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Selective electrocarboxylation of bromostyrene at silver cathode in DMF

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ABSTRACT

The electroreduction behavior of bromostyrenes **1** in DMF has been detected by cyclic voltammetry (CV) on GC and Ag electrodes. Under the atmospheric pressure of CO_2, selective electrocarboxylation of **1** was carried out in an undivided cell at Ag cathode under potentiostatic conditions, with the corresponding vinyl-benzoic acid methyl ester **3** as the principal product, accompanied by styrene **2**. Moderate to good electrocarboxylation yields were obtained by preparative electrolysis. Synthetic parameters such as supporting electrolyte, applied potential, electric charge, and temperature, were found to influence the carboxylation efficiencies. Both CV and electrolysis confirm that the positions of C–Br and C=C groups strongly affect the electrocarboxylation. Higher yields were obtained by changing from *ortho* to *meta* to *para* isomers.

1. Introduction

Although several different types of gases contribute to the greenhouse effect (caused by the accumulation of these gases in the upper atmosphere), CO_2 is the largest contributor to the effect.[1] And the sharply increasing atmospheric CO_2 concentration resulting from consumption of fossil fuel is becoming an important environmental issue today.[2] Meanwhile, CO_2 is recognized to be a naturally abundant, cheap, recyclable and non-toxic carbon source that can sometimes replace toxic chemicals such as phosgene, isocyanates or carbon monoxide.[3] However, its high chemical stability has made its conversion and utilization ecologically and economically challenging for chemists. Therefore, much attention has been paid to utilize CO_2 under mild conditions. There are various ways to make use of CO_2, among which electrocarboxylation is one of the most practical routes. Many substrates, such as ketones,[4–8] alkenes,[9–12] organic halides,[13–22] imines,[23–25] amines,[26,27] and so on, could be electrochemical carboxylated into their corresponding organic carboxylic acids in the presence of CO_2.

So far, most studies about electrocarboxylation focused on the substrates with only one reducible functional group, while a few papers concerned with substrates bearing two reducible groups.[28–31] It could be anticipated that the two reducible groups will compete with each other during the electrolysis, complicating the reaction pathway. Consequently, selectivity is a very important issue. In our previous study,[31] electrocarboxylation of haloacetophenones has been carried out. Thanks to the extraordinary electrocatalytic activities of Ag towards the reduction of organic halides,[17,20,21] the enhanced reactivity of C–X bond compared with that of the C=O bond has been achieved. Even so, because the bulk electrolysis was carried out under galvanostatic conditions, three kinds of products were obtained, and the yields were a little low.

As extension of our studies, we have now investigated the selective electrocatalytic carboxylation of three bromostyrenes, such as 2-bromostyrene (**1a**), 3-bromostyrene (**1b**) and 4-bromostyrene (**1c**). Cyclic voltammograms have been used to study the electroreduction behaviors, and the bulk electrolysis have been performed under potentiostatic conditions. The influence of various synthetic parameters, such as supporting electrolyte (SE), electric charge (Q), and temperature (T), have also been investigated in detail.

2. Experimental

2.1. General

^1H NMR spectras were recorded on a Bruker 400 MHz spectrometer, with Me_4Si as an internal standard. Mass spectra were obtained on a 5973N spectrometer connected with an HP 6890 gas chromatograph. Cyclic voltammograms were measured with CHI600c electrochemical station (Shanghai Chenhua Instruments

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Company) in an undivided glass cell, with an Ag or GC (d=2 mm) as the working electrode, a platinum spiral (Pt) as the counter electrode and an Ag/AgI/n-Bu_4NI (0.1 mol L^{-1}) in DMF as the reference electrode. *N,N*-Dimethylformamide (DMF) was kept over 4 Å molecular sieves. Other reagents were used as received.

