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Received July 18, 1966.

## On the Nature of Charge-carriers in Liquid Se Containing Cl

MARGARETA LUNDKVIST and  
LARS GUNNAR SILLÉN

*Department of Inorganic Chemistry,  
Royal Institute of Technology (KTH),  
Stockholm 70, Sweden*

The conductivity of liquid selenium is considerably increased by addition of small amounts of chlorine. It was recently pointed out by us<sup>1</sup> that it might be advantageous to apply a "chemical" approach for finding the nature of the charge-carriers. From studies of the conductivity of a melt at equilibrium with  $\text{SeCl}_2(\text{g})$  at various partial pressures  $p(\text{SeCl}_2)$ , it should be possible to apply the law of mass action and conclude how many charged particles are formed for each  $\text{SeCl}_2$ .

The preliminary experiments, reported in that paper, seem to indicate that the increase in conductance,  $\kappa - \kappa_0$ , is proportional to the square root (power 1/2) of  $p(\text{SeCl}_2)$ , which would indicate that only two charged particles are formed per  $\text{SeCl}_2$  dissolved. Several possible mechanisms were suggested.

In the meantime, however, we have made more accurate measurements and especially have been able to use electrodes and cell materials that are less attacked by the melt than those used earlier. This has led us to a modification of our conclusions.

*Cell material.* All experiments described here were carried out on Se(l) at 280°C. The first cells were made of soda glass, for practical convenience, but it was found that they gave a higher value for the conductivity of pure Se,  $\kappa_0$ , than cells of quartz glass. So, in the following, quartz was used in the cells.

*Electrode material.* At first Pt electrodes were used. However, they were slowly attacked by the melt, and other electrode materials were thus tried. With wolfram electrodes,  $\log \kappa_0 = -6.70 \pm 0.05$  was found, to be compared with  $-6.55 \pm 0.05$  for Pt electrodes. This might indicate that W interacts less with the melt than Pt; we found no evidence for a surface resistance. Unfortunately, the W electrodes did not work well when the melt was equilibrated with  $\text{SeCl}_2(\text{g})$ : only irreproducible data were obtained which indicates that there is a reaction between W and Cl in these surroundings.

During the Se Symposium in London, 1964,<sup>1</sup> we learnt about the availability of a vitreous form of carbon<sup>2</sup> which we then tried as an electrode material. We found with vitreous carbon electrodes the same low value,  $\log \kappa_0 = -6.70 \pm 0.05$ , as with the W electrodes, and moreover, there was

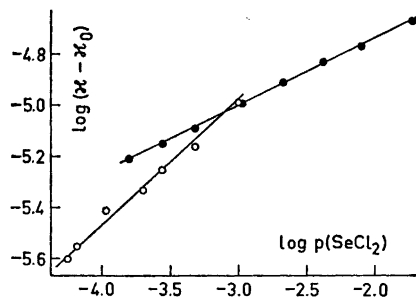
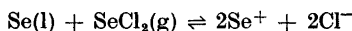


Fig. 1. Conductivity of liquid Se at equilibrium with  $\text{SeCl}_2(\text{g})$  of various partial pressures:  $\log(\kappa - \kappa_0)$  as a function of  $\log p(\text{SeCl}_2)$ . Open circles show earlier experiments with a soda glass cell with Pt electrodes. Filled circles show one series of experiments in a quartz cell with vitreous carbon electrodes. Other series give lines of the same slope but may be shifted parallelly by  $\pm 0.07$  units in  $\log(\kappa - \kappa_0)$ .

no indication that the vitreous carbon was attacked by the selenium melts, even in the presence of Cl.

Data with the new cell (Fig. 1) would hence be less influenced by impurities than our earlier data. Also, the correction for  $\kappa_0$  is smaller. The data now give a slope of 1/4 for  $\log \kappa$  versus  $\log p(\text{SeCl}_2)$ , which indicates that each  $\text{SeCl}_2$  gives four charged particles. The simplest way of writing such a reaction is the following:



As usual for equilibrium data, it is not possible to say how many molecules of the solvent (Se) are attached to each particle. So the formulas might be written  $\text{Se}_n^+$  and  $\text{Se}_n\text{Cl}^-$ . This "chemical" picture can easily be seen to be equivalent to a "physical" picture of electron holes and of excess electrons, connected with Cl atoms. A certain electron hole need not necessarily stay with the same Se atom: on the contrary, a large part of the "mobility of  $\text{Se}^+$ " may really be caused by jumps of an electron hole from one Se atom to another. Analogously the high apparent mobilities of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  in water are only to a small extent connected to the movement of the same  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  particle but result from jumps of protons or proton holes between the water molecules.

The "chemical" picture has the advantage that it allows one, by traditional ways of thinking, to predict how  $\kappa$  will vary with  $p(\text{SeCl}_2)$ .

We wish to thank the *European Selenium-Tellurium Committee and United States Air Force*, grant No. AF EOAR 65-22, for supporting this work, and Mr. Mati Lellep for skillful help with the experiments.

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Received July 29, 1966.

## The Molecular Structure of 1,3,5,7-Cyclo-octatetraene

MARIT TRÆTTEBERG

*Kjemisk institutt, Norges lærerhøgskole,  
Trondheim, Norway*

The molecular structures of 1,3-butadiene<sup>1</sup> and 1,3,5,7-cyclo-octatetraene<sup>2</sup> (COT) have previously been studied by the gas electron diffraction method. According to these investigations the carbon-carbon double bond distances were approximately the same in the two molecules, while the carbon-carbon single bond distance was found to be 0.021 Å larger for 1,3-butadiene than for COT. These results are hard to explain on the basis of  $p$ -electron delocalization. In view of the importance of the problem simultaneous reinvestigations of COT and 1,3-butadiene have therefore been carried through. The structural results for 1,3-butadiene are being published elsewhere<sup>3</sup> while the parameters determined for COT are presented here.

The molecular structure of COT was determined by the sector electron diffraction method, using a modified  $s^3$  sector. The intensity data were treated according to the usual procedure,<sup>4</sup> yielding an  $sM(s)$ -intensity function in the  $s$ -region from  $s = 1.25 \text{ \AA}^{-1}$  to  $s = 60 \text{ \AA}^{-1}$ . The intensity data in the outer  $s$ -region ( $s \geq 45 \text{ \AA}^{-1}$ ) were not too good and the outer  $s$ -limit was therefore set equal to  $45 \text{ \AA}^{-1}$ .

The carbon-carbon single and double bond distances were determined by applying auto- and cross-correlation functions<sup>5</sup> to the intensity data, a method that is particularly well suited to determine closely spaced bond distances as they occur in the COT molecule.

The structural parameters for the molecule as a whole were determined by a least-squares refinement of the molecular intensity function. The results obtained from the least-squares adjustment are presented in Table 1. The numbering of the carbon atoms in the molecule is demonstrated in Fig. 1, which also shows the geometrical shape of the COT molecule. Fig. 2 shows the experimental molecular intensity function ( $sM(s)$ -function) and the corresponding theoretical function calculated on the basis of the parameters presented in Table 1. The  $sM(s)$ -functions shown in Fig. 2 were both multiplied with