

Cyclic Voltammetric Investigations of 3-aryl-4-bromo Sydnone and its Derivatives at Glassy Carbon Electrode

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Mesoionic 3-aryl-4-bromo sydnone has been studied at glassy carbon electrode in non-aqueous media and its derivatives in aqueous media under different acidic conditions using cyclic voltammetric technique. Effect of cathodic peak potential (E_{pc}) and cathodic peak current (i_{pc}) has been discussed. The effect of sweep rate, concentration, pH, substituents and solvents have been evaluated. The overall electrode processes were shown to be diffusion controlled. The cationic and non-ionic surfactants were inhibited the reduction process. The effect of these surfactants on E_{pc} and i_{pc} has been discussed. The electrolytic products were characterized by controlled potential electrolysis.

Keywords: Cyclic voltammetry; 3-aryl-4-bromo Sydnone; Glassy carbon electrode and Surfactant.

1. INTRODUCTION

Sydnone constitutes a well-defined class of mesoionic compounds [1-5]. Sydnone is the most important representative of mesoionic compounds because they undergo a wide variety of reactions and also possess varied physiological activity. Sydnone finds use as an anti-inflammatory, anti-microbial, anti-cancer and anti-analgesic agent [6-10]. They are known to undergo easy cyclo-addition with acetylenes to give pyrazoles. The reaction involves a 1, 3-dipolar cyclo-addition of the sydnone, behaving like a cyclic azomethine imine [11].

Though biological electron transfer reactions are complicated, both biological and electrochemical electron transfer reactions have many things in common. Both involve essentially heterogeneous electron transfer processes which are pH and temperature dependent and occur at electrode /

electrolyte interface or at membrane / solution interface. The explanations based on electrochemistry have played significant and important role in interpreting and understanding the biological phenomena [12].

The electrochemical reduction mechanism of some derivatives of 3-aryl-4-cyano sydnones have been investigated at hanging mercury drop electrode (HMDE) using cyclic, linear sweep and differential pulse voltammetric methods in Britton-Robinson buffer [13]. These studies have also been reported using square wave voltammetry [14]. The electrochemical reduction of some 3-aryl sydnones have been investigated at wax-impregnated carbon paste and glassy carbon electrode using cyclic voltammetric method in Britton-Robinson buffer [15].

The electrochemical reduction of some 3-aryl sydnones have been investigated at glassy carbon electrode using cyclic voltammetric method in sulfuric acid media [16].

The above mentioned compounds have undergone two electron reduction and on the basis of these observations we have now extended this study to some 3-aryl-4-bromo sydnones. However, surprisingly we found that 3-aryl-4-bromo sydnones have undergone one electron reduction and not two as observed in the 3-aryl sydnones and 3-aryl-4-cyano sydnones because of the presence of bromine group. In the present work, we now report the experimental details and a probable mechanism for one electron reductive dimerization of some 3-aryl-4-bromo sydnones.

2. EXPERIMENTAL PART

2.1. Instrumentation and Apparatus

Electrochemical measurements were done using the electrochemical analyzer EA-201 fabricated by Chemi Link Systems, Mumbai, India. Experiments were conducted in three compartment electrochemical cell. The main compartment of the electrochemical cell consisted of a three-neck flask and contained the solution under investigation. A second compartment, separated from the main compartment by a glass membrane, contained the counter electrode. A platinum foil was employed as the counter electrode. A third compartment contained the reference electrode and a solution with the same composition as that of the main compartment. Contact was made with the main compartment through a stopcock. The reference electrode was saturated calomel.

If not mentioned otherwise, the solutions were purged with nitrogen for 10 min to remove dissolved oxygen and a stream of nitrogen gas was blanketed over the solutions. The surface of glassy carbon electrode was subjected to the below pretreatment.

Before each measurement the glassy carbon surface was polished with alumina (BAS CF-1050) on an alumina polish kit (BAS MF-1040) for 50s and then rinsed with distilled water.

All solutions were prepared using double distilled high purity water and this water is used in all cleaning procedures electrode treatment. Sulphuric acid double distilled PPB/Teflon grade Dimethyl formamide (DMF), Dimethyl sulfoxide (DMSO) and acetonitrile was obtained from Aldrich Chemical Co. Inc. Milwaukee, WI.

