



BULK ELECTROORGANIC SYNTHESIS OF SCHIFF'S BASE AND IT'S ELECTRICAL BEHAVIOUR

**S. A. SHREEKANTA^a, T. V. VENKATESH^{*}, P. PARAMESWARA NAIK^a
and N. MURUGENDRAPPA^b**

Department of Chemistry, Kuvempu University, SHANKARAGHATTA – 577451 (Karnataka) INDIA

^aDepartment of Chemistry, Sahyadri Science College, SHIMOGA – 577203 (Karnataka) INDIA

^bDepartment of Electronics, Kuvempu University, SHANKARAGHATTA – 577451 (Karnataka) INDIA

ABSTRACT

Schiff's bases has been synthesized by bulk electrochemical method from 5-amino-2-hydroxy benzaldehyde and salicylaldehyde. The product was characterized by spectroscopic techniques. It involves the electrochemical reduction of 5-nitro-2-hydroxy benzaldehyde. The electrochemical reaction has been carried out at copper and silver electrodes in the presence of sodium chloride as supporting electrolyte in water/methanol (50 : 50) solution. The electrochemical reaction has also been performed in presence of sodium sulphate as supporting electrolyte. The electrochemical behaviour of the product was investigated in aqueous methanolic solution at different time interval. The electrochemical reaction has been carried out at copper cathode and silver anode. The electrochemical synthesis was carried at the cell voltage of 30 V and highest current density required for the reduction of nitro group has been achieved.

Key words: Electrochemical reduction, 5-nitro-2-hydroxybenzaldehyde, Salicylaldehyde, Bulk synthesis, Copper cathode, Silver anode.

INTRODUCTION

The electrical properties of simple organic molecules and their polymers have important applications in organic electronics. The electroorganic devices such as OLED (organic light emitting diodes) and organic photovoltaic cells (OPV) are considered to provide the display technology of the future. Components made of organic semiconductors are cheap in their production¹.

The importance of Schiff bases are mainly due to their physical properties²⁻⁴. The electron withdrawing or electron releasing ability of the N-substituent, their position and stereochemistry, as well as hydrogen bond donor-accepter properties, can stabilize one or another tautomer in the crystal. salicylaldimines are thermodynamic compounds. The

* Author for correspondence; E-mail: drtvvenkatesha@yahoo.co.uk

organic molecule containing functional group such as nitro, aldehyde, hydroxyl, amine, acid group are having important role in organoelectronics¹. The organoelectronics that utilize carbon based molecules as conductor. They appreciated for low costs, light weight and rubbery flexibility. The electrochemical behavior of imine group were studied by cyclic voltametry by many researcher¹. The three functional groups nitro, hydroxyl and aldehyde of 5-nitro-2-hydroxy benzaldehyde are electroactive groups. Among these nitro group reduced electrochemically at the highest current densities as shown in the Fig. 1. The -NH₂ group then condensed with aldehyde group of salicylaldehyde forming an imine. This condensation is catalysed by the electrode during the electrochemical process. The percentage yield of the imine is appreciable when compare to the percentage yield of the product in conventional method. The current densities required for the reaction was achieved by using different supporting electrolytes as shown in the tables. The ratio of the water and the organic solvent was adjusted to increase the conductivity of the electrolytic solution. At the beginning the conductivity was due to aqueous organic solvent and the supporting electrolyte. After 50 minutes, the current increases suddenly due to the interaction of organic molecule with the surface of the cathode. The reduction of nitro group begins, the current density increases drastically, the frequency ($F = 1/T$) decreases²⁻⁴.

Schiff bases are the compounds having wide range of biological activities and industrial application. They have been found to possess the pharmacological activities such as antiviral, antibacterial, antifungal, antimalarial, anti-inflammatory, anticancerous¹⁻⁸. The biological activity and industrial applications provoked the chemists for their investigation. Synthesis of Schiff's base by conventional method required more time.⁹ Bulk method is used for the reduction of nitro compounds¹⁰. The chiral properties, biological activity and industrial applications provoked the chemists for their investigation¹¹⁻¹⁵. Chemist have used Electroreduction method for the reduction of nitro compounds^{16,17}.

