscopy as well as by static magnetic susceptibility measurements as $\Delta H(3) = 148 \pm 5$ kJ/mol (see Table II). So far, only S$_8$ and S$_\mu$ have been discussed in the literature as a source of the observed radicals but due to their endothermic nature S$_6$ and S$_7$ must dissociate more easily than both S$_8$ and S$_\mu$.

TABLE I

Enthalpy of formation of $S_7$ and $S_6$ from $S_8$ under different conditions (in kJ/mol ($S_8$))

| Phase | $\Delta H(1)$ | $\Delta H(2)$ | Temperature | Ref. |
|-------|-----------|-----------|-------------|------|
| vapor | 27 | 35 | 127°C | 6 |
| vapor | 28 ± 2 | 35 ± 2 | 239°C | 7 |
| vapor | 28 | 34 | 25°C | 8 |
| melt | 21 | 27 ± 3 | 115–160°C | 9 |
| $CS_2$ solution | 24 ± 1 | 32 ± 1 | 130–155°C | 10 |

TABLE II

Enthalpy $\Delta H(3)$ of radical formation in liquid sulfur as determined from the temperature dependence of the number of unpaired electrons in the regions indicated

| Technique | $\Delta H(3)$ in kJ/mol | Temperature (°C) | Ref. |
|-----------|---------------------|------------------|------|
| e.s.r. spectrosc. | 140 ± 20 | 240–368 | 12 |
| magnet. susceptibility | 145 | 150–580 | 13 |
| e.s.r. spectrosc. | 149 | 230–550 | 14 |
| magnet. susceptibility | 153 | 550–950 | 15 |

Let us assume that the measured dissociation energy represents the enthalpy of the reaction

$$S_8^R \rightleftharpoons S_8^C \qquad \text{R: ring, C: chain} \qquad (4)$$
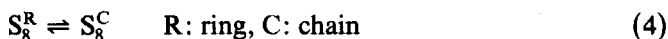
i.e. $\Delta H(4) = D_8 = 148$ kJ/mol. Since $S_8$ is the most stable cyclic sulfur molecule[6–10] it will have the highest bond dissociation energy; this results in the strongest temperature dependence of the homolytic dissociation and that is what has been measured in the experiments cited in Table II.

The enthalpy of formation of chain-like $S_8^C$ from $S_8$ at 160–200°C amounts to about 2 kJ/mol (SS bonds).[2] Therefore, the homolytic bond dissociation energy of $S_\mu^C$ should be $D_\mu = D_8 - 2 = 146$ kJ/mol. Since sulfur chains should be free of bond angle and torsional strain it can be assumed that $D_\mu$ is independent of the chain length at least for chains of 6 and more atoms in which the terminal atoms are far enough apart from each other and from the central bonds whose number varies with varying chain length. The mean bond energies of $S_9$ and $S_{10}$ have also been found to be very similar to that of $S_8$.[6]

Any radicals formed from either $S_8$ or $S_\mu$ will rapidly equilibrate with those of other chain length, e.g.

$$2S_8^C \rightleftharpoons S_7^C + S_9^C \qquad (5)$$

$$2S_8^C \rightleftharpoons S_6^C + S_{10}^C \qquad (6)$$

and the new radicals must be in equilibrium with the corresponding rings, e.g.

$$S_7^R \rightleftharpoons S_7^C \qquad \Delta H(7) = D_7 \qquad (7)$$

$$S_6^R \rightleftharpoons S_6^C \qquad \Delta H(8) = D_6 \qquad (8)$$
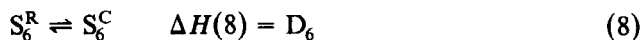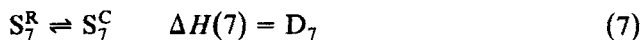
Therefore, the dissociation energies $D_7$ and $D_6$ must be related to $D_8$ by the

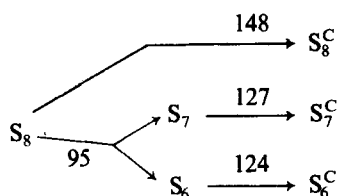following thermodynamic cycles in which it has been assumed that $D_\mu$ is independent of the chain-length:

$$\tfrac{8}{7}S_7^C \xleftarrow{\ \tfrac{1}{7}D_\mu\ } S_8^C \xrightarrow{\ \tfrac{1}{3}D_\mu\ } \tfrac{4}{3}S_6^C$$

$$-\tfrac{8}{7}D_7 \Big\downarrow \qquad\qquad \Big\uparrow D_8 \qquad\qquad \Big\downarrow -\tfrac{4}{3}D_6$$

