



Research Article

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## Anodic behaviour of mono substituted aromatic benzenoids in acetonitrile-water solvent on graphite surface under protic conditions

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### ABSTRACT

Electrochemical oxidation of selective aromatic benzenoid compounds have been attempted in 1:1 MeCN - Water solvent mixture under protic conditions using 4M sulfuric acid on Graphite electrode in a locally fabricated divided H-Cell. Working potentials were arrived at and suitable electroanalytical interpretations are offered. Electrochemical acetamidation along with Hydroxylation and dimerization have been reported to occur. Products were identified with pmr. Suitable electrochemical reaction routes are proposed for ECEC pathway.

**Key words:** Electrochemical, Graphite, MeCN-Water, acetamidation, N-aryl acetamide

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### INTRODUCTION

The importance of N-aryl acetamide has been widely studied in the field of chemical, agricultural [1] and pharmaceutical fields [2-5]. The synthetic aspects of these derivatives assume paramount importance as they are patented. Most of the synthetic formulations involved circuitous, multi-staged and complicated chemical techniques with an inevitable strain of resorting to the process of separation. In recent years, alternative electrochemical methods of syntheses, involving both direct and indirect anodic oxidative methods have been reported [6-9]. Having realized the importance and crucial applications of N-aryl acetamides, an effective and alternative electrochemical synthetic route has been attempted.

To consolidate the electrochemical and electroanalytical parameters, anodic acetamidation on selective homo aromatic benzenoids, has been designed with an intention of getting the insight into its electrochemical pathway, as very little work on this process has been reported.

### EXPERIMENTAL SECTION

The anodic process was carried out with six mono substituted benzenes-four with electron donating and two with electron withdrawing substituents. 0.1 M solutions of substrates in 1:1 MeCN-H<sub>2</sub>O were subjected to electrolyses in protic condition with 4 M H<sub>2</sub>SO<sub>4</sub> on graphite surface. Electrolyses were carried out in divided H- cell with a G4 sintered disc separator with 2 mm thickness and of 2.5 cm diameter in an inert atmosphere of Nitrogen gas circulated above the level of electrolyte. Rectangular pretreated graphite rods were employed as working and auxillary electrodes. Potentials were measured as electrode potentials with reference to saturated calomel electrode [SCE] coupled with the anode through a drawn luggin capillary super-filled with saturated KCl solution.

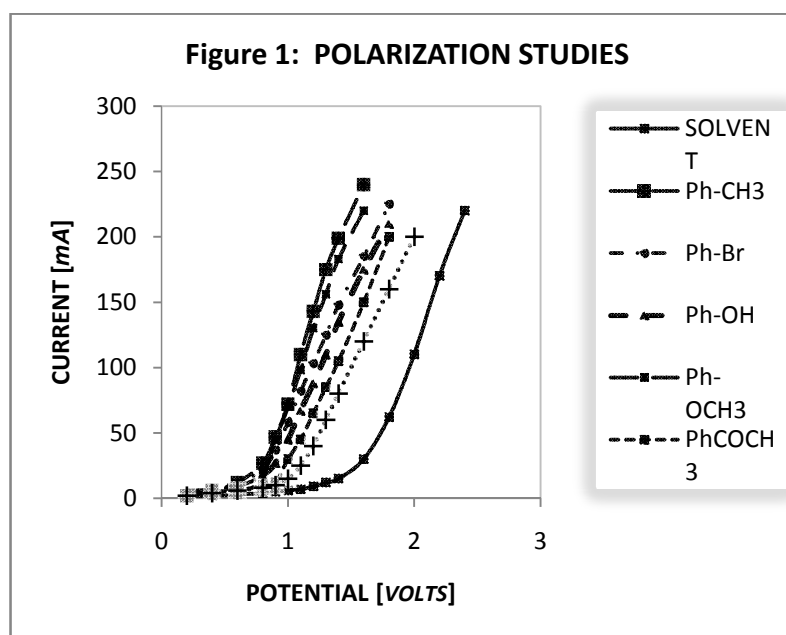
Working potentials were arrived at by polarization studies. The intensities of current realized at a wide range of potentials were recorded and tabulated [Table 1]. Graphical representation of these values was obtained [Fig.1]. A blank run of current-potential behavior was obtained with solvent- electrolyte combination. The quantum of current to be passed at the appropriate working potential maintained for each system is arrived at from Faraday's laws,

taking into consideration the current realized at the maintained potential with the effective surface area of the electrode material. After the passage of calculated quantum of current, both analytes and catholytes were independently subjected to ether extraction process.

