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SYNTHESIS OF 2-CHLORO-P-XYLENE FROM P-XYLENE THROUGH TWO PHASE ELECTROLYSIS

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By employing a precious metal oxide coated over titanium as anode, electrolysis of p-xylene in an aqueous hydrochloric acid medium yielded a mixture of mono and dichloro-p-xylene in the ratio of 3.5:1. A detailed investigation, employing various electrochemical parameters, resulted in a high yield of these products. These products were separated in 100% pure form and analysed through NMR and other common organic analysis. The products were found to be 20-chloro-p-xylene and 2,5-dichloro-p-xylene.

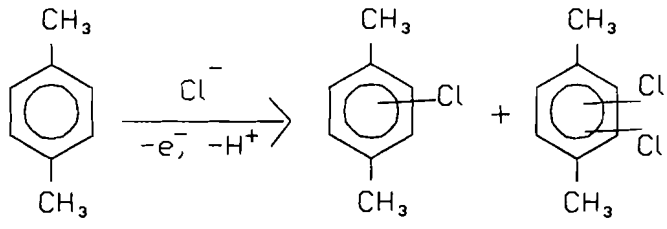
Keywords: 2-chloro and 2,5-dichloro-p-xylene, electrochemical preparation, temperature and mixing effect.

INTRODUCTION

Chlorinated p-xylenes are used as key intermediates in the manufacturing of pesticides, pharmaceuticals, peroxides, dyes and other intermediates [1]. The electrochemical chlorination of aromatic hydrocarbons has been carried out by many workers to develop a new practical process and to understand the mechanism of many electrochemical oxidations. The anodic chlorination of toluene in CH_3CN containing some Lewis acids was carried out as reported in [2]. Electrochemical chlorination of toluene in methanol/LiCl for obtaining chlorotoluene was also carried out [3-4]. However no chloro derivatives substituted in methyl group have been reported as formed by electrochemical methods. Two phase electrolysis to chlorinate the benzene ring of the toluene has been reported [5-6]. The chlorination of toluene has also been demonstrated [7]. There are some reports concerning about the chlorination of toluene through zeolite [8-9].

The process described in this paper involves the electrochemical chlorination of p-xylene in aqueous 2 *M* HCl using precious metal oxides coated over titanium as anode [10]. The noble metal oxide coated over titanium substrate anode has some specific advantages over the anodes in bringing up a facile reaction for chlorine evolution like (1) stability and workability of the anode, (2) longer life, (3) ability to function at higher current density and (4) power savings due to lower chlorine over voltage, lesser bubble effect resulting from higher free surface for escape of chlorine and lower cell voltage [10]. However few publications are available in electroorganic synthesis using these electrodes [11-15].

Here we have demonstrated the electrochlorination of p-xylene through "two-phase electrolysis" using precious metal oxide coated over titanium under galvanostatic condition. This method is the most useful for the synthesis of monochloro-para-xylene (See scheme 1).



Scheme 1

EXPERIMENTAL

Laboratory scale experiments were carried out in one litre capacity divided glass cell. The cell cover had the facility for introducing porous diaphragms, electrodes, stirrer and thermometer. The anode was precious metal oxide coated over titanium and rectangular graphite sheet placed on both sides of the anode inside the porous diaphragm were used as the cathodes. p-xylene used was L.R. grade. The anolyte was stirred by a glass stirrer.

Aqueous 2 *M* HCl acted as a supporting electrolyte as well Cl^- source. The organic phase was neat solution of 20 g of p-xylene.

Electrochemical chlorination was carried out under galvanostatic condition at various amount of charge passed (i.e.) 1F, 2F, 4F, 6F and 8F per mole of p-xylene at two different temperatures 278 and 303 K with and without stirring. The current density was 5 $A.dm^{-2}$ in all the experiments and the anode area was $100cm^2$. After electrolysis the reaction products were extracted with ether, the ethereal layer washed with ice cold water, then dried over anhydrous sodium sulphate and finally distilled. The residue obtained was examined for its contents by High Performance Liquid Chromatography (HPLC) (Shimadzu 8LC, Japan). To elucidate the mechanism of the chlorination reaction, chlorination by chemical method was also carried out.

RESULTS AND DISCUSSION

The electrolysis was carried out to a charge of 4F at two different temperatures namely 278 and 303 K (Table I). It was found that electrolysis at 278 K gave better yield. The rate of stirring was 300 rpm which gave better stirring. The product mixtures were analysed by HPLC (Table II). It is found from the table that electrolysis to four Faraday gives better yield and gives single major product (product A) retention time and 2 minor products 4.6 min (product B and product C) having retention time 5.3 min and 3.8 min respectively. The remaining portion is the reactant.