$$\tfrac{8}{7}S_7^R \xrightarrow{\ -\Delta H(1)\ } S_8^R \xleftarrow{\ -\Delta H(2)\ } \tfrac{4}{3}S_6^R$$
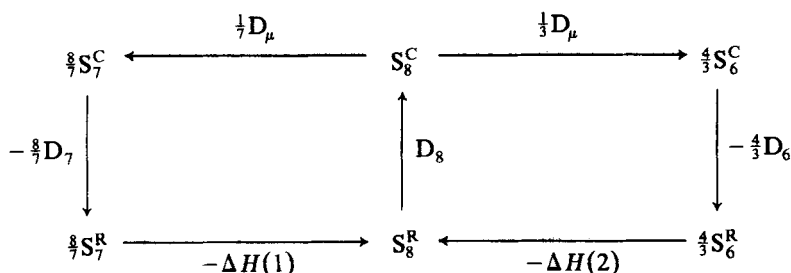
Application of the energy conservation law yields:

$$D_6 = \tfrac{3}{4}\Big[D_8 - \Delta H(2) + \tfrac{1}{3}D_\mu\Big] = 124\ \mathrm{kJ/mol}$$

$$D_7 = \tfrac{7}{8}\Big[D_8 - \Delta H(1) + \tfrac{1}{7}D_\mu\Big] = 127\ \mathrm{kJ/mol}$$

As expected, $D_7$ and $D_6$ are by the enthalpy of formation of $S_7$ and $S_6$, respectively, lower than $D_8$ because $D_8 \approx D_\mu$. However, due to the lower concentrations of $S_7$ and $S_6$ in the equilibrium melt reactions (7) and (8) will lead to the same equilibrium concentration of unpaired electrons per mol of sulfur atoms as reaction (4). With other words, the overall enthalpy to generate free spins in liquid sulfur is independent of the reaction pathway. This is of course a consequence of the reversible nature of reactions (1) through (8) and of the chemical equilibrium between all species involved. Since the concentrations of $S_7$ and $S_6$ relative to $S_8$ must increase with temperature their lower dissociation enthalpies finally result in the same temperature dependence of the concentration of unpaired electrons as in the case of $S_8$.

While the enthalpy of radical formation is independent of the reaction pathway the activation energy ($E_a$) is not. $E_a$ of reactions (1) and (2) has been determined in $CS_2$ solution as 95 kJ/mol;[10] $E_a$ of reactions (4), (7) and (8) will be about equal to the reaction enthalpies. It follows that the formation of chain-like radicals from $S_7$ or $S_6$ is much more favorable, i.e. faster, than by dissociation of $S_8$. The following scheme shows the activation energies of the different reaction steps (in kJ/mol):

$$S_8 \begin{cases} \xrightarrow{148} S_8^C \\ \xrightarrow{95} S_7 \xrightarrow{127} S_7^C \\ \searrow S_6 \xrightarrow{124} S_6^C \end{cases}$$

It can be concluded that the polymerization of liquid sulfur on heating to temperatures above 159°C leading to the formation of chain-like macromolecules ($S_\mu^C$) is initiated by the dissociation of $S_7$ and $S_6$ rather than $S_8$. This view is supported by

the following experimental observations:

a. Pure $S_6$ and $S_7$ polymerize in the liquid state at temperatures below $100°C^{16}$ as a result of their lower dissociation enthalpies.

b. Addition of 2% $S_6$ to an equilibrium sulfur melt at 150°C results in immediate polymerization of the melt[16] since obviously the higher concentration of $S_6$ yields a much higher concentration of radicals compared with the equilibrium conditions when the $S_6$ content is only about 1%.[3] After addition of 2% $S_6$ to a sulfur melt at 115°C the halflife of the $S_6$ amounts to about 90 min.[17]

c. When pure $S_8$ is fairly rapidly heated the polymerization does not take place at 159°C but at much higher temperatures which depend on the heating rate (e.g. at 203°C with 40°/min).[18, 19] Only extrapolation to zero heating rates yields a polymerization temperature of 159°C.[19] The explanation of this phenomenon is that in the absence of $S_7$ and $S_6$ radicals can be formed from $S_8$ only which requires a considerably higher activation energy. However, when the melt is kept at 138°C for 20 min (to allow for the formation of some $S_\pi$) and is then rapidly heated the polymerization takes place at a considerably lower temperature.[18] The activation energy of this polymerization has been determined as $120 \pm 12$ kJ/mol[18] which agrees well with the values of $D_7$ and $D_6$ calculated above.

It is likely that the vulcanization of rubber by sulfur is also initiated by $S_7$ rather than $S_8$. Recently it has been observed that polymeric sulfur (laboratory made or commercial products) depolymerizes on heating (80–120°C) to give a mixture of mainly $S_8$ and $S_7$ (molar ratio 1 : 1 to 2 : 1) together with traces of other sulfur rings (detected by HPLC).[20] Since polymeric sulfur is widely used for rubber vulcanization which takes place at temperatures near 100°C and since $S_7$ is more reactive than both $S_8$ and $S_\mu$ the cycloheptasulfur may well be responsible for at least the start of the reaction.

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