



Short communication

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



Serena Arnaboldi <sup>a</sup>, Alberto Bonetti <sup>a</sup>, Ester Giussani <sup>a</sup>, Patrizia Romana Mussini <sup>a,\*</sup>, Tiziana Benincori <sup>b</sup>, Simona Rizzo <sup>c</sup>, Abdirisak Ahmed Isse <sup>d,\*\*</sup>, Armando Gennaro <sup>d</sup>

<sup>a</sup> Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy

<sup>b</sup> Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, via Valleggio 11, 22100 Como, Italy

<sup>c</sup> ISTM-CNR, via Golgi 19, 20133 Milano, Italy

<sup>d</sup> Dipartimento di Scienze Chimiche, Università degli Studi di Padova, via Marzolo 1, 35131 Padova, Italy

### ARTICLE INFO

#### Article history:

Received 12 August 2013

Received in revised form 9 October 2013

Accepted 18 October 2013

Available online 26 October 2013

#### Keywords:

Molecular electrocatalysis

Dissociative electron transfer

Anchoring groups

Bromothiophenes

Gold electrodes

Silver electrodes

### 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.

© 2013 Elsevier B.V. All rights reserved.

## 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

\* Corresponding author. Tel.: +39 02 50314211.

\*\* Corresponding author. Tel.: +39 049 8275677.

E-mail addresses: [patrizia.mussini@unimi.it](mailto:patrizia.mussini@unimi.it) (P.R. Mussini), [abdirisak.ahmedisse@unipd.it](mailto:abdirisak.ahmedisse@unipd.it) (A.A. Isse).

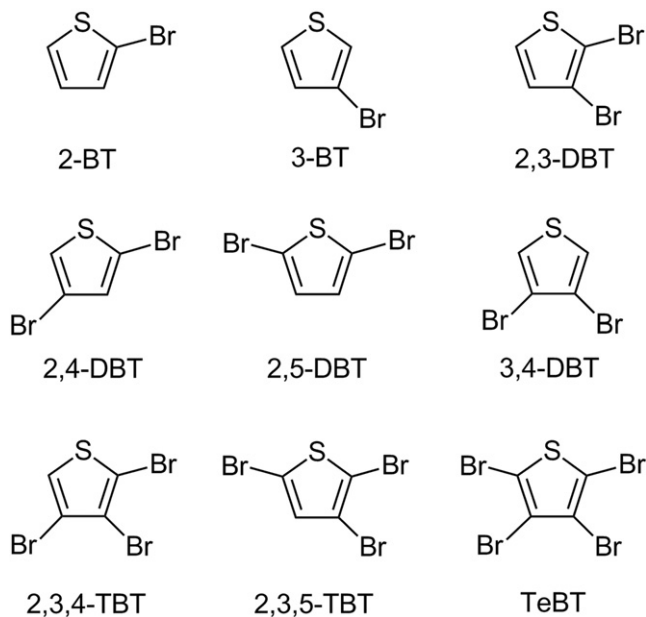


Fig. 1. A synopsis of the investigated bromothiophenes.

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 CH<sub>3</sub>CN (Merck and Sigma-Aldrich, HPLC grade) with 0.1 M (Et<sub>4</sub>N)BF<sub>4</sub> (Fluka 99%) at 0.05 – 2 V s<sup>-1</sup>. 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<sup>+/0</sup>|Fc, jacketed in a compartment filled with the working medium to prevent leakage of water and Cl<sup>-</sup> 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

