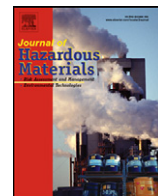




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Complete electrochemical dechlorination of chlorobenzenes in the presence of various arene mediators

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ABSTRACT

Electrochemical dechlorination of chlorobenzenes in the presence of various arene mediators such as naphthalene, biphenyl, phenanthrene, anthracene, and pyrene, was studied. The amount of mediator required was able to be reduced to 0.01 equiv. for all mediators except for anthracene, with the complete dechlorination of *mono*-, *1,3-di*- and *1,2,4-trichlorobenzene* still achieved. This catalytic amount of mediator plays an important role in accelerating the dechlorination through the rapid formation of radical anions prior to reduction of the chlorobenzenes.

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1. Introduction

Polychlorinated aromatic compounds are environmentally persistent chemicals, and are resistant to degradation, bioaccumulate in fatty tissue and show carcinogenic and mutagenic activity. Thus, they are a class of pollutants of special environmental concern [1]. Various degradation techniques have been studied with the aim of destroying these toxic chemicals. These techniques include incineration [2], biological reduction [3,4], photocatalytic oxidation [5,6], heterogeneous [7,8] and homogeneous [9,10] catalysis, and complexation with metals and metal hydrides [11,12]. However, these methods require high temperatures, long operation times, are expensive, and may also produce more hazardous by-products, such as dioxins and furans, due to incomplete combustion. Therefore, considerable effort has been expended in the search for a more efficient and cheaper method of degradation. For example, electrochemical degradation, which is simple in operation, has a

high-energy efficiency, is economic, and also produces less toxic by-products compared to other techniques [13–15].

Recently, we reported a simple electrochemical system for the complete dechlorination of monochlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene in the presence of a naphthalene mediator in a one-compartment cell fitted with a platinum cathode and zinc anode [16]. This new system overcame the problem of the insulating film that forms on the electrode surfaces during electrolysis [17–19], and gave complete dechlorination of chlorobenzenes. The reaction time could be also reduced by one-half compared to electrochemical dechlorination in the absence of naphthalene.

Matsunaga and co-workers have reported the electrochemical reduction of several chlorobenzenes in the presence of aromatic radical anions and its application to PCBs [20]. They also reported a rapid and complete dechlorination of an excess amount of 1-chloronaphthalene, which simultaneously reacts as a reactant and a mediator [21]. Nevertheless, the use of a catalytic amount of mediator is necessary for devising low-cost and simple purification methods for dechlorination systems [22]. In view of this, we herein report the use of a catalytic amount of a naphthalene mediator for the complete dechlorination of monochlorobenzene (MCB). The performance of four different types of arene mediators, biphenyl, phenanthrene, anthracene, and pyrene, and their appli-

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cation for the dechlorination of 1,3-dichlorobenzene (*m*-DCB) and 1,2,4-trichlorobenzene (TCB) will also be discussed.

2. Materials and methods

2.1. Reagents, materials and solutions

MCB, *m*-DCB, TCB, tetraethylammonium bromide solution, and naphthalene were purchased from Fluka Chemical. Perchloric acid and hydrochloric acid were obtained from MERCK and anhydrous ether was purchased from J.T. Baker. Acetone and acetonitrile were purchased from HmbG Chemical and methanol was purchased from RPE Reagent Pure Erba. Zinc and platinum plates of more than 99.9% purity 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), which was used as a supporting electrode in electrolysis, was prepared as follows. A saturated aqueous solution of 190 ml (1 mol) of tetraethylammonium bromide (Et₄NBr) solution in 600 ml of water was treated with 60 ml of aqueous 60% perchloric acid (HClO₄, 1 mol). After filtration of the resulting insoluble perchlorate salts, the salts were washed with cold water and dried. Recrystallization from methanol and drying under reduced pressure gave pure Et₄NClO₄ as white needles in 90% yield.

2.2. Apparatus and procedures

A one-compartment cell equipped with a magnetic stirring bar, a zinc plate (2 cm × 2 cm) as an anode and a platinum plate (2 cm × 2 cm) as a cathode were used. Electrolysis was carried out in acetonitrile solution at a constant current of 60 mA/cm² at 0 °C. The progress of the reaction was monitored with a Hewlett Packard-Agilent Technologies gas chromatograph equipped with an HP-5 capillary column until complete dechlorination was achieved.

