

## Electrocatalytic Reduction of Bromothiophenes on Gold and Silver Electrodes: an Example of Synergism in Electrocatalysis

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The reductive cleavage of C–Br bonds on silver electrodes can be regarded as an ideal model of dissociative electron transfer (DET) in electrocatalytic conditions, modulated by many factors, among which the molecular structure is of particular relevance. A detailed mechanistic study based on a large set of compounds with different molecular structures allowed us a full rationalization of the process for the case of aryl bromides in acetonitrile. [1]

Now we are extending this research to heteroaromatic halides, in which the heteroatom not only makes the aromatic ring asymmetric from the perspective of the electron density but also can have its own specific interactions with the electrode surface, in addition to those of the halide ions. [2] As a first approach, we have selected the mono-, di-, tri- and tetra-bromothiophene series, plus a series of substituted bromothiophenes together with the corresponding bromobenzenes as benchmarks, investigating (by CV, supported by EIS in selected cases) the electrochemical reduction of the whole family: (i) on glassy carbon, GC, assumed as a non-catalytic reference electrode accounting for intrinsic reactivity; (ii) on the highly catalytic silver electrode; (iii) on gold electrode, showing in former halide cases lower catalytic effects than silver but having the highest affinity for the sulphur atom in the thiophene ring. While the results on GC and on Ag are fully consistent with the formerly studied aryl bromide case on the same two electrodes [1] the catalytic effects of Au appear to be neatly modulated by the relative position of the –Br leaving group with respect to the sulphur atom. This feature is quite evident and reproducible in the whole series (including polysubstituted cases provided by our organic partner group), and points to the S atom acting as an asymmetrically anchoring group for the molecule on the Au surface.

[1] S. Arnaboldi, A. Gennaro, A.A. Isse, P.R. Mussini (2015) *Electrochimica Acta*, 158, 427-436

[2] S. Arnaboldi, A. Bonetti, E. Giussani, P.R. Mussini, T. Benincori, S. Rizzo, A.A. Isse, A. Gennaro (2014) *Electrochemistry Communications*, 38, 100-103