

ESR MEASUREMENTS ON THE POLYMERIZATION OF LIQUID SELENIUM

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In an earlier communication ESR measurements on de-oxygenized selenium were announced. The present paper reports on further ESR measurements on liquid de-oxygenized selenium carried out in a temperature interval $240^{\circ}\text{C} < T < 420^{\circ}\text{C}$. The g -value of the ESR signal is found to be 2.03 ± 0.02 . The temperature dependence of the intensity and linewidth are interpreted as caused by a polymerization process. The heat of scission selenium-selenium bonds in chains was calculated to be 29 ± 3 kcal/mole. It seems that this is the first time, that ESR signals from pure liquid selenium have been reported.

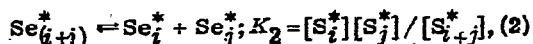
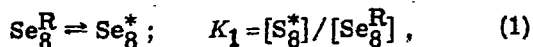
1. EXPERIMENTAL

The ESR measurements were carried out using an E-15 Varian spectrometer with a Varian dual sample cavity, modified for performing measurements at high temperatures without loss in sensitivity. To obtain interpretable results at each temperature the signal of the empty cavity had to be subtracted from the selenium ESR recording.

Samples were made from selenium pellets, commercially obtained from Johnson and Matthey (catalogue nr JM 781, purity 1 in 10^5). The pellets were evacuated at 10^{-5} torr for one hour at 20°C , and were then heated in vacuum at a rate of 15°C/hr until a temperature of 190°C was reached. The selenium was then outgassed and distilled at approximately 10^{-5} torr for 2 hours in the liquid state ($\approx 350^{\circ}\text{C}$). When this purification was finished the samples were sealed in quartz ESR sample tubes which had no detectable paramagnetic impurities.

2. THEORY

To describe the polymerization equilibrium the following reaction can be chosen*:



where

Se_i^* = selenium diradical with i atoms;

Se_8^{R} = selenium ring molecule with 8 atoms.

From the polymerization theory for sulphur developed by Gee [1] the following formula for the temperature dependence of the number of chainends (free radicals) can be derived:

$$\ln \left(\frac{N_s}{2M_0\phi^{1/2}} \right) = - \frac{\Delta H_2}{2RT} + \frac{\Delta S_2}{2R} , \quad (3)$$

where N_s is the concentration of free radicals (kmole/kg), ϕ the weight fraction polymer, M_0 the concentration of selenium atoms (kmole/kg), ΔH_2 the heat of reaction (2) (heat of scission), and ΔS_2 the entropy change of reaction (2).

3. RESULTS

As illustrated by fig. 1 the linewidth (ΔH) found in selenium is very large. Because the spin concentration (N_s) is comparable to that in liquid sulphur, it is found that the signal amplitude (A) is extremely small [$A = CN_s(\Delta H)^{-2}$]. For this reason broad cavity signals must be carefully eliminated.

The average g -value is found to be 2.03 ± 0.02 .

* K_2 is identical to K_5 , used by Gee [1].

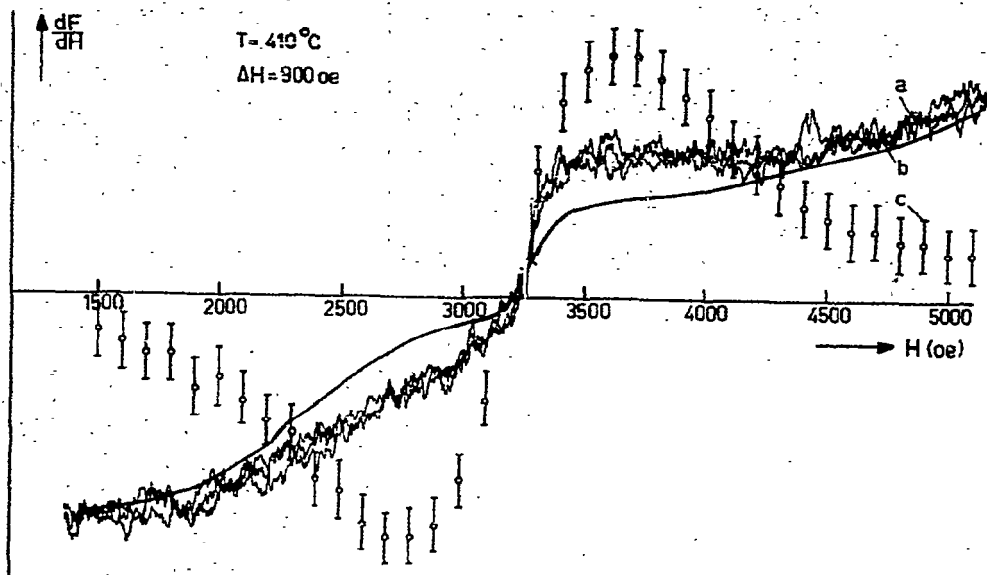


Fig. 1. a) ESR spectrum of liquid selenium superimposed on the cavity background signal. b) Cavity background signal; noise averaged by hand. c) The dotted points give the difference ($\times 5$) between curve (a) and (b) (selenium ESR signal).

