Article

Electrocarboxylation of Dichlorobenzenes on a Silver Electrode in DMF

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Abstract: Carbon dioxide (CO_2) is the largest contributor to the greenhouse effect, and fixing and using this greenhouse gas in a facile manner is crucial. This work investigates the electrocarboxylation of dichlorobenzenes with the atmospheric pressure of CO_2 in an undivided cell with an Ag cathode and an Mg sacrificial anode. The corresponding carboxylic acids and their derivatives, which are important industrial and fine chemicals, are obtained. To deeply understand this reaction, we investigate the influence of various reaction conditions, such as supporting electrolyte, current density, electric charge, and reaction temperature, on the electrocarboxylation yield by using 1,4-dichlorobenzene as the model compound. The electrochemical behavior of dichlorobenzenes is studied through cyclic voltammetry. The relation among the distinct electronic effects of dichlorobenzenes, the electrochemical characteristics of their reduction, and the distribution law of target products is also established.

1. Introduction

The growing carbon dioxide (CO_2) content in the atmosphere is the major contributor to the greenhouse effect and global warming [1]. Measures to address the greenhouse effect can be implemented in two ways. The first one is to create a low-carbon economic development model that conserves energy and controls energy from the source. The second method is to convert CO_2 into useful organic chemicals [2–4]. Continuous emission of CO_2 is expected to occur for a long time due to human dependence on fossil fuel. Therefore, identifying effective means to convert and utilize CO_2 has become a pressing issue in this modern society; moreover, the fixation of CO_2 into useful products of industrial significance has elicited considerable attention [5–9].

Although CO_2 is the main gas that causes the greenhouse effect, CO_2 is an abundant, cheap, non-toxic, recyclable C1 building block for organic synthesis. However, CO_2 conversion is a challenge to chemists because of the high chemical and thermodynamic stability of this gas. Electrochemical techniques [10] that deal with a clean reagent, the electron, can realize CO_2 activation at normal temperature and pressure [11–13]. Therefore, electrocarboxylation is a facile method of CO_2 fixation from ecological and economic viewpoints. Many substrate types, alcohols [14], epoxides [15,16],

imines [17], organic halides [13,18–28], ketones [11,12,29–32], aldehydes [33], alkenes [34–38], and alkynes [39] have been used in previous studies.

Carboxylic acids and their derivatives are an important class of compounds, and several of them are fine chemicals of industrial interest, especially in the production of anti-inflammatory drugs. Electrocarboxylation of organic halides is a potential facile means to synthesize carboxylated products. Homogeneous [40–42] and heterogeneous [19,21,22,43,44] catalytic methods have been adopted to optimize this reaction because of the negative reduction potential of organic chlorides. A good catalytic electrode material can effectively reduce the reduction potential and improve the reaction. Hg has been the main material choice for a long time. However, Hg is discarded for environmental reasons. Meanwhile, studies have indicated that silver (Ag) exhibits extraordinary electrocatalytic activities toward the reduction of organic halides [13,18–23,43,44]. Although many studies have investigated electroreduction and electrocarboxylation of organic chlorides, most of them focused on monochloride compounds [19,21,22,40–44]. Only a few studies have examined the electroreduction of polyhalidecompounds [45–59], such as dichloromethane, trichloromethane, tetrachloromethane, and hexachlorocyclohexane.

