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Research Article

INTERPHASIAL OXIDATION OF ALKYL AROMATICS ELECTROCATALYZED BY SODIUM NITRATE MEDIATOR

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ABSTRACT

Nitrate mediated selective oxidation of alkyl aromatics by emulsion electrolysis gives the corresponding carbonyl compounds at moderately high yield (34-84%). The substrate was dissolved in $CHCl_3$ and the aqueous solution consisted of 2% sodium nitrate as a mediator containing a catalytic amount of H_2SO_4 as supporting electrolyte. The interphasial reaction has been effectively carried out at a stirring rate of 80 rpm in a single compartment cell with a pair of platinum electrodes at 35-40 °C.

Keywords: alkyl aromatics, selective oxidation, emulsion electrolysis, sodium nitrate.

INTRODUCTION

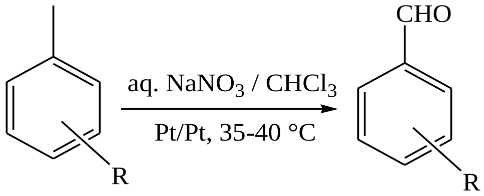
The controlled oxidation of alkyl aromatics to corresponding carbonyl compounds is a well-known and valuable reaction in synthetic organic chemistry. The carbonyl compounds are used as versatile intermediates for the synthesis of specialty chemicals such as pharmaceutical intermediates and dyestuffs[1]. There are various methods available for the partial oxidation of toluene using catalytic mediators such as Ag(I)/Ag(II)[2], $Ru(acac)_3$[3], $(NH_4)_2Ce(NO_3)_6$ (CAN)[4], ceric methanesulfonat[5] and tetramethylammonium nitrate[6]. The Boron-Doped Diamond (BDD) electrode material[7], ultrasound assisted electrochemical oxidation[8], molecular oxygen under pressure[9] and techniques like vapour phase catalytic oxidation using vanadyl pyrophosphate[10] were also reported for the selective oxidation of toluene. The catalyst such as V_2O_5-ZrO_2 complex[11], $[n\text{-}Bu_4N]_3H_3[PW_9V_3O_{40}]$[12], copper manganese nanoscale oxides[13] and $CeO_2/NaBrO_3$[14] were used to improve the yield of carbonyl compounds. The major drawbacks of the above mentioned processes are the use of costly catalysts, hazardous reagents and low selectivity. Recently, it has been reported that the nitrate mediated electrochemical oxidation of *p*-xylene at emulsion condition which results in higher yield (84%) of *p*-tolualdehyde[15]. In order to find out the scope and limitations of the method for various substrates, herein the electrochemical oxidation of alkyl aromatic derivatives using sodium nitrate mediator at emulsion condition (scheme 1) has been undertaken.

MATERIALS AND METHODS

A solution of *o*-chloro toluene 1.265g (10 mmol) in chloroform (25 mL) was taken in an undivided cell. To the above solution, 50 mL of 2% $NaNO_3$ (1.0 g, 11.7 mmol) and (2.25 g, 0.46 M) sulphuric acid was added. Two platinum sheets with an area of 15 cm^2 each were placed in the reaction mixture and it was stirred moderately with a magnetic stirrer at a rate of 80 rpm in such a way that to form an emulsion. A *DC* power source (Aplab) was used as the direct current source for constant current electrolysis. The current density of 75 mA cm^{-2} was applied until the maximum yield of the desired product was obtained as indicated in Table 1. The electrolysis was monitored by a Shimadzu HPLC with ODS 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. After completion of the electrolysis, the stirring was stopped to allow the separation of two phases and the aqueous phase was extracted twice with chloroform (2×25 mL) and the combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed by distillation to afford 1.375g of crude product. HPLC analysis of the residue indicated the presence of 79% *o*-chloro benzaldehyde along with 20% starting material.