We have worked-out the formation imine group, CH=N with NH₂ in one of its aromatic ring by electrochemical method in undivided cell. The electroreduction of 5-nitro-2-hydroxy benzaldehyde in aqueous methanolic solution was carried out at copper cathode and platinum anode. It was also carried out using copper cathode and silver anode. The yield at various conditions was shown in the Table 1.

Table 1: Yield of product as various conditions

Cathode	Anode	Solvent	Supporting electrolyte	Isolated yield of the product
Copper	Platinum	Acetic acid-water (20 : 80)	NaOH (E-1)	90%
Copper	Silver	Methanol-water (50 : 50)	NaCl (E-2) Na ₂ SO ₄ (E-3)	85% 75%

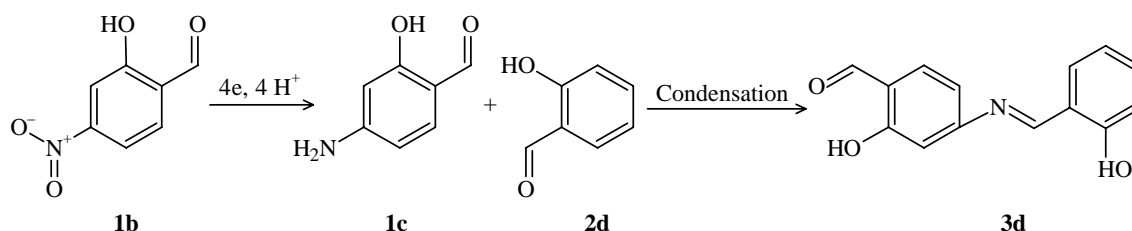
The product was also confirmed by infrared spectral analysis. A broad band at 3426 to 3100 cm^{-1} is due to free -N-H stretching modes. A strong band at 1288 cm^{-1} is due to the C-O stretching vibration of -OH groups. The presence of a strong band between 1686 cm^{-1} indicates the presence of C=O functional group in the aldehyde and C=N group indicated by 1603 cm^{-1} .

The structure of the product was also confirmed by CHN analysis.

EXPERIMENTAL

Apparatus and reagents

The reaction equipments were as follows, the glassware electrolytic cell equipped with zinc plate anode ($3 \times 4 \text{ cm}^2$) and copper plate ($3 \times 4 \text{ cm}^2$) cathode, all chemicals were reagent grade materials. These chemicals were used without further purification.



Scheme

Experimental procedure of the scheme (Experiment-1): Electrode reaction was carried out by dissolving nitrosalicylaldehyde (3 mmol) and salicylaldehyde (3 mmol) in solution containing 20 mL acetic acid and 80 mL water. NaOH (2 g) was added into solution. DC source voltage was adjusted to 30.0 V. The undivided cell was equipped with a copper cathode (Cu-) and a silver anode. Current was measured at different time interval. The dark brown ppt was separated by filtration. The progress of the reaction was monitored by TLC. The product was extracted by dry ether and was recrystallised by acetone. After recrystallisation, product was characterised by IR, ^1H NMR, CHN analysis. The isolated yields of crystallized product was reported in the Table 1.

Experimental procedure of the scheme (Experiment 2): The Electrode reaction was carried out by dissolving nitrosalicylaldehyde (3 mmol) and salicylaldehyde (3 mmol) in solution containing 50 mL methanol and 50 mL water. NaCl was added into solution. DC source voltage was adjusted to 12.9 V (0.34 A). The undivided cell was equipped with a

copper cathode and a platinum anode. The electrolysis was completed in 30 min. the dark brown ppt was separated by filtration. The progress of the reaction was monitored by TLC. The product was extracted by dry ether and was recrystallised by acetone. After recrystallisation, product was characterised by IR, ^1H NMR, CHN analysis. The isolated yields of crystallized product was reported in the Table 1.