In this study, electroreduction of dichlorobenzenes on an Ag electrode in the presence of CO_2 under mild conditions is described (Scheme 1). The aim of this investigation is to set up an alternative methodology for electrocarboxylation of dichlorobenzenes with CO_2 to the corresponding carboxylic acid, thus providing an environmentally friendly method for the electrochemical fixation of CO_2 with dichlorobenzenes possessing aromatic carboxylic acids and their derivatives, which are useful for pharmaceutical or industrial application.
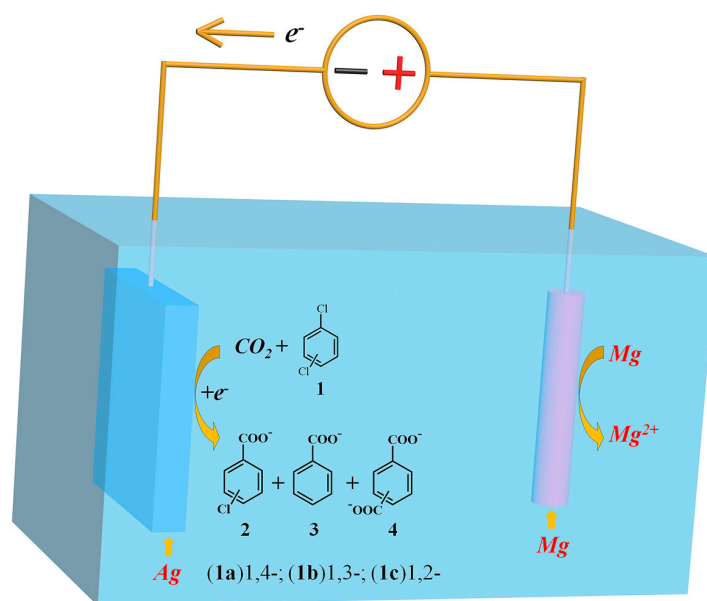
Scheme 1. Electrocarboxylation of dichlorobenzenes.

2. Results and Discussion

2.1. Electroanalytical Measurement of 1,4-Dichlorobenzene

Figure 1 presents the voltammetric characteristic of 1,4-dichlorobenzene (**1a**) in *N*,*N*-dimethylformamide (DMF) containing 0.1 M tetraethylammonium tetrafluoroborate (TEABF$_4$) on glassy carbon (GC), and Ag electrodes at a scan rate of 0.1 V/s. As shown in curve a, no redox peak on the GC electrode existed within the scan range, which revealed a favorable potential window in the region of −0.6 to −2.5 V. Two successive irreversible cathodic peaks were detected at −2.04 V and −2.30 V (curve b) after **1a** was added to the solution. The first reduction peak currents varied

linearly with $v^{1/2}$ (Figure S1, Supplementary Materials), which confirmed the diffusion control for the electroreduction process. The voltammetric characteristic of chlorobenzene on the GC electrode was also recorded for comparison. Curve c displayed an irreversible reduction peak at -2.30 V corresponding to the two-electron transfer of the C–Cl bond of chlorobenzene, similar to the second reduction peak of **1a** on the GC electrode [50]. This result implies that the first cathodic peak was caused by the two-electron reductive cleavage of one of the C–Cl bonds, and the second one was caused by the reduction of another C–Cl bond. The gas chromatography–mass spectrometry (GC–MS) analysis also confirmed the synthesis of chlorobenzene through potentiostatic electrolysis at the first reduction peak in the presence of N_2. When the voltammetric characteristic of **1a** was recorded in DMF saturated with CO_2 (0.2 M) [51], a different behavior was observed. As shown in curve d of Figure 1, the first reduction peak current increased, with its potential appreciably shifting to a more positive place, indicating that a chemical reaction may have occurred between the electroreduced intermediate and CO_2. Meanwhile, the second reduction peak disappeared. The voltammetric characteristic of **1a** was checked on the Ag electrode for comparison. As shown in curves b and e, the two reduction peaks shifted to a more positive potential because of the electrocatalytic properties of the Ag electrode. The electrocatalytic activities of electrode materials for the reduction of organic halides have been the subject of many studies [18,19,21,22,52–54]. These studies have shown that Ag exhibits powerful electrocatalytic activities toward the reduction of various organic halides. Therefore, the electroreduction of dichlorobenzenes on the Ag cathode was investigated herein.
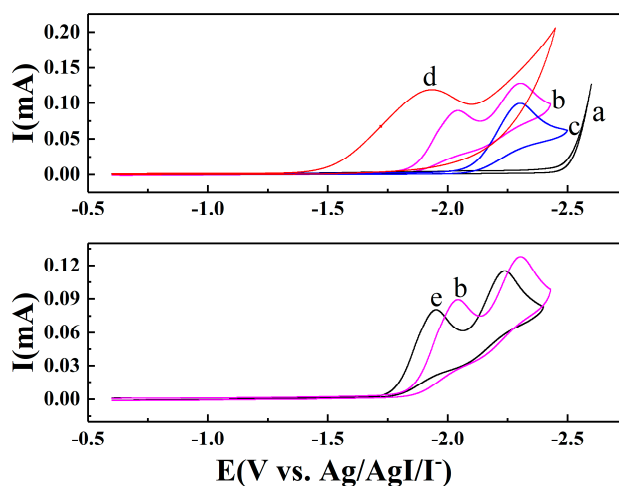

