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ELECTROSYNTHESIS OF CHLORINE SUBSTITUTED ORGANIC COMPOUNDS EMPLOYING A CATALYTIC ELECTRODE - TSIA

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Chloroaromatic compounds are used as intermediates in the manufacture of many industrially important chemicals. Electrosynthesis of chloro aromatic compounds using ruthenium oxide/titanium oxide coated on titanium substrate (TSIA) in aqueous hydrochloric acid yielded a mixture of ortho and para chloro aromatic compounds. A detailed investigation was carried out under different conditions to maximise the product yield.

Keywords: Electrochemical chlorination, TSIA electrode, rubber latex and CNSL

INTRODUCTION

Chloro aromatic compounds both ortho and para isomers are used as key intermediates in the manufacture of pesticides, pharmaceuticals, peroxides, dye and other intermediates [1]. Gourcey et al. carried out the anodic chlorination of benzene, toluene and other substituted benzene in acetonitrile containing aluminium chloride [2]. Y.Matsuda et al. carried out the electro- chlorination of toluene in CH_3OH/LiCl and obtained chlorotoluenes [3]. They have also carried out at a later stage two phase electrolysis of toluene and obtained benzyl chloride in addition to ortho & para chlorotoluenes [4]. However yields of mono chlorotoluene is very low. In our present work we have tried to develop a process for the preparation of ortho and para chloro aromatic compounds. The process involves the electrochemical chlorination of aromatic compounds in aqueous hydrochloric acid using TSIA and obtained ortho and para chloro aromatic compounds in higher yield.

The noble metal oxide coated over titanium substrate anodes have some specific advantages over other 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 densities and (4) power savings due to lower chlorine overvoltage, lesser bubble effect resulting from higher free surface for escape of chlorine and lower cell voltage [5]. Such electrodes have been extensively used in chlor-alkali industry. However only a very few preliminary publications are available in electro organic synthesis using these electrodes [6- 10].

EXPERIMENTAL

Lab scale experiments

Laboratory scale experiments were carried out in one litre capacity divided glass cell. The cell cover had the provision for introducing porous diaphragm, electrodes stirrer and thermometer. The anode was TSIA (on expanded mesh) and a graphite sheet placed inside a porous diaphragm was used as a cathode. LR grade chemicals were used for the electrolysis.

The electrolysis was carried out under galvanostatic condition in a temperature range of 288-293 K. The product having a higher density, settled at the bottom of the cell which was easily separated from the electrolyte. The product was distilled and analysed by gas chromatography. Studies on the chlorination werealso carried out with other anodes like platinum and graphite.

Experiments under the same condition in an undivided cell was also tried to prepare mono chlorotoluenes.

RESULTS AND DISCUSSION

The amount of electricity passed for electrolysis is equivalent to that required for a 2 e^- for oxidation of compounds like toluene, anisole, benzene. The electrochemical chlorination of toluene is initiated by the oxidation of chloride ion (Cl^-) since the oxidation potential of toluene is higher than that of Cl^- [6]. The ortho to para ratio for the chloro toluene was about 2:1 in all experiments.

Table I shows the electrochemical chlorination of toluene in different electrodes. In the case of graphite electrode, the product yield was low and the disintegration of the electrode was noticed. The disintegration of the graphite electrode increased the cell voltage in subsequent electrolysis. Of the other two electrolysis TSIA was found to be a better electrode than platinum for the reasons cited elsewhere [5].

Table II shows the effect of temperature for chlorination in divided cell and also the studies in undivided cells. The current efficiency for the chlorination and hence yield of the product tended to increase with increase in temperature.

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TABLE I: Electrochemical chlorination of toluene in divided cell, current density 5 Am/dm^2 and temperature 293 to 298 K

Sl. No.	Anode	Amt. of toluene in ml	Yield (%)			Remarks
			Ortho	Para	Total	
1.	Graphite	50.0	—	—	6.0	***
2.	Platinum	50.0	36.7	18.4	55.1	***
3.	TSIA	50.0	56.3	28.1	84.4	***

*** electrode disintegrates during electrolysis

TABLE II: Electrochemical chlorination of toluene with TSIA electrode

Sl. No.	Type of cell	Current density Amp/dm^2	Temp K	Ortho	Para	Total
1.	divided	5	293-298	56.3	28.1	84.4
2.	divided	5	318-323	57.7	28.8	86.5
3.	undivided	5	293-298	42.3	21.1	63.4

TABLE III: Electrochemical chlorination of some aromatic compounds in divided cell with TSIA electrode

Sl. No.	Compound taken ml	Temp. K	Current density Amp/dm^2	Yield %
1.	Benzene	293-298	5	38.0
2.	Toluene	293-298	5	86.5
3.	Anisole	293-298	5	72.0

However higher temperature led to coating loss of the electrode and hence the activity of the electrode decreased in subsequent electrolysis.

In case of undivided cell, the product yield is less than that of divided cell. This may be due to the recombination of hydrogen and chlorine in the cell itself.

Table III shows the effect of chlorination of various aromatic compounds in divided cell. It was found that toluene gives a better yield of monochlorinated product than benzene. This is due to the orientation of methyl group. In case of anisole and cashew nut shell liquid (CNSL) the electrode is slowly getting deactivated.

Table IV shows the effect of total current passed and the percentage of chlorine content in chlorinated cashew nut shell liquid for the chlorination of cashew nut shell liquid (CNSL) in divided cell. The percentage of chlorine content in CNSL tended to increase with increase in total current passed.

TABLE IV: Electrochemical chlroination of CNSL in divided cell with TSIA electrode and current density 3 A/dm^2

Sl. No.	Amt. of rubber latex ml	Current passed amp.hr	Wt. of chlorinated CNSL(gm)	% of chlorine
1.	10	7.5	11.26	21.0
2.	10	15.0	12.00	20.8
3.	10	22.5	15.94	32.0
4.	10	30.0	15.28	37.8

TABLE V: Electrochemical chlorination of rubber latex in divided cell with TSIA electrode, current density 5 Amp/dm^2 and temp 293-298 K

Sl. No.	Amt. of rubber latex ml	Current passed amp.hr	% of chlorine content in chlorinated rubber
1.	5.0 (3.0 gm)	2.4	15
2.	5.0 (3.0 gm)	7.2	29
3.	5.0 (3.0 gm)	14.8	33 to 35
4.	5.0 (3.0 gm)	28.8	47 to 50

Table V shows the effect of total current passed and the percentage of chlorine content in chlorinated rubber for the chlorination of rubberlatex dissolved in chloroform in divided cell. The percentage of chlorine content in chlorinated rubber tended to increase with increase in total current passed. In electro chemical chlorination of rubber latex the electrode is covered with a layer of rubber latex and hence the passage of current is difficult in course of reaction.

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