

Review

# Complete electrochemical dechlorination of chlorobenzenes in the presence of naphthalene mediator

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Received 23 February 2007; received in revised form 4 May 2007; accepted 7 June 2007

Available online 12 June 2007

## Abstract

Electrochemical dechlorination of chlorobenzene in organic solutions was studied. Electrolysis of chlorobenzene in acetonitrile solution in a one-compartment cell fitted with a platinum cathode and a zinc anode at 60 mA/cm<sup>2</sup> and 0 °C was found to be the optimum conditions, which gave complete dechlorination of chlorobenzene. However, similar result could not be achieved when applying these conditions to 1,3-dichlorobenzene and 1,2,4-trichlorobenzene. We found that the use of naphthalene which reacted as a mediator in the appropriate system could accelerate the reduction and gave complete dechlorination of those chlorobenzenes. Moreover, in the presence of naphthalene the reaction time could be shortened by half compared to dechlorination in the absence of naphthalene.

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**Keywords:** Electrolysis; Dechlorination; Chlorobenzenes; Naphthalene; Mediator

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## 1. Introduction

Polychlorinated aromatic compounds are environmentally persistent chemicals, recalcitrant toward degradation, which bioaccumulate in fatty tissue and show carcinogenic and muta-

genic activity, so they are a class of pollutants of special environmental concern [1]. Various degradation techniques have been studied in order to destroy these toxic chemicals such as by incineration [2–5], various reducing reagents, namely hydrogen together with catalysts in both heterogeneous [6–10] and homogeneous systems [8,11,12], Raney Nickel alloy [13–15], metals [16–18] and metal hydrides [19–21]. However, these methods required high temperature, expensive and may also produce more hazardous byproducts such as dioxins and furans due to the incomplete combustion. In addition, detoxifying of those

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organic chlorides by other techniques at low temperature have been also developed such as by biological reduction [22–25], photocatalytic oxidation [26,27], and catalytic hydrodechlorination [28,29]. Although these techniques could be carried out under mild conditions without formations of dioxins and furans, they have disadvantages in the large-scale applications such as highly cost and long time operation [30]. Therefore, another alternative method which is much cheaper and efficient is expected.

Among the several existing techniques, electrochemical reduction has become a well-known alternative method for detoxification of chlorinated organic compounds due to its simple operations, promise of high-energy efficiency, economic and also produces much less toxic products compared to other technique such as biodegradation [31–34]. However, complete dechlorination almost rarely occurs since the insulating films which produced on the electrode surfaces during the electrolysis will prohibit the progress of the reduction [35]. This is due to the potentials for the electrolyses are close to the lower limits of the potential windows of the solvents and supporting electrolytes [33]. Kargina et al. reported that electrolyses on a glassy carbon electrode using mediators can solve this problem since chlorinated benzene will be reduced at the redox potentials of mediators which are close to the standard reduction potentials of chlorinated benzenes [33,35]. Nevertheless, they founded that few chlorinated benzenes still remained in the solution and less than the expected amount of benzene was detected even after passing enough charge to dechlorinate trichlorobenzene [36]. Besides, Hoshi et al. reported the voltammograms of the reduction of chlorobenzene in the presence of naphthalene mediator on various metal electrodes [33]. They found that the activity of the reduction depends on the type of metal electrodes as follows:  $Pt=Zn < Ag$ . According to the above studies, we supposed that combination of appropriate electrolysis system and mediator are very important factor in achieving a complete dechlorination of those chloroaromatic compounds. Therefore, aiming for this purpose, in this paper we reported a complete dechlorination of monochlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene in the presence of naphthalene mediator in a simple one-compartment cell fitted with platinum cathode and zinc anode. Monochlorobenzene was used as a model substrate in order to find the optimum condition of the electrolysis since it is the simplest aromatic organic chloride, which forms the framework of highly toxic organic compounds such as polychlorobiphenyl (PCB), dioxins and furans.

## 2. Materials and methods

### 2.1. Reagents, materials and solutions

Chlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene, tetraethylammonium bromide solution, and naphthalene were purchased from Fluka Chemica. Perchlorate acid and hydrochloric acid were obtained from MERCK and ether anhydrous from J.T. Baker. Acetone and acetonitrile solution were purchased from HmbG Chemical and methanol from RPE Reagent Pure Erba. Zinc and platinum plates of more than 99.9%

purities were obtained from Nilaco, Japan, and were used as electrodes. Before electrolysis, the electrodes were washed with 2N HCl, methanol and acetone.