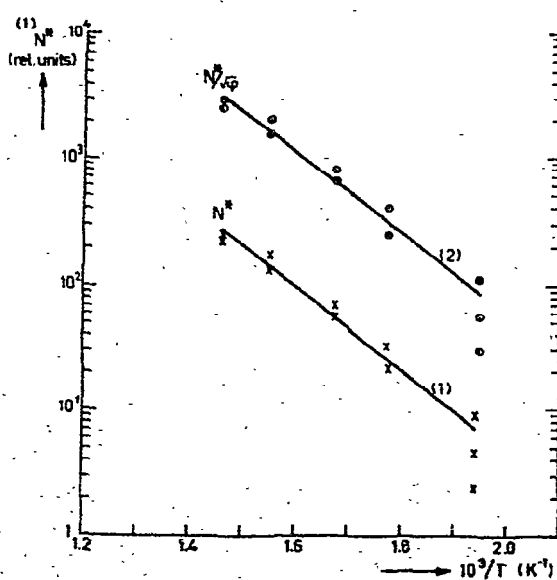


Fig. 2. Relative concentration of free radicals in liquid selenium. N^* (curve 1) and $N^*/\phi^{1/2}$ (curve 2) versus $1000/T$. The straight line (curve 2) was calculated with the method of least squares. Curve 1 was determined with help of curve 2.

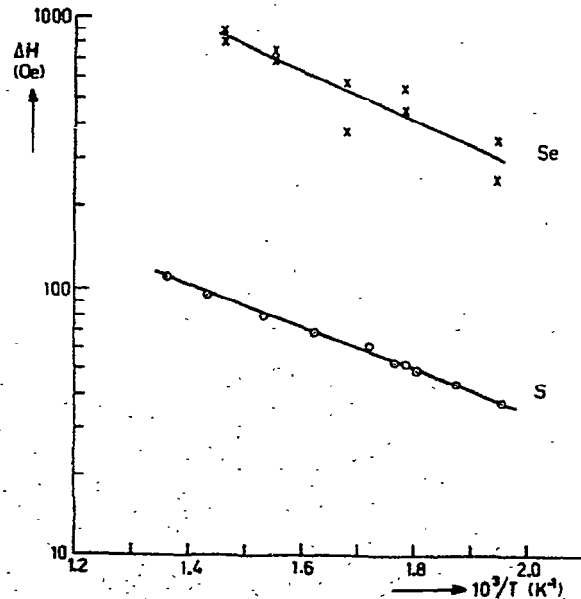
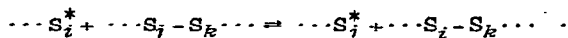


Fig. 3. Linewidth (ΔH) versus $1000/T$ of ESR spectra of liquid selenium (\times) and sulphur (\circ). The data for sulphur were obtained from ref. [4].

In fig. 2 N^* and $N^*/\phi^{1/2}$ are given as a function of $1000/T$, where N^* is the relative concentration of free radicals, which is proportional to $N_S/2M_0$. Values for the weight fraction polymer (ϕ) were obtained from data given by Briegleb [2]. From the slope of the straight line (2) in fig. 2 we obtain a heat of scission $\Delta H_2 = 29 \pm 3$ kcal/mole.

In fig. 3 the linewidth of the ESR signals of liquid selenium and liquid sulphur are given as a function of $1000/T$. Gardner and Fraenkel [3] proposed that the finite lifetime of the sulphur chainend spinstate is determined by the radical displacement reaction:



A similar mechanism is consistent with our ESR measurements on liquid selenium. In both cases the slope of the straight line gives the activation energy of the reaction involved. The activation energy is in both cases nearly the same. It may however be noted that the pre-exponential factor

differs considerably. The evaluation of this information concerning entropy change will be postponed until the number average chainlength has been determined by absolute spin calibration measurements.

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