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Electrocatalytic carboxylation of aliphatic halides at silver cathode in acetonitrile

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ABSTRACT

A simple and efficient electrocarboxylation reaction of aliphatic halides has been developed using silver as cathode, magnesium as anode and CH_3CN saturated CO_2 as solvent in an undivided cell. The influence of some key factors (such as the nature of electrode materials, supporting electrolytes and temperature) on this reaction was investigated. Under the optimized condition, the corresponding carboxylic acids were obtained in moderate to good yields (22–89%). The electrochemical behaviour was studied at different electrodes (Ag, Cu, Ni and Ti) by cyclic voltammetry, which showed significant electrocatalytic effect of the silver electrode towards the reductive carboxylation of aliphatic halides.

1. Introduction

The global warming due to the increased atmospheric CO_2 concentration resulting from increasing consumption of fossil fuel is becoming an important environmental issue today.[1] On the other hand, 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.[2] Under these circumstances, conversion of carbon dioxide to industrially useful compounds has been a challenge for synthetic chemists and has recently attracted much interest in view of the so-called 'sustainable society'[3] and ' green chemistry'[4] concepts.

Aliphatic halides represent one of the most challenging categories of organic pollutants (applied as pesticides), not only for their highly toxic, even carcinogenic characters, but also for their volatility. It is of great practical importance that aliphatic halides combine with CO_2 to prepare carboxylated products that are fine chemicals of industrial interest. The electrocarboxylation of aliphatic halides has been studied in the past decades, however, the existing methods are not very efficient. A drawback to use aliphatic halides as starting material is that their reduction at the most commonly used cathodes occurs at very negative potentials, where concomitant reduction of CO_2 may take place, resulting in undesired products and a decrease of current efficiency.[5] Homogeneous catalytic route involving reduction of aliphatic halides in solution far from the electrode has been proposed to avoid the use of negative potentials required by the direct electroreduction process.[6] In spite of the good yields achieved with several metal complexes, the use of expensive catalytic materials makes the reaction system and the separation impractical.

Very recently, a series of studies dealing with the reduction of organic halides at Ag electrode have been reported.[7] The most important result emerging from such studies is that silver exhibits extraordinary electrocatalytic activities towards the reduction of organic halides. The possibility of exploiting the electrocatalytic nature of silver for the electrocarboxylation of aliphatic halides has not been established yet. In this work, we investigated in a detailed way the influence of operative parameters on the electrocarboxylation of aliphatic halides in CO_2–saturated CH_3CN solution at Ag cathode, aiming to optimize the process and to define an applicable methodology. The voltammetry and kinetics of aliphatic halides have been examined in the absence and presence of CO_2 in CH_3CN.

2. Results and discussion

2.1. Cyclic voltammetric behaviour of aliphatic halides

Cyclic voltammograms recorded for reduction of 3-chloro-2-methylpropene (**1a**) at Ag electrode in CH_3CN containing 0.1 M tetraethylammonium chloride (Et_4NCl) are depicted in Figure 1. As shown in curve A of Figure 1, reduction of **1a** gives rise to a single irreversible peak (E_p) under an nitrogen atmosphere at −1.56 V that

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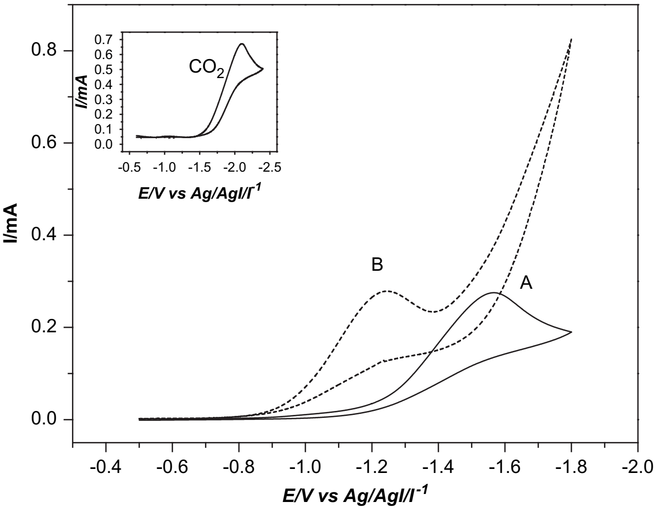


Figure 1. Cyclic voltammograms of 20 mM 3-chloro-2-methylpropene (**1a**) recorded at Ag electrode in CH_3CN–0.1 M Et_4NCl in the (A) absence and (B) presence of CO_2, $v=100$ mV s^{-1}, $T=25$ °C. Inset: cyclic voltammogram of CO_2 in CH_3CN–0.1 M Et_4NCl at Ag electrode.

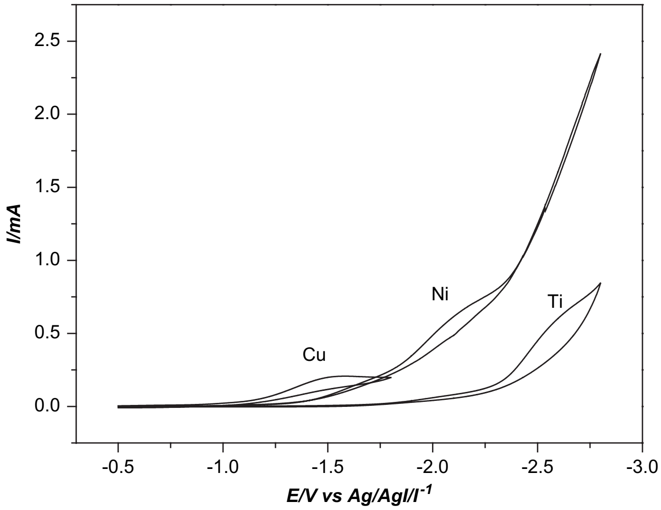


Figure 2. Cyclic voltammograms of 20 mM 3-chloro-2-methylpropene (**1a**) in CH_3CN–0.1 M Et_4NCl recorded at Cu, Ni and Ti electrodes, $v=100$ mV s^{-1}, $T=25$ °C.

