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## Electrochemical evidence of sulfinic acid derivative as an intermediate in the reduction of aromatic sulfonyl chloride in an aprotic medium

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**Abstract:** The electrochemical reduction of p-nitrobenzenesulfonyl chloride (NBSCl) in dimethylsulfoxide (DMSO) solution is used here as a model to investigate the role of sulfinic acid derivative in this compound's global reduction process. Cyclic voltammetric experiments reveal the production of sulfinic acid derivative, which is important in chemical reactions involving the original compound and other intermediates. This paper also discusses the probable mechanisms of the reduction.

**Keywords:** electrochemistry; sulfonyl compounds; sulfinic acid and derivatives; mechanism.

### Introduction

Sulfinic acids are highly unstable organic compounds that do not usually participate in chemical reactions. However, sulfinic acid derivatives are normally observed as intermediates or products of a wide range of electrochemical reactions.

Simonet and Jeminet [1] conducted polarographic studies with aromatic sulfones to investigate the influence of the aromatic substituent in these compounds' reduction process. In a protic medium, they obtained a bielectronic wave corresponding to the production of sulfinate ions and hydrocarbon as an electroinactive substituent. Two monoelectronic waves were observed in an aprotic medium, and the authors suggested the production of the p-toluenesulfinate ion in the global reduction process.

Gourcy et al. [2] studied the electrochemical reduction of aromatic sulfonyl chlorides in acetonitrile and dimethylformamide solutions in the presence of alkyl halides. The reduction of these compounds in an aprotic medium produces sulfinate and sulfide ions, which react with the alkyl sulfide,

producing the corresponding sulfone or sulfide. In dimethylformamide, probably due to the alkaline character of that solvent, the global process indicates the production of chloride, sulfide and sulfonic ions.

Jeminet et al. [3] reported results on their studies of the electrochemical reduction of sulfonyl chlorides in aprotic and protic mediums on mercury, pointing out the role of the acidic nature of the electrolytic solution in the electroreduction process. The global process the authors described indicates the production of sulfinate ions by the faradaic step.

Johansson and Persson [4], who studied the electrochemical reduction of aromatic sulfonyl chlorides on mercury and glassy carbon electrodes in acetonitrile, demonstrated the production of chloride and benzenesulfinate ions using cyclic voltammetry and coulometry on glassy carbon.

The cathodic behavior of long chain aromatic sulfones in a low acidic medium was investigated by Mabon et al. [5]. Their studies conducted in dimethylformamide solutions using cyclic voltammetry and electrolysis under a controlled potential showed cleavage of the C-S bond with the production of sulfinate ions and hydrocarbon.

In a 1991 review, Simonet [6] pointed out the occurrence of the sulfinate ion in the reduction of sulfonyl chlorides via a two-electron cleavage process of the S-Cl bond. Such a cleavage can be considered a source of sulfinate ions as intermediates of the reduction process.

A few years ago, Angelo and Stradiotto [7] proposed a mechanism for the electrochemical reduction of aromatic sulfinic acids in an aprotic medium, demonstrating the importance of the chemical reactions of derivative intermediates.

The above findings lead us to conclude that the production of sulfinate ions in the sulfonyl halide and sulfone reduction process is an essential step. Although sulfonyl halides also lead to the production of the halide ion, and sulfone leads to that of the corresponding hydrocarbon, these studies found no evidence of the role of sulfinic acid derivatives in the global process.

p-nitrobenzenesulfonyl chloride (NBSCl) was elected as a model compound to shed light on the role of the sulfinic acid derivative in the electrochemical reduction process. The electron-removal character of the nitro substituent allows the compound to be reduced at less negative potentials and also to produce stable intermediates. The aim of this work is to find electrochemical evidence of the participation of the aromatic sulfinic acid derivative in the electrochemical reduction process of the corresponding sulfonyl chlorides.

## Experimental

Commercially available NBSCl (Merck) was used as received. The purity of the compound was analyzed using melting point, nuclear magnetic resonance and infrared spectrometry techniques.

