

Short Communications

Polarographic Investigations of Organic Selenium Compounds

VI. The Polarographic Reduction of Diphenyl Diselenide and Diphenyl Disulphide

BENGT NYGÅRD

Research Division, AB Pharmacia, Uppsala, Sweden

The current polarographic investigations of organic selenium compounds,¹ with special reference to the scission of the diselenide bond, have so far been restricted to aliphatic open-chain and cyclic diselenides. For a more complete understanding of the polarographic reduction mechanism of this type of bond, investigations have now been extended to the aromatic diselenides. The present communication deals with the preliminary results of some polarographic measurements on the unsubstituted diphenyl diselenide.

Because of its technical application as an initiator in polymerization processes, the corresponding aromatic disulphide has received special attention and has also been studied polarographically. Several papers²⁻⁴ discuss the polarographic behaviour of a number of aromatic disulphides without giving a precise interpretation of the polarographic waves. Recently Kapoor *et al.*⁵ proposed a reduction mechanism for the diphenyl disulphide. However, in the light of our present knowledge of organic selenium polarography, certain objections could be raised against the proposed reaction scheme. In order to obtain a direct comparison between sulphur and selenium compounds

under similar experimental conditions, two aromatic disulphides have been incorporated in this investigation.

The limited solubility of these substances in water necessitated the use of low depolarizer concentrations in a solvent containing not more than 35 % (by volume) of ethanol. Some typical d.c. polarograms are seen in Fig. 1. All exhibit a double wave, characteristic for both the selenium and the sulphur compounds. Furthermore, at the lowest concentration (1×10^{-4} M) only the upper part i_A of the double wave persists (Fig. 1 a). The appearance of this special type of polarographic wave, characteristic of several organic selenium compounds, could be explained by a reaction mechanism in which the homolytic fission of the Se-Se bond constitutes the first step. This is immediately followed by the formation of mercury compounds. A small post-wave with adsorption properties corresponds to the reduction of a surface compound. The more positive wave is controlled by diffusion and varies linearly with the depolarizer concentration. Thus, this polarographic step corresponds to the reduction of the non-adsorbed part of the mercury intermediate. The electrode reac-

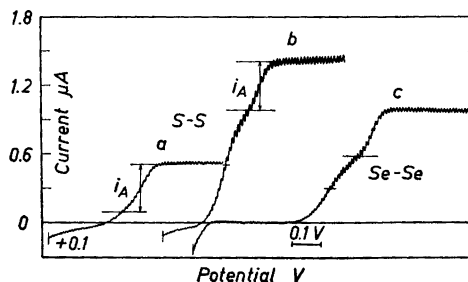
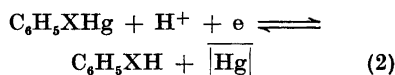
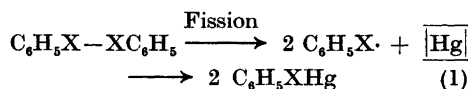


Fig. 1. D.C. polarograms. Perchlorate solution pH 1.15. 35 % ethanol. (a) Diphenyl disulphide 1×10^{-4} M; (b) 2.5×10^{-4} M; (c) diphenyl diselenide 2×10^{-4} M.

* Ref. 1 is referred to as I. II-V will be in press in *Arkiv Kemi*.

tion proceeds under *thermodynamically reversible* conditions at the covered surface of the mercury electrode. The experiments furnish convincing evidence that the reduction of the diphenyl disulphide proceeds by an analogous reaction mechanism. The following reaction scheme is applicable.



with X = S or Se

The diffusion controlled main wave, corresponding to the reaction step (2), is attributed to a one-electron process. The experimental results of Kapoor *et al.*⁵ also lead to this conclusion but their interpretation is based on the assumption of a total reaction consisting of two successive one-electron steps.

The pH-dependence of the half-wave potentials of the more positive wave (Fig. 2) consists of two linear parts, one of which has a slope about 0.059 V/pH, in agreement with the theory. It has been concluded earlier that the extrapolated intersection points¹ correspond to the pK' values* of benzenethiol and benzene-

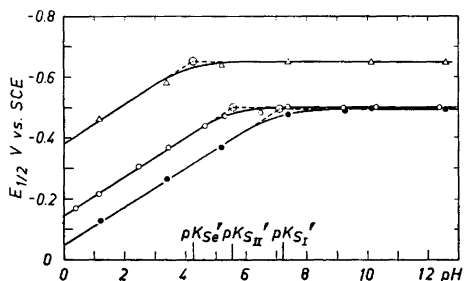


Fig. 2. The pH-dependence of the half-wave potentials in 35 % ethanolic solution. (●) Diphenyl disulphide 5×10^{-4} M; (○) diphenyl-disulphide-3,3'-dicarboxylic acid 5×10^{-4} M; (Δ) diphenyl diselenide 2×10^{-4} M.

* Valid under the present experimental conditions of ionic strength and alcohol content.

