



Short communication

Electrocatalytic reduction of bromothiophenes on gold and silver electrodes: An example of synergy in electrocatalysis



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ABSTRACT

The electroreduction of bromothiophenes on Au and Ag provides a striking model of synergy in electrocatalysis, when a second group specifically interacting with the catalytic surface is present besides the reacting one, providing an auxiliary anchoring effect. The high catalytic activity of Ag for bromobenzene reduction is enhanced in the bromothiophene case. Moreover, Au, having for bromobenzene a much lower and less reproducible catalytic effect than Ag on account of the repulsive effect of its very negative surface charge in the working potential range, approaches Ag activity in the case of 2-bromothiophene, where the anchoring S group is adjacent to the Br group to be cleaved. The beneficial anchoring effect is lower when it has to be shared between two Br leaving groups adjacent to the S group, and becomes negligible in the case of a bromide leaving group in 3-position.

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1. Introduction

Reductive cleavage of carbon–halogen bonds (C–X) on Ag electrodes provides a good model for dissociative electron transfer (DET) in electrocatalytic conditions. In recent years the process has been shown to be modulated by many factors, among which is the molecular structure, in terms of both the halide leaving group [1–3] and the aromatic [4], aliphatic [5], or benzylic residue [3]. Recently, a detailed mechanistic study led to propose a rationalization of the process for the case of aryl bromides in acetonitrile [4]. Catalytic effects linearly increase with increasing significance of the heterogeneous ET barrier in the overall DET kinetics and decrease with increasing electron-withdrawing ability of substituents on the aryl ring, implying increasing localization of the negative charge away from the halide leaving group.

We are extending our investigations to the heteroaromatic halides, in which the heteroatom (a) makes the aromatic ring asymmetric from the perspective of the electron density and (b) can itself have specific

interactions with the electrode surface, in addition to those of the C–X group, thus acting as an “adsorption auxiliary group” [6] on the catalytic surface.

A good example is provided by halothiophenes, since both Au and Ag, catalytic for C–X bond cleavage, also have strong specific interactions with sulfur atoms, promoting formation of self-assembled monolayers (SAMs) [7,8]. Studies on thiophene SAMs on Au(111) confirm a direct chemical interaction between the sulfur head groups in the thiophene rings and the metal surface [9]. Moreover, it is confirmed that, in thiophene-SAM formation, the involvement of the S atom results in simple molecular adsorption with no chemical reactions, unlike disulfides that might be reductively cleaved, and alkanethiols which might be reduced to thiolates or oxidized to disulfides [10].

In this context, the whole bromothiophene family (Fig. 1) is investigated at (i) glassy carbon (GC), assumed as a non-catalytic reference accounting for intrinsic reactivity only [11], (ii) Ag, highly catalytic for DET to C–X bonds [1–3,12] and (iii) Au, having the highest intrinsic affinity for both S and X ions, but with much lower catalytic effects than Ag for the reduction of organic halides on account of its high negative surface charge in the working potential range [12,13]. It is particularly interesting to see whether this scenario changes if the molecule contains “adsorption auxiliary groups” such as sulfur capable of interacting strongly

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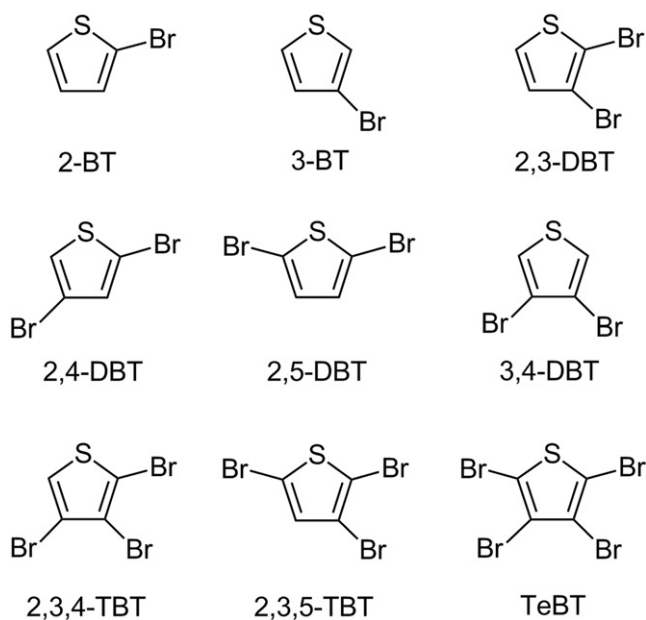


Fig. 1. A synopsis of the investigated bromothiophenes.

with the metal. To our knowledge this preliminary study is the first work specifically focusing on the effect of anchoring groups on electrocatalysis.