Tetraethylammonium perchlorate (TEAP) that was used as a supporting electrode in this electrolysis was prepared as follows. A saturated aqueous solution of 190 ml (1 mol) of tetraethylammonium bromide ( $Et_4NBr$ ) solution in 600 ml of water was treated with 60 ml of aqueous 60% perchlorate acid,  $HClO_4$  (1 mol). After filtration of the resulting insoluble perchlorate salt, the salt was washed with cold water and dried. Recrystallization from methanol and drying under reduced pressure give a pure  $Et_4NClO_4$  as white needles in 90% yield.

### 2.2. Apparatus and procedures

A one-compartment cell equipped with a magnetic stirring bar, zinc plate ( $2\text{ cm} \times 2\text{ cm}$ ) as an anode and platinum plate ( $2\text{ cm} \times 2\text{ cm}$ ) as a cathode was used. Electrolysis was carried out in acetonitrile solution at a constant current of  $60\text{ mA/cm}^2$  at  $0^\circ\text{C}$ . The progress of the reaction was monitored by Hewlett Packard–Agilent Technologies gas chromatograph equipped with HP-5 capillary column until complete dechlorination was achieved. The conversion was calculated by the disappearance of chlorobenzene.

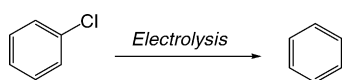
## 3. Results and discussion

### 3.1. Dechlorination in the absence of naphthalene

Initially, chlorobenzene was used as a model reactant and the reaction was carried out in *N,N*-dimethylformamide (DMF) solution in the absence of a mediator. Various parameters were studied in order to find the optimum conditions of dechlorination such as temperature, current density, type of solvent and also electrode. The result of the dechlorination in the absence of naphthalene mediator under air atmosphere is shown in Table 1. Entries 1 and 2 show that the reaction under either air or nitrogen atmosphere did not have much effect on dechlorination. Furthermore, conventional stirred reaction gave only 43% of conversion (entry 5) which means that the current passed is significant for dechlorination. The results of the effect of temperature are shown in entries 2–4. Reaction at  $0^\circ\text{C}$ , room temperature and  $50^\circ\text{C}$  gave 77, 52 and 63% of conversion, respectively. The reaction at low temperature gave better result while at high temperature the voltage increased gradually and resisted the current passed. The reactions at  $30\text{ mA/cm}^2$  (entry 6),  $60\text{ mA/cm}^2$  (entry 3) and  $80\text{ mA/cm}^2$  (entry 7) gave 57, 77 and 63% of conversion, respectively. Reaction in acetonitrile solution and mixture of DMF and acetonitrile with water were also studied with a view to apply this method to wastewater treatment. However, as shown in entry 9, acetonitrile was an optimum solvent which gave complete dechlorination. The presence of water did not seem suitable in this system (entries 8 and 10). In addition, we found that aluminium, copper and carbon could not be used as an anode material (entries 11–13).

As a result, the electrolysis of chlorobenzene in acetonitrile solution under air atmosphere at  $0^\circ\text{C}$  and  $60\text{ mA/cm}^2$  of current

Table 1  
Dechlorination of chlorobenzene in the absence of naphthalene



Entry	Reaction conditions	Conversion (%)
1	(-)Pt–Zn(+), 60 mA/cm <sup>2</sup> , r.t., in nitrogen, DMF	54
2	(-)Pt–Zn(+), 60 mA/cm <sup>2</sup> , r.t., in air, DMF	52
3	(-)Pt–Zn(+), 60 mA/cm <sup>2</sup> , 0 °C, in air, DMF	77
4	(-)Pt–Zn(+), 60 mA/cm <sup>2</sup> , 50 °C, in nitrogen, DMF	63
5	(-)Pt–Zn(+), without current, r.t., in air, DMF	43
6	(-)Pt–Zn(+), 30 mA/cm <sup>2</sup> , 0 °C, in air, DMF	57
7	(-)Pt–Zn(+), 80 mA/cm <sup>2</sup> , 0 °C, in air, DMF	63
8	(-)Pt–Zn(+), 60 mA/cm <sup>2</sup> , 0 °C, in air, DMF:H <sub>2</sub> O (8:2)	22
9 <sup>a</sup>	(-)Pt–Zn(+), 60 mA/cm <sup>2</sup> , 0 °C, in air, CH <sub>3</sub> CN	100
10	(-)Pt–Zn(+), 60 mA/cm <sup>2</sup> , 0 °C, in air, CH <sub>3</sub> CN:H <sub>2</sub> O (9:1)	33
11	(-)Pt–Al(+), 60 mA/cm <sup>2</sup> , 0 °C, in air, CH <sub>3</sub> CN	Precipitation
12	(-)Pt–Cu(+), 60 mA/cm <sup>2</sup> , 0 °C, in air, CH <sub>3</sub> CN	Precipitation
13	(-)Pt–C(+), 60 mA/cm <sup>2</sup> , 0 °C, in air, CH <sub>3</sub> CN	Precipitation

Current passed: 8 F/mol.