Figure 1. Cyclic voltammograms obtained with the scan rate of 0.1 V/s in DMF + 0.1 M TEABF$_4$-: (**a**) blank cyclic voltammetry on GC electrode; (**b**) as (a) +5 mM 1,4-dichlorobenzene; (**c**) as (a) +5 mM chlorobenzene; (**d**) as (**b**) in the presence of CO_2; (**e**) cyclic voltammetry of 5 mM 1,4-dichlorobenzene on Ag electrode.

2.2. Electrocarboxylation of Dichlorobenzene

Considering that electrolysis carried out under galvanostatic conditions is a much more convenient procedure than that implemented under potentiostatic conditions, the reaction conditions for the galvanostatic electrolysis of **1a** were examined and are summarized in Table 1. The yields of mono- and di-carboxylation products were affected by the choice of supporting electrolyte (SE), current density (*J*), electric charge (*Q*), and reaction temperature (*T*).

SE strongly determined the effects of the electrocarboxylation of **1a**. Tetrabutyl ammonium chloride (TBACl) was the best SE, and resulted in 36.7% total electrocarboxylation yield (Table 1, entry 5). Notably, with the same tetraalkylammonium cation, the total carboxylation yield dependences on the anion were in the following order: $Cl^{-1} > Br^{-1} > I^{-1}$ (Table 1, entries 1–3, 5–7). Although negatively charged in the Ag electrode, inorganic halide anions have been reported to remain

powerfully absorbed in the Ag electrode in the sequence of $Cl^{-1} \leq Br^{-1} \leq I^{-1}$ and are thus accorded with many well-known halide properties, such as the solubility of products with Ag ions [18,55]. In addition, with the same anion of Cl^{-1}, Br^{-1}, and I^{-1}, the synthesis carried out with the TBA^+ cation provided better yields than those of the TEA^+ cation cases (Table 1, entries 1–3, 5–7), indicating that the cations exerted some influence on the electrolysis.

Table 1. Electrocarboxylation of 1,4-dichlorobenzene under various synthetic parameters [a].

| Entry | SE | J (mA/cm^2) | Q (F/mol) | T (°C) | Carboxylation Product Yields (%) [b] | | | Total Yield (%) [b] |
					2	3	4	
1	TEACl	10	4	0	3.1	trace	1.0	4.1
2	TEABr	10	4	0	2.1	trace	1.0	3.1
3	TEAI	10	4	0	1.2	trace	1.0	2.2
4	TEABF4	10	4	0	2.3	trace	trace	2.3
5	TBACl	10	4	0	31.2	3.2	2.3	36.7
6	TBABr	10	4	0	24.3	3.4	2.4	30.1
7	TBAI	10	4	0	25.3	trace	1.0	26.3
8	TBACl	8	4	0	16.1	4.2	2.2	22.5
9	TBACl	13	4	0	35.7	4.3	2.9	42.9
10	TBACl	14	4	0	37.6	3.3	2.7	43.6
11	TBACl	15	4	0	34.4	4.9	3.3	42.6
12	TBACl	16	4	0	26.8	2.6	2.2	31.6
13	TBACl	14	2	0	14.9	2.6	1.7	19.2
14	TBACl	14	3	0	23.0	2.6	1.6	27.2
15	TBACl	14	4.2	0	37.2	4.7	3.4	45.3
16	TBACl	14	4.5	0	26.8	3.9	2.3	33.0
17	TBACl	14	5	0	24.8	3.5	2.2	30.5
18	TBACl	14	4.2	−10	41.6	1.0	1.0	43.6
19	TBACl	14	4.2	−5	40.7	1.9	1.8	44.4
20	TBACl	14	4.2	5	38.4	4.6	3.3	46.3
21	TBACl	14	4.2	10	38.6	4.1	3.1	45.8
22	TBACl	14	4.2	25	24.2	6.7	3.1	34.0

[a] General conditions: DMF = 10 mL, SE = 0.1 M, 1,4-dichlorobenzene = 0.1 M, Ag as cathode, Mg as anode, P_{CO_2} = 1 atm; [b] The yield based on starting substrate is determined by GC.