Britton Robinson Buffer was used as a supporting electrolyte for variation of pH, which was prepared by mixing 0.04 M each of acetic acid, phosphoric acid and boric acid, sodium hydroxide and hydrochloric acid was obtained from Fischer chemical, Fischer scientific, Fair Lawn NJ.

The 3-aryl-4-bromo sydnones used in our study were prepared in our laboratory according to the reported method [17].

3. RESULTS AND DISCUSSION

3.1. Aqueous media

The cyclic voltammograms of 3-aryl-4-bromo sydnone at a concentration of 2mM in aqueous DMF medium using 50 mM H₂SO₄ as the supporting electrolyte, with a sweep rate of 50 mVs⁻¹ at glassy carbon electrode Fig. 1. It is found to undergo a one electron reductive dimerization.

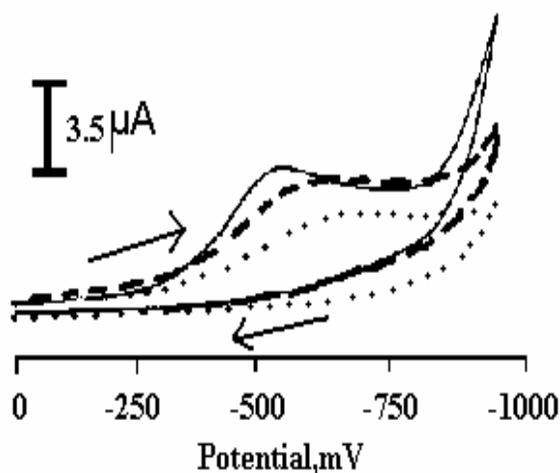


Figure 1. Cyclic voltammogram of 2mM (a) Solid curve: 3-methoxy-4-bromosydnone. Dashed curve: 3-aryl-4-bromo sydnone, Dotted curve: 3-methyl-4-bromosydnone, Scan rate = 50 mVs⁻¹ at glassy carbon electrode (aqueous media).

From the differential pulse voltammogram recorded for the reduction of 3-aryl-4-bromo sydnones, the half peak with ($\Delta W_{1/2}$) is obtained (data is not shown) using the equation [18].

$$\Delta W_{1/2} = 90.4/n \quad (1)$$

The number of electrons (n) involved in the reduction process is found to be one [19] on the basis of the above results the following mechanism is proposed for the electrochemical reduction of 3-aryl-4-bromo sydnones.

From the theoretical method also we calculated the number of electrons by using Randles-Sevcik equation [20].

$$i_p = 2.99 \times 10^5 n(\alpha n)^{1/2} A D_0^{1/2} \nu^{1/2} C_0^* \quad (2)$$

Where, i_p is the peak current μA , α is the charge transfer coefficient. D_0 is the diffusion coefficient cm^2/s , A is the surface area of the electrode cm^2 , ν is the scan rate mVs^{-1} , C_0^* is the concentration in mM .

Here the value of n is equals to one. Further evidence was given by the spectral data in the next section.

3.2. Identification of product analysis

Controlled potential electrolysis was carried out using H-type cell by applying a potential of -630 mV vs. SCE. Products of the electrolysed species were isolated by bulk electrolysis at the glassy carbon electrode and the reduced product was characterized by NMR and mass spectral studies.