<sup>a</sup> Complete dechlorination was achieved at 5 F/mol of current passed.

density with platinum plate as a cathode and zinc plate as an anode was considered as an optimum condition for this dechlorination. Next, this reaction was applied to 1,3-dichlorobenzene and 1,2,4-trichlorobenzene in order to achieve complete dechlorination of such compounds (Fig. 1).

However, as shown in Fig. 1, complete dechlorination could be only achieved by chlorobenzene, at 5 F/mol of current passed. And the maximum conversion that could be achieved by 1,3-dichlorobenzene and 1,2,4-trichlorobenzene were only 93 and 88% at 16 and 26 F/mol of current passed, respectively. This is may be due to the insulating films that are produced on the electrode surfaces during the electrolyses prohibit the progress of the electrolysis. Therefore, we added naphthalene in order

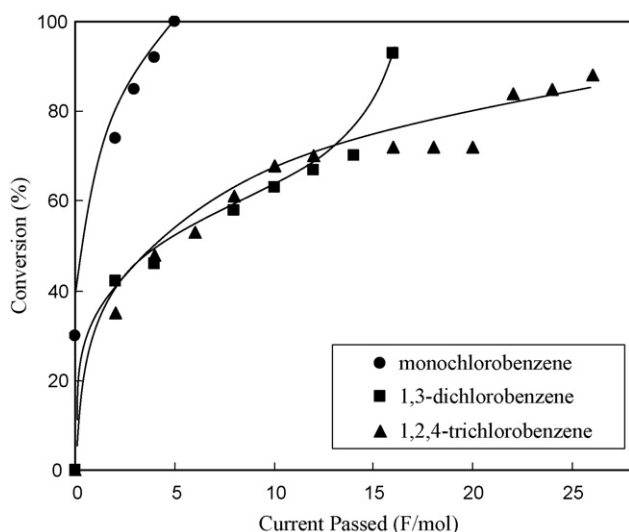
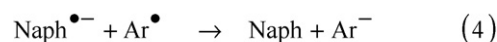
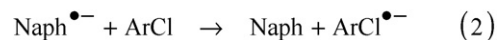


Fig. 1. Dechlorination of chlorobenzenes in the absence of mediator.



Scheme 1. Reaction mechanism.

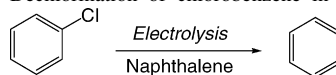
to achieve a complete dechlorination of those chloroaromatics [35].

### 3.2. Dechlorination in the presence of naphthalene

The reaction mechanism of dechlorination of chlorobenzene in the presence of naphthalene mediator is shown in Scheme 1 [37]. At the cathode, a one-electron reduction of naphthalene molecule readily occurred to give naphthalene radical anion preferentially. From our observation, the formation of the naphthalene radical anions was shown by the dark brown color which appeared on the surface of the cathode soon after the current was started. Then the chlorobenzene was reduced by the naphthalene radical anion to give its radical anion (2). The neutral radical thus formed (3) may then undergo another naphthalene reduction to form aryl anion (4), which then protonated by the solvent or the quaternary ammonium cation of the supporting electrolyte (5), to an overall hydrogenolysis of the carbon–chlorine bond. As a result, two electrons were consumed per chlorine removed.

Table 2 shows the effect of equivalents of naphthalene on the dechlorination of chlorobenzene. In DMF solution, 2 equivalents of naphthalene gave the maximum conversion (87%) of chlorobenzene (entry 3) compared to 0.5 and 1.0 equivalent that only gave 67 and 74% of conversion, respectively (entries 1 and 2). However, when the reaction was carried out in acetonitrile, complete dechlorination was achieved at only 4 F/mol of current passed (entry 4<sup>b</sup> and also in Fig. 2), about 13 min earlier than the reaction in the absence of naphthalene (entry 9, Table 1).