**Table 1: CURRENT - POTENTIAL RELATIONS**

[SUBSTRATE] : 0.1 M  
 SOLVENT : 1:1 MeCN – WATER  
 ANODE : C ;  
 CATHODE : C  
 TEMP :  $30 \pm 1^\circ\text{C}$   
 ELECTROLYTE : 4M  $\text{H}_2\text{SO}_4$   
 CELL : DIVIDED CELL

S.No	Potntial [volts]	CURRENT [ mA ] (vs SCE)						
		Solvent	Ph-CH <sub>3</sub>	Ph-Br	Ph-OH	Ph-OCH <sub>3</sub>	PhCOCH <sub>3</sub>	PhCOOEt
1	0.2	2	2	4	5	3	2	2
2	0.4	2	6	7	6	5	5	4
3	0.6	3	12	12	10	9	6	6
4	0.8	4	27	22	18	19	10	8
5	0.9	5	47	37	27	45	12	10
6	1	6	72	58	45	70	30	15
7	1.1	7	110	82	67	98	45	25
8	1.2	9	143	103	88	130	65	40
9	1.3	12	175	125	110	156	85	60
10	1.4	15	199	148	135	183	105	80
11	1.6	30	240	185	175	220	150	120
12	1.8	62		225	210		200	160
13	2	110						200
14	2.2	170						
15	2.4	220						



The product mixture was apportioned and identified by *Co-tlc* and preparative *tlc* techniques using plates with 2mm thickness of silica gel-G, TLC grade (BDH). The products were characterized by chemical and spectrochemical (*pmr* BRUCKER-400mhz in  $\text{CDCl}_3$ ) analyses. Toluene, Anisole, Bromobenzene and phenol were the set of substrates with electron donating substituents and acetophenone and ethyl benzoate with withdrawing influence.

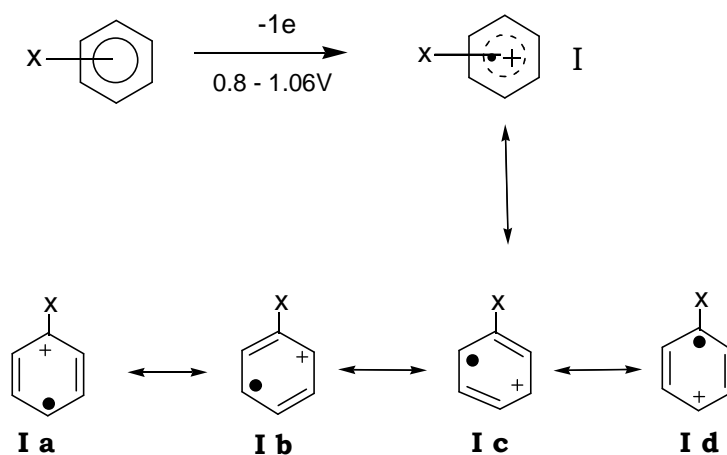
In the present study *meta* / *para* acetamido substituted aromatic derivatives along with phenolic products were observed as major products. A couple of dimers were formed in smaller proportions as minor products along with traces of identified side products. The comparative product yields were realized by employing *glc* [Toshniwal RLO4 (3mmx2.5mm SS column packed with SE chromosorb WHP)]