3. Results and discussion

3.1. Analysis of chlorobenzenes

Dechlorination efficiency was calculated by the conversion of chlorobenzene, which was determined by the disappearance of chlorobenzene in the system. Fig. 1 illustrates the GC chromatogram of the reaction mixture during the dechlorination of TCB. TCB is first transformed to *m*-DCB, and then quickly reduced to benzene.

3.2. Dechlorination of MCB

In a previous paper, we reported that MCB could be completely dechlorinated with 48×10^4 C/mol² of electric quantity (at 5 F/mol of current passed) in the absence of a mediator (Table 1, entry 1). We then found that the addition of naphthalene is important

in accelerating the reaction (entry 2) and facilitating the dechlorination of chlorobenzenes that contain more than one chlorine atom. A complete dechlorination of MCB, *m*-DCB and TCB could be achieved in the presence of 2 equiv. of naphthalene in an acetonitrile solution with 39×10^4 (at 4 F/mol), 58×10^4 (at 6 F/mol) and 116×10^4 C/mol² (at 12 F/mol) of electric quantity, respectively [16]. Other researchers have also reported the use of excess amounts of mediators in dechlorinations [20–21]. However, the use of a catalytic amount of arene is more desirable in this dechlorination system. Therefore, we attempted to reduce the amount of naphthalene from 2 to 0.01 equiv. (Table 1, entries 2–7).

We found an increase in electric quantity, which corresponds to the reaction time, when the amount of naphthalene was reduced. This is may be due to the amount of naphthalene radicals reduced because of the decrease in the naphthalene amount [16]. Thus, more electric quantities or longer times were required for the electron transfer steps and reproduction of the naphthalene radicals compared to the system with a greater amount of naphthalene. Entries 6 and 7 show that complete dechlorination could be achieved by using 0.05 and 0.01 equiv. of naphthalene with 68×10^4 and 77×10^4 C/mol² of electric quantity, respectively. This result demonstrates a dechlorination using a catalytic amount of mediator in our system. However, due to the observed reaction rates, current stability and reaction times, we chose 0.05 equiv. as the optimum level.

3.3. Dechlorination of MCB in the presence of various types of mediators

Next, with the aim of studying the effect of various types of arenes, we carried out the dechlorination of MCB in the presence of 0.05 equiv. of biphenyl, anthracene, phenanthrene and pyrene. As shown in Fig. 2, all of the reactions in the presence of those mediators gave complete dechlorination of MCB, except the reaction in the presence of anthracene, which gave only a maximum conversion of 83% with 97×10^4 C/mol² of electric quantity. This limitation was due to precipitation during the reaction that may be caused by the dimerization of anthracene. In addition, the reduction potential of anthracene is more positive compared to MCB and other mediators, which is less effective for this arene-mediated dechlorination [20]. In the presence of biphenyl, phenanthrene and naphthalene, complete dechlorinations were achieved with 42×10^4 , 42×10^4 and 68×10^4 C/mol² of electric quantity, respectively. Pyrene was found to be the most effective mediator in this system, which yielded the highest reaction rate compared to the other arenes, and gave complete dechlorination with only 34×10^4 C/mol² of electric quantity. The use of pyrene could shorten the reaction time by one-half compared to the use of naphthalene. According to the literature, the tendency of arenes and chlorobenzenes to be reduced follows the order: biphenyl > naphthalene > phenanthrene > pyrene > MCB > *m*-DCB > TCB > anthracene [15,20,23–24]. Therefore, the effectiveness of pyrene may be due to its smaller difference in reduction potential with MCB compared to the other mediators [15,20].

These results verified that the reducing power of the arenes does not entirely depend on the number of benzene rings, but on the other factors such as reduction potential, occurrence of side reactions and deterioration of the arene [15,25]. Notably, we found that a catalytic amount of mediator could also facilitate the complete dechlorination of MCB.

3.4. Dechlorination of *m*-DCB and TCB

We next studied the effectiveness of a catalytic amount of the aforementioned arenes on the dechlorination of *m*-DCB (Fig. 3) and TCB (Fig. 4). As shown in Figs. 3 and 4, all of the mediators except

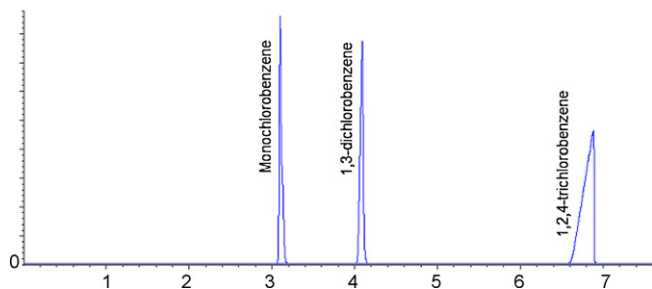
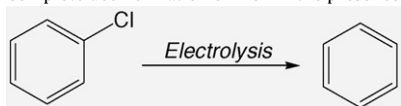
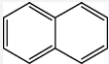


Fig. 1. GC chromatogram of the reaction mixture during the dechlorination of TCB.

