



## **ELECTROREDUCTION OF SCHIFF'S BASES ON GRAPHITE ELECTRODE**

**D. ABIRAMI and T. K. KRISHNAMOORTHY**

Department of Chemistry, AVVM Sri Pushpam College (Autonomous),  
POONDI – 613 503 (TN) INDIA

### **ABSTRACT**

Cathodic reduction of Schiff's bases has been carried out on graphite electrodes in 1 : 1 ethanol–water solvent mixture under acidic conditions. The major reduction product is a 2<sup>o</sup> amine along with dimers and unsaturated 2<sup>o</sup> amines in traces. The most probable mechanism has been proposed. Influence of substituents on the product yield has been studied.

**Key words :** Electro reduction, Schiff's bases, Graphite electrode.

### **INTRODUCTION**

Preliminary electrochemical studies on Schiff's bases are reported in literature<sup>1</sup>. Imines are reported to exhibit a well developed, diffusion controlled polarographic wave, under acidic conditions, while two–electron waves at higher pH values<sup>2</sup>.

In the present work, cathodic process on substituted Schiff's bases has been carried out on graphite electrode in 1:1 ethanol–water solvent mixture. The Schiff's bases of aniline/o–toluidine with benzaldehyde/anisaldehyde/salicylaldehyde/cinnamaldehyde were employed.

### **EXPERIMENTAL**

#### **Materials**

Amines and aldehydes (BDH) were purified by vacuum distillation and kept dry on anhydrous calcium chloride. Their purities were checked by boiling points and confirmed by TLC. Schiff's bases were prepared by conventional methods and their purities were confirmed by TLC.

### **ELECTROCHEMICAL PROCESS**

The electro reduction was carried in a divided cell with a locally fabricated 5V–100 mA regulated DC power supply. The potentials were measured as cell voltages. Current voltage studies were performed with graphite anode, in 1:1 ethanol–water mixture containing 5 mL of concentrated hydrochloric acid. The studies were repeated with 1M solutions of Schiff's bases, under identical conditions.

The catholyte contained 0.1 M Schiff's base in 1:1 ethanol–water mixture and 5 mL of concentrated hydrochloric acid. Assuming a  $2e^-$  process to occur, depending on the intensity of current realized at the given potential, the duration of current passed was fixed. Whenever current decrease was unduly large either the polarity was reversed or potential was taken to zero volt for a short period, as practiced in established electro synthetic works.<sup>3,4</sup>

### Product Analysis

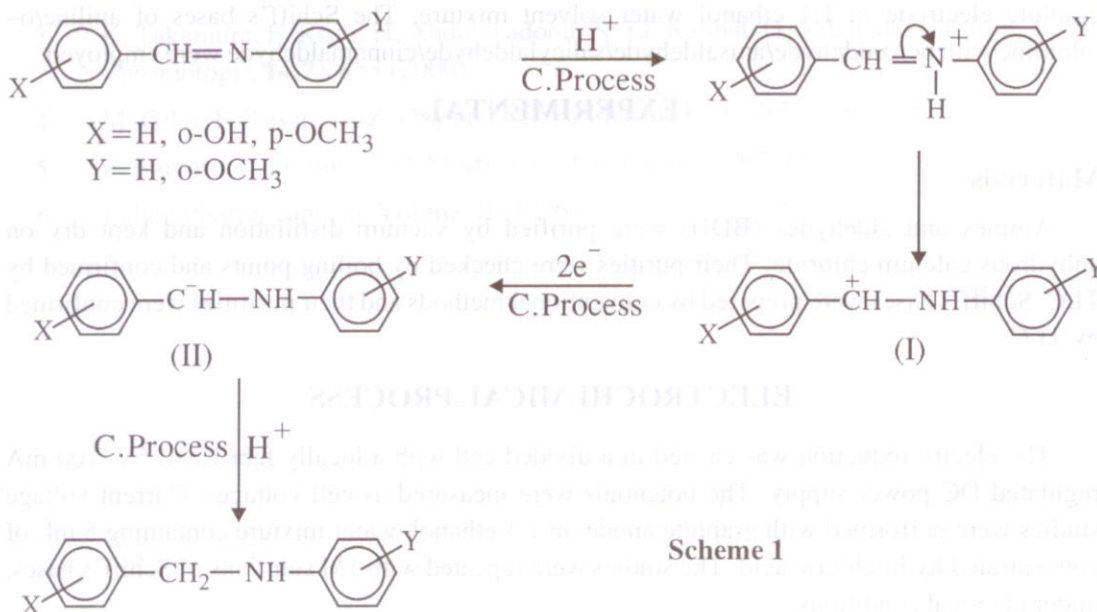
The organic product mixture was separated by ether extraction and resolved on TLC test plate, using 10:4 hexane–ether mixture as eluent. The products were identified by means of co-TLC, physical constants and chemical analysis.

