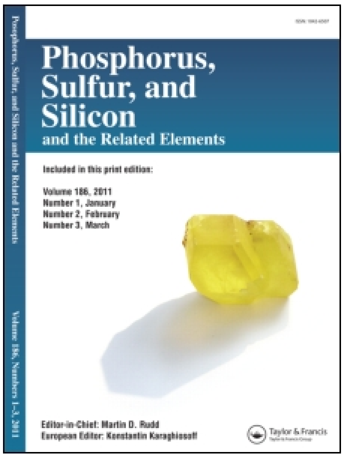

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Ludvik, Jiří(1998) 'Organic Dichalcogenides and their Mercury Complexes: Electrochemical Reduction Mechanism in Aprotic Media', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 413 — 416

To link to this Article: DOI: 10.1080/10426509808545967

URL: http://dx.doi.org/10.1080/10426509808545967

Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 413–416
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ORGANIC DICHALCOGENIDES AND THEIR MERCURY COMPLEXES: ELECTROCHEMICAL REDUCTION MECHANISM IN APROTIC MEDIA

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The electroreduction mechanism of diselenides and ditellurides on mer-cury electrodes has been described, and two types of intermediate Hg- complexes were isolated and characterized. The cathodically generated S- and Se-precursors were used for addition reactions.

Keywords: aromatic dichalcogenides, electrochemical reduction mechanism, Hg-complexes, electrosynthetic use of reduction intermediates.

INTRODUCTION

The presented paper is a part of a broader comparative mechanistic and electrosynthetic investigation of organic dichalcogenides where the relationship *structure - redox properties - reactivity* is studied and the reduction of diselenides is compared with that of analogous disulfides [1].

Electrochemical reduction mechanism of disulfides has been already studied (e.g. cystine and its analogues.). However, this is not the case of diselenides and ditellurides although their physiological, pharmaceutical and electrosynthetic significance increases. Due to the fact that selenium, as a biologically essential element, often accompanies or substitutes sulfur in the organism, even in the coordination sites of proteins, our attention was attracted especially to the interactions of these two elements with heavy metals. On the other hand, the detailed knowledge of the electroreduction mechanism enables the use of electrochemically generated intermediates (radicals or ions) containing a chalcogen atom for selective organic syntheses.

REDUCTION MECHANISMS AND MERCURY COMPLEXES

In general, all dichalcogenides are reduced in aprotic solvents by two electrons giving rise corresponding chalcogenolate anions

$REER + 2e^- \longrightarrow 2\,RE^-$ (R = alkyl, aryl; E = S, Se, Te)

In a more detailed view, this reaction proceeds via different pathways depending on the chalcogen atom, type of solvent and electrode material.

Aromatic disulfides are reduced in a single irreversible wave by two electrons following the ECE mechanism [2] at Hg, Pt or GC electrodes:

electrode (E) step: $RSSR + e^- \longrightarrow [RSSR]^{-\cdot}$

chemical (C) step: $[RSSR]^{-\cdot} \longrightarrow RS^- + RS^\cdot$

electrode (E) step: $RS^\cdot + e^- \longrightarrow RS^-$

The presence of the radical intermediate $RS^\cdot$ was proved by electrochemically generated luminescence [2].

In contrast to that, diselenides (as well as ditellurides) are reduced on mercury in two diffusion controlled waves, the ratio of their limiting currents is 1:2 with a total consumption of two electrons. The reversi-bility of both steps [3] is evident from cyclic voltammetry experiments. Although the final product is also RSe^- (RTe^-), the radical intermediate $RSe^\cdot$ ($RTe^\cdot$) has not been detected. The reason of the different reduction pathway is the spontaneous antecedent reaction of the diselenide (ditelluride) with mercury metal under formation of a mercury complex $Hg[RE]_2$ which is in fact the reduced species. These mercury compounds were isolated and fully characterized by ^{1}H,^{13}C,^{77}Se NMR, MS, elem.analysis, PES and X-ray difraction [4]. For the above mentioned unusual electro-chemical behavior the following mechanism has been suggested:

Antecedent reaction: $RSeSeR + Hg \longrightarrow RSe\text{-}Hg\text{-}SeR$

1st wave (2/3 el.): $RSe\text{-}Hg\text{-}SeR + 2e^{-} \longrightarrow 2\,RSe^{-} + Hg$

$2\,RSe^{-} + 2\,RSe\text{-}Hg\text{-}SeR \longrightarrow 2\,[Hg(RSe)_3]^{-}$

2nd wave (4/3 el.): $2\,[Hg(RSe)_3]^{-} + 4e^{-} \longrightarrow 6\,RSe^{-} + 2\,Hg$

The proposed mechanism involves the formation of another intermedi-ate mercury complex $[Hg(RSe)_3]^{-}$ which is formed by a nucleophilic attack of the anion RSe^{-} on the positively charged mercury atom of the primary complex. The anionic "propeller shaped" complex has been isolated as a tetraalkylammonium salt and characterized by elemental analysis, NMR, and AAS, as well as by electrochemical and spectro-scopic *in situ* experiments. This compound represents a possible model of a coordination center of metalloregulatory proteins [5].

The cyclic voltammetry and phase-selective ac-polarography revealed that between the two Nernstian waves an adsorption controlled process (a post-wave) appears due to a strong adsorption of primary complex [1].

ELECTROSYNTHETIC USE

The above mentioned electrochemically generated anions (in the case of disulfides also radicals) were used as nucleophilic (or radical) reagents for addition reactions on double bonds of unsaturated organic molecules. As substrates, chlortrifluoroethene, 1,2-dichlorodifluoroethene and methyl-2,5-dihydro-2,5-dimethoxy-3-furancarboxylate were used. All of them fulfil the prerequisite that their reduction potential should be substantially more negative than that of the dichalcogenide. Besides di-phenyldichalcogenides, an alicyclic diselenide was also used which forms a dianion during reduction. Nucleophilic and radical addition reactions proceeded in non-aqueous acetonitrile on the mercury pool electrode. Products were characterized by IR and ^{1}H, ^{19}F and ^{77}Se NMR spectra[6].

CONCLUSIONS

The redox behavior of organic diselenides, their specific interaction with mercury and the reduction of thus formed complexes can serve as a model for the origin and functions of metalloregulatory protein active centers containing selenium. The difference in the electroreduction pathways of disulfides, diselenides and ditellurides has been described and basing on this, new synthetic routes to aryl(fluorethyl)selenides and -sulfides have been found. The addition reactions of cathodically generated chalcogen containing precursors on compounds bearing activated double bonds have been thus proved as a suitable electro-synthetic procedure due to its selectivity and mild reaction conditions.

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