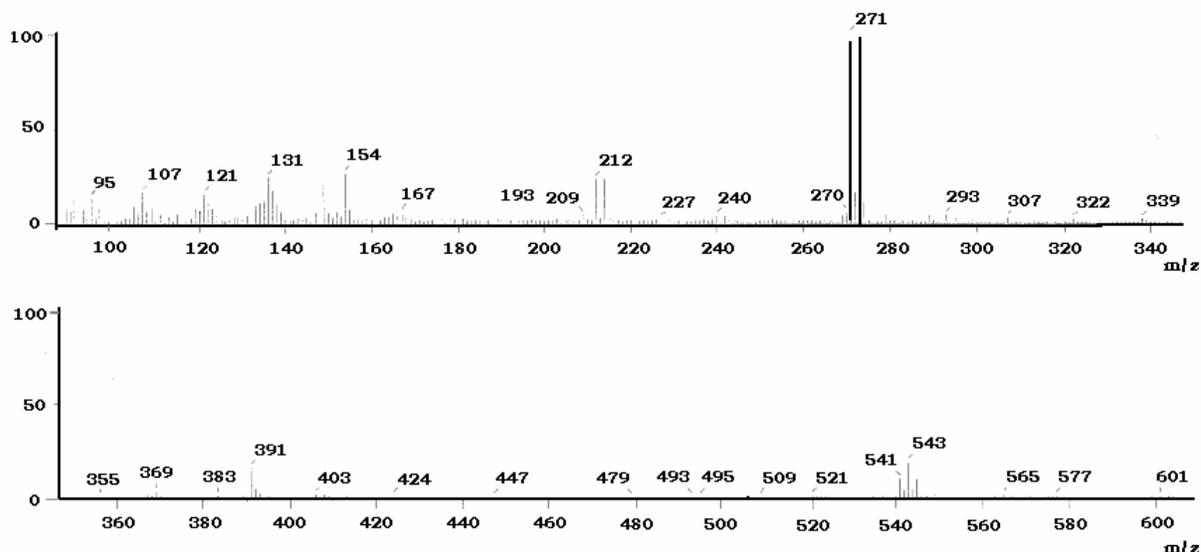


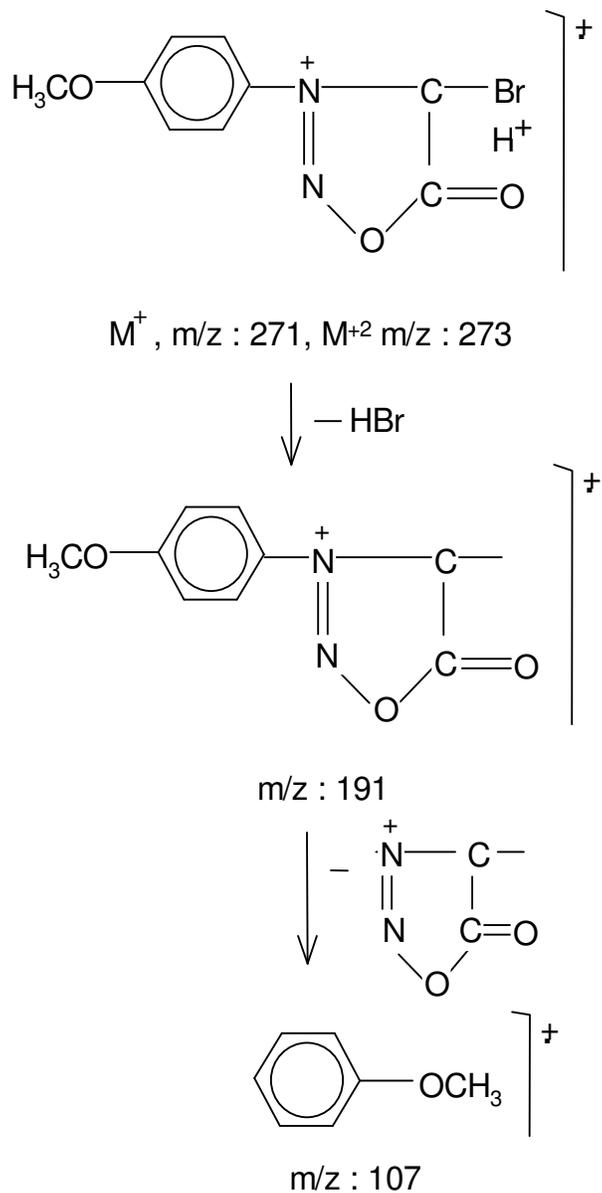
Figure 2. Mass spectra of the reduced 3-methoxy-4-bromosydnone

The formation of a stable protonated species is further evidenced by the spectral data.

^1H NMR spectra of 3-methoxy-4-bromo sydnone shows a singlet at δ 3.87 for the methoxy protons and two doublets at δ 7.25-7.22 and δ 7.75-7.72 for the four aromatic protons (AA'BB' pattern). The spectrum of 3-methoxy-4-bromo sydnone after reduction exhibits a multiplet integrating for five protons in the aromatic region which accounts for an additional proton (either on NH, CHBr or OH are all deshielded).

Electron impact mass spectrum has two molecular ion peaks at m/z 271 and 273 (ratio 1:1) agrees with the molecular weight of the protonated species.