Table 1
Complete dechlorination of MCB in the presence of a naphthalene mediator.



Entry	Mediator	Equivalents	Electric quantity ($\times 10^4$ C/mol ²) ^a	Conversion (%)
1	None	0	48	100 ^b
2		2	39	100 ^b
3		1	43	100
4		0.50	48	100
5		0.25	58	100
6		0.05	68	100
7		0.01	77	100

(Cathode)Pt–Zn(anode), 60 mA/cm², 0 °C, under air atmosphere.

^a 9.65×10^4 C/mol² = 13 min.

^b Refer to [18].

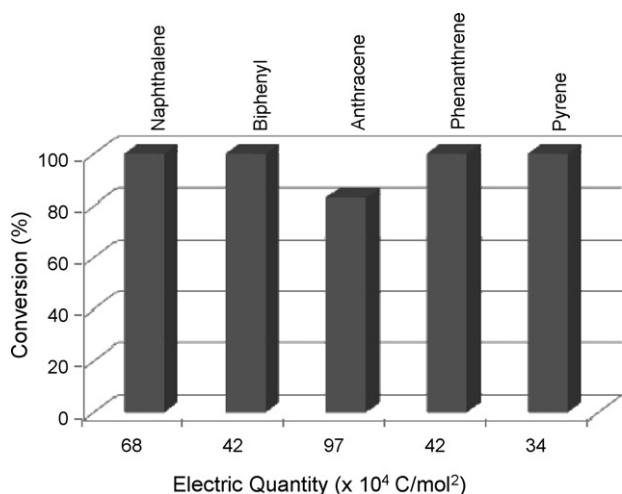


Fig. 2. Dechlorination of MCB in the presence of various types of mediators.

anthracene gave complete dechlorination of *m*-DCB and TCB. Similar to MCB, the reduction potential of *m*-DCB and TCB is also more negative than anthracene, which caused problems in prior reductions, and always ended with precipitation in the system [20,24].

In the dechlorination of *m*-DCB, pyrene and phenanthrene demonstrated better performance as a mediator compared to the other compounds, and completed the reaction with the same elec-

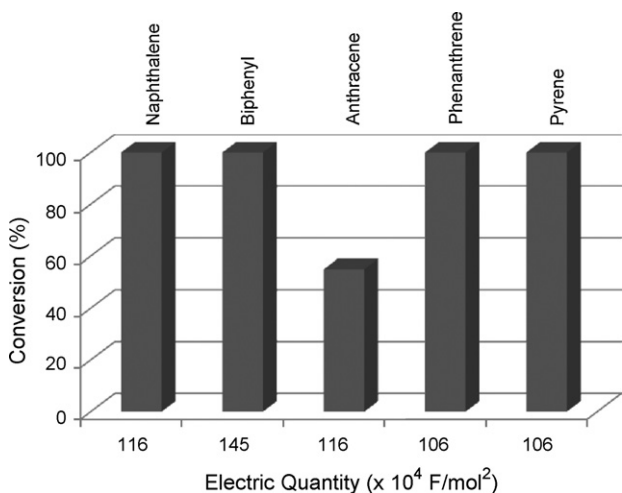


Fig. 3. Dechlorination of *m*-DCB in the presence of various types of mediators.

tric quantity of 106×10^4 C/mol² (Fig. 3). These results also showed that a lesser difference in reduction potential between the mediators and the chlorobenzenes requires a smaller the electric quantity for reduction. Phenanthrene was the most effective mediator in the dechlorination of TCB, and required the same electric quantity of 106×10^4 C/mol² (Fig. 4). Naphthalene and biphenyl were the next most effective mediators after phenanthrene in both dechlorinations (Figs. 3 and 4). However, the dechlorination of TCB in the presence of pyrene required about two times as much electric quantity compared to the same reaction of *m*-DCB. In fact, this reaction showed an early rapid progress, like the reaction of TCB in the presence of biphenyl, but was sluggish at the final step of the reaction. This is may be due to the concentrated solution that finally prohibited the progress of the reaction.

