

Electrochemical chlorination of toluene by two-phase electrolysis

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Abstract

A simple method for the preparation of benzyl chloride from toluene by two-phase electrolysis is reported. The major product is benzyl chloride in contrast to chlorotoluenes in homogeneous electrolysis. Electrolysis was carried out at 30 °C in chloroform solvent. Toluene conversion ranges from 80 to 85% and the selectivity is as high as 95%. The effect of different electrodes, temperatures, and current density are studied and the optimum condition is reported.

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1. Introduction

The conversion of methyl group in toluene to benzyl chloride is a fundamental reaction in the synthesis of a variety of organic compounds [1,2]. Halogenated aromatic compounds are a useful class of intermediates as they are precursors to a number of organo metallic species useful in the synthesis of natural products and pharmaceutically important compounds.

Benzyl chloride is an industrially more important compound produced in large quantity. Benzyl chloride is mainly converted to butyl benzyl phthalate, a vinyl resin plasticizer and benzyl alcohol. It is also a raw material for numerous derivatives such as flavor, perfume chemicals, disinfectants and dyes [3].

Benzyl chloride can be prepared by the action of sulfoxyl chloride on toluene in the presence of peroxide, by the reaction of benzyl alcohol with hydrogen chloride and with zinc chloride as a catalyst, by the action of phosphorous trichloride or pentachloride on benzyl alcohol or by chloromethylation of benzene. All these methods have no commercial significance since the starting materials are too expensive. In commercial practice benzyl chloride is manu-

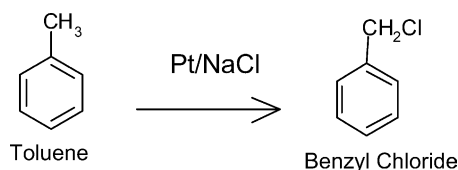
factured by photochemical chlorination of toluene at about 100–140 °C [4].

Electrochemical reaction has an advantage over regular homogenous processes in as much as they do not require the use of large quantities of noxious or corrosive reagents as in this case with elemental chlorine and hydrochloric acid. Electrochemical chlorination produces chlorine in vivo as an intermediate from non-corrosive chlorides and it can be easily controlled. Selective chlorination can be achieved in electrochemical technique [5].

Electrochemical chlorination of toluene has been attempted by many workers [6], Gourcy et al., [7] for instance, carried out the anodic chlorination of toluene in CH₃CN containing some Lewis acids and obtained *o*- and *p*-chloro toluenes, Matsuda et al., [8] have also obtained chloro-toluenes with high yield through the electrolysis of toluene in CH₃OH/LiCl. However, no chloroderivative substitution in methyl group has been reported as formed by electrochemical methods.

Forsyth and Pletcher [9] have discussed “Two-phase electrolysis” as an advantageous process in practical organic synthesis. Mortita et al., [10] showed that two-phase electrolysis can yield different products from conventional homogeneous electrolysis. In their work they obtained 26% benzylchloride as well as chlorotoluenes (26%) by the electrolysis of toluene in immiscible two-phase systems.

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Scheme 1. Electrochemical chlorination of toluene to benzyl chloride by two-phase electrolysis.

In continuation of our earlier work [11], now we wish to report a simple and efficient electrochemical method for chlorination of toluene to benzyl chloride in a two-phase system (Scheme 1). The chlorinating agent is electrochemically generated in an aqueous phase containing sodium chloride by oxidation of chloride ion and is transported to the organic phase where the side chain chlorination occurs.

2. Experimental

2.1. Materials and analysis

All the employed chemicals are commercially available and were used as received. Deionised water was used for preparing sodium chloride solution. Aplab power source was used as a direct current source for the electrolysis. A beaker type glass cell (120 ml capacity) equipped with a magnetic stirrer was used for the electrolysis. In electrochemical chlorination two platinum sheets were used as electrodes (both had areas of 10 cm²). Saturated solution of sodium chloride containing catalytic amount of sulphuric acid (2 g) was used as electrolyte. The electrolysis was monitored by HPLC (Shimadzu, Japan, Model. no. CLASS. VP-10) using Shimpack ODS-18 column (125 mm × 4.5 mm) as stationary phase. The eluent consisted of methanol/water (70:30) at a flow rate of 1 ml/min. Samples were analysed at a wavelength of 254 nm with a UV detector (Shimadzu UV-vis detector) coupled to a printer. Authentic samples of benzylchloride, *o*- and *p*-chlorotoluenes are used to calculate the peak areas of the respective experimental products for yield calculation.