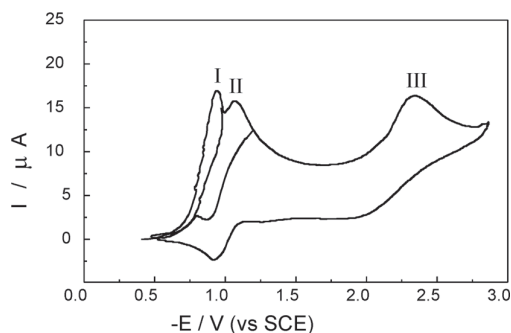
The electrochemical experiments were performed in dimethylsulfoxide (DMSO, Merck) solutions using tetrabutylammonium tetrafluoroborate ( $\text{Bu}_4\text{NBF}_4$ , Merck) as the supporting electrolyte, at 25°C. The solutions were deaerated by bubbling nitrogen gas before each experiment. A two-compartment glass cell was used in the cyclic voltammetric experiments, and a three-compartment cell was used in the potential-controlled electrolysis experiments. The counter electrodes were a platinum ring for cyclic voltammetry and a platinum grid for electrolysis. A glassy carbon disk with an area of 0.07

$\text{cm}^2$  (Tokai Carbon Co.) was used as a working electrode for cyclic voltammetry, and a glassy carbon plate with an area of 9.2  $\text{cm}^2$  (CTA) was the working electrode in our electrolysis studies. All the potentials cited in this work are referred to an SCE, saturated calomel electrode (Analion).

An EG&G Princeton Applied Research model 173 potentiostat-galvanostat coupled to an EG&G Model 175 Universal Programmer was used for the electrochemical studies. The data obtained were recorded with a Houston Instruments Model RE0091 recorder. For rapid scan rates, an IBM-compatible PC interfaced by an ADC card to the above mentioned potentiostat was used.

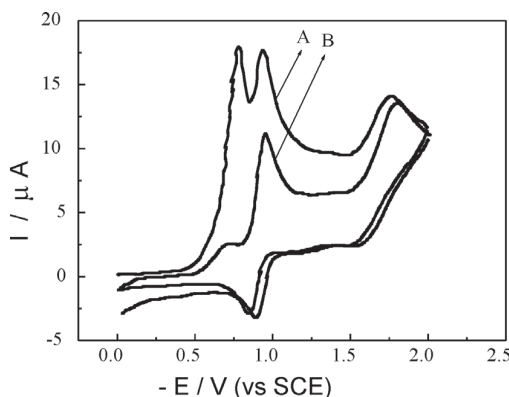
## Results and Discussion

Figure 1 displays cyclic voltammograms obtained for the reduction of NBSCl in DMSO/ $\text{Bu}_4\text{NBF}_4$  on a glassy carbon electrode. Three cathodic peaks are visible at -0.84 V (peak I), -1.0 V (peak II) and -2.2 V (peak III) and one anodic peak at -0.92 V. Peaks I and III did not show the corresponding anodic peaks even when a sweep rate as high as 10  $\text{V s}^{-1}$  was applied, suggesting their irreversible character due to a fast coupled chemical reaction and/or an irreversible charge transfer reaction. On the other hand, peak II indicates the corresponding anodic process located at -0.92 V. The profile is characteristic of the reduction of aromatic sulfur compounds activated by a nitro substituent in aprotic medium.



**Figure 1.** Cyclic voltammograms for NBSCl in DMSO solution at 25°C ( $v=0.10 \text{ V s}^{-1}$ ), with the cathodic sweep reverted after each cathodic peak.

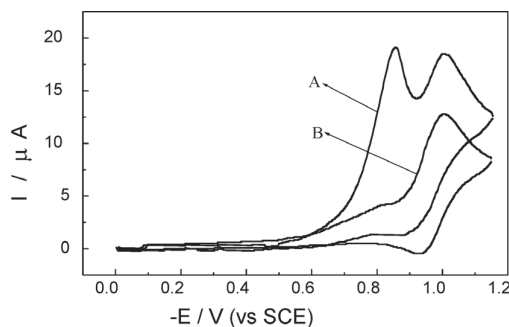
The effect of repetitive scans on the shape of the cyclic voltammograms is shown in Figure 2. In addition to a decline in the current peak due to the concentration gradient, an almost complete suppression of peak I was observed in the successive scans, suggesting that, close to the electrode, NBSCl was consumed through a chemical step following the second and third electron transfer steps.