Table 2  
Dechlorination of chlorobenzene in the presence of naphthalene mediator



Entry	Reaction conditions	Conversion <sup>a</sup> (%)
1	DMF, 0.5 equivalent naphthalene	67
2	DMF, 1 equivalent naphthalene	74
3	DMF, 2 equivalent naphthalene	87
4 <sup>b</sup>	MeCN, 2 equivalent naphthalene	100

(Cathode)Pt–Zn(anode), 60 mA/cm<sup>2</sup>, 0 °C, in air atmosphere.

<sup>a</sup> Data were taken at 8 F/mol of current passed.

<sup>b</sup> Complete dechlorination was achieved at 4 F/mol of current passed.

Table 3  
Dechlorination of chlorobenzenes in the absence and presence of naphthalene

Entry	Chlorobenzene	Without naphthalene		With naphthalene	
		Current passed (F/mol)	Conversion (%)	Current passed (F/mol)	Conversion (%)
1	Monochlorobezene	5	100	4	100
2	1,3-Dichlorobenzene	16	93	6	100
3	1,2,4-trichlorobenzene	26	88	12	100

Subsequently, this condition was applied to 1,3-dichlorobenzene and 1,2,4-trichlorobenzene. As shown in Fig. 2, in the presence of naphthalene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene could be completely dechlorinated at 6 and 12 F/mol, respectively. These efficient results show that the use of appropriate reaction system with naphthalene mediator is significant factor in accomplishing the reduction of chlorobenzenes. This is may be due to the formation of naphthalene radical anion on different electrodes would affect the acceleration of the electron-transferring step during the reaction.

Table 3 shows that in the case of monochlorobenzene, it could be completely dechlorinated either with or without naphthalene. However, the reaction in the presence of naphthalene is faster than that in the absence of naphthalene, which is the difference of the current passed is about 1 F/mol (entry 1). In addition, in the absence of naphthalene the dechlorination of 1,3-dichlorobenzene and 1,2,4-trichlorobenzene could not be completed, which is the maximum conversion that could be achieved were only 93 and 88%, respectively (entries 2 and 3). While, by adding naphthalene both chlorobenzenes could be completely dechlorinated (entries 2 and 3) at 6 and 12 F/mol, respectively, which was about two times faster compared to the reaction in the absence of naphthalene. These results may be owing to the difference of electrolysis potentials in those two systems [35] which caused the formation of insulating film and also affected the rate of electrons transferring step in each reactions.

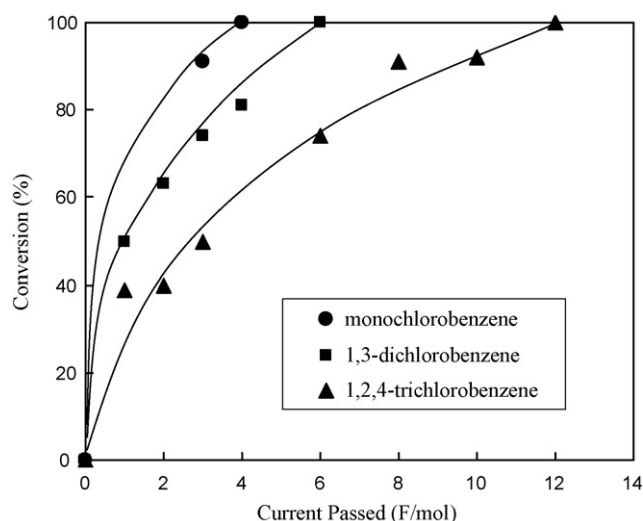


Fig. 2. Dechlorination of chlorobenzenes in the presence of naphthalene mediator.

#### 4. Conclusion

Complete dechlorination of monochlorobenzene was achieved by electrolysis in acetonitrile solution on the platinum cathode and zinc anode. However, the same result could not be obtained when applying this system to 1,3-dichlorobenzene and 1,2,4-trichlorobenzene. This problem was solved by adding naphthalene into the system. As a result, naphthalene which reacts as a mediator could accelerate the reduction of those chlorobenzenes and finally complete dechlorination could be achieved in about two times faster compared to the reaction in the absence of naphthalene. These results showed that the combination of appropriate reaction system and the use of naphthalene mediator are important factor in attaining complete dechlorination of chlorobenzenes.

#### Acknowledgement

Our gratitude goes to Universiti Teknologi Malaysia for its financial supports under the Fundamental Research Grant (No. 75042) and to Professor Emeritus Masao Tokuda at Hokkaido University, Japan, for his useful guidance and advice. We would also like to thank the Hitachi Scholarship Foundation for their support especially for the Gas Chromatography Instruments Grant.

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