Table 2: DC Source; 30.0V, cathode copper wire, anode silver wire, electrolyte 5-nitro-2-hydroxy benzaldehyde, 50 cc methanol, 50 cc water, distance between electrode 2 cm, electrode dipped 2.5 cm

Time in minute	Amount of NaCl in g	Current in mA	Cell voltage	Current density ampere/m ²
0	0	-0.006	0.008	0.24
10	1	-0.008	0.008	0.32
20	2	-0.015	0.008	6.0
30	3	-0.036	0.008	1.44
40	4	-0.067	0.014	2.68
50	5	-0.117	0.017	4.68
60*	6	-0.240	0.013	9.6
70	7	-0.472	0.054	18.88
80	8	-0.480	0.003	19.2
90	9	-0.393	0.026	15.72
100	10	-0.426	0.007	17.04

*Salicylaldehyde is added at this stage, After ten minute schiff's base is formed.

Yield of schiff's base = 85%

Experimental procedure of the scheme (Experiment-3): The Electrode reaction was carried out by dissolving nitrosalicylaldehyde (3 mmol) and salicylaldehyde (3 mmol) in solution containing 50 mL methanol and 50 mL water. Na_2SO_4 was added into the solution. DC source voltage was adjusted to 30.0 V. The undivided cell was equipped with a copper cathode (Cu-) and a silver anode. Current was measured at different time interval. The dark brown ppt was separated by filtration. The progress of the reaction was monitored

by TLC. The isolated yields after crystallization were reported in the Table 1. In Experiment 2 and 3 the electrochemical reaction has been carried out almost in neutral condition (pH = 6)

Highest current density was obtained as in Fig. 1 of Table 2.

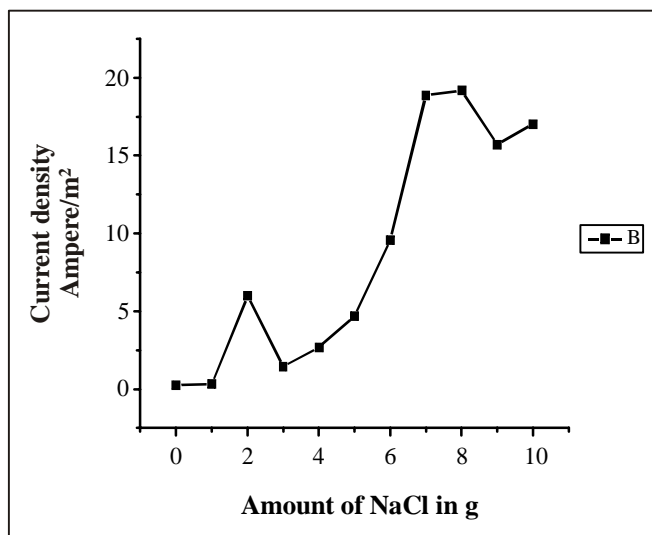


Fig. 1:

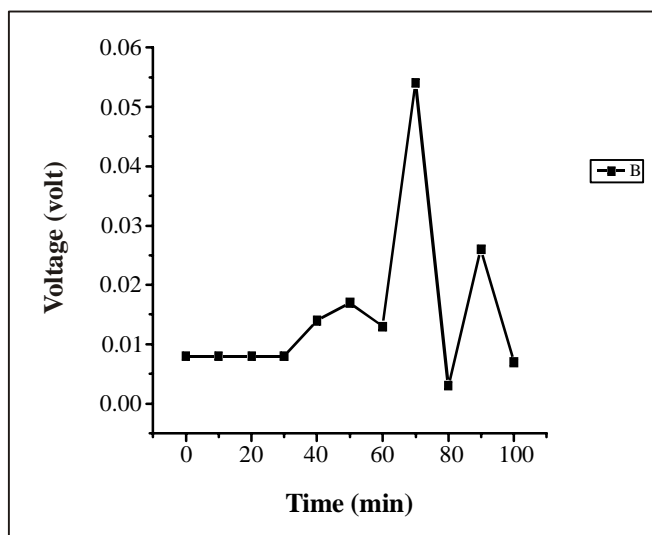


Fig. 2:

Highest voltage has been achieved at 70 min., it shows the electrochemical reaction of above scheme.