The electrocarboxylation yields were also strongly affected by J (Table 1, entries 5, 8–12). The highest total electrocarboxylation yield of 43.6% was achieved with 14 mA/cm^2 (Table 1, entry 10). The total electrocarboxylation yield decreased regardless of whether the current density was higher or lower than 14 mA/cm^2. On the one hand, the electrode potential became negative when the current density was high. Hence a series of side reactions, such as the reduction of Mg^{2+} or CO_2 to C1 or C2 compounds (carbonate, oxalate, and CO), occurred on the electrode surface and reduced the total electrocarboxylation yield [56]. On the other hand, the electrode potential became positive when current density was low. Therefore, the proportion of the Faradaic current was reduced, thus decreasing the carboxylation yield.

The influence of Q was also investigated (Table 1, entries 10, 13–17). The Faradaic efficiency did not reach 100% due to the existence of non-Faradaic current. Accordingly, an amount that is more than the theoretic charge was consumed to improve the yield in general. The best total yield of 45.3% was obtained when the passed electric charge reached 4.2 F/mol (Table 1, entry 15). Before the point of 4.2 F/mol, the total yield increased rapidly with the increase in the passed charge. Afterward, the total yield decreased to 30.5% for 5 F/mol.

T also influenced the electrolysis reaction and mainly affected the thermodynamics and kinetics of the electrocarboxylation reaction and the solubility of CO_2 in the solvent [51]. In general, a low T increases the solubility of CO_2 in DMF, and is conducive to the reaction. A low T also reduces the rate of mass transport and increases the activation energy of the reaction, both of which are dangerous to the electrocarboxylation of **1a**. To investigate the effect of T, a set of electrolysis experiments were carried out at different T values (Table 1, entries 15, 18–22). Increasing T from −10 °C to 5 °C favored

the reaction, but further increasing *T* resulted in a low total carboxylation yield of **1a**. The best total carboxylation product with 46.3% yield was achieved at 5 °C (Table 1, entry 20).

2.3. Electrocarboxylation of Other Dichlorobenzenes

To investigate the effect of the C–Cl bond position on the benzene ring, cyclic voltammograms and electrolysis were extended to 1,3-dichlorobenzene (**1b**) and 1,2-dichlorobenzene (**1c**) under the optimized reaction conditions.

As shown in Figure 2, two successive irreversible cathodic peaks corresponding to the two-electron transfer reaction of the C–Cl bond were detected for all the three dichlorobenzenes on the Ag electrode. The cathodic peak potentials of the three dichlorobenzenes were very close. Electrolysis of **1b** and **1c** was conducted under the optimized conditions. As shown in Table 2, halogenated monocarboxylation product **2** was obtained for all the three dichlorobenzenes, and the yield of **2** decreased from 43.7% to 38.4% in the following order: **2c** > **2b** > **2a**. The yield correlated with the first peak current of **1** (Figure 2): **1c** (0.103 mA) > **1b** (0.097 mA) > **1a** (0.079 mA). High yields were obtained when the first peak current of **1** was large. In addition, dehalogenated monocarboxylation product **3** was detected for all the three dichlorobenzenes. Surprisingly, dicarboxylation products **4b** and **4c** were not detected. To understand this phenomenon, the proposed pathways for the electrocarboxylation of dichlorobenzene were studied, and energy calculations were performed using the Gaussian09W program (Revision A.1, Gaussian, Inc., Wallingford, CT, USA, 2009).
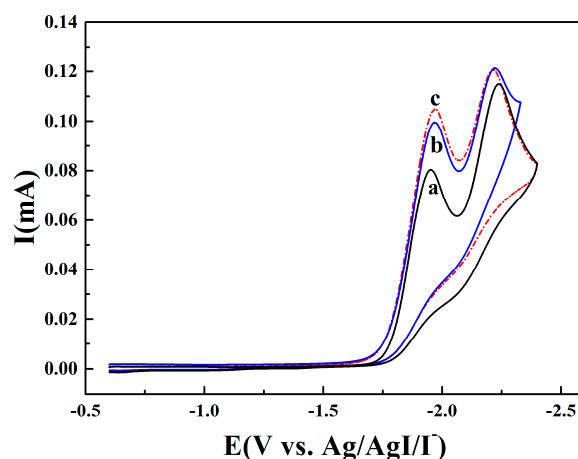

