

Article

Carbon Dioxide Fixation Method for Electrosynthesis of Benzoic Acid from Chlorobenzene

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Abstract: Carbon dioxide fixation technique was developed as an alternative dechlorination method of chlorobenzenes. Electrolysis of chlorobenzene was carried out in a one-compartment cell fitted with an aluminium anode and a platinum cathode. Electrolysis in *N,N*-dimethylformamide (DMF) solution containing 0.1 M of tetrapropylammonium bromide (TPAB) at 0 °C, 100 ml/min of CO₂ flow rate and 120 mA/cm² of current density was found to be the optimum conditions of this electrocarboxylation, which gave 72% yield of benzoic acid from chlorobenzene. These conditions were then applied to 1,2-dichlorobenzene and 1,3-dichlorobenzene in order to convert them to their corresponding benzoic acids.

Key words: carbon dioxide; fixation method; electrosynthesis; chlorobenzene; benzoic acid

1. Introduction

Carbon dioxide (CO₂) is the most abundant waste produced by human activities and one of the greenhouse gases [1]. Utilization of CO₂ as a renewable raw material thus becomes greater in industrial chemistry and biotechnology which are an area of current interest [2]. At present, CO₂ is used in manufacturing urea, salicylic acid and para-hydroxy benzoic acids, methanol and cyclic carbonates [2]. Chemical fixation of CO₂ into organic substances is one of the most attractive methods as there are many possibilities for CO₂ to be used as a safe and cheap C₁ building block in organic synthesis, and it is environmentally benign (nontoxic, noncorrosive, and nonflammable) [3]. Much works have been conducted for the synthesis of organic compounds from CO₂ fixation method. For instance, Yoshida *et al.* reported the palladium-catalyzed reaction of 6-methoxycarbonyloxy-2,4-hexadien-1-ols to

produce 1,3-dienyl-substituted cyclic carbonates *via* CO₂-fixation process [1]. Synthesis of cyclic carbonate *via* cycloaddition of CO₂ to epoxide is one of the effective routes of CO₂ fixation and it was reported by Sun *et al.* [3]. Cyclic carbonates have been found to be of extensive use as excellent aprotic polar solvents, electrolytes in secondary batteries, and intermediates in the production of pharmaceuticals and fine chemicals such as dialkyl carbonates, glycols, carbamates, pyrimidines, purines, *etc.* In contrast, this study uses CO₂ fixation method for electrosynthesis of benzoic acid from chlorobenzene [4].

Chlorobenzene is the simplest aromatic chloride, and forms the frame work of highly toxic organic chlorides such as polychlorobiphenyls (PCBs), dioxins and furans [5]. Such components which are produced in a broad range of industrial processes are hazardous due to their carcinogenic and mutagenic activity. There are various methods for elimination of organochlorine compounds such as biological treatment [6], steam reforming [7], catalytic reactions [8], and incineration.

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However, these methods require longer reaction time and high temperature, expensive reagents, and could also produce more toxic materials such as dioxins and furans if the combustion is incomplete [9]. Therefore, another alternative technique is necessary in order to overcome these problems.

One of the promising methods is that using electrochemical reduction which is expected to offer an effective consequence of dechlorination. This technique is safe, clean, cheap and easy to control since it uses electron as a reagent [10]. In many cases, organic halides can be simply reduced by electrolysis at room temperature and ambient pressure. Furthermore, studies on the fast and efficient electrolysis of chlorobenzene may contribute to a new technology for the safe detoxification of PCB and dioxins with low energy consumption [11]. Although this technique is efficient and desirable among the other treatment methods, the final purification of electrochemical waste which contains chlorine ions, precipitant or complexes still is a problem. Therefore, herein we report another alternative electrochemical dechlorination of chlorobenzene by using carbon dioxide fixation method. The product of benzoic acid not only simplifies the disposal process of electrochemical waste but also offers a great number of advantages, for example, in preparing compounds bearing substituents (F, CN, CO₂ R, CO, and OR) that are not compatible with the preparation of organometallic compounds [12]. In addition, this fixation of carbon dioxide method can be done by using a very simple one-compartment cell. Electrochemical carboxylation by using a sacrificial anode has been reported to be one of the useful methods in converting organic chlorides to useful products [13–15].

2. Materials and methods

2.1. Materials

The substrates used in this experiment were chlorobenzene, 1,2-dichlorobenzene and 1,3-dichlorobenzene, whereas, the solvents were tetrahydrofuran (THF), dimethylacetamide (DMA), *N*-methyl-2-pyrrolidinone (NMP), acetonitrile (MeCN), and *N,N*-dimethyl-formamide (DMF). Supporting electrolytes used in this study were tetraethylammonium perchlorate (TEAP), tetraethylammonium bromide (TEAB), and tetrapropylammonium bromide (TPAB). They were all purchased from Fluka Chemika and used as received.

