SELECTIVE ELECTROCATALYTIC OXIDATION OF TOLUENE MEDIATED BY SODIUM NITRITE IN BIPHASIC MEDIUM

[1]E.K. Joice, [2]M. Balaganesh, [3]Anitha Varghese and [1]S. Joseph Selvaraj [*]

[1]Department of Chemistry, St. Joseph's College, Tiruchirappalli- 620 002, India.

[2]Department of Chemistry, BWDA Arts and Science College, Kolliyankunam- 604304, India.

[3]Department of Chemistry, Christ University, Bangalore- 560 029, India.

Abstract: Sodium nitrite as an effective redox mediator was used in the electrochemical oxidation of toluene in biphasic medium at ambient temperature. Reaction conditions were optimized to obtain maximum oxidation efficiency on toluene to benzaldehyde. It is a transition metal-free catalytic oxidative conversion. An efficient radical scavenger Butylated hydroxytoluene (BHT) was used in the reaction mixture in order to confirm the presence of nitrite free radical which plays an important role in the oxidation of toluene. Variety of toluene derivatives were converted in to corresponding aldehydes or ketones to test the generality of the reaction.

Keywords: Biphasic electrolysis; Butylated hydroxytoluene; Oxidation; Radical scavengers; Sodium nitrite; Toluene.

1.   INTRODUCTION

The electrochemical conversion of alkyl aromatics into corresponding carbonyl compounds is one of the interesting fields of research for organic chemists. Toluene is an important industrial chemical which is used as a starting material to synthesis benzaldehyde. Benzaldehyde is a versatile intermediate for the production of pharmaceutical intermediates, food additives and dyestuffs [1-3].

There are many research studies on the electrochemical conversion of toluene to benzaldehyde was reported in the literature. Many metal ions such as Ce^{4+}/Ce^{3+}, Co^{3+}/Co^{2+}, V^{5+}/V^{4+}, Mn^{3+}/Mn^{2+}, $Cr_2O_7^{2-}/Cr^{3+}$, $CuCr_2O_4$ spinel nanoparticle catalyst and Co(II) in N-butyl-N-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide ionic liquid have been widely used in anodic oxidation on alkyl aromatics [4-13]. The oxidation of toluene to benzaldehyde and benzyl alcohol is accomplished over chitosan(CTS)-supported Co(II)TPP catalyst [Co(II)TPP/CTS] [14] under a relatively mild reaction condition using air in absence of reductants and solvents. Poly(methylphenylene) films were prepared by direct oxidation of toluene in the mixed electrolytes of boron trifluoride diethyl etherate and trifluoroacetic acid [15]. Graphite/Nafion membrane composite electrodes were used for the electrochemical oxidation of p-methoxytoluene through preparative electrolysis. But along with p-methoxybenzaldehyde, a small amount of p-methoxybenzoic acid was also detected in the product mixture [16]. Metalloporphyrins as catalysts were also used for the oxidation of toluene substrates [17-19]. Most of the reported methods have limitations such as costly catalysts, hazardous reagents and low selectivity. These metal-based oxidation reactions may leave toxic traces of heavy metals in the products. Therefore, it shows that there is a need for developing efficient nonmetallic catalysts for the oxidation of alkyl aromatics under mild conditions.

Some non-metallic catalysts have been reported on the electrochemical oxidation reactions $NaBF_4$ and $Et_4N.BF_4$ as a supporting electrolyte at graphite anodes [20], sodium nitrate [21], sodium bromide [22], sodium chloride [23] have been used for electrochemical oxidation of benzyl alcohol in biphasic medium.

Few reports are available for sodium nitrite as a catalyst in the conventional chemical method. Sodium nitrite $(NaNO_2)/O_2$ system has been reported as a highly efficient transition metal-free protocol for aerobic oxidation of alcohols [24-26]. The deoximation of oximes by Amberlyst-15, $NaNO_2$ under mild conditions [27], oxidative dibromination of alkenes with aqueous HBr and $NaNO_2$ as a catalyst [28], A metal-free catalyzed oxidative bromination of aromatic compounds and aryl ketones utilizing a combination of aqueous hydrobromic acid, molecular oxygen and sodium nitrite as the catalyst [29]. A similar system was also used for aerobic iodination [30].