2.2. Experimental condition

An amount of 4.3 gm (46 mmole) of toluene was dissolved in 25 ml chloroform and the solution was transferred into the electrolytic cell. Sixty millilitre of saturated sodium chloride solution containing 2 gm H₂SO₄ was added over the above solution. The aqueous upper phase acted as a supporting electrolyte and chloride source. Two Platinum electrodes (10 cm²) were placed in the aqueous phase (upper phase) without touching the organic phase (lower phase) but very close to the interphase between the above layers. The organic phase alone was stirred with magnetic stirrer at a rate of 40 rpm in such a way that the organic layer does not touch the electrodes. i.e. leaving the immiscible phases separated

(stationary electrolysis). The electrolysis was conducted galvanostatically (current 300 mA) for 15 h. The electrochemical cell contents were maintained at 30 °C throughout the electrolysis and an aliquot of sample was drawn periodically from chloroform layer and analysed by HPLC. After completion of electrolysis the lower organic phase was separated, water washed (2 × 25 ml), dried over anhydrous sodium sulphate and the solvent was removed by distillation. HPLC analysis of the residue indicate the presence of 81% benzylchloride (4.78 g) and 9% chlorotoluene along with 9% unconverted toluene.

3. Result and discussion

3.1. Two-phase electrolysis

Generally elemental chlorine was generated by simple constant current electrolysis of dichloromethane solution of tetra methyl ammonium chloride in presence of a substrate. This kind of chlorination is called homogeneous chlorination as the electrolyte, electrode, solvent and substrate are present in single phase. Lithium chloride in methanol can also be used in homogeneous electrolytic chlorination. Using the above systems toluene was chlorinated and no chloro derivative substituted in the methyl group has been reported. Only ring-chlorinated products i.e. *o*- and *p*-chlorotoluenes are reported as products [8].

Two-phase electrolysis is one where the electrolyte and the substrate are present in different phases. When electrolysis occurs, electrolytically generated species travels from aqueous phase to organic phase and attacks the substrate. The products obtained in two-phase electrolysis will not be the same as in the homogenous electrolysis. If the two-phases are made into emulsion by vigorous stirring, then this type of electrolysis is called emulsion electrolysis.

In our earlier studies [11] we could get 66% *o*-chlorotoluene and 33% *p*-chlorotoluene by emulsion electrolysis of toluene in 10% HCl solution at 25 °C. No benzyl chloride was obtained.

Our recent studies revealed that when the two-phases (aqueous and organic phases) are stirred in such a way without disturbing the two layers i.e., leaving the immiscible phases separated (stationary electrolysis), the products obtained from two-phase electrolysis is entirely different from homogenous electrolysis.

Although the benzyl chloride yield was satisfactory (81%), the fact that some amount of the substrate toluene remains unreacted prompted us to perform several experiments in which more than 3.5 F/mole charge was consumed. The amount of unchanged substrate in the reaction mixture decreased to trace amounts by simple prolongation of electrolysis time, however did not result in an enhancement of the yield. Instead, several new side products, which would not be separated and unidentified are appeared. Also additional experiments were carried out with an increased current

density (upto 70 mA/dm²) in order to shorten the electrolysis time. However, increased amounts of unknown side products were obtained.

3.2. Ratio of electrolyte and organic phase

In the present study saturated sodium chloride solution is used as upper phase and chloroform containing toluene as lower phase. The chlorinating species is generated electrochemically in aqueous phase by oxidation of chloride ions and is transported to the organic phase where the side chain chlorination occurs. i.e. the reaction takes place at the interphase of the two-phases. Hence more the interphase area, higher the transport of chlorinating species, faster the reaction rate. The cell is designed in such a way that the height–diameter ratio of the cell is 1:1. The electrodes were placed close to the interphase of the two-phases without touching the organic phase.

3.3. Comparison on chemical and electrochemical chlorination

To understand whether electrochemical chlorination is behaving as the chemical chlorination mode, electrochemical chlorination conditions were simulated and instead of passing current, chlorine gas was generated chemically (by the action of potassium permanganate on concentrated hydrochloric acid) and it was passed into saturated sodium chloride solution (top layer). As the reaction proceeds the products formed in the organic phase was monitored by HPLC at regular interval. Though the reaction rate was very slow, it yields benzyl chloride (35%) as the primary product and equal amount of *o*- and *p*-chlorotoluenes (35%) i.e. 24% *o*-chlorotoluene and 11% *p*-chlorotoluene along with 30% unconverted toluene. Continuation of chlorine gas passage leads to decrease in benzylchloride concentration and ultimately ring chlorinated benzyl chloride was formed as mixture of isomers (9% of *o*-chlorobenzyl chloride and 6% of *p*-chlorobenzyl chloride 15% benzyl chloride and 35% *o*- and *p*-chlorotoluenes). Hence it is understood that the mechanism involved in electrochemical chlorination is not exactly the same as in chemical chlorination.