2.2. Electrocarboxylation of bromostyrenes (typical procedure)

The potentiostatic electrolysis was carried out in 10 mL of dry DMF solution containing 0.1 mol L^{-1} bromostyrene and 0.1 mol L^{-1} TBABr as a supporting electrolyte in an undivided glass cell, which was equipped with an Ag cylinder (8 cm^2) as cathode, a Mg rod as anode and an Ag/AgI/n-Bu_4NI (0.1 mol L^{-1}) in DMF as the reference electrode. Prior to every experiment, the solution was bubbled with CO_2 for 30 min to be saturated. Continuous CO_2 flow was maintained throughout the duration of the whole electrolysis process.

After the electrolysis, the reaction mixture was esterified by adding anhydrous K_2CO_3 (2 mmol) and MeI (5 mmol) and stirring the mixture at 55 °C for 5 h. The solution was treated with aq HCl and extracted four times with ethyl acetate, and the organic layers were washed with H_2O, dried over $MgSO_4$, and evaporated. The conversion of the substrate and the yields of products were determined by GC using n-decane as the internal standard.

*2.2.1. 2-Vinyl-benzoic acid methyl ester **3a**.* GC–MS (m/z, %):162 (M^+, 100), 147 (33), 131 (85), 103 (72), 77 (45), 51 (18); ^1H NMR (400 MHz, DMSO): δ 3.83 (s, 3H), 5.36 (d, J=10.8 Hz, 1H), 5.77 (d, J=17.6 Hz, 1H), 7.32 (dd, J=17.2 Hz, J=10.8 Hz, 1H), 7.40 (t, J=7.6 Hz, 1H), 7.57 (t, J=7.6 Hz, 1H), 7.70 (d, J=8 Hz, 1H), 7.78 (dd, J=7.6 Hz, J=0.8 Hz, 1H).

*2.2.2. 3-Vinyl-benzoic acid methyl ester **3b**.* GC–MS (m/z, %):162 (M^+, 71), 131 (100), 103 (36), 77 (14), 51 (5); ^1H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H), 5.32 (d, J=11.2 Hz, 1H), 5.85–5.80 (m, 1H), 6.75 (dd, J=17.6 Hz, J=10.8 Hz, 1H), 7.41–7.39 (m, 1H), 7.59 (d, J=7.6 Hz, 1H), 8.08–7.91 (m, 1H), 8.08 (s, 1H).

*2.2.3. 4-Vinyl-benzoic acid methyl ester **3c**.* GC–MS (m/z, %):162 (M^+, 44), 131 (100), 103 (29), 77 (20), 51 (7); ^1H NMR (400 MHz, $CDCl_3$): δ 3.91 (s, 3H), 5.38 (d, J=10.8 Hz, 1H), 5.87 (dd, J=17.6 Hz, J=0.4 Hz, 1H), 6.75 (dd, J=17.6 Hz, J=10.8 Hz, 1H), 7.47–7.45 (m, 2H), 8.01–7.98 (m, 2H).

3. Results and discussion

3.1. Cyclic voltammetry of 4-bromostyrene

Bromostyrene contain two different reducible groups, namely C–Br and C=C on phenyl ring. Competition between these groups may complicate the electrocarboxylation pathway. 4-Bromostyrene (**1c**) was chosen as the model substrate for the investigation of bromostyrene electrocarboxylation. To begin with, we focused on its electroreduction behavior. Cyclic voltammograms recorded for reduction of **1c** at GC and Ag electrodes in DMF containing 0.1 mol L^{-1} $TEABF_4$ are depicted in Fig. 1. As shown in curves a and b, at both electrodes, reduction of **1c** gives rise to two irreversible peaks in the region of −1.0 to −2.5 V at the scan rate of 0.1 V s^{-1}. Moreover, these two reduction peak currents vary linearly with $\nu^{1/2}$, which confirms diffusion control for the electroreduction processes. In the case of GC electrode, the first reduction peak of **1c** was detected at −1.80 V, and the second one was at −2.21 V. For Ag electrode, the first reduction peak shifted to more positive potential at −1.40 V, while the second one remains constant. In the previous studies, metallic silver was recognized as a powerful catalytic material for the electroreduction of C-X bond,[32–34] while the electroreduction of C=C bond was scarcely catalyzed. For comparison, cyclic voltammograms of styrene at both GC and Ag electrodes were also recorded (Fig. 1 curves c and d), which display an irreversible reduction peak at −2.25 V and −2.23 V, respectively, similar as the second reduction peak of **1c** on both electrodes. It implies that the first reduction peak is attributed to the two-electron reductive cleavage of the C–Br bond, and the second one is ascribed to the reduction of the C=C bond. GC–MS analysis confirmed the synthesis of styrene through potentiostatic electrolysis at the first reduction peak in the presence of N_2. The above information reveals that Ag electrode shows better catalytic effect for the reduction of C–Br bond than GC electrode, therefore, for the reduction of C–Br bond convenience, Ag electrode is chosen as the proper material in our follow-up study.