## RESULTS AND DISCUSSION

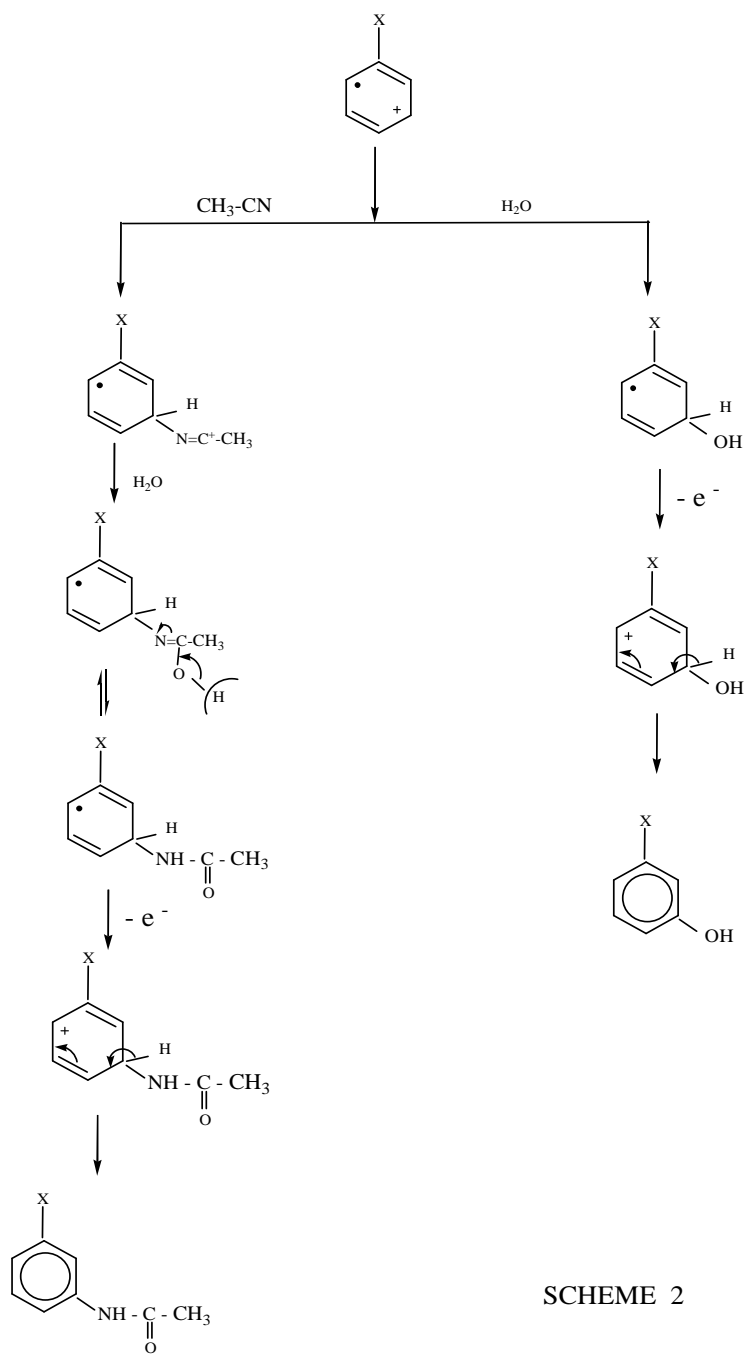
The fact that the polarization curves for the systems under study tread well below the decomposition potential of the solvent-electrolyte combinations, the feasibility of the electrode processes of all these systems is ascertained. The trend in the working potential values of the various substrates seems to have relevance to the field effects of the substituents present in them. Hyperconjugative, inductive and mesomeric influences either opposed or reinforced with each other influence the ease of electron transfer at the anode. The pattern by which shifts in working potential occurred indirectly conveys a crucial fact that it is by the same manner electron transfer occurs. Furthermore, the observation leads to an inevitable involvement of aromatic  $\pi$  cloud at the initiation step. This proposition is quantitatively supplemented by earlier reports through a wide range of periods [10-13].

Electrochemical oxidations on aromatic system at graphite surface have been exhaustively reported. Some interesting observations involving the participation of additives during the electrolysis are worth consideration. The role of solvent and supporting electrolyte in the electrode process is of primary importance [14].