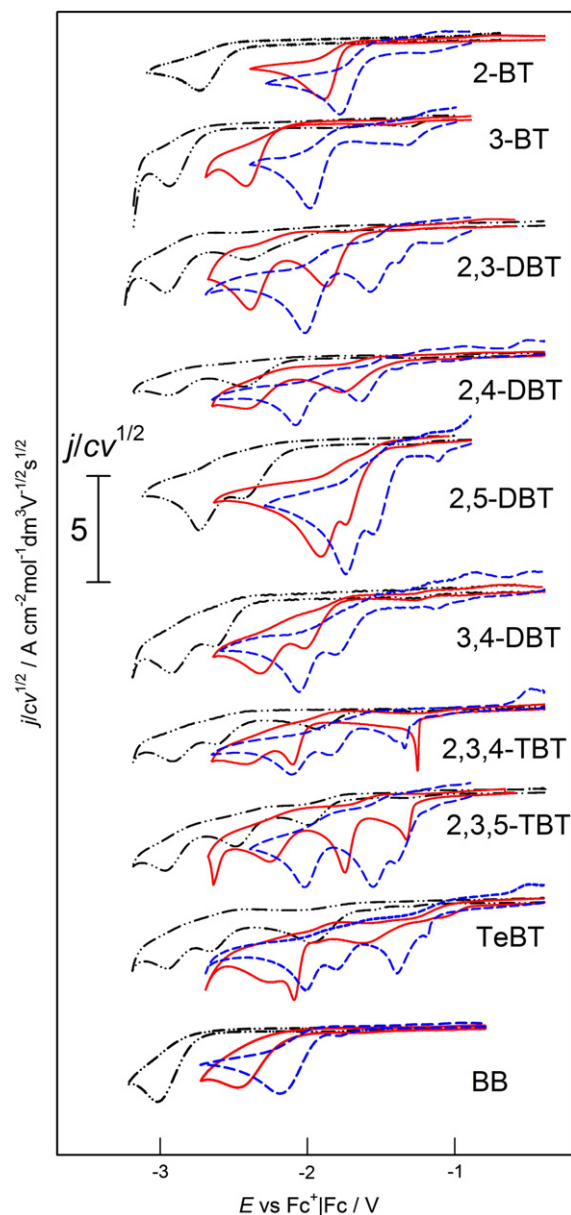


Fig. 2. Normalized CV features of the investigated bromothiophenes (0.00075 M) recorded on GC (–•–•), Au (–) and Ag (– –) electrodes in CH<sub>3</sub>CN + 0.1 M (Et<sub>4</sub>N)BF<sub>4</sub> at 0.2 V s<sup>-1</sup>.

accounted for by a kinetic parameter  $\kappa$  [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  $\kappa$  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  $\kappa$  values point to a concerted mechanism in which the electron uptake is concurrent with bond breaking:



**Table 1**  
Key CV features of the investigated bromothiophenes recorded on GC, Au, and Ag electrodes in CH<sub>3</sub>CN + 0.1 M Et<sub>4</sub>NBF<sub>4</sub> at 0.2 V s<sup>-1</sup>.

Entry	R-Br	Electrode	$E_{pl}$ vs Fc <sup>+</sup> /Fc/V	$\kappa^a$	$E_{pl(M)} - E_{pl(CC)}/V$	$E_{pl}$ vs Fc <sup>+</sup> /Fc/V
1	<b>2-BT</b>	GC	-2.74	0.35		
2		Au	-1.89	0.54	0.85	
3		Ag	-1.78	0.45	0.96	
4	<b>3-BT</b>	GC	-2.93	0.41		
5		Au	-2.42	0.35	0.51	
6		Ag	-1.98	0.46	0.95	
7	<b>2,5-DBT</b>	GC	-2.44	0.33		-2.73
8		Au	-1.76	0.41	0.68	-1.91
9		Ag	-1.54	0.47	0.90	-1.74
10	<b>3,4-DBT</b>	GC	-2.64	0.41		-2.93
11		Au	-2.02	0.48	0.62	-2.32
12		Ag	-1.80	0.43	0.84	-2.05
13	<b>2,3-DBT</b>	GC	-2.40	0.35		-2.96
14		Au	-1.87	0.40	0.53	-2.39
15		Ag	-1.56	0.46	0.84	-2.03
16	<b>2,4-DBT</b>	GC	-2.43	0.32		-2.93
17		Au	-1.77	0.36	0.66	-2.41
18		Ag	-1.64	0.49	0.79	-2.08
19	<b>2,3,4-TBT</b>	GC	-1.92	0.44		-2.62
20		Au	-1.26		0.66	-2.10
21		Ag	-1.38		0.54	-1.83
22	<b>2,3,5-TBT</b>	GC	-1.99	0.43		-2.49
23		Au	-1.83		0.16	-1.75
24		Ag	-1.40		0.59	-1.55
25	<b>TeBT</b>	GC	-1.97	0.23		-2.67
26		Au	-1.63	0.43	0.38	-2.09
27		Ag	-1.37	0.49	0.64	-1.80
28	<b>BB<sup>b</sup></b>	GC <sup>c</sup>	-3.00	0.45		
29		Au	-2.47	0.25	0.53	
30		Ag <sup>c</sup>	-2.15	0.29	0.85	

Bold characters have been used to highlight the compound acronyms to facilitate table reading, considering that there are three entries for each compound.

<sup>a</sup> Average of the values calculated from Eqs. (3) and (4) for GC; values from Eq. (3) for Au and Ag.

<sup>b</sup> BB = bromobenzene.

<sup>c</sup> From ref. [4].

The concerted mechanism is typical of alkyl halides, but can be observed in some cases also with aryl halides on a catalytic surface. In a previous study of halobenzenes [4]  $\kappa$  values were found to be in the 0.5–1 range on GC (except for a few cases like bromobenzene,  $\kappa = 0.45$ ), but in many cases  $< 0.5$  on Ag, pointing to the stepwise process on the catalytic electrode being controlled by the ET step, and, in some cases, to a mechanism change from stepwise to concerted.