Table 1

Effect of charge passed on the electrochemical chlorination of toluene by two-phase electrolysis

S. no.	Charge passed (F)	Yield (%)			Selectivity (%)		Current efficiency on benzyl chloride formation (%)
		Toluene	Benzyl chloride	Chloro toluene	Benzyl chloride	Chloro toluene	
1	2	23	73	4	95	5	77
2	3	20	76	4	95	5	52
3	4	14	81	5	94	6	43
4	5	12	80	8	91	9	35
5	6	12	80	8	91	9	29
6	7	11	80	8	91	9	25

Anode: Platinum (area = 10 cm²), cathode: platinum (area = 10 cm²), current density = 30 mA/cm², toluene = 46 mmoles (4.3 g), electrolyte: aqueous solution of saturated NaCl, solvent: chloroform, stirring rate: 20–40 rpm, cell volume: 120 ml, type of cell: undivided glass cell, temperature = 30 °C.

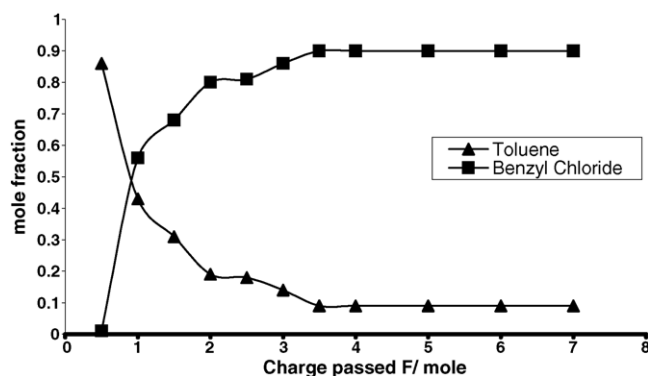


Fig. 1. The effect of charge passed on the electrochemical chlorination of toluene and the formation of benzyl chloride by two-phase electrolysis.

3.4. Effect of charge passed

In electrochemical chlorination at optimum conditions, 81% of benzyl chloride and 9% of unconverted toluene was obtained after passing 3.5 F charge per mole of toluene. The curves in Fig. 1 shows the relative quantities of toluene, benzyl chloride as a function of charge passed on electrochemical chlorination of toluene. The maximum concentration of benzyl chloride is reached at a charge of 3.5 F/mole. There is no increase in the product yield even after passing upto 7 F/mole of toluene, is shown in Table 1.

3.5. Effect of temperature

Table 2 shows the effect of temperature on the amount of benzyl chloride formed and toluene conversion. There is an increase in benzyl chloride yield with decrease of temperature from 40 to 30 °C. Further decrease of temperature from 30 to 20 °C indicates the rate of reaction is very slow and at 0 °C no reaction takes place even after 8 F charge is passed.

3.6. Effect of various anodes

Table 3 shows the various types of anodes employed in electrochemical chlorination of toluene by two-phase electrolysis. Platinum, Platinised platinum over titanium and

Table 2
Effect of temperature on the electrochemical chlorination of toluene by two-phase electrolysis

S. no.	Temperature (°C)	Yield (%)			Current efficiency on benzyl chloride formation (%)
		Toluene	Benzyl chloride	Chlorotoluene	
1	40	56	40	4	22
2	30	12	81	5	43
3	20	22	67	5	34
4	10	78	9	4	4
5	0	84	6	2	3

Anode: platinum (area = 10 cm²), cathode: platinum (area = 10 cm²), current density = 30 mA/cm², toluene = 46 mmoles (4.3 g), electrolyte: aqueous solution of saturated NaCl, solvent: chloroform, stirring rate: 20–40 rpm, cell volume: 120 ml, type of cell: undivided glass cell and charge passed = 3.5 F.