Figure 2. Cyclic voltammograms of 5 mM dichlorobenzene obtained on Ag electrode with the scan rate of 0.1 V/s in DMF + 0.1 M TEABF$_4$-: (**a**) 1,4-dichlorobenzene; (**b**) 1,3-dichlorobenzene; (**c**) 1,2-dichlorobenzene.
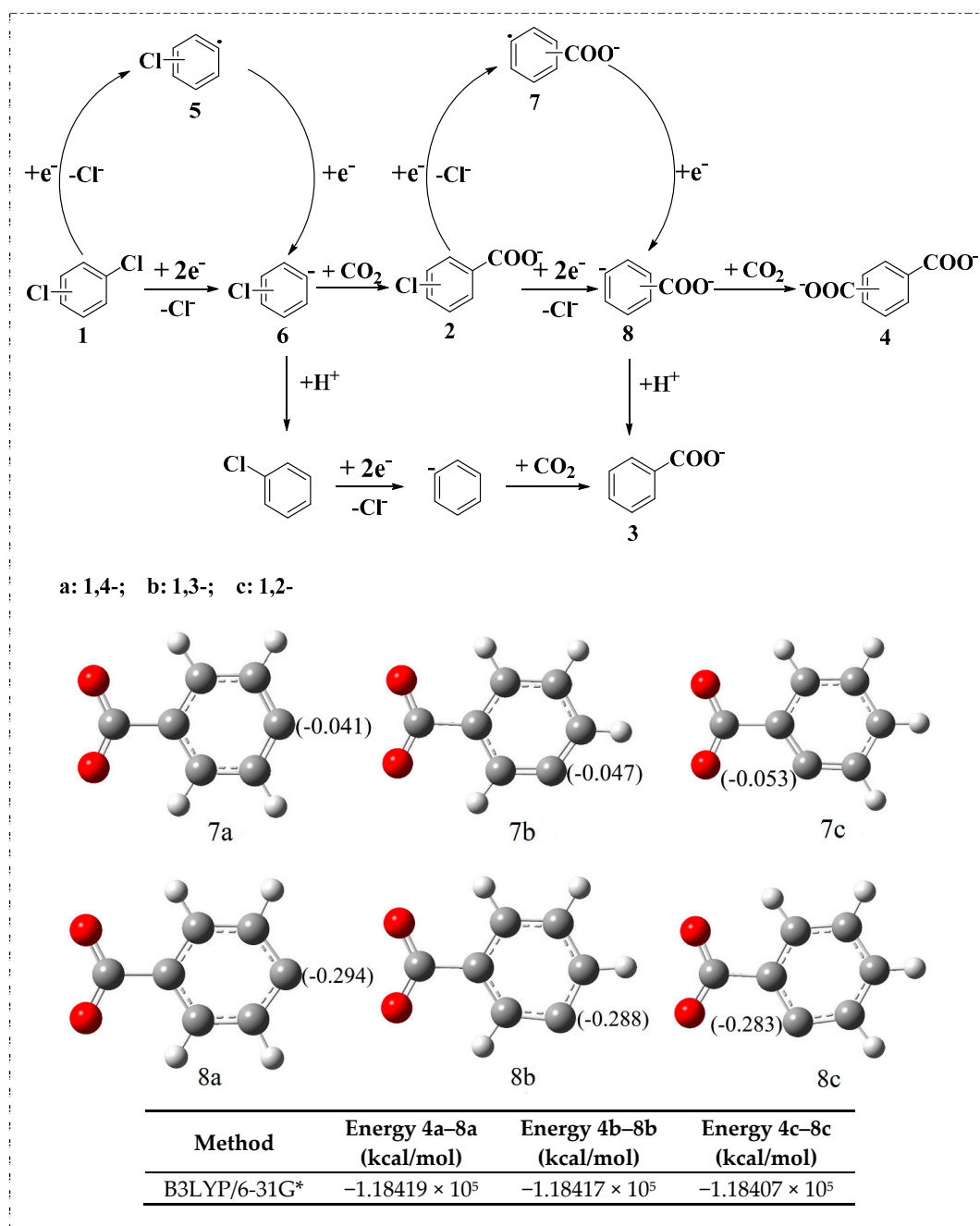
Table 2. Electrocarboxylation of dichlorobenzenes [a].