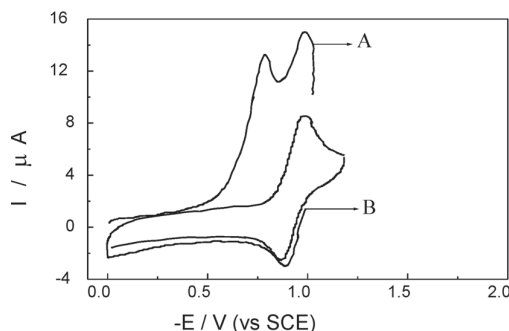
**Figure 2.** Cyclic voltammograms obtained for NBSCl in DMSO solution at 25°C ( $v=0.10 \text{ V s}^{-1}$ ), with the cathodic sweep reverted after peak (III). (A) 1<sup>st</sup> cycle, and (B) 7<sup>th</sup> cycle.

Cyclic voltammograms obtained with the scan limited to the potential of peak II (Figure 3) show the same behavior, indicating that the chemical step occurred with an intermediate produced from the second electron transfer step. This can be explained by the fact that radicals generated in organic compound reactions are usually highly reactive and, when present in the diffusion layer, can react with a variety of species, including the starting compound.

Cyclic voltammetry experiments were also performed by holding the potential immediately after reaching peak II. If the potential is held after peak II, the cyclic voltammogram recorded inhibits peak I, as indicated in Figure 4. This result reinforces the suggestion that an intermediate produced from the second cathodic process reacts with the starting compound through a chemical step. Moreover, it should be noted that a consecutive sweep experiment made after holding the potential allows one to reproduce the voltammetric profile of the sulfinic acid derivative in an aprotic medium [8,9].

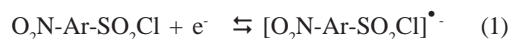


**Figure 3.** Cyclic voltammograms obtained for NBSCl in DMSO solution at 25°C ( $v=0.10 \text{ V s}^{-1}$ ); cathodic sweep reverted after peak (II). (A) 1<sup>st</sup> cycle, and (B) 8<sup>th</sup> cycle.



**Figure 4.** Cyclic voltammograms for NBSCl in DMSO solution at 25°C ( $v=0.10 \text{ V s}^{-1}$ ): (A) start holding for 30 s; (B) restarting of the sweep.

These cyclic voltammetric experiments suggest that the first step in the electrochemical reduction of NBSCl may be:



which is responsible for peak I and produces the starting radical-anion compound that leads to the R-Cl bond cleavage.



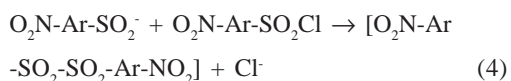
Hence, the sulfinic acid derivative (sulfinic acid radical) produced (eqn. 2) can either subtract a proton from the medium and generate p-

nitrobenzenesulfinic acid or participate in an electron transfer reaction. Furthermore, the same step produces the  $\text{Cl}^-$  ion which is commonly determined to be a product of the electrochemical reduction of sulfonyl chlorides.

Assuming that the sulfinate radical persists in the diffusion layer, such species could receive a second electron (peak II), producing the reactive sulfinate

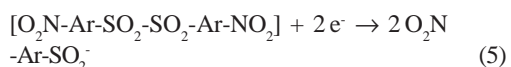


ion. This anion presumably attacks the starting compound via the nucleophilic chemical reaction:



which was probably responsible for the disappearance of peak (I) in the consecutive sweeps and potential-holding experiments. It must be pointed out that step (4) also produces the  $\text{Cl}^-$  ion. This process has also been reported by Lazar and Vinkler [10].