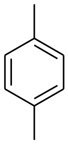
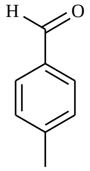
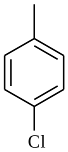
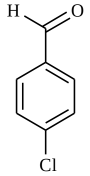
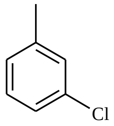
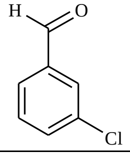
RESULTS AND DISCUSSION

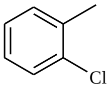
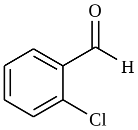
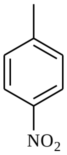
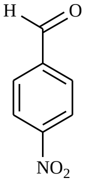
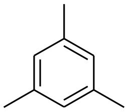
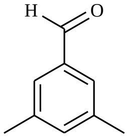
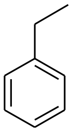
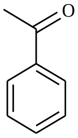
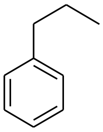
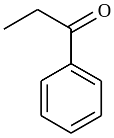
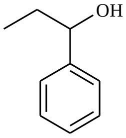
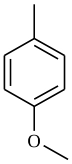
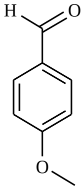
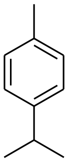
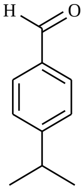
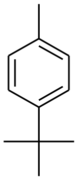
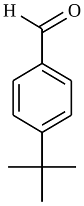
Oxidation of alkyl aromatic derivatives gives the corresponding carbonyl compounds using nitrate mediator by emulsion condition. The relative yield of product distributions is listed in Table 1. The products obtained from the experiments are compared with the authentic samples as a reference.



Scheme 1: Interphasial oxidation product of alkyl aromatics by emulsion condition

Table 1: Oxidation products of alkyl aromatic derivatives and their percentage yield

Entry	Substrate	Charge passed (F/mol)	Product	Yield (%)	Current efficiency (%)
1		6		84	56
2		6		83	55
3		8		67	33

4		7		79	45
5		8		0	0
6		6		66	44
7		8		78	39
8		8	 	45 29	37
9		8		34	17
10		8		38	19
11		8		36	18

Emulsion electrolysis condition: current density: 75 mA cm^{-2}; aqueous phase: 11.7 mmol $NaNO_3$ + 0.46 M H_2SO_4 in (50 mL) deionised water; organic phase: substrate (10 mmol) in 25 mL chloroform; electrode: Pt/Pt; stirring rate: 80 rpm; temperature: 35-40 °C.

From the table it is observed that, *p*-xylene gives a maximum of 84% yield. Among the isomers of chloro toluenes, *p*-chloro toluene provides 83% yield. But in the case of isomers of *m*- and *o*-chloro toluene (entry 3, 4) the corresponding aldehyde is obtained in 67% and 79% yield after passing a charge of 8 and 7 F/mol respectively. The highly deactivating nitro group substituted toluene (entry 5) did not undergo oxidation even after passing 8 F/mol of charge. In the case of n-propyl benzene (entry 8) two products i.e. propiophenone 45% and 1-phenyl-1-propanol 29% are obtained after passing a charge of 8 F/mol. It is interesting to note that the formation of alcohol is observed only in this case alone and in the other cases only trace amount is observed. It may be due to the formation of intermediate during the oxidation process. Electron donating groups like methoxy, iso-propyl, tert-butyl substituted toluene (entry 9-11) resulted in products with a yield of 34%, 38% and 36% respectively even after passing a charge of 8 F/mol. There are two kinds of benzylic protons present in the substrate 4-iso-propyl toluene. The iso-propyl group which is intact during oxidation may be attributed to lower of its hyperconjugation effect.

In this emulsion process, the *in-situ* generated nitrate radical[16] has an effective Hydrogen Atom Transfer capacity (HAT)[17] which subsequently reacted with substrate at the interphasial region of aqueous and organic phase to form the product efficiently. The possible mechanism of the nitrate mediated electrocatalytic oxidation of various alkyl aromatics is depicted in the earlier report[15].

CONCLUSIONS

To conclude, the electrochemical oxidation of alkyl aromatics to the corresponding carbonyl compounds using nitrate mediator has several advantages over conventional methods: i) simple reaction setup ii) absence of over oxidised secondary products iii) very cheap and readily available mediator iv) use of very low acid concentration v) ambient temperature reaction condition vi) low production cost vii) recycling of mediator viii) moderately high product yield (34-84%). Thus, it seems that in the present study, oxidation of alkyl aromatics with $NaNO_3$ by emulsion electrolysis is amenable for scale up as a greener process.

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