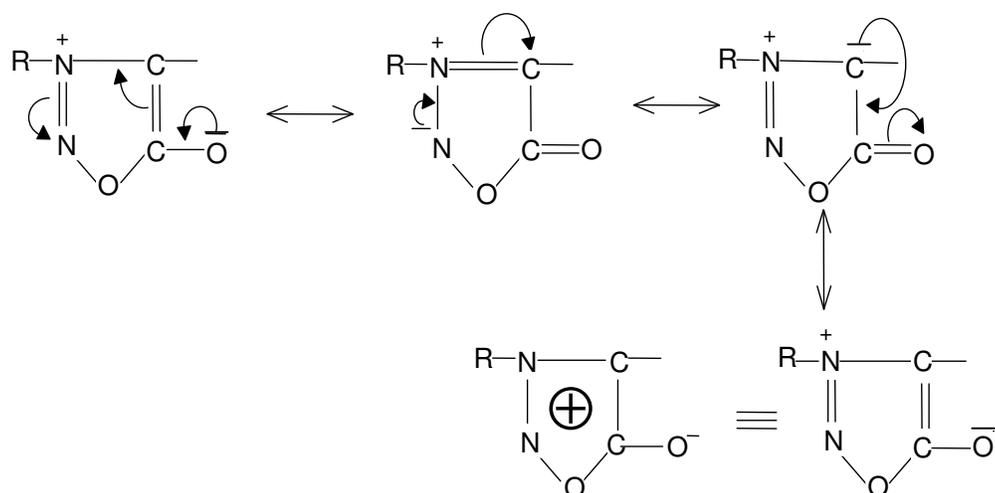
The possible mass fragmentation pattern is given below



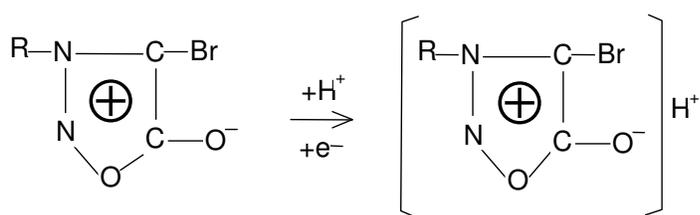
In mass spectrum we got peaks at m/z 541, 543 and 545 in the intensity ratio 1:2:1. It is shown in Fig. 2. It indicates that the compound has undergone one electron reductive dimerization containing two bromine atoms.

3.3. Reaction and mechanism

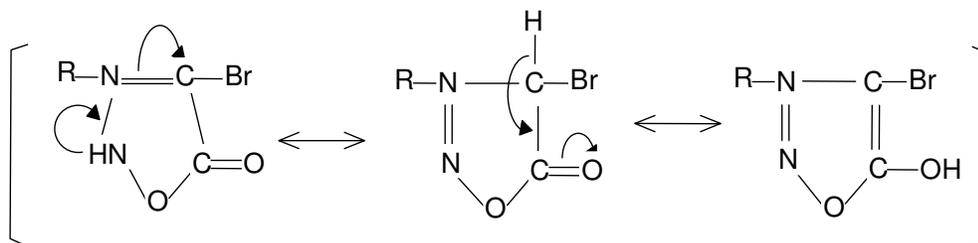
The sydnone ring is represented by resonance hybrid of dipolar and tetra polar structures.



Mesoionic structure



Protonated sydnone



This protonated species must be stable due to delocalization and phototropic shifts.

3.4. Effect of pH

The pH was varied in the range of 1.0 to 5.0 using Britton-Robinson Buffer as the supporting electrolyte at 2mM concentration of 3-aryl-4-bromo sydnone at a scan rate of 50 mVs⁻¹. The cathodic peak potential E_{pc} shift towards more negative potential from -547 mV at pH 1.0 to -943 mV at pH 5.0 (Fig. 3). There was no reduction peak observed in the basic media.

