

## Electrochemical Bromination of Acetanilide in Protic Media at Graphite and Platinum Anodes

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Electrochemical bromination of acetanilide with sodium bromide in 5 % acetic acid solution at graphite/platinum anode has been carried out. *o*- and *p*-Bromoacetanilides are the products on platinum where as *p*-bromoacetanilide and a benzidine derivative have been isolated at graphite and their identities confirmed by chromatographic and PMR spectral studies. While conventional aromatic electrophilic substitution with bromonium ion has been conceived at platinum electrode, a nucleophilic attack by bromide ion on a cation radical is the obvious choice at the graphite electrode.

**Key Words:** Electrochemical, Bromination, Acetanilide.

### INTRODUCTION

In earlier reports on anodic halogenations, it was argued that the bromination of certain aliphatic and aromatic compounds were not possible, because of the ease of oxidation of bromide ion to bromine<sup>1</sup>. In subsequent years, there was a break through in achieving electrochemical bromination of a number of aromatics under specific conditions<sup>2-4</sup>. Studies on electro bromination in earlier years have been reviewed in the literature<sup>5-7</sup>. Recent work on the bromination of aromatics suggests a reaction of cationic substrate with halide ion<sup>8</sup>. However four different propositions involving cationic intermediate, electrogenerated molecular halogen, radical and solvent, in the halogenation of aromatics have been suggested. Electro halogenation of the aromatic nucleus bearing an electron donating substituent has been reported to proceed in both regio- and product-selective fashions<sup>9</sup>. Among the various bromides employed, sodium bromide has been reported to be an effective electrolyte<sup>10-11</sup>, in bringing about the anodic process. In the present work, brominations of acetanilide at graphite and platinum electrodes with sodium bromide have been explored with an intention of probing their mechanistic and electro-analytical aspects.

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## EXPERIMENTAL

Acetanilide [S.D. Fine] was purified by recrystallization from dilute ethanol and characterized by its physical parameters. Sodium bromide (BDH) was purified by recrystallization from water. Electrolyses were carried out in the divided H-Cell designed in this laboratory, with rectangular graphite electrodes or with platinum strips. The graphite electrodes were cleaned, initially by polishing with emery papers with decreasing grain size, while platinum was activated with the deposition of platinum black using chloroplatinic acid. They were subsequently washed with water and with methylene chloride and were kept in distilled water till they were employed in the electrolytic cell. The voltages were recorded as cell voltages. A locally fabricated transistorized DC power supply [0-5 V, 500 mA range] was employed.

Current-Voltage studies were performed independently with graphite and with platinum anodes. Graphite/platinum was used as cathode accordingly. 0.5 M sodium bromide in 5 % acetic acid solution was distributed in the divided cell. Calculated quantity of acetanilide was added so as to realize a 0.1 M anolyte solution. Assuming a 2-electron oxidation at the aromatic ring, the duration of current passage was arrived at, in accordance with the current realized at the maintained potential so as to realize 2F/equivalent quantum of current. During the electrolysis, the anolyte was kept stirred with a magnetic stirrer. The products were extracted with ether from anolyte, resolved with thin layer chromatographic test plates and identified with conventional chemical tests and with PMR spectra (Bruker DSX- 300 MHz instrument in  $\text{CDCl}_3$  solvent.)

## RESULTS AND DISCUSSION

The background current-potential plot was pertaining to the protic solvent along with the electrolyte. The plots (Fig. 1) for solvent and solution at graphite anode indicate an electron transfer process occurring before the decomposition potential of the electrolyte. This suggests a possible oxidation at the substrate molecule.

