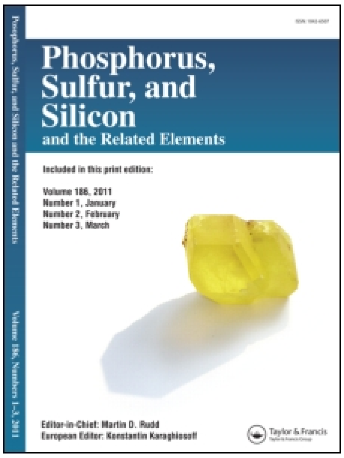

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Electrochemical Activation of Sulfur-Synthesis of Organic Mono and Trisulfides with a Sacrificial Carbon-Sulfur Anode

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ELECTROCHEMICAL ACTIVATION OF SULFUR - SYNTHESIS OF ORGANIC MONO AND TRISULFIDES WITH A SACRIFICIAL CARBON-SULFUR ANODE

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Abstract The electrooxidation of sulfur in organic solvents leads to the formation of the cationic species S^{2+}. Macroscale electrolyses are carried out with a sacrificial carbon-sulfur anode. S^{2+} can react either with aromatics to give monosulfides by electrophilic substitution, or with nucleophiles, thiols for example, to give trisulfides.

INTRODUCTION

For the first time electrooxidation of sulfur is conducted at room temperature in organic solvents. An estimated sixteen-electron process leads to the formation of S^{2+}.

$$S_8 \longrightarrow 8\ S^{2+} + 16\,e^-$$

Such electrogenerated sulfur cations are stable in non-nucleophilic solution for several days.

For carrying out macroscale electrolyses it has been used a sacrificial carbon-sulfur anode containing 2 parts of sulfur for 1 part of powdered graphite. This method circumvents advantageously the poor solubility of sulfur in the usual organic solvents.

In a first stage S^{2+} cations are generated by oxidation of this electrode at a working potential of 2.0 - 2.2 V, vs saturated calomel electrode. At the end of electrolysis, a stoicheiometric amount of a suitable substrate is added into the solution to react with.

RESULTS

The use of a sacrificial sulfur electrode for the generation of electrophilic species S^{2+} appears to be a good method of high interest for the electrochemical preparation of thioorganic compounds.

Preparation of monosulfides

These reactions involve attack of the benzene ring by the electrophilic reagent S^{2+}

according to the global mechanism:

$$2\,\mathrm{Ar{-}H} + \mathrm{S}^{2+} \longrightarrow \mathrm{Ar{-}S{-}Ar} + 2\,\mathrm{H}^{+}$$

Yields in diarylsulfides are rather high with aromatic ethers[1] , phenols and heterocycles [2], but contrastingly much lower with aromatic amines[2] . Yields can be improved if a Lewis acid is added.

We have observed a high regioselectivity which can be modified in some cases by the choice of the medium.

The proposed method presents advantages over the classical technique using sulfur chloride procedures known as hazardous and which emits noxious by-products.

Preparation of trisulfides

S^{2+} can also react with classical nucleophiles and here we give only the example of reaction with thiols or thiolates:[3]

$$2\,\mathrm{R{-}S}^{-} + \mathrm{S}^{2+} \longrightarrow \mathrm{R{-}S{-}S{-}S{-}R}$$

Under these conditions S^{2+} appears to play partially the role of an oxidizing species and therefore the formation of di and tetrasulfides is also observed as side-products. The selectivity is also directly influenced by the experimental conditions.

Consequently the carbon-sulfur electrode can be considered as a powerful tool for the preparation at room temperature of new thioorganic compounds under mild conditions and opens interesting perspectives,[4] which ought to be developed on an industrial scale when one considers the great importance of sulfur-containing compounds as pharmaceuticals, pesticides, etc.

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