2.2. Procedure

Electrolysis was carried out in a one-compartment cell equipped with a magnetic stirrer and a serum cap. The cell was fitted with a platinum plate cathode (2 × 2 cm²), aluminium bar anode, and a tube path for CO₂. The electrolysis was carried out in a DMF solution (10 ml) containing 0.1 M of TPAB, chlorobenzene and toluene as a standard material. Chlorobenzene was used as a model substrate and five parameters were studied in order to obtain the optimum conditions of this electrocarboxylation. The parameters were temperature, current density, type of anode materials, solvents and supporting electrolytes. Progress of the reaction was analyzed by FID gas chromatograph (Agilent Technologies) with HP-5 column.

3. Results and discussion

Blank test showed that conventional stirring reaction without current being passed gave only 20% conversion of chlorobenzene and no benzoic acid was produced. Therefore, in order to enhance the conversion of chlorobenzene and yield of benzoic acid, the effect of current density on the electrocarboxylation was first studied. Electrolysis was carried out at 0 °C with magnesium anode and platinum cathode under four different values of current density, which were 30, 60, 120 and 180 mA/cm². As shown in Figure 1, after 2 F/mol of current passed, the electrolysis at 120 mA/cm² gave the highest conversion of chlorobenzene (60%) and maximum yield of benzoic acid (10%). Therefore, we considered 120 mA/cm² as the optimum current density in this electrocarboxylation.

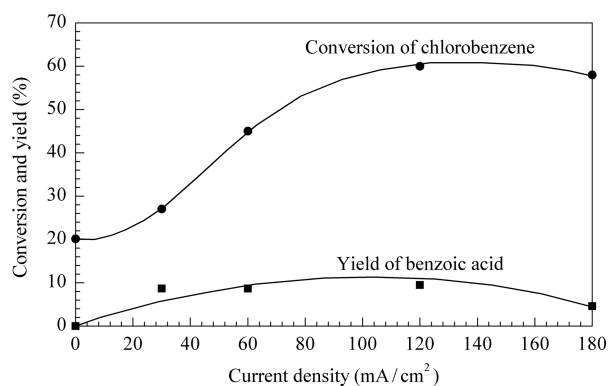


Figure 1. Effect of current density on electrocarboxylation of chlorobenzene

Conditions: (anode)Mg-Pt(cathode), 0.1 M TEAP-DMF, 2 F/mol current passed, 0 °C, chlorobenzene (2 mmol), toluene (2 mmol)

Next, the effect of the type of anode materials was studied and the results are shown in Table 1. All data were taken at 3 F/mol. A complete conversion of chlorobenzene was achieved when zinc was used as an anode; however, no benzoic acid was produced. The conversion became lower when magnesium, copper, and carbon were used, but the yield of benzoic acid was increased up to 3%–9%. It was found that aluminium was the optimum anode material in this electrocarboxylation which gave the highest yield (35%) of benzoic acid. On the other hand, zinc metal did not perform well in this non-aqueous solvent to produce benzoic acid because of the fact reported by Ito that zinc shows higher tendency in producing carbon monoxide, oxylate, and glyoxylate in the similar system [16]. The effect of the type of cathode materials was also studied by replacing the platinum cathode with carbon and stainless steel. However, both of them did not show better result than the case using a platinum cathode in this electrocarboxylation.

Table 1. Effect of type of anode material on electrocarboxylation of chlorobenzene

Type of anode material	Conversion (%)	Yield of benzoic acid (%)
Zn	100	—
Mg	61	9
Al	77	35
Cu	40	3
C	49	7

Conditions: (anode)M-Pt(cathode), 0.1 M TEAP-DMF, 0 °C, 120 mA/cm², chlorobenzene (2 mmol), toluene (2 mmol)

In order to find the optimum temperature of this electrocarboxylation, electrolyses were carried out at three different temperatures which were 0 °C, room temperature and 70 °C. As shown in Figure 2, electrolysis at 0 °C gave 77% conversion of chlorobenzene and the highest of benzoic acid (35%). However, the reaction at room temperature (24 °C) seems not to be appropriate in this system. The conversion was increased up to 93% when electrolysis was carried out at 70 °C, but this temperature was not suitable for converting chlorobenzene to benzoic acid. We can see that increasing the temperature will favor the decreasing of benzoic acid. Lower temperature may increase the solubility of carbon dioxide in dimethylformamide, which is classified as an aprotic solvent and this may enhance the stability of the reduction intermediate under such condition [11]. Therefore, aiming to a simple and mild condition of electrolysis, we

considered 0 °C as the optimum temperature in this electrocarboxylation.