In the investigated range of  $v$ , plots of  $E_p$  versus  $\log v$  give straight lines for all compounds regardless of the electrode type. In addition,  $I_p$  varies linearly with  $v^{1/2}$ , indicating that the overall process is under diffusion control. In this circumstance, Eqs. (3) and (4) can be applied to calculate  $\kappa$  [4] and indeed the two methods gave comparable values on GC (the average values are reported in the table). Since in several cases sharp peaks have been observed on the catalytic electrodes, we considered the method based on half-peak width not fully reliable and hence data calculated from Eq. (3) are reported for Ag and Au. The  $\kappa$  values reported in the table are in the 0.35–0.50 range for nearly all substrates, on both GC and the two catalytic electrodes. This points to a stepwise DET mechanism with the heterogeneous electron transfer barrier prevailing on that of the C–X bond cleavage even in the absence of catalytic effects.

### 3.2. Reactivity in non-catalytic conditions

The CV features recorded at the non-catalytic GC electrode account for the intrinsic reactivity of bromothiophene molecules. Comparing CV patterns for a decreasing number of Br groups confirms that on GC the DET processes involving the C–Br bonds result in progressive hydrodebromination, consistent with former literature [19,20]. All reduction potentials of the C–Br bonds are consistent with the inductive effects of the S atom and of the Br atoms present in the molecule: the 2-position is much more reactive than the 3-position (Table 1, entry

1 vs 4), and increasing the number of Br atoms shifts  $E_{pl}$  in the positive direction (entries 1, 13, 22, 25).

### 3.3. Reactivity in catalytic conditions

The catalytic effects of Au and Ag for the first C–Br cleavage, calculated as  $E_{pl(M)} - E_{pl(CC)}$ , are reported in Table 1. It is important to stress that this potential difference does not contain any contribution from inductive substituent effects but accounts only for the specific surface–substrate interactions leading to the observed anodic shift of  $E_p$ .

A conspicuous catalytic effect, which is much higher than in the bromobenzene case, is observed on Au for 2-BT (entries 2, 29). This catalytic enhancement must arise from synergic interactions of S and C–Br with the metal, which of course is not possible for bromobenzene. In the 3-BT case the catalytic effect is much lower than that found for 2-BT. The remarkable difference in catalytic activity for positions 2 and 3 must be justified in terms of different substrate–surface interactions. In particular, assuming the reductive cleavage process to evolve through an intermediate state in which Au coordinates the S atom of the thiophene ring, as in SAMs, the highest catalytic effect is expected when the molecular structure allows optimal synergic interactions of S and C–Br with the metal. Now, when the C–Br bond to be cleaved is adjacent to the S atom, it is in a more favorable position than 3-Br to benefit from the additional interaction with the catalytic surface offered by sulfur.

On Ag, the catalytic effects are even greater than on Au, and higher than those already observed for bromobenzene, but nearly identical for 2-Br and 3-Br. We assume that, also for Ag, the affinity of the surface for S results in a stronger coordination of the molecule and therefore in an increased catalytic effect for C–Br bond cleavage, but in this case the surface interaction with the Br atom is more determining than the Ag...S interaction.

The dibromothiophene reductions on Au appear consistent with the assumptions made in the case of the monobromothiophenes. On both

metals the highest catalytic effects are observed for 2,5-DBT, probably because both C–Br groups are in the most favorable position for sulfur-assisted surface interactions. It is important to stress, however, that the catalytic effect is lower than that observed for 2-BT (0.68 V vs 0.85 V for Au and 0.90 vs 0.96 for Ag), possibly on account of the anchoring group effect being shared by the two redox sites. Another interesting point is that high catalytic effects are observed for 3,4-DBT at both electrodes. This might suggest a coplanar disposition of the molecule with respect to the surface, affording surface interaction with the three heteroatoms at the same time. Finally, in the 2,3-DBT and 2,4-DBT cases, a higher catalytic effect is observed on Au when the Br atoms are in distal positions, whereas the opposite is true for Ag.

On both catalytic electrodes the tri- and tetra-bromo derivative cases are complicated by the presence of multiple specific adsorptions, as a consequence of the availability of at least 4 groups capable of specific interactions with the electrode surface in combination with the significantly less negative reduction potential range, allowing adsorption phenomena [21–23].

#### 4. Conclusions

The presence of an anchoring group promotes the electrocatalytic cleavage of C–X bonds on both Au and Ag, to an extent depending on the relative positions between the S atom and the halide leaving group.