Then, the electrochemical behavior of **1c** in the presence of CO_2 was investigated. Compared curve e with curve b (Fig. 1), the first reduction peak shifts to a slightly more positive potential with increasing peak current, indicating there may be a chemical reaction between the electroreduced intermediate and CO_2. Meanwhile, a new big irreversible reduction peak corresponding to the reduction of CO_2 (Fig. 1 curve f) appears at −2.0 V.

3.2. Electrocarboxylation of 4-bromostyrene under potentiostatic electrolysis

The more positive reduction potential of C–Br bond than that of C=C bond, especially at Ag electrode, suggests the possibility of selective electrocarboxylation of C–Br rather than C=C for **1c**. Potentiostatic electrolysis was carried out in CO_2 saturated DMF solution containing 0.1 mol L^{-1} **1c** in an undivided cell with Ag

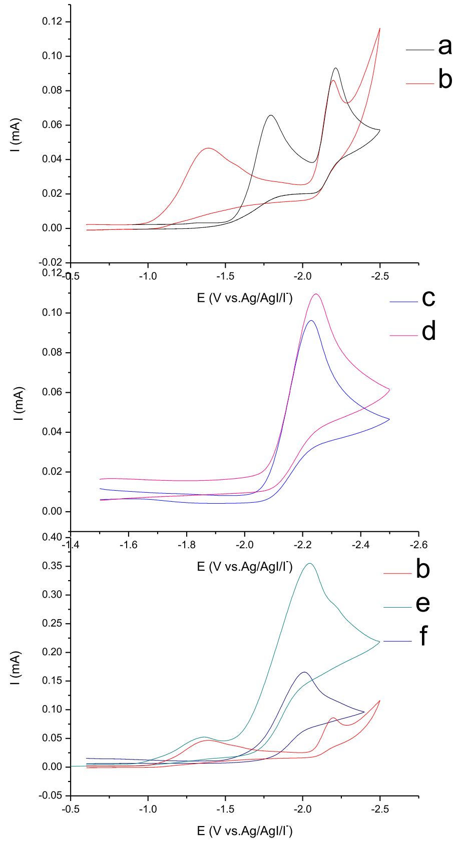

Fig. 1. Cyclic voltammograms recorded at Ag (b, d, e, f) or GC (a, c) electrode in DMF-$TEABF_4$, containing 5 mmol L^{-1} 4-bromostyrene (a, b, e) and styrene (c, d) in the presence of N_2 (a, b, c, d) and CO_2 (e, f). ν=0.1 V s^{-1}, T=25 °C.

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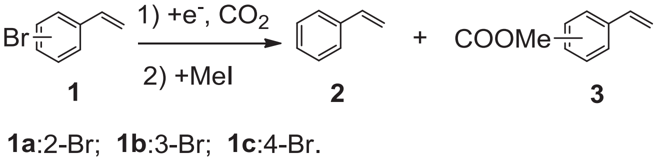
cathode and Mg sacrificial anode. As expected, 4-vinyl-benzoic acid methyl ester **3c** was obtained as the principal product, accompanied by styrene **2** (Scheme 1), at the applied potential (E_{app}) of −1.8 V, which is slightly more negative than peak potential of C–Br reduction. To deeply understand the selective electrocarboxylation of **1c**, the influence of various synthetic parameters, such as supporting electrolyte (SE), E_{app}, electric charge (Q), and temperature (T), was investigated. The results of the electrolysis were summarized in Table 1.