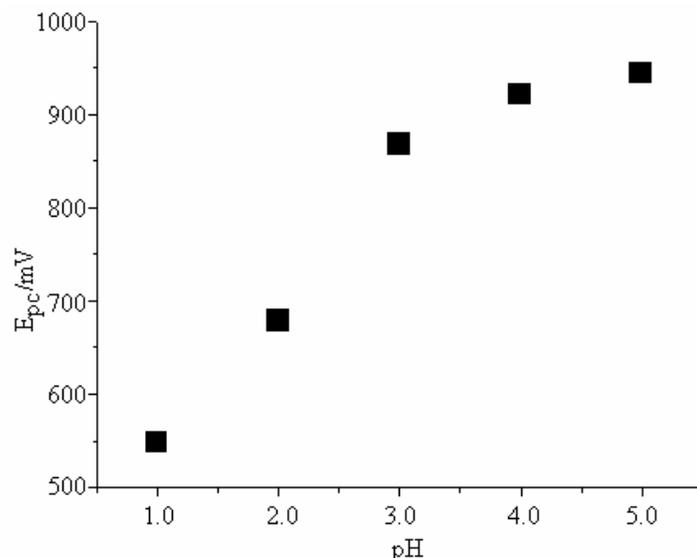


Figure 3. Effect of pH on peak currents of 2mM of 3-aryl-4-bromo sydnone at glassy carbon electrode (aqueous media).

3.5. Effect of concentration

The concentration of 3-aryl-4-bromo sydnone was increased from 1 mM to 5 mM in 50 mM H_2SO_4 as a supporting electrolyte at a sweep rate of $50 mVs^{-1}$. The cathodic peak current increases linearly with the concentration of sydnone and hence obeys Randles-Sevcik equation, which implies that the process is diffusion controlled (Fig. 4).

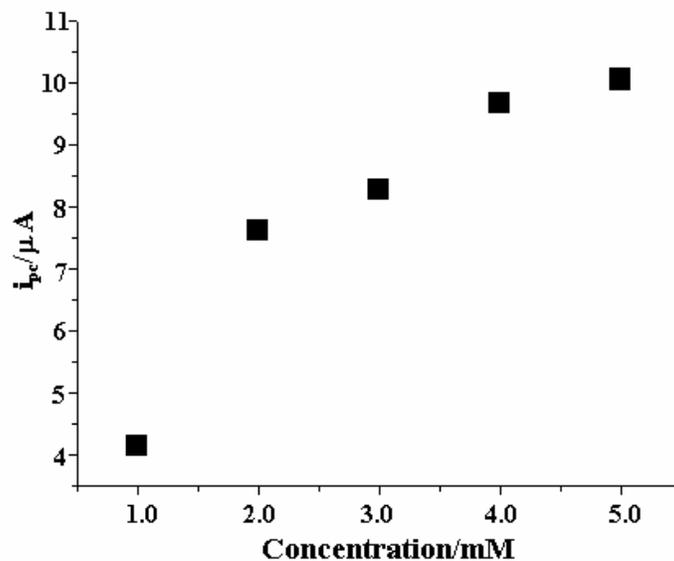


Figure 4. Effect of concentration on peak currents of 3-phenyl-4-bromosydnone at glassy carbon electrode (aqueous media).

It was also observed that the peak potential shift towards more negative values. This kind of shift in E_{pc} in the cathodic direction with increasing concentration of the sydnone indicates that the product of sydnone molecules are adsorbed over the electrode surface [21,22]. This kind of shift has been predicted theoretically [23] and observed experimentally for other reactions [24].

3.6. Effect of scan rate

The effect of scan rate on the electro reduction of 3-aryl-4-bromo substituted sydnones 2mM was examined in different aqueous solvent DMF, DMSO and acetonitrile in 50mM H_2SO_4 was used as a supporting electrolyte. The scan rate was varied from 10 to 200 mVs^{-1} . In all the cases, the cathodic peak current was proportional to the square root of the scan rate. Under these conditions the current process was diffusion controlled [20,25]. Fig. 5 shows the linear relationship between the square root of scan rate and cathodic peak currents of 3-aryl-4-bromo sydnone derivatives at glassy carbon electrode. The cathodic peak shifts towards more negative potential with increase in scan rate.

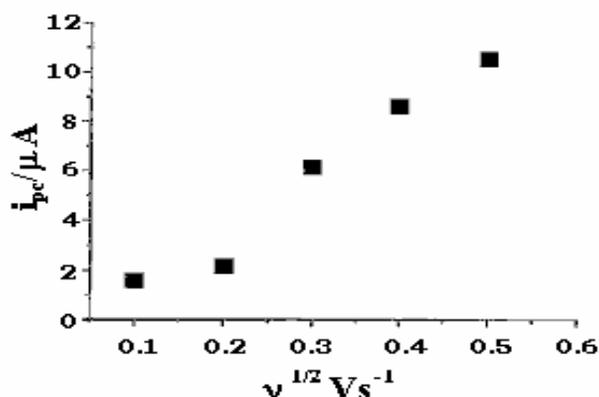


Figure 5. Effect of scan rate on peak currents of 2mM of 3-aryl-4-bromo sydnone at glassy carbon electrode (aqueous media).