In present work sodium nitrite has been chosen as a non-metal catalyst for the electrocatalytic oxidation of toluene to benzaldehyde. It is because, it is cheap, easily available, less expensive and less hazardous. Moreover, it is a highly selective catalyst for the electrocatalytic oxidation of toluene.   It is found to be an interesting alternative route for the conversion of toluene to benzaldehyde with the transition metal-free catalyst. Herein, we report the optimization studies of electrochemical oxidation of toluene to benzaldehyde using sodium nitrite as a mediator with Pt/Pt electrode combinations in biphasic medium (Scheme 1).
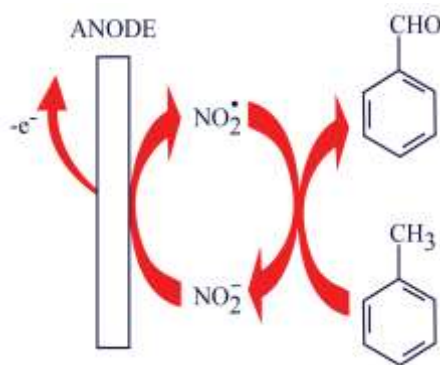
Scheme 1: Electrochemical oxidation of toluene using NaNO₂ in biphasic electrolysis

II. EXPERIMENTAL

The reaction was monitored by a Shimadzu HPLC with LC-8A column (250 mm×4.6 mm) as the stationary phase. The eluent consisted of acetonitrile/water (80:20) at a flow rate of 1 mL/min. Samples were analysed by UV detector at a wavelength of 254 nm. Authentic samples were used to compare and calculate the peak areas of the experimental products for yield calculation.

Electrochemical oxidation of toluene was performed on Electrochemical analyzer, CHI609C (CH Instruments, Inc. USA).

2.1 Electrocatalytic oxidation of toluene using NaNO₂ in biphasic medium

A solution of toluene (1.0 g, 10 mmol) in chloroform (20 mL) was taken in beaker of capacity 200 mL. To this solution, 20.39 mmol of sulphuric acid and 72.46 mmol of sodium nitrite in 80 mL of water were added. Here, in this reaction mixture, sodium nitrite was considered as a mediator and sulphuric acid as a supporting electrolyte. The reaction mixture was developed with two phases. Two platinum electrodes (each of 15 cm² area) with inter electrode distance of 2 cm were introduced through upper aqueous phase and electrodes were positioned in the aqueous phase without touching the organic phase but very close to the interphacial region. The experimental setup has been shown in Figure 1.
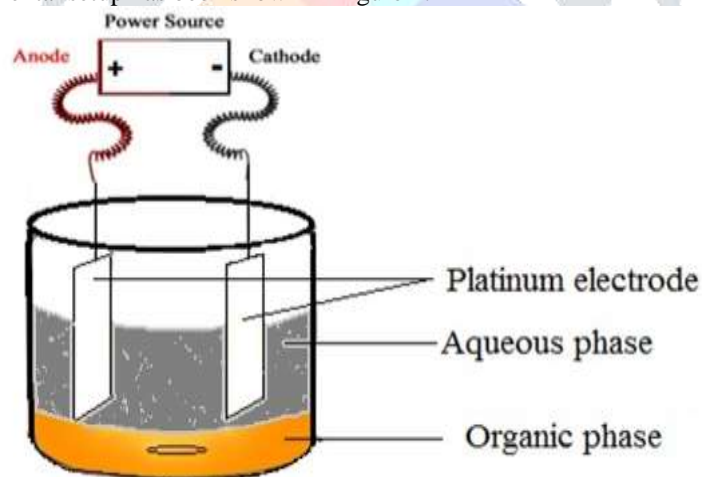

Figure 1: The experimental setup for oxidation of toluene in biphasic medium.

The electrolysis was conducted galvanostatically at a current density of 50 mA cm⁻², at room temperature. A magnetic stirrer was employed in the solution and the whole solution was stirred at the rate of 600 rpm. The magnetic stirring was stopped after passing 7F/mol of charge. After the completion of the electrolysis, the two phases were separated by a separating funnel. The aqueous phase was washed with chloroform (2×25 mL). The organic phase was washed with water (2×25 mL) and dried over anhydrous sodium sulphate. The solvent was removed by distillation. HPLC analysis of the residue was done and the characteristic peak of benzaldehyde in HPLC spectrum indicated the formation of benzaldehyde and the product was isolated by column chromatography.