2. Experimental

Voltammograms were recorded for each substrate (Sigma-Aldrich or synthesized according to literature procedures [14–19]) in deaerated 0.00075 M solutions in CH₃CN (Merck and Sigma-Aldrich, HPLC grade) with 0.1 M (Et₄N)BF₄ (Fluka 99%) at 0.05 – 2 V s⁻¹. The investigations were carried out by an Autolab PGSTAT potentiostat/galvanostat with positive feedback (EcoChemie, The Netherlands) run by a PC with GPES software. The working electrodes were Teflon®-embedded disks of GC (Sigradur, grade G), Au and Ag (AMEL, *d* = 0.2 cm for Au and 0.3 cm for GC and Ag) polished with 1-μm diamond powder (Sigma-Aldrich) on a wet cloth (DP-Nap, Struers). The reference electrode was an aqueous saturated calomel electrode with a potential of –0.39 V vs Fc^{+/0}|Fc, jacketed in a compartment filled with the working medium to prevent leakage of water and Cl⁻ into the working solution. The counter electrode was a platinum wire or disk.

3. Results and discussion

A synopsis of the CV features of the investigated bromothiophenes on the three electrodes is provided in Fig. 2 and Table 1, which reports data on the first and second reduction peaks. For comparison, bromobenzene data are also reported.

3.1. Dissociative electron transfer mechanism

As for the electrochemical reduction of aryl halides [4], all the CV patterns account for an overall irreversible process, following a stepwise DET mechanism [19]:



The relative heights of the activation barriers of reactions (1) and (2) in the global DET process have recently been shown to be nicely

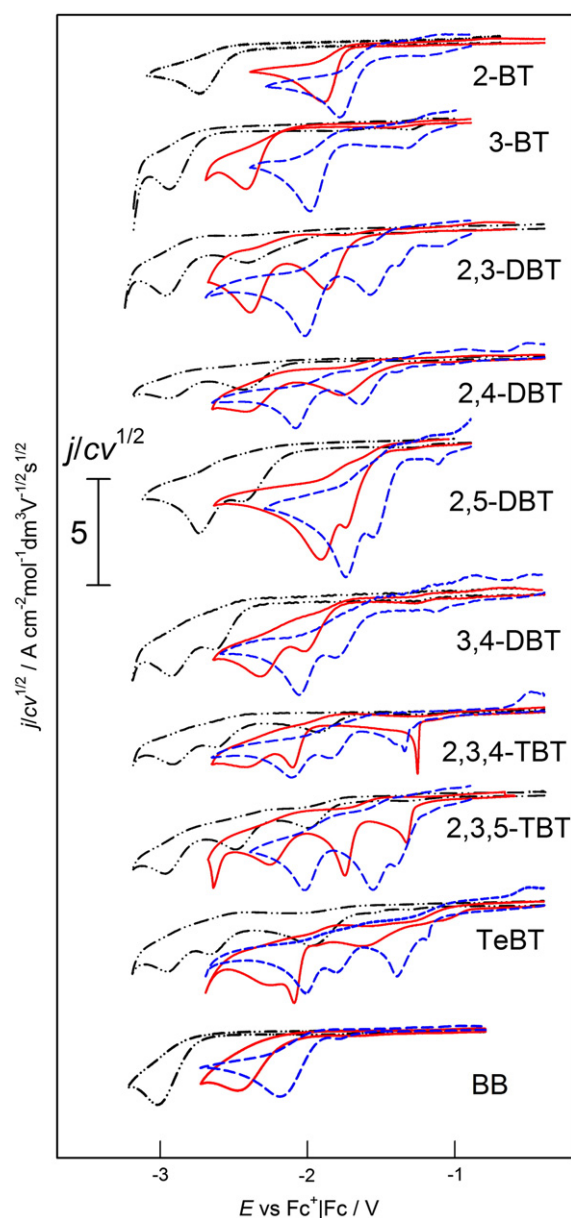


Fig. 2. Normalized CV features of the investigated bromothiophenes (0.00075 M) recorded on GC (–•–), Au (–) and Ag (– –) electrodes in CH₃CN + 0.1 M (Et₄N)BF₄ at 0.2 V s⁻¹.

accounted for by a kinetic parameter κ [4], calculated along two possible criteria:

$$\kappa' = -\frac{1.51RT/F}{\partial E_p / \partial \log v} = -\frac{0.0296}{\partial E_p / \partial \log v} \text{ at } 25^\circ \text{C} \quad (3)$$

$$\kappa'' = -\frac{1.857RT}{F(E_p - E_{p/2})} = -\frac{0.0477}{E_p - E_{p/2}} \text{ at } 25^\circ \text{C}. \quad (4)$$

The higher the κ value, the more determining the chemical barrier, which can be assumed to prevail in the $0.5 < \kappa < 1$ range, whereas the electrochemical barrier prevails for $0.35 < \kappa < 0.5$; lower κ values point to a concerted mechanism in which the electron uptake is concurrent with bond breaking:



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