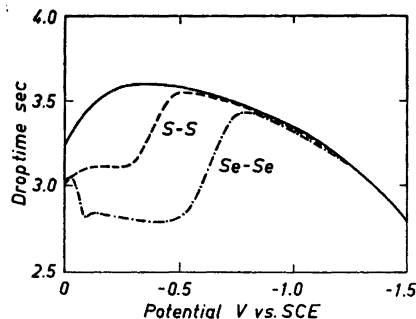


Fig. 3. Electrocapillary curves. Acetate buffer pH 5.2. 35 % ethanol. 1 M NaCl. --- Diphenyl disulphide 2×10^{-4} M; -.-.- diphenyl diselenide 2×10^{-4} M.

selenol, respectively. Further proof of the proposed analogy between the reaction mechanisms of the sulphur and selenium compounds may be deduced from their electrocapillary curves (Fig. 3). Within a limited potential region both substances have a strong capillary activity, depressing the drop-times. At the reduction potentials of the adsorbed mercury compounds the drop-times increase rapidly under equilibrium conditions and the corresponding electrocapillary curves approach that of the blank solution. Over the same concentration range the diselenide depresses most the surface tension at the mercury electrode. This may be related to the structural properties of the mercury compounds formed on the surface. In addition, oscillopolarographic and a.c. polarographic (according to Breyer) methods as well as the study of the *i-t*-curves are in complete accordance with a *reversible* electrode process (2). A more comprehensive report of these investigations, including studies on additional model substances, will be presented later.

As has been pointed out earlier, polarographic methods permit the determination of the protolytic constants of selenols and certain thiols, without need for isolation, by using the corresponding oxidized forms, which are generally more stable. The benzeneselenol (pK' 4.2) is a considerably stronger acid than benzenethiol (pK' 7.2), a property which is in accordance with the trends in the dissociation constants of the hydrogen

compounds among the VI A group elements.

The polarographic pattern conclusively proves that the S—S bridge in the diphenyl disulphides has a lower bond energy than the aliphatic disulphides. X-Ray investigations of the diphenyl diselenide⁶ have verified a dihedral angle of 82°. Bergson⁷ also emphasizes, that to a certain extent there will exist a delocalization of the lone-pair electrons with π -symmetry on sulphur and selenium. The disulphide and diselenide molecules must, as a first approximation, be regarded as consisting of two "insulated" π -electron systems which may separately interact with single sulphur or selenium atoms. As a result the bond energies of the S—S and Se—Se bridges will decrease to such an extent that a currentless fission of these bonds and subsequent formation of mercury compounds can take place. The rates of these reactions are high enough to be without measurable influence on the rates of the electron transfer processes, studied by the slower d.c. polarographic methods. They will therefore proceed under reversible conditions.

Experimental. The substances investigated were recrystallized samples and their analytical data was in accordance with the literature. The polarograms were recorded on a Radiometer Polariter P 04. The capillary constant was $m^{1/2} t^{1/2} = 2.120 \text{ mg}^{1/2} \text{ sec}^{-1/2}$. The electrocapillary curves were registered with an automatic equipment.⁸

The author is much indebted to Professor Arne Fredga for kindly supplying the samples used in this investigation and for valuable discussions.

1. Nygård, B. *Acta Chem. Scand.* **15** (1961) 1039.
2. Hall, E. M. *Anal. Chem.* **25** (1953) 556.
3. Colichman, E. and Love, D. *J. Am. Chem. Soc.* **75** (1953) 5737.
4. Karchmer, J. H. and Walker, M. T. *Anal. Chem.* **26** (1954) 271.
5. Kapoor, R. C., Asthana, M. and Nigam, H. L. *J. Polarog. Soc.* **10** (1964) 41.
6. Marsh, R. E. *Acta Cryst.* **5** (1952) 458.
7. Bergson, G. Some New Aspects of Organic Disulphides, Diselenides and Related Compounds, *Abstr. of Uppsala Diss. in Science* 1962.
8. Nygård, B., Johansson, E. and Olofsson, J. *J. Electroanal. Chem. In press.*

Received June 20, 1966.

New Phases in the Zr-P and Zr-As Systems

TORSTEN LUNDSTRÖM

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The existence of the three phases ZrP_2 , ZrP , and a subphosphide in the Zr-P system was reported by Strotzer *et al.*¹ on the basis of tensimetric analysis and X-ray work. Two polymorphs of ZrP were described by Schönberg² and by Irani and Gingerich.³ However, Bachmayer *et al.*⁴ mentioned only the hexagonal β - ZrP . Recently, Hulliger⁵ published X-ray data for ZrP_2 , ZrAs and ZrAs_2 , were characterized by Trzebiatowski *et al.*⁶ In the present paper, two new zirconium phosphides and one arsenide are described.

A master alloy with the approximate composition $\text{ZrP}_{1.2}$ was prepared in the following way. Turnings of zirconium (claimed purity 99.9 %, less than 0.03 % oxygen) and red phosphorus (better than 99 % purity) were enclosed under a slight over-pressure of argon in a zircalloy cylinder equipped with a tight-fitting screw lid. The cylinder was then sealed under vacuum in a silica capsule and heated for three days at 860°C. The synthetic technique described should greatly reduce the possibilities for oxygen contamination of the product. The reaction product, containing mainly β - ZrP and some ZrP_2 , was arc-melted under pure argon with the addition of various amounts of zirconium metal. The zirconium arsenide was synthesized by heating zirconium turnings and arsenic (Johnson, Matthey & Co., spectrographically standardized) in evacuated and sealed silica capsules, an inner alumina crucible being used to prevent direct contact between the metal and silica.

Powder diffraction films were taken with Guinier-Hägg type cameras using strictly monochromatized $\text{CuK}\alpha_1$ and $\text{CrK}\alpha_1$ radiation. The cell dimensions given in Table 1 are based on silicon as internal calibration standard with $a = 5.43054 \text{ \AA}$. A least-squares refinement of the lattice parameters was made with a program called CELSIUS, written by J. Tegenfeldt⁹ for a CDC 3600 computer. As may be seen from Table 1 the standard deviations indicate a high degree of precision; however, it is possible that systematic errors in some cases are of greater magnitude than those indicated by the standard deviations.