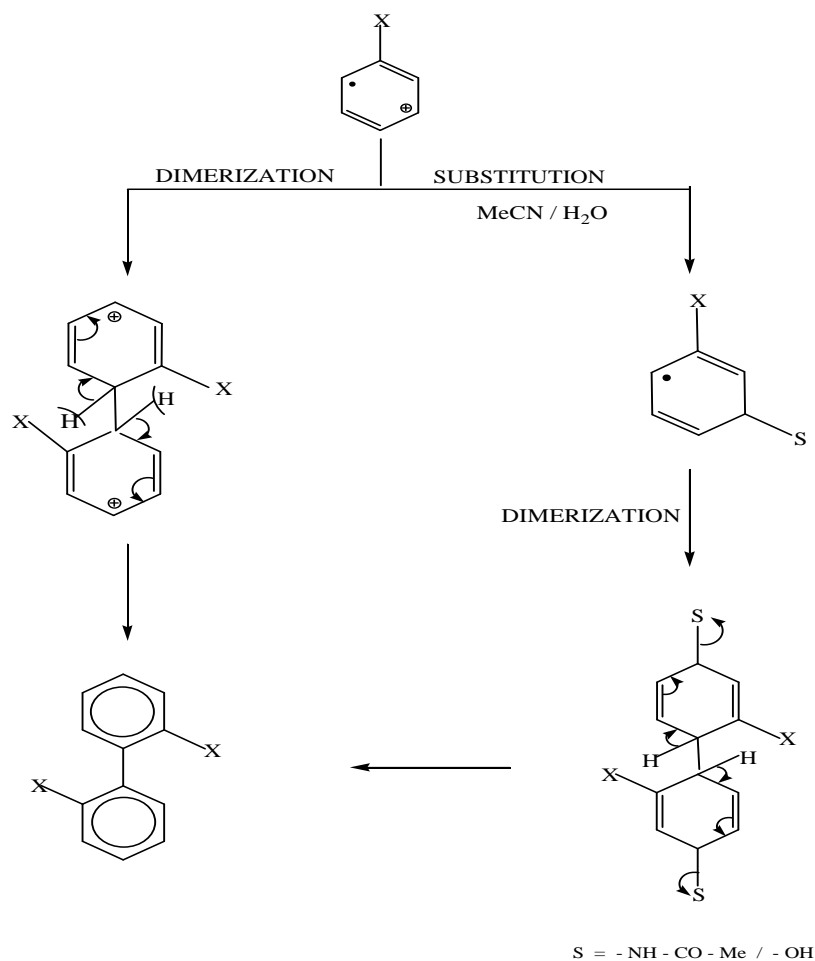
Accommodating the above valid observations, a prospective ECEC electrochemical pathway for the process under investigation is proposed. The working potentials maintained in the present experimental exploration fall around the reported decomposition potential for the aromatic  $\pi$  system, viz .0.82 volts (vs SCE). As a logical sequence, the initial step involved is assumed to be the abstraction of an electron from the aromatic  $\pi$  cloud at a potential depending on the nature of the substitute. This results in the generation of a radical cation I from the chemisorbed substrate molecule [Scheme 1]. As and when the radical cation get generated, desorption at the graphite electrode occurs, pushing the radical ion into the solvent across the electrical double layer. Consequently the radical cation I becomes vulnerable to the attack of either a radical or a nucleophile in the medium. In the present experimental environment, either acetonitrile molecule with the nitrogen terminus or the water molecule with oxygen terminus may attack the radical cation. This situation leads to the formation of the initial  $\pi$  complex leading to a  $\sigma$  complex which happens to be a radical. Such radicals are left with alternate options of undergoing dimerization or of subjecting themselves to the second 1- electron oxidations [ Scheme 2 &3]. The resulting dimer intermediate or a carbocation exist under considerable stress due to non-homogeneity in the hybridization levels inside the ring. This unfavorable situation may act as a driving force for aromatization to occur, ultimately resulting in acetamido substituted derivative [N-Aryl acetamides].



SCHEME 1



SCHEME 2



SCHEME 3

### CONCLUSION

Preliminary works on electrochemical acetamidation has accomplished the working potentials for chosen mono substituted Benzenoids. A probable reaction pathway proposed has to be established by further work which is being on the anvil. Electroanalytical studies are being studied to offer physico chemical interpretations on the present investigation.

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