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The Anodic Acetoxylation of Alkylarylselenides

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Abstract: Electrooxidation of alkylarylselenides in methanol in the presence of sodium acetate leads to the acetoxylation of the methylene group of selenides

The organic compounds of selenium, particularly phenylseleno compounds, 2 can be of wide use in the processes of electrochemical functionalization of organic molecules. As a rule, the transformations do not affect the phenylseleno group, and it is the organic saturated radical on the selenium that undergoes functionalization. Generally, these reactions result in the formation of a double bond between α and β carbon atoms after elimination of the phenylseleno fragment. We have shown, however, that this is just one of the two possible reaction pathways of the cation radicals of alkylphenylselenides, the two pathways being rupture of a Se-C_{sp3} bond (dealkylation) and deprotonation⁴.

For a large number of alkylarylselenides, carrying ArSe moiety, the primary products of electrooxidation in "dry" acetonitrile were shown by commutative voltammetry at the rotating disk electrode to be cation radicals. While radical cations of thioanisoles and arylsulfides, being relatively stable, react in second order reactions⁵, a consecutive reaction of the cation radicals of isologous selenides occurs very rapidly as a first order one ($\Delta E_{1/2}/\Delta lg \omega = 30 mV$).

Exhaustive electrooxidation of arylselenides with different alkyl substituents on the selenium produces corresponding diaryldiselenides as the final selenium-containing products. A sequence of transformations leading to diaryldiselenide begins with the fission of the Se-C_{sp3} bond of the cation radical. The resulting ArSe⁺ cation exists for some time in solution, probably as a complex with acetonitrile; hydrolysis of this complex by residual water leads to a diselenide:⁶

ArSeAlk
$$\xrightarrow{-2e}$$
 ArSe $\xrightarrow{+}$ ArSe $\xrightarrow{+}$ \longrightarrow Ar₂Se₂

ArSe $\xrightarrow{+}$ + NCCH₃ \longrightarrow ArSe-N=C-CH₃ $\xrightarrow{+1}$ ArSeNHCCH₃

ArSe-N=C-CH₃ $\xrightarrow{-1}$ ArSeNHCCH₃

ArSeOH + H₂NCCH₃

2 ArSeOH \longrightarrow ArSeH + ArSeO₂H

ArSeOH + ArSeH \longrightarrow Ar₂Se₂ + H₂O

Seleninic acid, being a strong oxidant, reacts with components of the solution to give Ar₂Se₂ as well.