3.7. Effect of solvents

The reduction of 3-aryl-4-bromo sydnone 2mM was studied in three different aqueous organic solvents in 50mM H_2SO_4 as the supporting electrolyte with a sweep rate of 50 mVs^{-1} . The reduction potentials were found to be -697, -544 and -622 mV in DMF, acetonitrile and DMSO respectively (Table 1). The easier reduction was observed in the case of acetonitrile. It is reasonable to explain that many properties in solution are affected by interactions between the analyte and solvent molecules. These interactions may be non specific (polarity and polarizability effects) and specific (e.g. resulting from the hydrogen bonding between analyte and the solvent). The solvation process takes place in two steps. In the first, the complex through the hydrogen bonding is formed. These complexes are solvated

by non-specific interactions in the second step. In all other cases the general trend is due to an increase in the dielectric constant, which has the highest value in DMSO [15].

Table 1. Effect of organic solvent and the scan rate on the peak current and peak potentials of 3-aryl-4-bromo sydnone (2mM) at glassy carbon electrode

Scan rate $v(\text{mVs}^{-1})$	DMF		DMSO		Acetonitrile	
	$-E_{pc}$ (mV)	i_{pc} (μA)	$-E_{pc}$ (mV)	i_{pc} (μA)	$-E_{pc}$ (mV)	i_{pc} (μA)
10	561	1.57	542	2.28	414	1.14
20	579	2.16	572	3.78	477	2.19
50	697	6.14	622	5.12	544	3.97
100	760	8.64	677	7.03	602	5.26
200	852	10.5	699	9.92	773	8.55

3.8. Effect of substituents

Electron-withdrawing groups accelerate reduction whereas electron donating groups lowers reduction [26]. Accordingly, methyl and methoxy sydnone undergo reduction at -707 and -566 mV respectively. Both methyl and methoxy groups stabilize the positive charge. The methyl group has positive inductive and hyper conjugative effect whereas the methoxy donates electrons by resonance, i.e., positive mesomeric effect and the dipole associated with it operates in the opposite direction, i.e., negative inductive effect. The hyper conjugation effect of the methyl group operates through the framework of the benzene ring.

The negative inductive effect of methoxy group substantially decreases with distance but its positive mesomeric effect is greatly felt by the aromatic ring as well as the heterocyclic ring in conjugation with it. Therefore, the methoxy group increases the electron density in the aromatic part even more than what the methyl does, which is observed in the peak potential. Therefore, it will be more difficult to reduce the methoxy-substituted sydnone as compared to the methyl-substituted one, as it is evident from the reduction potentials.

3.9. Effect of Surfactants

Surfactants even in trace quantities can exert a strong effect on the electrode process. Adsorption of such substances at the electrode may inhibit the electrolytic process, bring about the irregularity in the voltammogram and cause shift in the wave to more negative potential [27-29].

Surface active substances have the common tendency of accumulation at interfaces. The lack of affinity between the hydrophilic portion of the surfactant and water leads to a repulsion of these substances from the water phase as a consequence of reduction of the microscopic 3-aryl-4-bromo sydnone water interface [30].

These particles thus accumulate at the surface of the electrode and thus decrease the current. Addition of surfactant results in the shift of E_{pc} towards more negative potential. This may be attributed to the direct adsorption of the surfactants at the glassy carbon electrode surface are replaced by the surfactant molecules. At higher concentration of surfactant there was no reduction observed (Table 2). Similar effect was observed for anionic and non-ionic surfactants.

Table 2. Effect of CTAB on the peak current and peak potentials of 3-aryl-4-bromo sydnone (2 mM) at 50 mVs^{-1} in $50 \text{ mM H}_2\text{SO}_4$ at glassy carbon electrode

Concentration x 10^{-5} M	CTAB	
	$-E_{pc}$ (mV)	i_{pc} (μA)
1	681	8.73
2	635	7.87
3	624	7.27
4	620	5.76
5	538	3.75

3.10. Non-aqueous media

The cyclic voltammetry of 2mM 3-aryl-4-bromo sydnones were recorded in the potential range -350 to -1000 mVs^{-1} at glassy carbon electrode in 0.1 M tetra butyl ammonium iodide (TBAI) with DMF. It exhibits in the forward scan one reduction wave and in the backward scan one oxidation wave at 50 mVs^{-1} as shown in Fig. 6. The reduction wave was increased with the sweep rate and oxidation wave in the backward scan. The current was linear when the concentration increases from 2 mM to 12 mM .