TABLE-1  
POLARIZATION STUDIES

Substance: 0.1M acetanilide; Solvent : 5 % acetic acid in water; Electrolyte: 0.5 M sodium bromide; Temperature:  $30 \pm 1$  °C; Anode : Graphite/platinum; Cathode: Graphite/platinum

Potential (volts)	Current (mA)		
	Solvent	Solution (in Pt)	Solution (in C)
0.5	2	2	5
1.0	2	2	6
1.5	5	7	15
2.0	11	15	26
2.5	25	27	24
3.0	44	49	84
3.5	66	75	120

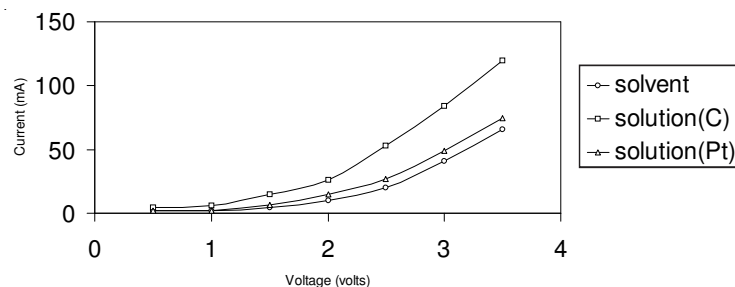
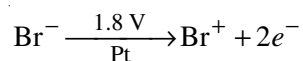


Fig. 1.

On the other hand, on platinum electrode, both the curves (Fig. 1) almost overlap with each other, indicating the oxidation of electrolyte and not of the substrate. This observation has much relevance to the earlier reports that carbon electrodes favor 2-electron oxidation, providing cationic species, while platinum electrodes are liable to bring about no more than 1-electron oxidation, generating radicals<sup>12</sup>.

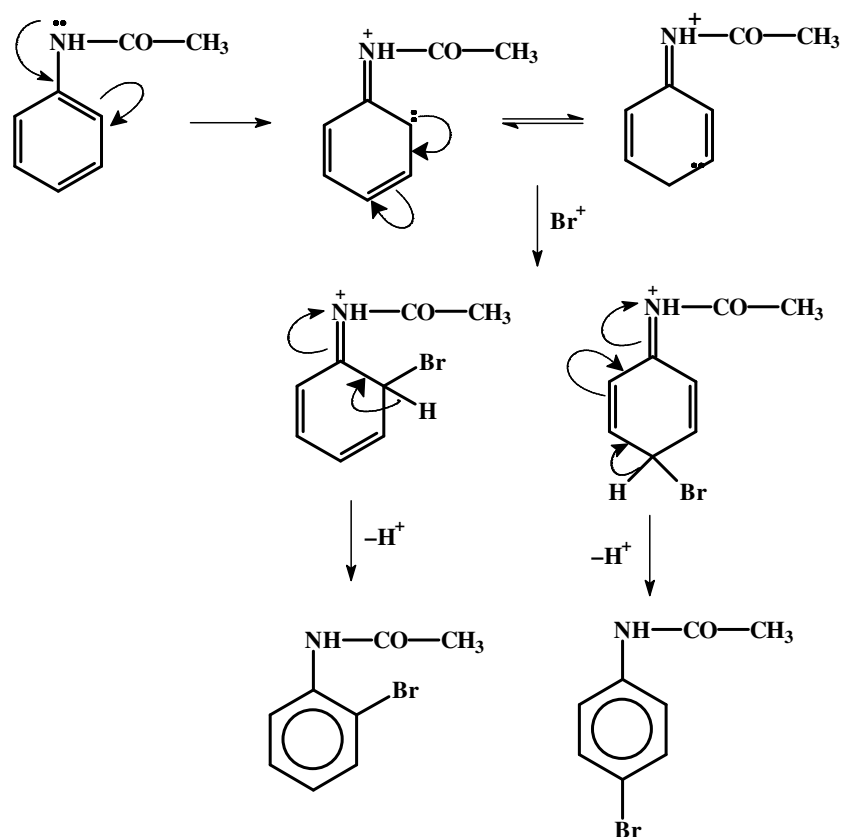
On the basis of observations from polarization studies and with reference to earlier works, two varied mechanistic pathways have been proposed. While conventional aromatic electrophilic substitution with bromonium ion has been conceived at platinum electrode, a nucleophilic attack by bromide ion on a cation radical is the obvious choice for the graphite electrode.