Entry	Substrate	Carboxylation Product Yields (%) [b]			Total Yield (%) [b]
		2	**3**	**4**	
1	1,4-dichlorobenzene (**1a**)	38.4	4.6	3.3	46.3
2	1,3-dichlorobenzene (**1b**)	41.4	7.8	0	49.2
3	1,2-dichlorobenzene (**1c**)	43.7	5.8	0	49.5

[a] General conditions: DMF = 10 mL, TBACl = 0.1 M, haloacetophenone = 0.1 M, Q = 4.2 F/mol, J = 14 mA/cm^2, T = 5 °C, P_{CO_2} = 1 atm, Ag as cathode, Mg as anode; [b] The yield based on starting substrate is determined by GC.

For monoaromatic halide compounds, carboxylated products were normally obtained by the reaction of CO_2 with the anions that were generated by the two-electron transfer of monoaromatic halides [20,25,57,58]. Therefore, the possible electrocarboxylation pathway of dichlorobenzene is Scheme 2. The first electron reduction of **1** results in the carbon radical **5**. After the second electron

transfer, **5** is reduced to carbon anion **6**, which reacts with CO_2 to form halogenated monocarboxylation product **2**. The phenomenon in which two successive irreversible cathodic peaks were detected for all the three dichlorobenzenes (Figure 2) is indicative of two two-electron transfer reactions for all three dichlorobenzenes. Therefore, **2** may undergo further two-electron transfer to the corresponding carbon anion **8**, which would react with another CO_2 to form decarboxylation product **4**. Given that a small amount of water is still present in the solvent, the protonation process competes with carboxylation [13,58,59]. Then, dehalogenated monocarboxylation product **3** is formed by either carboxylation following protonation or protonation following carboxylation.

a: 1,4-;　b: 1,3-;　c: 1,2-

Method	Energy 4a–8a (kcal/mol)	Energy 4b–8b (kcal/mol)	Energy 4c–8c (kcal/mol)
B3LYP/6-31G*	-1.18419×10^5	-1.18417×10^5	-1.18407×10^5

Scheme 2. Proposed pathways for electrocarboxylation of dichlorobenzenes (Insertion: Optimized structures of expected carboxylated intermediate for dichlorobenzenes, grey—C atom, red—O atom, white—H atom).

On the basis of the electrolysis result (Table 2) and the proposed electrocarboxylation pathway, dicarboxylation products **4b** and **4c** were not obtained from **1b** and **1c**, respectively. This finding indicates that several steps may have been blocked from **2b** to **4b** and from **2c** to **4c**. To determine the reason, the Gaussian09W program was used to perform gas-phase geometry optimizations and energy calculations using the density functional theory (DFT) B3LYP/6-31G* method [60]. The optimized structures with the net charges on the carbon radicals are shown in Scheme 2. The charge numbers of the carbon radical of **7a**, **7b**, and **7c** were −0.041, −0.047, and −0.053, respectively. Electrophilicity decreased in the following order: **7a** > **7b** > **7c**. **8** was difficult to obtain with weak electrophilicity. Generally, strong electron donation of the substrate goes against electrocarboxylation [29]. When **1b** or **1c** was used as a substrate, the weak electrophilicity of the carbon radical of **7b** or **7c** might have significantly prevented **7b** or **7c** from undergoing further one-electron transfer to the corresponding carbon anion **8b** or **8c**. Scheme 2 indicates that the charge numbers of the carbon anion of **8a**, **8b**, and **8c** were −0.294, −0.288, and −0.283, respectively. Nucleophilicity decreased in the following order: **8a** > **8b** > **8c**. When the electrocarboxylation was carried out using **1b** or **1c** as a substrate, the weak nucleophilicity of the carbon anion of **8b** or **8c** might have prevented **8b** or **8c** from attacking CO_2 in a nucleophilic manner even when a small amount of **8b** or **8c** was generated [18]. Furthermore, based on the energy calculations, the energy differences of **4b**–**8b** and **4c**–**8c** were surprisingly higher than that of **4a**–**8a** (Scheme 2). Accordingly, the gas-phase geometry optimizations and energy calculations corroborated the phenomenon that the corresponding dicarboxylation products, **4b** and **4c**, were not obtained.