## RESULTS AND DISCUSSION

The current–voltage curves for all the systems recommend a working potential range of 3.3 to 4.2 V (as cell voltages) for the cathodic processes. By a  $2e^-$  process on graphite cathode, Schiff's base gets transformed into secondary amine as the major product, a dimer in traces and an  $\alpha, \beta$ -unsaturated  $2^0$  amine in the case of Schiff's base of cinnamaldehyde.

### (a) Formation of Secondary Amine

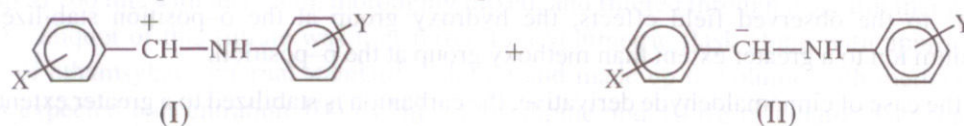
The reduction is initiated by the protonation of the Schiff's base. The positive charge relocates on the adjacent carbon to form a carbonium ion (I). This proposition is supported by earlier works on such carbonium ions at a graphite electrode<sup>5</sup>. Subsequent  $2e^-$  process reduces (I) to carbanion (II), which gets protonated to  $2^0$  amine (Scheme 1).



Such proposal is in conformity with the polarographic studies carried out on imines in acid medium<sup>6</sup>. Earlier studies on electrochemical reductions of ketimines of cyclo-alkanones also report the formation of 2<sup>o</sup> amines<sup>7</sup>.

### (b) Formation of Dimer

When (II) couples with (I), the dimerized product results (Scheme 2).



Scheme 2

Normally dimerizations have been reported by radical combinations. But earlier electrochemical reports reveal that radical initiated electrode processes are being favored on platinum<sup>8</sup>, while carbonium ion forming reactions on graphite electrodes. This prompted us to propose the coupling between (I) and (II) as a secondary process, as indicated by the formation of the dimer in traces.

### (c) Formation of $\alpha, \beta$ -Unsaturated 2<sup>o</sup> Amine

In the case of cinnamaldehyde derivative, the other canonical structure of (II) would have yielded  $\alpha, \beta$ -unsaturated 2<sup>o</sup> amine on protonation. The formation in lesser yield of this product may be attributed to the suppression of resonance effect in the field of electrostatic repulsive forces around cathode.

### Effect of Substituents

Proportional to the intensities of spots in chromatogram, the comparative yields of various secondary amines are arrived at, among these systems.

The increased stability of carbonium ion (**I**) leads to better yields of 2° amine. The decreasing order in the yields of 2° amines may be categorized in terms of aldehyde and aniline moieties, as follows

Aldehyde based : *Salicylaldehyde* > *Anisaldehyde* > *Benzaldehyde* > *Cinnamaldehyde*

Aniline based : *o-Toluidine* > *Aniline*

Due to the observed field effects, the hydroxy group at the o-position stabilizes the carbonium ion to a greater extent than methoxy group at the p-position.

In the case of cinnamaldehyde derivative, the carbanion is stabilized to a greater extent than carbonium ion due to the fact that the presence of lone pair on adjacent nitrogen enhances resonance stabilization of carbanion while inhibits that of carbonium ion.

### REFERENCES

1. R. N. Renaud, *et al.*, *Can. J. Chem.*, **61**, 1376 (1983).
2. H. J. Gardner, *et al.*, *J. Chem. Soc.*, 4180 (1956).
3. Lines Robert and H. P. Utley James, *J. Chem. Soc. Perkin Trans. II*, 803 (1977).
4. N. Porter Quentin, *et al.*, *J. Chem. Soc. Perkin Trans. I*, 1973 (1984).
5. W. J. Koehl Jr., *J. Am. Chem. Soc.*, **91**, 1227 (1969).
6. H. Lund, *Acta. Chem. Scand.*, **13**, 249 (1959).
7. A. J. Fry and R. Reed, *J. Am. Chem. Soc.*, **91**, 6448 (1969).
8. W. J. Boyd, *et al.*, *J. Am. Chem. Soc.*, **102**, 3856 (1980).

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