3.5. Proposed reaction path of *m*-DCB and TCB dechlorinations

Scheme 1 shows the proposed reaction mechanism of the arene-mediated dechlorination of chlorobenzenes. At the cathode, two-electron reduction of the mediator readily occurs to preferentially give mediator radical anion (1). From our observation, the formation of the mediator radical anion is shown by particular colors of each mediator that appeared on the surface of the cathode soon after the current is started. For example, dark green, dark brown and dark grey colors were shown by the radical anions of naphthalene, pyrene and phenanthrene, respectively. Next, the TCB (2) is reduced by the mediator radical anion to give its radical anion

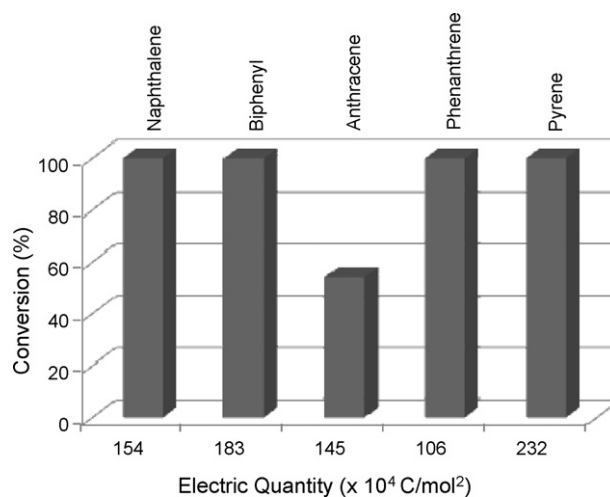
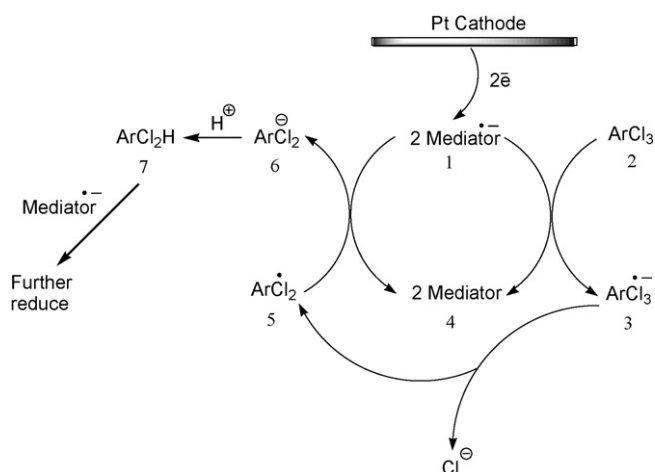


Fig. 4. Dechlorination of TCB in the presence of various types of mediators.

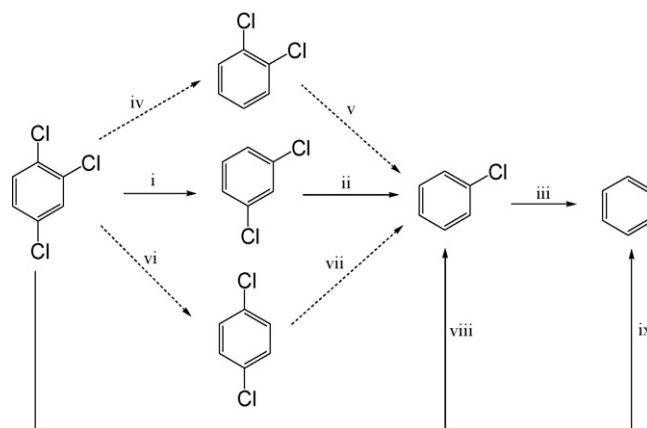


Scheme 1. Proposed reaction mechanism of arene-mediated dechlorination of chlorobenzenes.

(3). The neutral radical thus formed (5) may then undergo another mediator reduction to form an aryl anion (6), which is then protonated by the solvent or the quaternary ammonium cation of the supporting electrolyte to give DCB (7). Next, further reduction will occur with the consumption of two electrons per chlorine removal until complete dechlorination is achieved.

Fig. 5 shows the dechlorination of TCB in the presence of a naphthalene mediator (2 equiv.). The amount of TCB decreased rapidly with the first $10 \times 10^4 \text{ C/mol}^2$ of electric quantity (at 13 min of reaction), while *m*-DCB started to increase followed by an increase of MCB. This was due to the elimination of a chlorine atom from TCB to form *m*-DCB and then MCB. Subsequently, the amount of *m*-DCB gradually decreased, while the amount of MCB was constant for about 40 min before the reaction was completed by $116 \times 10^4 \text{ C/mol}^2$ of electric quantity. The main peaks that were detected by GC during the dechlorination were TCB, *m*-DCB and MCB, while only trace amounts of intermediate chlorinated compounds were detected. Therefore, we assumed that all of the chlorobenzenes were converted completely to benzene.