High catalytic effects for bromothiophene reduction, even approaching those of Ag in a few cases, are observed on Au, which instead has a significantly lower catalytic activity than Ag for bromobenzene reduction. The anchoring sulfur atom allows the Au surface to recover most of its intrinsically high catalytic activity, overcoming the repulsive effect of the surface charge in the working potential range which, being much more negative than the PZC, significantly hampers Au catalysis for aryl halides. Such an effect appears neatly modulated by the relative position of the Br leaving group with respect to the S atom: the catalytic effects for the reduction of 2-Br positions are significantly higher than those for the 3-positions (nearly approaching the very high catalytic effects of Ag); moreover, they decrease when the beneficial anchoring effect is to be shared between two redox sites.

Also Ag catalytic effects are significantly enhanced in the bromothiophene case with respect to the bromobenzene one, albeit the position of the leaving group is less determining, on account of pre-vailling silver–halide interactions.

The study provides a nice example of the important synergic role of anchoring groups in enhancing molecular electrocatalysis.

#### References

- [1] A.A. Isse, L. Falciola, P.R. Mussini, A. Gennaro, *Chem. Commun.* 3 (2006) 344–346.
- [2] A.A. Isse, G. Berzi, L. Falciola, M. Rossi, P.R. Mussini, A. Gennaro, *J. Appl. Electrochem.* 39 (2009) 2217–2225.
- [3] A.A. Isse, A. De Giusti, A. Gennaro, L. Falciola, P.R. Mussini, *Electrochim. Acta* 51 (2006) 4956–4964.
- [4] A.A. Isse, P.R. Mussini, A. Gennaro, *J. Phys. Chem. C* 113 (2009) 14983–14992.
- [5] A.A. Isse, G. Sandonà, C. Durante, A. Gennaro, *Electrochim. Acta* 54 (2009) 3235–3243.
- [6] S. Rondinini, P.R. Mussini, P. Muttini, G. Sello, *Electrochim. Acta* 46 (2001) 3245–3258.
- [7] A. Ulman, *Chem. Rev.* 96 (1996) 1533–1554.
- [8] J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, G.M. Whitesides, *Chem. Rev.* 105 (2005) 1103–1169.
- [9] J. Noh, E. Ito, K. Nakajima, J. Kim, H. Lee, M. Hara, *J. Phys. Chem. B* 106 (2002) 7139–7141.
- [10] M.H. Dishner, J.C. Hemminger, F.J. Feher, *Langmuir* 12 (1996) 6176–6178.
- [11] A. Gennaro, A.A. Isse, C.L. Bianchi, P.R. Mussini, M. Rossi, *Electrochem. Commun.* 11 (2009) 1932–1935.
- [12] C. Bellomunno, D. Bonanomi, L. Falciola, M. Longhi, P.R. Mussini, L.M. Doubova, G. Di Silvestro, *Electrochim. Acta* 50 (2005) 2331–2341.
- [13] M. Fedurco, J. Sartoretti, J. Augustynski, *Langmuir* 17 (2001) 2380–2387.
- [14] E. Ertas, T. Ozturk, *Tetrahedron Lett.* 45 (2004) 3405–3408.
- [15] L. Brondsma, H.D. Verkruijse, *Synth. Commun.* 18 (1988) 1763–1764.
- [16] D.W. Hawkins, B. Iddon, D.S. Longthorne, P.J. Rosyk, *J. Chem. Soc., Perkin Trans. 1* 19 (1994) 2735–2744.
- [17] S. Gronowitz, Y. Zhong, A.-B. Hoernfeldt, *Acta Chem. Scand.* 46 (1992) 654–660.
- [18] D.L. Ladd, P.B. Harrsch, L.I. Kruse, *J. Org. Chem.* 53 (1988) 417–420.
- [19] M.S. Mubarak, D.G. Peters, *J. Org. Chem.* 61 (1996) 8074–8078.
- [20] D. Deffieux, D. Bonafoux, M. Bordeaux, C. Biran, J. Dunogués, *Organometallics* 15 (1996) 2041–2046.
- [21] S. Ardizzone, G. Cappelletti, P.R. Mussini, S. Rondinini, L.M. Doubova, *J. Electroanal. Chem.* 532 (2002) 285–293.
- [22] P.R. Mussini, S. Ardizzone, G. Cappelletti, M. Longhi, S. Rondinini, L.M. Doubova, *J. Electroanal. Chem.* 552 (2003) 213–221.
- [23] L. Falciola, P.R. Mussini, S. Trasatti, L.M. Doubova, *J. Electroanal. Chem.* 593 (2006) 185–193.