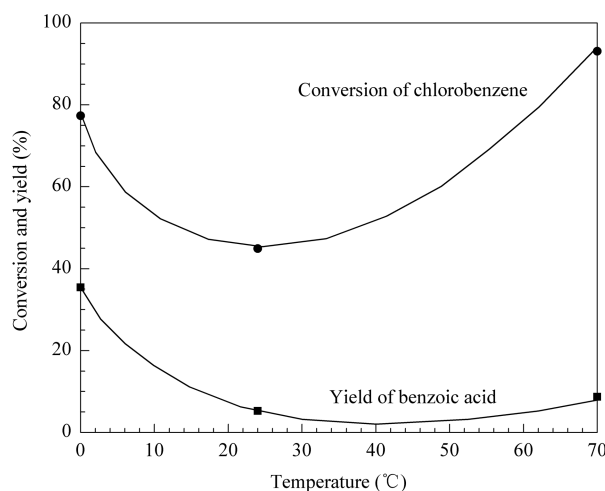


Figure 2. Effect of temperature on electrocarboxylation of chlorobenzene

Conditions: (anode)Al-Pt(cathode), 0.1 M TEAP-DMF, 3 F/mol current passed, 120 mA/cm², chlorobenzene (2 mmol), toluene (2 mmol)

The effect of the solvent was also studied in order to enhance the yield of benzoic acid. As tabulated in Table 2, the sequence of the optimum solvents is DMF > NMP > MeCN > DMA > THF. DMF gave the highest yield of carboxylic acid (18%) compared with other solvents after 2 F/mol of current was passed. Thus, DMF is considered to be the optimum solvent for this electrocarboxylation. This is probably because of its highest dielectric constant among the other solvents. DMSO also is a good solvent for many inorganic salts and organic compounds since it has the highest dielectric constant. However, it is not appropriate in this reaction since its melting point is at 18.4 °C. On the other hand, electrolysis in acetonitrile or less polar solvents would increase the voltage as a result of the precipitation on the surface of the electrode during the reaction.

Table 2. Effect of type of solvent on electrocarboxylation of chlorobenzene

Type of solvent	Conversion (%)	Yield of benzoic acid (%)
Tetrahydrofuran (THF)	—	—
Dimethylacetamide (DMA)	0	0
<i>N</i> -Methyl-2-pyrrolidone (NMP)	23	trace
Acetonitrile (MeCN)	7	trace
<i>N,N</i> -Dimethylformamide (DMF)	76	18

Conditions: (anode)Al-Pt(cathode), 0.1 M TEAP-solvent, 0 °C, 120 mA/cm², chlorobenzene (2 mmol), toluene (2 mmol)

Next, the effect of the types of supporting electrolytes is also an important parameter in this electrocarboxylation. As shown in Table 3, supporting electrolytes used in the experiments were tetraethylammonium perchlorate, tetraethylammonium bromide and tetrapropylammonium bromide. According to the results which were all taken at 2 F/mol, the sequence of the effectiveness of supporting electrolytes are TEAP > TEAB > TPAB. The increase in size of the cation will decrease the rate constant of electron transfer from electrode to substrate [17]. This is the

reason behind the lowest yield (8%) of benzoic acid by tetrapropylammonium bromide at 2 F/mol compared with the tetraalkylammonium ions of TEAP and TEAB. However, the smaller rate constant of the tetrapropylammonium ion benefits the electrolysis when the yield of benzoic acid increases through time and causes a later termination of current passed. Table 3 shows, compared with other supporting electrolyte, TPAB is the only salt which could continue conducting the current passed to 14 F/mol and eventually give the highest yield (61%) of benzoic acid.

Table 3. Effect of type of supporting electrolyte on electrocarboxylation of chlorobenzene

Type of supporting electrolyte (SE)	Conversion (%)	Yield of benzoic acid (%)
Tetraethylammonium perchlorate (TEAP)	76	18
Tetraethylammonium bromide (TEAB)	83	10
Tetrapropylammonium bromide (TPAB)	31	8
Tetrapropylammonium bromide (TPAB)*	90	61

Conditions: (anode)Al-Pt(cathode), 0.1 M SE-DMF, 0 °C, 120 mA/cm², chlorobenzene (2 mmol), toluene (2 mmol).

*Data was taken at 14 F/mol of current passed

Therefore, we considered the electrolysis at 0 °C and 120 mA/cm² in DMF solution containing tetrapropylammonium bromide with aluminium anode and platinum cathode as the optimum conditions in this electrocarboxylation. Finally, we studied the effect of the flow rate of carbon dioxide and the results are shown in Table 4.