III. RESULTS AND DISCUSSION

The optimum reaction conditions for the electrochemical oxidation of toluene were established by varying one of the parameters keeping the others constant.

The effect of charge passed was examined in the range of 4-8 F/mol. The percentage of yield was increased gradually with increase of the charge. The maximum yield was obtained at 7 F/mol. There was no further increase in the yield by increasing the charge after 7F\mole. Therefore, the optimized charge for conversion of toluene to the oxidised product was taken as 7F/mol.

Table 1: Influence of charge passed

S.no.	Charge passed (F/mol)	Benzaldehyde yield (%)	Current efficiency (%)
1	4	44	44
2	5	61	49
3	6	66	44
4	7	70	40
5	8	70	35

Experimental conditions: Organic phase: 10 mmol toluene in 20 mL CHCl$_3$; Aqueous phase: 72.46 mmol NaNO$_2$ + 20.39 mmol H$_2$SO$_4$ in 80 mL deionised H$_2$O; Current density: 50 mA cm^{-2}; Charge passed: 4-8 F/mol; Stirring rate: 600 rpm.

Effect of current density was studied in the range of 30 to 60 mA cm^{-2} as shown in the Table 2. The maximum yield was observed with current density of 50 mA cm^{-2} and it was taken as optimum current density.

Table 2: Influence of current density

S.No.	Current density (mA cm^{-2})	Benzaldehyde yield (%)	Current efficiency (%)
1	30	64	36
2	40	67	38
3	50	70	40
4	60	62	35

Experimental conditions: Organic phase: 10 mmol toluene in 20 mL CHCl$_3$; Aqueous phase: 72.46 mmol NaNO$_2$ + 20.39 mmol H$_2$SO$_4$ in 80 mL deionised H$_2$O; Current density: 30-60 mA cm^{-2}; Charge passed: 7 F/mol; Anode/Cathode: Pt/Pt; Stirring rate: 600 rpm.

The effect of different acids on the reaction was investigated by using HCl, HNO$_3$, H$_2$SO$_4$ and HClO$_4$. Among these, sulphuric acid was found effective in facilitating electrochemical oxidation of toluene in presence of NaNO$_2$ under mild conditions. Higher product yield was observed, when sulphuric acid is used in the reaction. This is due to the good electrolytic behavior of sulphuric acid [11,31], by accelerating the conductivity of the electrolyte [8]. The experiments were also shown that the higher *Ka* value [32], enhances the efficiency of the reaction. In that perspective, H$_2$SO$_4$ (70%) gave higher product yield in this reaction but HClO$_4$ (10%) could only produce a lesser yield.

Table 3: Influence of acid

S.No.	Acid	Benzaldehyde yield (%)	Current efficiency (%)
1	HCl	21	12
2	HNO$_3$	28	16
3	H$_2$SO$_4$	70	40
4	HClO$_4$	10	06

Experimental conditions: Organic phase: 10 mmol toluene in 20 mL CHCl$_3$; Aqueous phase: 72.46 mmol NaNO$_2$ + 20.39 mmol various acids in 80 mL deionised H$_2$O; Current density: 50 mA cm^{-2}; Charge passed: 7 F/mol; Anode/Cathode: Pt/Pt; Stirring rate: 600 rpm.

Table 4: Influence of sulphuric acid concentration

S.No.	Sulphuric acid concentration (mmol)	Benzaldehyde yield (%)	Current efficiency (%)
1	20.39	70	40
2	30.59	66	37
3	40.78	68	39
4	50.98	69	39

Experimental conditions: Organic phase: 10 mmol toluene in 20 mL CHCl$_3$; Aqueous phase: 72.46 mmol NaNO$_2$ + 20.39-50.98 mmol H$_2$SO$_4$ in 80 mL deionised H$_2$O; Current density: 50 mA cm^{-2}; Charge passed: 7 F/mol; Anode/Cathode: Pt/Pt; Stirring rate: 600 rpm.