The aspect of the voltammogram is the same for all the scan rates $50, 100, 150, 200, 300, 400$ and 500 mVs^{-1} and concentrations. The voltammograms were recorded in a restricted potential range with a ten times better resolution for potential value readings at different scan rates. Analysis of the wave located $\sim -0.9 \text{ V}$ according to the usual electrochemical tests, shows that it corresponds to a quasi-reversible mono electronic charge transfer.

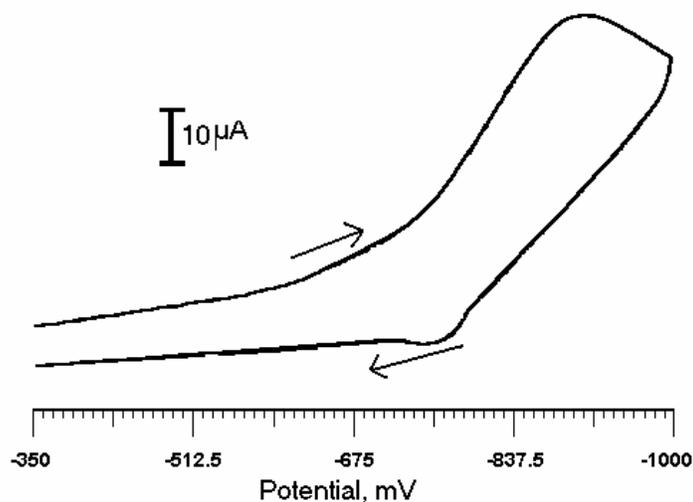


Figure 6. Voltammogram of (2mM) of 3-aryl-4-bromo sydnone, scan rate 50 mVs^{-1} at glassy carbon electrode in 0.1 M TBAI (non-aqueous media)

The standard rate concentration k_s of the charge transfer process was calculated using the Nicholson [31] between the anodic and cathodic peak potentials separation ΔE_p and the function Ψ

$$\Psi = 28.8 k_s v^{-1/2} \quad (3)$$

One obtains $k^s \cong 2 \times 10^{-3} \text{ M}$ indicating an intermediate charge transfer process [32].

The peak current for all compounds increases with square root of the sweep rate $v^{1/2}$. A plot of i_p as a function of $v^{1/2}$ is linear, characteristic for a diffusion controlled process (Fig. 7).

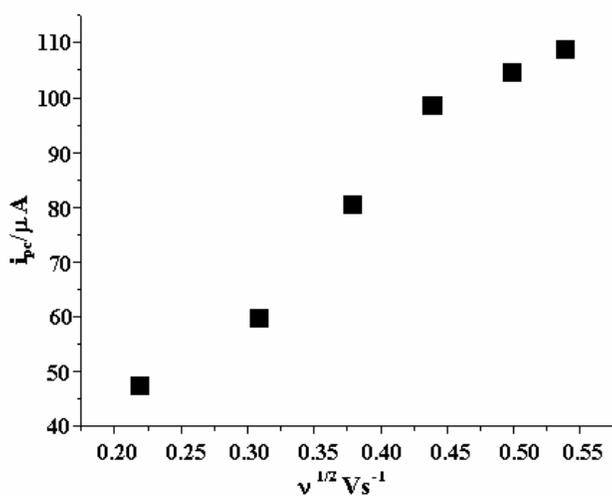


Figure 7. Effect of scan rate on peak currents of 2mM of 3-aryl-4-bromo sydnones at glassy carbon electrode (non-aqueous media).

4. CONCLUSIONS

3-aryl-4-bromo sydnones undergoes one electron reductive dimerization. Cathodic peak current increases linearly with the square root of scan rate and also with the concentration of the electro-active species. This suggests that the overall electrode process is a diffusion controlled. The electro-donating group lowers reduction and electron-withdrawing group accelerate reduction. Inductive and mesomeric effects play a dominant role in the reduction process.

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