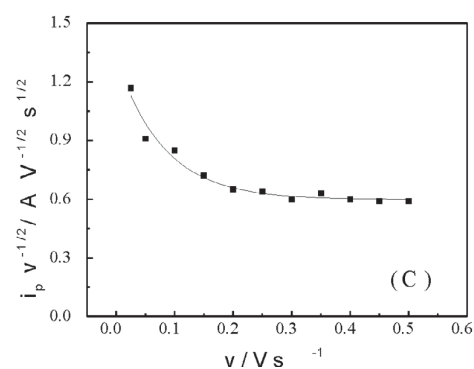
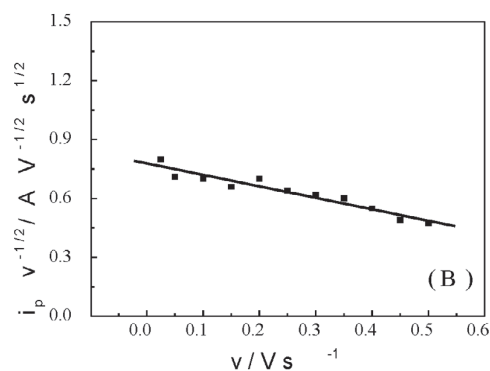
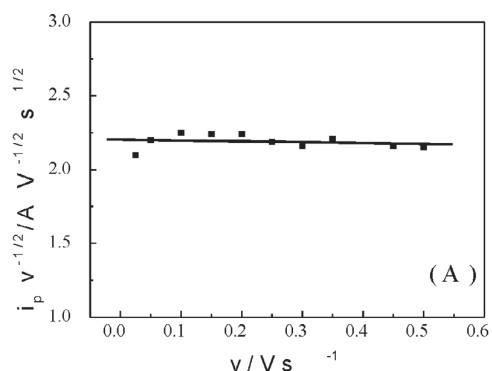
Peak (III) can be formed in response to the electrochemical cleavage of the disulfone produced in step (4):



which also produces the sulfinate ion that can react with the starting compound via step (4). At this point, the global process may acquire a complex and loop like a singularity, in which the nucleophilic attack from the sulfinate ion to the starting compound assumes a prevalent role.

To better understand the cathodic process, the influence of the sweep rate ( $v$ ) on the reduction peaks was investigated. The data obtained, which was plotted as  $i_p/v^{1/2}$ , is shown in Figure 5. The peak current declined slightly with the sweep rate in the first and second cathodic processes of NBSCl reduction. Figure 5 also reveals a pronounced decrease with the sweep rate in the third NBSCl reduction process. These results indicate a chemical reaction occurred in each electron transfer step. Note that this assumption was suggested earlier,

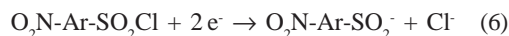
based on the successive sweeps and holding experiments conducted in this study.



**Figure 5.** Influence of the sweep rate on the current function ( $i_p/v^{1/2}$ ) for electrochemical reduction of NBSCl in DMSO at 25°C. (A) peak I; (B) peak II; and (C) peak III.

Our analysis of the influence of the sweep rate on the cathodic peaks also revealed a shift in  $E_p$  (potential of the cathodic peak) as a function of  $\log v$  (sweep rate). The  $\partial E_p / \partial \log v$  values calculated from these plots were 0.031 V, 0.015 V and 0.040 V, respectively, for the first, second and third cathodic step of the NBSCl reduction. These values indicate a significant cathodic shift in the  $E_p$  as the sweep rate increased. Based on the diagnostic criteria, these values suggest a coupled chemical reaction following each faradaic step. It should be pointed out that the magnitudes of such values are established by the kinetic characteristics of the chemical reactions involved, which depend on the stability of the intermediates produced from the faradaic steps.

The overall equation that represents the proposed mechanism is:



which indicates that each molecule of the starting

compound appears to transfer 2 electrons. The constant potential electrolysis experiments produced a number equal to 2.1, which is in good agreement with the predicted value.

The proposed mechanism is congruous with the experimental findings of this work and confirms the reaction products already determined by others [2-4,6]. Therefore, we have shown electrochemical evidence of the participation of the sulfinic acid derivative as an intermediate in the electrochemical reduction of the model compound NBSCl in DMSO solution.

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A. C. D. Angelo, S. M. A. Jorge, N. R. Stradiotto: Evidência eletroquímica do derivado ácido sulfínico como intermediário na redução do cloreto de sulfonila aromático em meio aprótico

**Resumo:** A redução eletroquímica do cloreto de p-nitrobenzenosulfonila (NBSCl) em dimetilsulfóxido (DMSO) foi utilizada como um modelo para o estudo da participação do derivado sulfínico no processo global de redução deste composto. Para isso foram utilizados ensaios de voltametria cíclica, onde foi evidenciada a produção do derivado sulfínico que assume papel preponderante nas reações químicas envolvendo o composto original e outros intermediários. São também discutidos os prováveis mecanismos de redução.

**Palavras-chave:** eletroquímica; compostos sulfonila; ácido sulfínico e derivados; mecanismo.

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