Table 3
Types of anodes employed in two-phase electrolysis of toluene

S. no.	Anode	Yield (%)			Current efficiency on benzyl chloride formation (%)
		Toluene	Benzyl chloride	Chlorotoluene	
1	Pt	14	81	5	43
2	Pt/Ti	14	81	5	43
3	MMO-Cl ₂	10	80	7	43

Anode: platinum (area = 10 cm²), cathode: platinum (area = 10 cm²), current density = 30 mA/cm², toluene = 46 mmoles (4.3 g), electrolyte: aqueous solution of saturated NaCl, solvent: chloroform, stirring rate: 20–40 rpm, cell volume: 120 ml, type of cell: undivided glass cell and temperature = 30 °C.

MMO-Cl₂ anodes were used in electrolysis and found that all three electrodes have more or less same efficiency.

3.7. Influence of acid in two-phase electrolysis

The electrochemical chlorination of toluene was carried out in aqueous solution of saturated NaCl containing catalytic amount of sulphuric acid and maximum yield of benzylchloride obtained was 81.0%. It was found that when the electrolysis was conducted in the absence of sulphuric acid 55.0–67.0% benzylchloride was formed and after that the concentration of benzyl chloride start decreasing. But in the presence of an acid no decomposition of benzylchloride occurs and the concentration increased upto 81.0%. Hence the acid may be used to neutralise the basicity that was generated as the electrolysis proceeds.

3.8. The probable mechanism for the two-phase electrolysis

The mechanism of this reaction seems to be very simple, which is shown in Scheme 2. The substitution of hydrogen by chlorine in the side chain chlorination is following a radical chain reaction. Free radical chain reaction comprise of following three different steps:

- I. Initiation
- II. Propagation
- III. Termination.

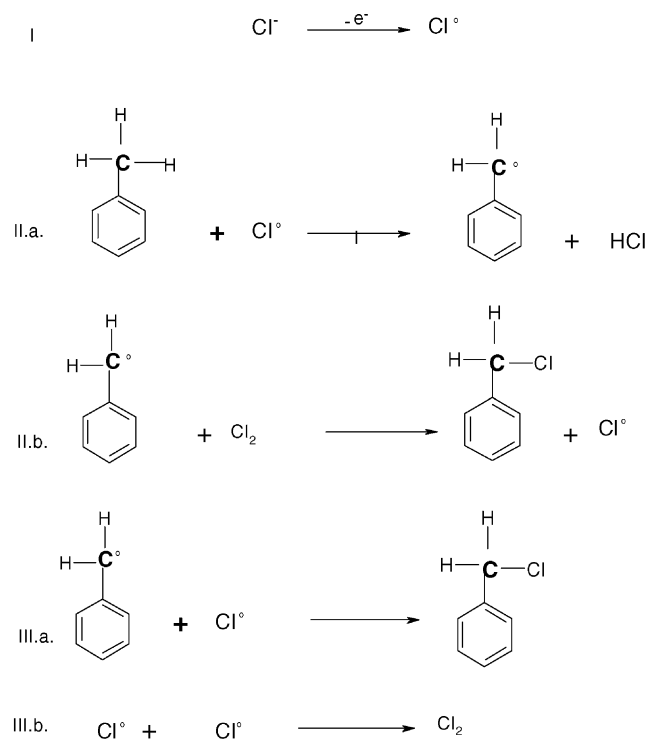
3.8.1. Initiation step

In this step, the reactive intermediate chlorine atom is generated. The chloride ion gets oxidized on the anode giving chlorine atom is the generation of a reactive intermediate: a

short lived, highly reactive species that is never present in large concentrations due to its reactive nature.

3.8.2. Propagation step

The reactive chlorine atom collides with a toluene molecule and abstracts a hydrogen atom. One of the C–H bond electrons stays on the carbon atom. The first propaga-



Scheme 2. The probable mechanism for the electrochemical chlorination of toluene by two-phase electrolysis.

tion step is the generation of the reactive intermediate. The radical reacts and generate another radical. The reactive intermediate thus produced (benzyl radical) reacts in the second propagation step. In the course of generation of the product benzyl chloride, another chlorine radical is produced and thus the propagation continues (step II.a and II.b. in [Scheme 2](#)).

3.8.3. Termination step

If a radical undergoes a reaction, which does not generate another radical, then the chain reaction slows and stops. The termination steps involve the combination of two free radicals either of two chlorine atoms or chlorine atom with benzyl radical (step III.b and III.a. in [Scheme 2](#)).

4. Conclusions

In conclusion, the electrochemical method involving the chlorination of toluene to benzyl chloride by two-phase electrolysis constitutes a novel and efficient alternative method over conventional chemical methods. The reactions are carried out under mild condition with a very simple electrochemical setup and present several advantages as free

as possible of secondary products, low cost of production, selective chlorination, high conversion and yield.

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