Scheme 1. Electrocarboxylation of bromostyrenes under CO_2 atmosphere.

3.2.1. Influence of supporting electrolyte. For the same tetraethylammonium cation (TEA^+), the yields of **3c** were very close to each other, under 40% (Table 1, entries 1–3), while **1c** conversion and yields of **2** were also analogous, respectively. In the case of tetrabutylammonium cation (TBA^+), higher yields of **3c** were obtained, both with 49% (Table 1, entries 4–5), while **1c** conversion and yields of **2** changed little. In both cases, the differences in yield of **3c** were minor when different anions were used in the electrolyte. TBA^+ gave better yields than TEA^+, indicating that cations had great influence on the synthesis (Table 1, entries 1–5) to some extent. Although magnesium ions could stabilize the electrogenerated carboxylate anion,[17,31] the initial concentration of magnesium ions was too low to make it. Since they were generated gradually by electrolytic dissolution of the Mg anode. When tetraalkylammonium (TRA^+) salt was used as supporting electrolyte, carboxylate anion could be stabilized by forming an ion pair $\{TRA^+–RCO_2^{-1}\}$, which was helpful to the electrosynthesis.[17] In the presence of TBA^+ and TEA^+, significant amounts of tributylamine and triethylamine were detected by GC–MS during the electrolysis, suggesting that these salts underwent electrochemical reduction. Moreover, predecessors found that TEA^+ was much easier to be reduced than TBA^+.[35,36] That is, TEA^+ salt surely expanded much more electric charge than TBA^+ salt in the selective electrocarboxylation of **1c**, lowering the carboxylation yield to a greater extent. On the other hands, higher **3c** yield could be obtained when TBAI was added into the electrolyte with TEAI as supporting electrolyte after electrolysis, indicating that TBA^+ have better performance to promote the esterification. Therefore, TBABr is the most suitable supporting electrolyte for the target electrocarboxylation.

Table 1
Electrocarboxylation of 4-bromostyrene under various conditions[a]

Entry	SE	E_{app} (V vs Ag/AgI/I^-)	Q (F)	T (°C)	Conversion[b] (%)	Product yields (%)[b]	
						2	3c
1	TEAI	−1.8	2.0	25	97	18	33
2	TEABr	−1.8	2.0	25	98	15	39
3	$TEABF_4$	−1.8	2.0	25	96	18	33
4	TBAI	−1.8	2.0	25	99	20	49
5	TBABr	−1.8	2.0	25	100	17	49
6	TBABr	−1.5	2.0	25	94	24	35
7	TBABr	−1.6	2.0	25	98	20	37
8	TBABr	−1.7	2.0	25	98	22	38
9	TBABr	−1.9	2.0	25	97	18	50
10	TBABr	−2.0	2.0	25	97	15	38
11	TBABr	−1.8	1.2	25	70	15	27
12	TBABr	−1.8	1.4	25	79	19	36
13	TBABr	−1.8	1.6	25	86	18	39
14	TBABr	−1.8	1.8	25	88	11	44
15	TBABr	−1.8	2.2	25	100	16	50
16	TBABr	−1.8	2.4	25	100	18	50
17	TBABr	−1.8	2.6	25	100	14	51
18	TBABr	−1.8	2.0	10	91	19	47
19	TBABr	−1.8	2.0	0	98	4	59
20	TBABr	−1.8	2.0	−5	97	6	73
21	TBABr	−1.8	2.0	−10	95	14	66

[a] General conditions: DMF=10 mL, SE=0.1 mol L^{-1}, 4-bromostyrene=0.1 mol L^{-1}, P_{CO_2}=1 atm, Ag as cathode, Mg as anode, Ag/AgI/I^- as reference electrode.