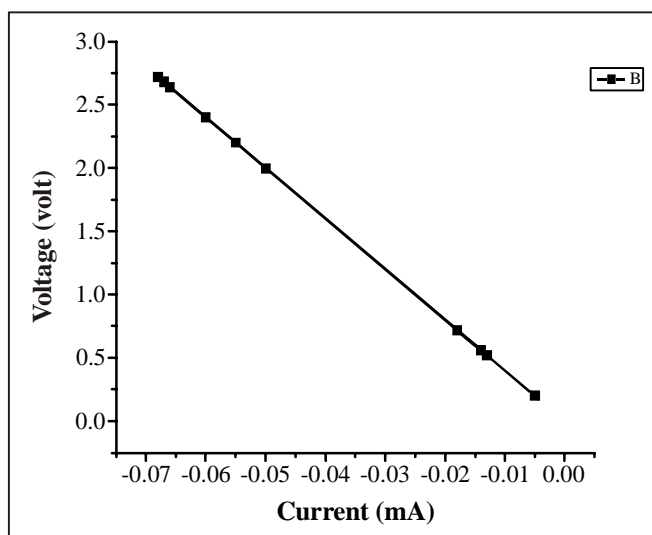


Fig. 3:

A Volt–Ampere characteristic of scheme

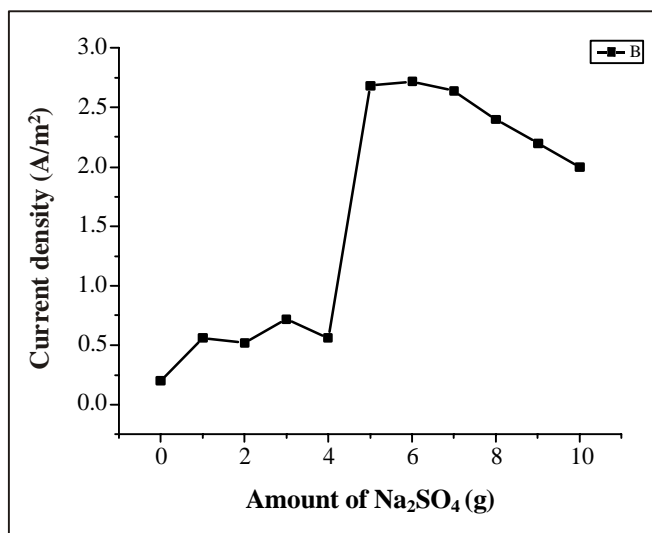


Fig. 4:

Highest current density was obtained as in Fig. 4 of Table 3.

Table 3: DC Source; 30.0V, cathode copper wire, anode silver wire, electrolyte 5-nitro-2-hydroxy benzaldehyde, 50 cc methanol, 50 cc water, distance between electrode 2 cm, electrode dipped in the solution 2.5 cm

Time in minute	Amount of Na ₂ SO ₄ in g	Current in mA	Cell voltage	Current density ampere/m ²
0	0	-0.005	0.008	0.2
10	1	-0.014	0.008	0.56
20	2	-0.013	0.008	0.52
30	3	-0.018	0.008	0.72
40	4	-0.014	0.034	0.56
50	5	-0.067	0.027	2.68
60*	6	-0.068	0.011	2.72
70	7	-0.066	0.011	2.64
80	8	-0.060	0.010	2.4
90	9	-0.055	0.008	2.2
100	10	-0.050	0.007	2.0

*Salicylaldehyde is added at this stage, after ten minute schiff's base is formed.