The effect of concentration of sulphuric acid was studied for the reaction. For that, the concentrations range of 20.39 to 50.98 mmol of sulphuric acid were carried out and analyzed. The yield of benzaldehyde was found almost the same for all the concentrations of sulphuric acid. So, the minimum concentration of 20.39 mmol sulphuric acid was taken for optimum condition

In order to study the effect of concentration of sodium nitrite on the electochemical oxidation of toluene, various concentrations of sodium nitrite ranging from 43.48 mmol to 86.96 mmol were examined. The maximum yield was found at 72.46 mmol to sodium nitrite and it was taken as the optimum sodium nitrite concentration as shown in Table 5.

Table 5: Influence of sodium nitrite concentration

S.No.	Sodium nitrite concentration (mmol)	Benzaldehyde yield (%)	Current efficiency (%)
1	43.48	56	32
2	57.97	59	34
3	72.46	70	40
4	86.96	64	37

Experimental conditions: Organic phase: 10 mmol toluene in 20 mL CHCl$_3$; Aqueous phase: 43.48-86.96 mmol NaNO$_2$ + 20.39 mmol H$_2$SO$_4$ in 80 mL deionised H$_2$O; Current density: 50 mA cm^{-2}; Charge passed: 7 F/mol; Anode/Cathode: Pt/Pt; Stirring rate: 600 rpm.

Selection of solvent as a medium for the reaction is another important parameter for the study. The effect of solvent was investigated in both biphasic [22] and homogeneous medium. Among the solvents that were studied, chloroform gave the maximum percentage of yield the experiment to be carried out in biphasic medium (Table 6).

Table 6: Influence of solvent

S.No.	Solvent	Benzaldehyde yield (%)	Current efficiency (%)
1	CH$_2$Cl$_2$	68	39
2	CHCl$_3$	70	40
3	CCl$_4$	54	31
4	CH$_3$CN	64	37

Experimental conditions: Organic phase: 10 mmol toluene in 20 mL various solvent; Aqueous phase: 72.46 mmol NaNO$_2$ + 20.39 mmol H$_2$SO$_4$ in 80 mL deionised H$_2$O; Current density: 50 mA cm^{-2}; Charge passed: 7 F/mol; Anode/Cathode: Pt/Pt; Stirring rate: 600 rpm.

The reaction mixture was subjected to agitation from 200 to 800 rpm in biphasic medium. The product yield increased as the agitation rate increased. The maximum yield was observed at the agitation rate 600 rpm and further increase of agitation rate did not show any change in the yield of the product.

Table 7: Influence of agitation

S.No.	Agitation (rpm)	Benzaldehyde yield (%)	Current efficiency (%)
1	200	52	29
2	400	66	37
3	600	70	40
4	800	69	39

Experimental conditions: Organic phase: 10 mmol toluene in 20 mL CHCl$_3$; Aqueous phase: 72.46 mmol NaNO$_2$ + 20.39 mmol H$_2$SO$_4$ in 80 mL deionised H$_2$O; Current density: 50 mA cm^{-2}; Charge passed: 7 F/mol; Anode/Cathode: Pt/Pt; Stirring rate: 200-800 rpm.

Different concentrations of toluene ranging from 5 mmol to 20 mmol were examined and calculated the product yield. The results in Table 8 show that, 10 mmol of toluene concentration gave the maximum product yield.

Table 8: Influence of substrate concentration

S.No.	Substrate concentration (mmol)	Benzaldehyde yield (%)	Current efficiency (%)
1	5	66	37
2	10	70	40
3	15	54	31

4	20	64	37

Experimental conditions: Organic phase: 5-20 mmol toluene in 20 mL CHCl₃; Aqueous phase: 72.46 mmol NaNO₂ + 20.39 mmol H₂SO₄ in 80 mL deionised H₂O; Current density: 50 mA cm⁻²; Charge passed: 7 F/mol; Anode/Cathode: Pt/Pt; Stirring rate: 600 rpm.

The aqueous phase was separated from the organic phase with a separating funnel and the separated aqueous phase was extracted twice (2×20 mL) with chloroform. This extracted solution containing sodium nitrite was collected and reused thrice for the oxidation of toluene. The results were presented in the Table 9. There was observed a gradual decrease in the product yield because of the loss of sodium nitrite which had been used for successive experiments.