TABLE I

Electrolysis of p-xylene : Effect of temperature
Anode : TSIA
p-xylene (g) : 20
Cathode : Graphite
Catholyte : 2 M HCl
Anolyte : 2 M HCl
Current density : 5 $A.dm^{-2}$
Charge passed : 4 FM^{-1}

Conditions	Yield (%)
5°C (300 rpm)	68.8
30°C (300 rpm)	29.7
5°C (> 300 rpm)	20.0
5°C (without stirring)	0.0

Product A was separated by column chromatography (Silica gel/hexane) and analysed for purity in HPLC. It was found that the compound was 97% pure. The product A was colourless liquid having b.p. 186°C and the sample was analysed through ^1H NMR. The result showed that two different environmental protons were present ^1H (90 MHz, $CdCl_3$) (2-chloro- p-xylene) δ = 6.9-7.3 (m, 3H, aromatic H), 2.3 (s, 6H, methyl 2-CH_3). The NMR result and the literature values confirmed that the product A was 2-chloro-p-xylene.

Product B was a colourless solid, m.p. 68°C (97% pure). ^1H NMR results for the above solid shows the presence of two different protons (^1H (90 MHz, $CdCl_3$) (2,5-dichloro0-p-xylene) δ = 7.1-7.3 (m, 2H, aromatic H), 2.3 (s, 6H, methyl 2-CH_3) confirming the compound as 2,5-dichloro-p-xylene.

The third product was a highly viscous liquid and having very high b.p. (> 200°C) and probably the multichlorinated products.

Mechanism of the reaction

Three different mechanisms have been proposed for the chlorination of aromatic hydrocarbons.

Mechanism I

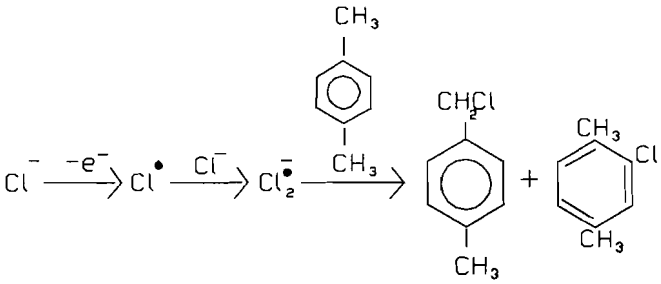
$$2Cl^- \longrightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + C_6H_4R_2 \longrightarrow C_6H_3R_2Cl + H^+ + Cl^- \quad (2)$$

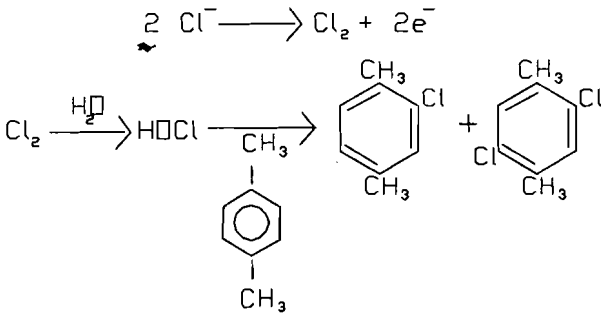
TABLE II: HPLC analysis of the chlorinated products of p-xylene
Electrolysis temperature : 278
RPM of anode : 300
Other conditions as in Table I

Charge (F)	Yield (%) at different retention time (min)		
	4.2 (product A)	4.6 (product B)	5.3 (product C)
1	16.0	—	11.0
2	15.2	3.2	47.0
4	68.8	2.1	3.9
6	25.4	4.8	25.8
8	24.3	6.5	27.3

Mechanism II



Mechanism III



On the basis of the following reasons the mechanism III may hold good for the chlorination of p-xylene.

- The amount of chlorine present in HCl/water is 9.97 g/l system at 283 K and is 1.27 g/l at 363 K and becomes nil at boiling point of water [16]. So once chlorine is formed under the galvanostatic condition, dissolves in water to form HOCl and this reacting species reacts with p-xylene to give the products.
- Under stirred condition the water and p-xylene are in emulsion condition. So, the possibility of HOCl reacting with p-xylene is higher and thereby giving the product in the higher yield.
- Experiments were carried out to produce chlorine under similar condition but without p-xylene. After completing the electrolysis, p-xylene was added to it and was stirred for about 2 hours and the chlorinated products formed were in low yield. This confirms that only very small amount of HOCl was present at any time in the electrolyte. During electrolysis once the HOCl was formed, it reacted with p-xylene and thereby giving way for the formation of fresh HOCl.
- Chlorine was produced chemically in the separate compartment with potassium permanganate and concentrated HCl and passed through the solution containing water, 2 *M* HCl and p-xylene. This experiment also give similar result as in the case of 4F galvanostatic electrolysis of p-xylene-2 *M* HCl confirming the mechanism proposed in III.

CONCLUSION

The chlorination of p-xylene in two phase electrolysis under galvanostatic condition using TSIA as anode in a divided cell at 278 K and stirring of electrolyte at 300 rpm rate give 68% 2-chloro-p-xylene product. This method is mostly useful for the selective chlorination. Electrochlorination of other aromatic substrates are also being investigated and the results will be published in the near future.

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