[b] Conversion of the substrate and yields of two products were determined by GC, based on the starting material.

3.2.2. Influence of applied potential. The applied potential is the key factor for the selective electrocarboxylation. To avoid competitive electrocarboxylation of C═C bond on phenyl ring, a series of electrolysis were carried out under potentials more positive than −2.2 V, under which C═C bond could be electroreduced (Fig. 1). As shown in Table 1 (entries 5–10), the conversion is insensitive to E_{app}. By shifting E_{app} from −1.5 V to −2.0 V, the yield of **3c** first increased and then decreased, while the yield of **2** decreased gradually. That may be ascribed to that a negative potential is in favor of the reduction of the C–Br bond to some extent. A reduction process carried out at more negative potential would normally provide higher reaction rate due to the larger overpotential. However, some side reactions, such as electroreduction of CO_2 and the supporting electrolyte TBABr, may take place, if the applied potential is too negative. Actually, tributylamine was detected in the final products by GC–MS. In that case, we may see that too negative potential would go against the reduction of the C–Br bond. In the cases of electrolysis under −1.8 V and −1.9 V (Table 1 entries 5 and 9), the yields of **3c** are almost the same. With a view to energy saving, the optimal applied potential is −1.8 V, providing **3c** in yield of 49%.

3.2.3. Influence of electric charge. The electrocarboxylation of **1c** was also examined under various electric charges (Table 1, entries 5, 11–17). Below 2.0 F mol^{-1}, the conversion of **1c** and the yield of **3c** increased rapidly with increasing charge. When electric charge passed 2.0 F mol^{-1}, the conversion of **1c** reached 100%, indicating that **1c** was completely participated. The yield of **3c** and **2** remained constant, while much more tributylamine was detected in the electrolyte, which suggesting the excess charge consumed in the electrolysis was used for electroreduction of supporting electrolyte rather than **2** and **3c**.

3.2.4. Influence of temperature. It is well known that CO_2 solubility in DMF depends on temperature, which is larger at lower temperatures,[37] indicating that low temperature favors the carboxylation reaction to some extent. However, as temperature decreases, mass transport decelerates in solution while activation energy increases during electrolysis. To check the effect of temperature, a set of electrolysis was performed at different temperatures (Table 1, entries 5, 18–21). The results indicated that the optimal temperature was −5 °C. So far, under the optimized condition, the highest yield of **3c** was 73% (Table 1, entries 20).

3.3. Electrocarboxylation of other bromostyrenes

To investigate the influence of the C═C position on phenyl ring, cyclic voltammograms of bromobenzene (**4**), 2-bromostyrene (**1a**) and 3-bromostyrene (**1b**) at Ag electrode were carried out (Fig. 2).

As shown in Fig. 2, one irreversible reduction peak for **4**, corresponded to two-electron reductive cleavage of C–Br bond is detected at −1.61 V. The same as **1c**, two irreversible reduction peaks, ascribed to electroreduction of C–Br and C═C, respectively, are obtained for **1a** and **1b**. Due to the conjugative effect of C═C