Table 9: Influence of reusability of sodium nitrite mediator

S.No.	Amount of sodium nitrite (mmol)	Benzaldehyde yield (%)	Current efficiency (%)
1	72.46	70	40
2	Reuse 1	66	37
3	Reuse 2	63	36
4	Reuse 3	62	35

Experimental conditions: Organic phase: 10 mmol toluene in 20 mL CHCl₃; Aqueous phase: 72.46 mmol NaNO₂ + 20.39 mmol H₂SO₄ in 80 mL deionised H₂O; Current density: 50 mA cm⁻²; Charge passed: 7 F/mol; Anode/Cathode: Pt/Pt; Stirring rate: 600 rpm.

In order to check the reproducibility of the reaction, the experiment was repeated for 4 times. The yield of benzaldehyde was found to be similar in all the four trials given in figure 2.
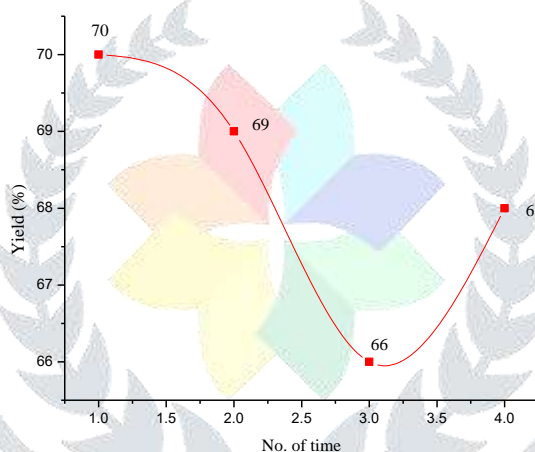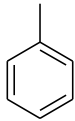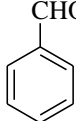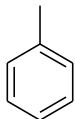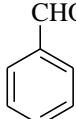

Figure 2: Influence of reproducibility on oxidation of toluene in biphasic medium

3.1 Determination of nitrite radical scavenging activity

To investigate the pathway of mechanism where the oxidation of toluene using sodium nitrite as a mediator in biphasic medium occurred, a few experiments were carried out. In the mechanism of oxidation of toluene to benzaldehyde, there found a possibility of forming nitrite free radical from sodium nitrite and this free radical has an important role in mechanism. This was confirmed by using a well-known radical scavenger 2,6-bis(1,1-dimethylethyl)-4-methyl phenol (Butylated hydroxytoluene) [33-35] in the reaction mixture. When the reaction was carried out with BHT, the oxidation reaction was inhibited and the yield was recorded as 0% (Table 10). This indicates that nitrite free radical was formed and was captured by Butylated hydroxytoluene.

Table 10: Influence of radical scavenger

S.No.	Substrate	Product	Yield (%)	Current efficiency (%)
1		CHO	70	40
2*		CHO	0	0

BHT radical scavenger was added

The optimization of reaction conditions necessary for the electrochemical oxidation of toluene using nitrite mediator are shown in Table 11.

Table 11: Optimal experimental condition

Optimal experimental condition	
Substrate	Toluene 10 mmol in 20 mL CHCl$_3$
Mediator	NaNO$_2$ 72.46 mmol in 80 mL deionised water
Supporting electrolyte	H$_2$SO$_4$ 20.39 mmol
Electrolysis method	Biphasic electrolysis
Current density	50 mA cm^{-2}
Charge passed	7 F/mol
Agitation	600 rpm
Electrode	Pt/Pt