According to Fig. 5, a reaction path of the dechlorination of TCB is proposed as shown in Scheme 2. It was hypothesized that TCB was transformed to *m*-DCB (route i), and then to MCB (route ii) before arriving at benzene (route iii) as the final product. This route is illustrated by a solid arrow in Scheme 1. Conversely, the route through



Scheme 2. Reaction path of the dechlorination of TCB.

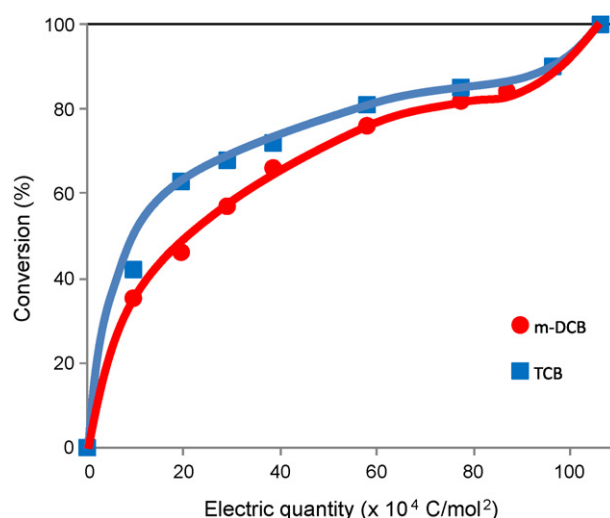


Fig. 6. Dechlorination of *m*-DCB and TCB in the presence of phenanthrene.

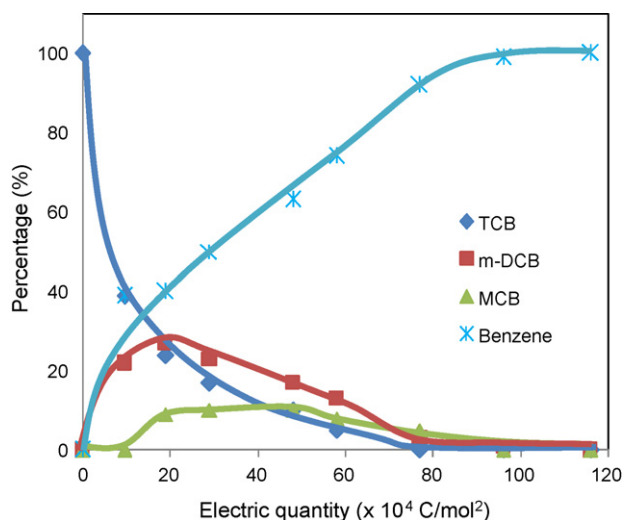


Fig. 5. Dechlorination of TCB in the presence of naphthalene.

o-DCB (route iv) and *p*-DCB (route vi) to produce MCB (routes v and vii), which is shown by a dashed line arrow, is not favorable for this reaction. In line with these results, Matsunaga also reported that due to delocalized electron density and steric hindrance, chlorine release from the radical anion of chlorobenzenes is fastest at the *p*-position and slowest at the *m*-position [20]. In addition, it was observed that in the presence of a phenanthrene mediator, the reaction rate of TCB is higher than that of *m*-DCB, indicating that the transformation of TCB to *m*-DCB is faster than *m*-DCB to MCB (Fig. 6). A direct dechlorination of TCB to MCB (route viii) and benzene (route ix) may also occur simultaneously (Scheme 1).

4. Conclusion

The amount of naphthalene mediator was reduced to 0.01 equiv. and gave complete dechlorination of monochlorobenzene with $77 \times 10^4 \text{ C/mol}^2$ of electric quantity. This catalytic amount was then applied to a similar reaction in the presence of four different types of arene mediators, biphenyl, phenanthrene, anthracene, and pyrene. Complete dechlorination was achieved in all of the reactions, except the one containing anthracene. Similar results were also obtained when applying this reaction to 1,3-*di*- and 1,2,4-*tri*chlorobenzene, with phenanthrene appearing to be the most effective mediator among those examined. These results showed that reduction potential plays an important role in this dechlorination system. The

occurrence of side reactions and the deterioration of the arenes also impede the progress of the reactions.

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