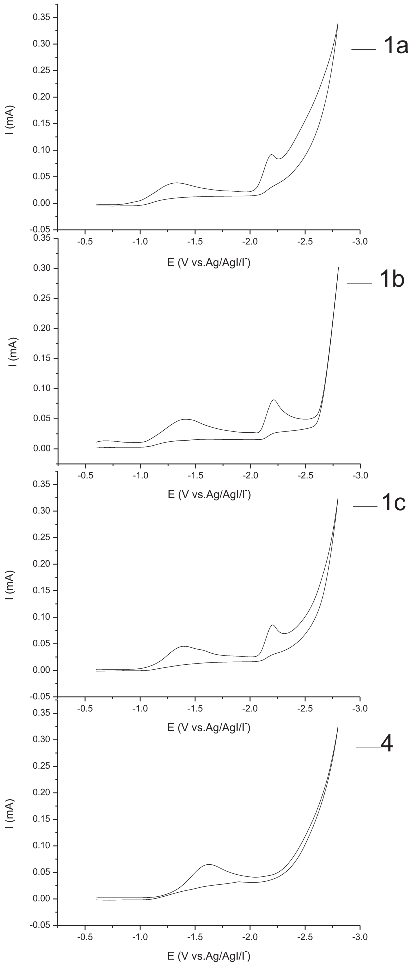


Fig. 2. Cyclic voltammograms of 5 mmol L^{-1} aromatic bromides in DMF-TEABF$_4$ recorded at Ag electrode in the presence of N$_2$, ν=0.1 V s^{-1}, T=25 °C.

group on phenyl ring, the reduction peak potentials of C–Br for **1a**, **1b** and **1c** are around −1.3 to −1.4 V, which are much more positive than that of unsubstituted bromobenzene **4**, indicating much easier reducibility of C–Br bond for **4**. Furthermore, the C–Br bond reduction peak potentials of the three tested bromostyrenes decreased in the following order: **1a** (−1.31 V)>**1b** (−1.39 V)>**1c** (−1.40 V).

Then a series of potentiostatic electrolysis of **1a** and **1b** were both carried out by varying the applied potential. The electrolysis data of **1a** and **1b**, accompanied with electrocarboxylation of **1c**, were displayed in Fig. 3. By shifting the potential to more negative value, the yields of **3** first increased, and then decreased. The optimized applied potential for **1a** and **1b** are −2.0 V and −1.8 V, respectively. Furthermore, the target carboxylation yields decreased in the following order: **3a**>**3b**>**3c**.

The possible reason would be spatial repellent effect of the benzene ring. Take 2-bromostyrene (**1a**) as an example, due to the short distance between C=C bond and C–Br bond, we guess the electron cloud of C=C bond would exclude that of C–Br bond, meanwhile hydrogen atoms of C=C bond would stretch outward and exclude C–Br bond, the above two reasons may reveal why C–Br bond gets weaker. We speculate that the shorter distance between C=C bond and C–Br bond, the weaker C–Br bond would become. Here we get novel information that C–Br bond strength gets weaker in the following order: **1c**>**1b**>**1a**, which is in the same sequence as the reduction peak potential of bromostyrenes.

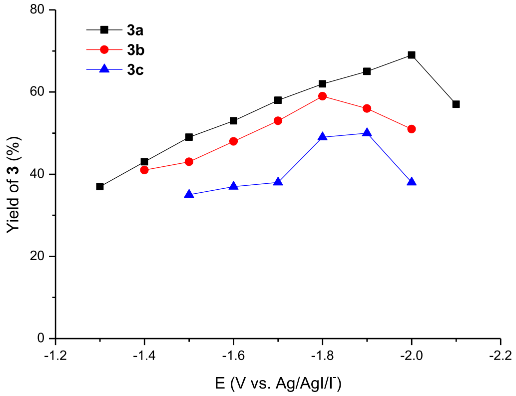


Fig. 3. Comparison of the yield of **3a**, **3b** and **3c**.

As a result, the target carboxylation yield of **3a** was the highest under the same conditions (Fig. 3).

4. Conclusions

In conclusion, we report a possible way to achieve the selective electrocarboxylation of bromostyrenes on Ag electrode. Cyclic voltammograms of bromostyrenes explained the competitive electrochemical reducibility between C–Br bond and C=C bond on phenyl ring. Since C–Br bond is much easier to be reduced than C=C bond, target electrocarboxylation product could be obtained by means of potentiostatic electrolysis. The performances of the process were found to be dependent on synthetic conditions. Both CV and electrolysis confirm that 2-bromostyrene was easier to reduce than 3-bromostyrene, which in turn than 4-bromostyrene.

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