**On platinum:** Anodic bromination may occur either through a charge transfer complex involving the aromatic nucleus with the electrogenerated molecular bromine or through a bromonium ion. As the availability of the  $\pi$ -electron at the aromatic ring possibly provided by the electron donating amino substituent, is partially subdued by the acetyl function, the proposition of the charge transfer complex under this context appears to be less probable. This is very much compatible with the characteristics of the polarization graph where no observable deviation in the curve even when the aromatic substrate is added. Henceforth, at the experimental potential which happens to be more positive than the oxidation potential of the substrate, bromide ion is visualized to undergo 2-electron oxidation, generating bromonium ion (**Scheme-I**).

**Scheme-I**

The generated bromonium ion functions as an electrophile and attacks electron rich *ortho* and *para* positions in the aromatic ring (**Scheme-II**).

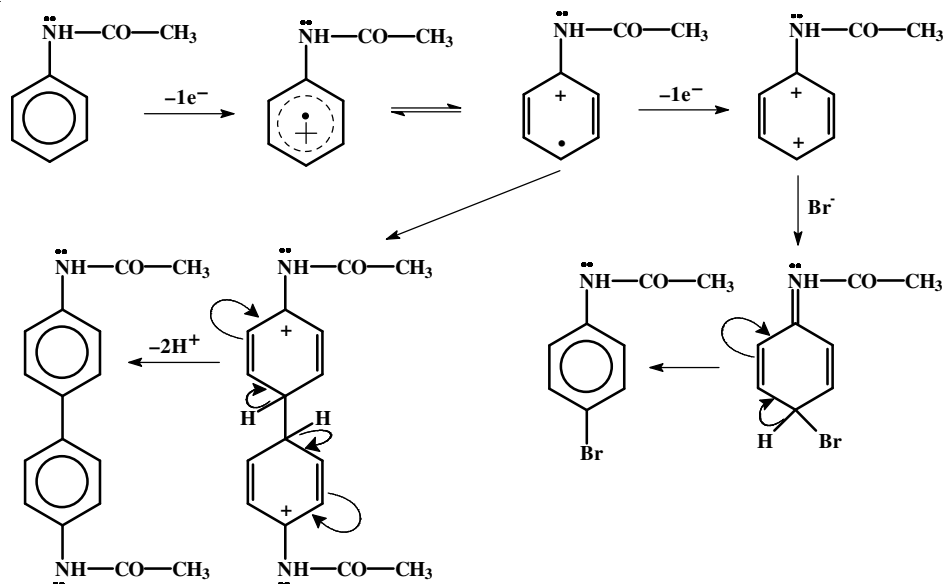
The TLC and PMR spectral studies confirm the formation of *p*-bromoacetanilide and *o*-bromoacetanilide. The better yield observed for *p*-isomer in comparison to *o*-isomer may be attributed to the steric factor associated with the aromatic electrophilic substitution in acetanilide. Earlier reports on the electrochemical bromination of anthracene serve as supportive evidence to this proposition<sup>8</sup>.

**On platinum****Scheme-II**

**On graphite:** The working potential on graphite is kept well below the decomposition potential of the solvent, corresponding to the oxidation potential of aromatic benzenoids. Under this stipulated electrochemical condition of the solvent-electrode-electrolyte, bromination is supposed to be effected through the initial oxidation of aromatic ring, generating a radical cation I. This may undergo dimerization to a benzidine derivative. Concurrently further one electron oxidation of I, may also result to generate the dication II which would have been accessed by bromide ions, to yield *p*-bromo acetanilide (**Scheme-III**).

The formations of *p*-bromoacetanilide and *N,N'*-diacetylbenzidine have been substantiated by TLC and PMR spectral data. The rejected proton would have been consumed by the alkali formed at the cathode. This proposal is conspicuous of the observation that there is a marginal increase in the pH at the end of the electrolysis.

Further work on electro analytical aspects like cyclic voltammetry on this system is being explored in order to draw concrete perceptions about this process.

**On platinum****Scheme-III****ACKNOWLEDGEMENTS**

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