Yield of schiff's base = 75%. In presence of NaCl, highest current density is produced

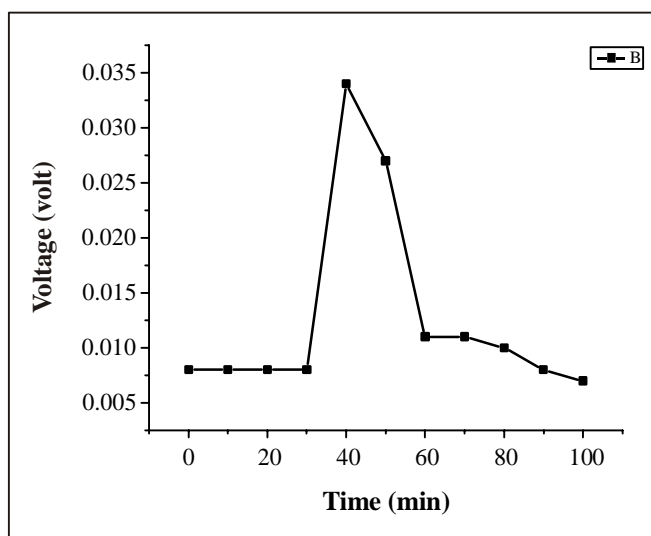


Fig. 5:

Highest voltage has been achieved at 50 min., it shows the electrochemical reaction of above scheme.

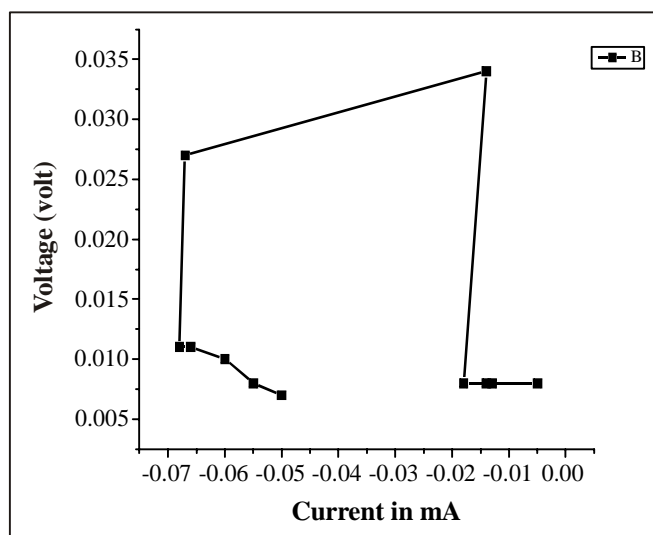


Fig. 6:

A Volt–Ampere characteristic of scheme.

Mechanism

The electrochemical conversion of 5-nitro-2-hydroxy benzaldehyde into 5-amino-2-hydroxy benzaldehyde and then to its schiffs base with salicylaldehyde as in the scheme involves the following mechanism.

The mechanism of reduction of nitro derivatives in various solvents as mentioned in the experimental section proceeds with the formation of hydroxyl amino compounds. The hydroxylamine reduced further into amino derivative in two steps.



The reaction of 5-amino-2-hydroxy benzaldehyde with salicylaldehyde in the scheme can be explained as follows. The aldehyde group condensed with amine group of the compounds and lose a molecule of water forming an imine compound. The process was catalysed by both anode and cathode.



The electrochemical reduction of the compound 5-nitro-2-hydroxy benzaldehyde in the scheme, was studied in the present work. The electrochemical reactions of 5-amino-2-hydroxy benzaldehyde with salicylaldehyde depends on the current densities. Therefore current densities were increased by adding NaCl as the supporting electrolyte. The high yield was found at the current density above 9.6-A/m^2 . This current density was produced by adding 6 g of sodium chloride as shown in Table 2.