Our investigation of the electrocarboxylation of dichlorobenzenes on an Ag electrode showed that the initial stage was the formation of carbon anions that could attack CO_2 in a nucleophilic manner to form halogenated monocarboxylation product **2** or dehalogenated monocarboxylation **3**. Afterward, **2** was further reduced by another two-electron transfer followed by a reaction with CO_2 to form dicarboxylation product **4**, or by protonation to **3**. The electronic effect of different C–Cl bond positions on the benzene ring played a decisive role in reaction efficiency and product distribution. When **1a** was used as a substrate, three carboxylation products were obtained. By contrast, no dicarboxylation product was available for **1b** or **1c** when the electrophilicity of the corresponding carbon radical, and the nucleophilicity of the corresponding carbon anion, were weak.

3. Materials and Methods

3.1. Materials and Product Measurement

All dichlorobenzenes were commercially available from J&K Chemical Co. (Beijing, China). DMF was kept over 4 Å molecular sieves. All other reagents were used as received. The cyclic voltammograms were measured with a CHI 760E electrochemical station (Shanghai Chenhua Instruments Co., Shanghai, China) at 25 °C in an undivided glass cell equipped with a gas inlet and outlet. Galvanostatic electrolysis was performed with a DC-regulated power supply HY5003M (Hangzhou Huayi Electronics Industry Co., Ltd., Hangzhou, China) in an undivided glass cell. The product yields were determined through GC-2014C gas chromatography (GC) (SHIMADZU, Tokyo, Japan).

3.2. General Electroanalytical Procedure

The electroanalytical experiments were performed in a DMF solution containing 0.1 M $TEABF_4$ as the SE. The working electrodes used for the electroanalytical experiments were GC with a diameter of 2 mm and Ag (*d* = 2 mm). The auxiliary and reference electrodes were a platinum (Pt) spiral and Ag/AgI/0.1 M TBAI in DMF, respectively. All experiments were performed at atmospheric pressure.

3.3. General Electrolysis Procedure

Galvanostatic electrolysis was conducted in a mixture of dichlorobenzenes (0.1 M) and SE (0.1 M) in 10 mL DMF solvent saturated with CO_2 in an undivided electrochemical cell equipped with an Ag cathode (8 cm^2) and a sacrificial Mg anode. At the end of each set of experiments, the reaction mixture was esterified in DMF by adding anhydrous K_2CO_3 (2 mmol) and MeI (9 mmol) at 55 °C for 5 h. Then, the solution was hydrolyzed and extracted with diethyl ether, and the combined organic layers were dried over anhydrous $MgSO_4$, filtered, and evaporated. The yields of methyl esters corresponding to acids were determined via GC with decane as the internal standard.

4. Conclusions

We demonstrated a simple and efficient electrochemical means to achieve the electroreduction of dichlorobenzenes in the presence of CO_2 on an Ag electrode. The impact of SE, *J*, *Q*, and *T* on the total electrocarboxylation yield was studied with 1,4-dichlorobenzene as the model compound. The electronic effect of different C–Cl bond positions on the benzene ring played a decisive role in reaction efficiency and product distribution. This work provides an environmentally friendly method for the electrochemical fixation of CO_2 with dichlorobenzenes possessing aromatic carboxylic acids and their derivatives, which are useful for pharmaceutical or industrial use. Thus, the applications of electrochemical methodology are expanded.

Author Contributions: Pei-Pei Luo, Ying-Tian Zhang and Bao-Li Chen conceived of and designed the experiments. Pei-Pei Luo, Ying-Tian Zhang, Bao-Li Chen, Shu-Xian Yu, Hua-Wei Zhou, Kong-Gang Qu, Yu-Xia Kong, Xian-Qiang Huang and Xian-Xi Zhang performed the experiments. Pei-Pei Luo and Bao-Li Chen analyzed the data. Pei-Pei Luo, Bao-Li Chen, Xian-Xi Zhang and Jia-Xing Lu wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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