3.2 Cyclic Voltammetric studies

A conventional three electrode system with platinum electrode as a working electrode, platinum wire as the auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode was used for electrochemical measurements. Electrochemical oxidation of toluene (2 mM) was carried out in 0.01M H$_2$SO$_4$ with 2 mM sodium nitrite in acetonitrile medium. Cyclic Voltammogram was recorded in the range between 0.00 V - 0.8 V at scan rate of 20 mVs^{-1}. A distinct oxidation peak at 0.587 V clearly indicates the oxidation of toluene where as reagent blank does not give any oxidation peak (Figure 3).
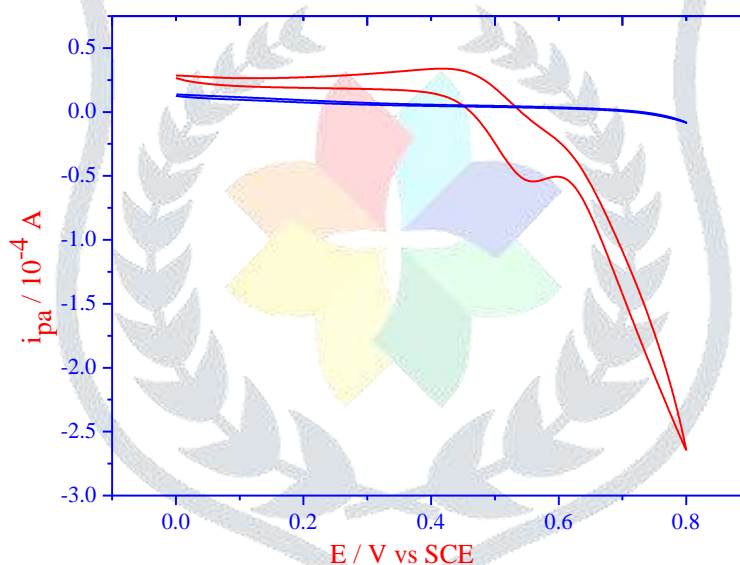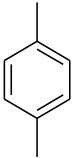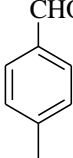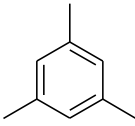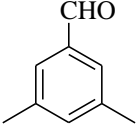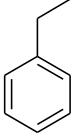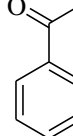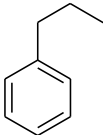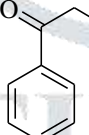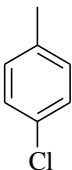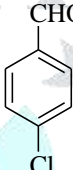

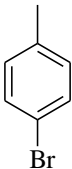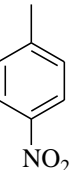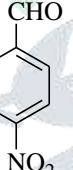**Figure 3: Cyclic Voltammetric studies of toluene sodium nitrite in acetonitrile medium.**

3.3 Effect of various substrates

To test the generality of the reaction, different alkyl aromatics were studied at the optimized electrochemical conditions and the results are presented in Table 12.

Table 12: Influence of substrate

Entry	Substrate	Charge passed (F/mol)	Product	Yield (%)	Current efficiency (%)
1	(toluene)	7	CHO (benzaldehyde)	70	40

| Entry	Substrate	Time	Product	Yield	Yield
2	(p-xylene)	7	(p-tolualdehyde, CHO)	61	35
3	(mesitylene)	7	(3,5-dimethylbenzaldehyde, CHO)	62	35
4	(ethylbenzene)	7	(acetophenone, O)	59	34
5	(n-propylbenzene)	7	(propiophenone, O)	53	30
6	(p-chlorotoluene, Cl)	7	(4-chlorobenzaldehyde, CHO, Cl)	69	39
7	(p-bromotoluene, Br)	7	(4-bromobenzaldehyde, CHO, Br)	61	35
8	(p-nitrotoluene, NO$_2$)	4-8	(4-nitrobenzaldehyde, CHO, NO$_2$)	0	0

When *p*-xylene (entry 2) is compared with toluene (entry 1), *p*-xylene is observed with lesser yield and it may be attributed to the steric effect of CH$_3$- group attached in the para position of aromatic moiety. The yield of mesitylene (entry 3) is less to toluene may be the steric effect exerted by two methyl groups attached to the aromatic moiety. Similarly, steric effect plays a role in ethyl benzene (entry 4) and n-propyl benzene (entry 5) so the yields are observed low, when compared with toluene (entry 1). *p*-chlorotoluene (entry 6) and *p*-bromotoluene (entry 7) also give comparatively lesser yield, when compared with toluene (entry 1). It may be due to -I and +R effect of the Cl- group. Entry 8 is observed 0% yield which may be caused by the deactivating effect of the substrates -NO$_2$ group.