The graphics of this table is shown in Fig. 1. It implies that as the concentration of supporting electrolyte increases. Electrode current also increases Cu cathode, Zn anode, 20 cm^3 methanol + 100 cm^3 water. The sodium sulphate was used as a supporting electrolyte, as the concentration of electrolyte increases the electron densities were also increased. The organic compound must atleast partially soluble in water. Therefore in the present work, the compound was dissolved in the mixture of water and methanol. Turbidity was produced while preparing the electrolytic solution. This was avoided by using the mixture of methanol and water in the ratio 20 : 80. The concentration of sodium hydroxide also varied to produce the high current density in the Table 2. This current density was produced by adding 2 g of sodium hydroxide. The sodium hydroxide concentration was increased, so that the pH of the solution increases above nine. This condition was found to be suitable for reduction. As the concentratin of NaOH increases, the current density also increases. It also implies that as the concentration alkali increase electrode current also increases.

RESULTS AND DISCUSSION

It is demonstrated that amino derivatives of Schiff base in the scheme produced by the electrochemically driven reduction of 5-nitro-2-hydroxy benzaldehyde. It was followed by electcatalysed condensation of 5-amino-2-hydroxy benzaldehyde with salicylaldehyde to produce the schiff' sbase. The electrochemical synthesis of schiff' sbase has been successfully performed in one pot in ambient conditions and in an undivided cell using an environmentally friendly method with high atom economy. The high current density was produced in presence of sodium chloride and sodium sulfate as supporting electrolyte. All compounds were obtained in good yield.

REFERENCES

1. M. Tscerner, C. Konrad, A. Bizzarri, M. Suppan, M. Cajlakovic and V. Ribitsch, I. J. 978-1-4244-5335-1/09.
2. Anita Blagus, Dominik Cincic, Tomislav, Branko Kaitner and Vladimir Stilinovic, Maced. J. Chem. Eng., **29**, 117-138 (2010).

3. M. A. Neelakantan, M. Esakkiammal, S. S. Mariappan, J. Dharmaraja and T. Jeyakumar, *Indian, J. Pharm. Sci.*, **72**, 216 (2010).
4. Shelar Mahendra Devidas, Shujat Hussain Quadri, Suresh Arjun Kamble, Faozia Mansoor Syed and Dipak, Y. Vyavhare, *J. Chem. Pharm. Res.*, **3**, 489-495 (2011).
5. Davood Nematollahi and Esmail Tammari, *J. Org. Chem.*, **70**, 7769-7772 (2005).
6. Abdullah Hussein and Kshash, *J. Chem.*, **2**, 2010 (2011).
7. A. M. Walter Lob, Lorenz, *Electrochemistry of Organic Compounds*, 3rd Ed., John Wiley and Sons, Chapman and Hall, Limited, London (1906).
8. Davood Nematollahi and Hassan Goodazi, *J. Org. Chem.*, **67**, 5036 (2002).
9. K. Manish Rawal, Amit Sahu, Rakshit Ameta, V. K. Sharma, Pinki B. Panjabi, *Int. J. Chem. Tech. Res. Coden. USA*, **1**, 1182 (2009).
10. Soonki Won, Wanjoong Kim, Hongbum Kim, *Bull. Korean Chem. Soc.*, **27(2)**, 195 (2006).
11. Santosh Kumar, M. S. Nirjan, K. C. Chaluvvaraju, C. M. Jamakhandi and Dayananda Kadadevar, *JCPR*, **01**, 39-42 (2010).
12. D. Ajay Kumar, Julkarni, A. Sangamesh Patil and Prema S. Badami, *Int. J. Electrochem.*, **4**, 117-729 (2009).
13. S. A. Abd and El-Maksoud, *Int. J. Electrochem., Sci.*, **3**, 528-555 (2008).
14. A. P. Mishra and Neha Sharma, *J. Ind. Council Chem.*, **26**, 125-129 (2009).
15. Percio Augusto, Mardini Farias and Margarida Bethlem Rodriguses Bastos, *Int. J. EElectrochem*, **4**, 458-470 (2009).
16. R. Sarganesh, K. K. Balasubramaniam and S. Venkatachalam, *Bull. Electrochem.*, **6**, 515 (1990).
17. C. J. Patel, A. S. Madhov, G. Ramachandraiah and D. N. Vyes, *Bull. Electrochem.*, **11**, 159 (1995).

Revised : 19.01.2013

Accepted : 22.01.2013