Table 4. Effect of CO₂ flow rate on electrocarboxylation of chlorobenzene

Flow rate of CO ₂ (ml/min)	Conversion (%)	Yield of benzoic acid (%)
30	26	3
80	60	—
100	54	16
100*	78	72
150	20	—
200	62	18
190*	89	11

Conditions: (anode)Al-Pt(cathode), 0.1 M TEAP-DMF, 0 °C, 120 mA/cm², chlorobenzene (2 mmol), toluene (2 mmol).

*Electrolysis was run until 6 F/mol of current passed

After 3 F/mol of current passed, we found that the conversion of chlorobenzene did not become higher than 62% even if the flow rate was raised up to 200 ml/min. However, it was observed that the yield of benzoic acid was increased with the increasing of flow rate. By allowing the current to pass until 6 F/mol for 100 and 190 ml/min, we found that conversions were increased up to 78% and 89%, respectively. Nevertheless, for 100 ml/min of flow rate

under the same conditions, the yield of benzoic acid also increased to maximum (72%) but not for the 190 ml/min. Therefore, we considered 100 ml/min as the optimum flow rate in this system. Next this condition was applied to 1,2-dichlorobenzene in order to convert it to its corresponding benzoic acid. However, probably because of the steric hindrance the conversion of 1,2-dichlorobenzene was 70% but no corresponding benzoic acid was produced at all.

The above stated reaction was also applied to 1,3-dichlorobenzene and the results are shown in Figure 3. In this case, complete conversion of 1,3-dichlorobenzene was achieved but the peak of isophthalic acid or 3-chlorobenzoic acid could not be traced. As shown in Figure 3, the yield of benzoic acid and chlorobenzene was increased with the increasing of the conversion of 1,3-dichlorobenzene. However, the maximum yield of benzoic acid was only 20% at 6 F/mol of current passed. The yield was then decreased and finally the current was terminated after 8 F/mol of current passed because of the increasing of voltage.

The probable reaction mechanism of this electrocarboxylation of chlorobenzene is shown in Figure 4. The reaction started at anode where aluminium was oxidized to give Al³⁺ cation and donated electrons, whereas, at cathode, a two-electron reduction of chlorobenzene would give phenyl anion. A nucleophilic addition of phenyl anion to carbon dioxide occurs to give benzoic acid after protonated by the solvent [18].

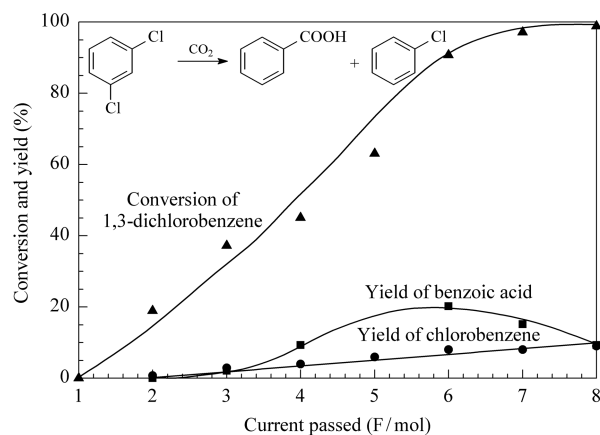


Figure 3. Electrocarylation of 1,3-dichlorobenzene

Conditions: (anode)Al-Pt(cathode), 0.1M TEAP-DMF, 3 F/mol current passed, 120 mA/cm², dichlorobenzene (2 mmol), toluene (2 mmol)

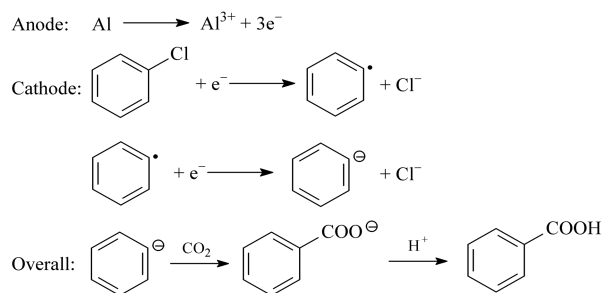


Figure 4. The proposed reaction mechanism of electrocarboxylation of chlorobenzene

4. Conclusions

In conclusion, an alternative dechlorination method of chlorobenzenes by using a simple electrolysis system *via* carbon dioxide fixation technique has been developed. Benzoic acid that was produced not only simplified the waste treatment of harmful compounds but also can be considered in converting those compounds to useful products such as carboxylic acids that have many uses especially in the field of pharmaceuticals.

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