3.4 The possible mechanism for the oxidation of toluene

A possible mechanism for nitrite mediated selective oxidation of toluene in biphasic electrolysis is presented in Scheme 2.

$$NO_2^- \xrightarrow[\text{anode}]{-e^-} NO_2^\bullet$$
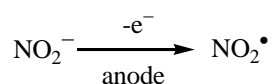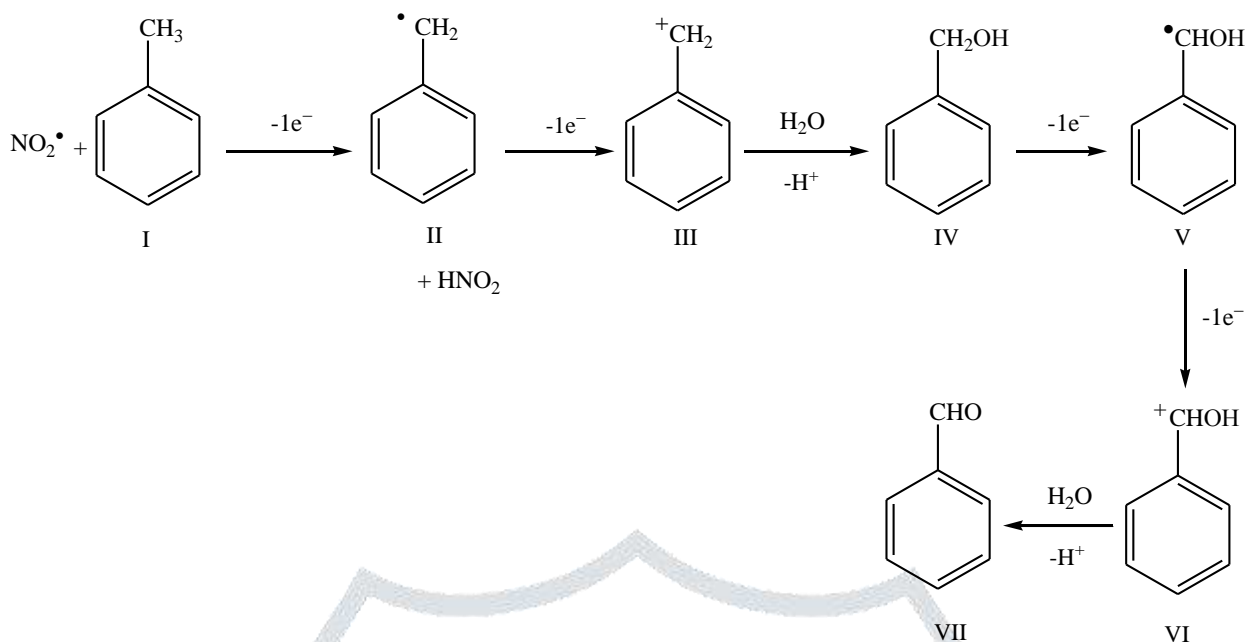
Scheme 2: Mechanism for the production of benzaldehyde product

Initially nitrite ion undergoes one electron oxidation at platinum anode in aqueous phase and then it abstracts α-hydrogen from toluene (I) which lies in the interphacial region to form a radical (II). The intermediate (II) undergoes one-electron oxidation to generate benzyl cation (III). The cation abstracts OH radical from water molecule to form benzyl alcohol (IV) which can be considered as the intermediate product. Benzyl alcohol further undergoes successive one-electron transfer leading to formation of the product. Loss of proton in an acidic solution can be justified by considering the electrical field in which the relieved proton can drift towards the cathode [36,37]. It can be seen that four electrons are removed per molecule of substrate during the oxidation [38].

IV. CONCLUSION

Selective oxidation of alkyl aromatics in biphasic medium yields corresponding carbonyl compounds. The reaction was carried out with platinum electrodes at 35–40℃. The electrochemical oxidation was optimized with various experimental parameters and resulted in high yield of products. Based on these electrochemical experiments and analytical studies, it is shown that the proposed method is a highly selective oxidative conversion of toluene to benzaldehyde with high conversion yield. The study has brought up several advantages in the field of synthetic organic chemistry. Maximum selectivity and yield can be attained with a single step experiment. Ambient temperature and pressure are maintained thought the experiment. The reactions are carried out under mild conditions, at room temperature with simple electrochemical set up. Easy separation of the product, free of possible secondary products and the low cost in production are projected the uniqueness of this study.

V. ACKNOWLEDGEMENT

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