corresponds to two-electron reductive cleavage of the carbon–halogen bond. The voltammetry behaviour of **1a** was very similar in appearance to those pictured in an earlier report[8] pertaining to the cathodic behaviour of alkyl halides at glass carbon electrodes. A study of peak current (i_p) for the main reduction process over the concentration range 2–10 mM revealed a linear relationship between i_p and concentration, showing that **1a** reduction proceeds rather cleanly at Ag electrode (that is, without serious filming effects). Variation of scan rate (v) from 20 to 100 mV s^{-1} produced a linear i_p versus $v^{1/2}$ plot, indicating diffusion-controlled behaviour. The inset chart is the reduction of CO_2 at Ag electrode. At −2.13 V is a irreversible peak that can be attributed to the one-electron of CO_2. It is noteworthy that E_p of **1a** is about 0.6 V more positive than that of CO_2 and becomes even more positive when the solution is saturated with CO_2 (Fig. 1B). This provides a potential window for electrocarboxylation of **1a** to be performed without any interference from reduction of CO_2. The E_p of **1a** is positively shifted from −1.56 to −1.24 V in the presence of CO_2 shows a rapid chemical reaction between CO_2 and electrogenerated radical anion.

In order to examine the electrocatalytic effect of Ag electrode towards the reduction of **1a**, the voltammetry behaviours of **1a** were also investigated at the most commonly used cathodes, e.g., Cu, Ni and Ti (Fig. 2). The reduction peak of **1a** at Cu electrode appeared at ca. −1.5 V, which is similar to that required for its reduction at Ag electrode (−1.56 V), but compared with Ag electrode, an obvious thin film was formed at Cu electrode after three voltammetry cycles, which is attributed to the absorption of electrogenerated intermediate species at Cu electrode, and will result in progressive degradation of Cu cathode during the electrocarboxylation of aliphatic halides. In addition, in our previously study,[9] we reported that Cu was also a good material for the reduction of CO_2. These two points mentioned above are unfavourable to electrocarboxylation of **1a**. A broad reduction peak ($E \geq -2$ V) appeared at Ni or Ti electrode, which is considerably more negative than the E_p value obtained at Ag, and very close to the reduction peak of CO_2.

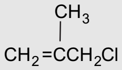
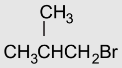
Voltammograms similar to those shown in Figure 1 were obtained for other aliphatic halides. The data are shown in Table 1.

2.2. Experimental investigations in preparative scale electrolysis

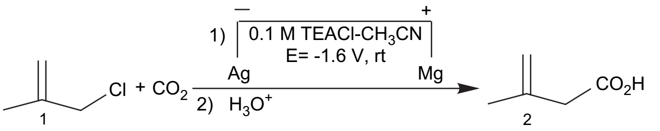
3-Chloro-2-methylpropene (**1a**) was first chosen as a model molecule to be investigated, and the obtained optimal reaction conditions were then applied to other aliphatic halides. The electrochemical carboxylation of **1a** and CO_2 followed the principle as shown in Scheme 1. In our experiments, controlled-potential electrolyses were carried out in CO_2–saturated CH_3CN containing 0.2 M **1a** in an undivided cell with Mg sacrificial anode. To optimize the yields, we focused our attention on the influence of various synthetic parameters on the process, such as electrode materials, supporting electrolytes and the temperature. The results of the electrolysis are summarized in Table 2.

Among all electrochemical reaction conditions, the choice of electrode materials has great influence on the yields or reactivity in CO_2 fixation. It is important to find a proper electrode that has good electrocatalytic effect to the reduction of aliphatic halides. The most relevant outcome of the above voltammetric investigation is that Ag shows a significant electrocatalytic effect towards the reduction of **1a**, so we first conducted the electrocarboxylation of **1a** at Ag electrode (Table 2, entry 1). Some experiments were performed at Cu, Ni and Ti electrodes as well for comparison (Table 2, entries 2–4). The electrocarboxylation yield decreased depending on the

Table 1
Voltammetric data for the reduction of aliphatic halides **1a–i** at $v=100$ mV s^{-1} in $CH_3CN+0.1$ M Et_4NCl[a]

Substrate	 $CH_2{=}\overset{\overset{CH_3}{\vert}}{C}CH_2Cl$	$CH_2{=}CHCH_2Cl$	$CH_2{=}CHCH_2Br$	n-C_3H_7Br	n-C_4H_9Br	 $CH_3\overset{\overset{CH_3}{\vert}}{C}HCH_2Br$	$BrCH_2COOC_2H_5$	n-$C_6H_{13}Br$	$C_6H_{11}CH_2Br$
	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**
E_p[b]/V	−1.56	−1.61	−1.58	−1.78	−1.87	−1.93	−1.29	−1.89	−1.71
E_p[c]/V	−1.24	−1.18	−0.97	−1.55	−1.65	−1.86	−0.91	−1.75	−1.59
ΔE	0.32	0.43	0.61	0.23	0.22	0.07	0.38	0.14	0.12

[a] Ag working electrode, $T=25$ °C, $C=20$ mM.
[b] Measured in the absence of CO_2, applied potential.
[c] Measured in the presence of CO_2.



Scheme 1.

employed cathode materials in the following order: Ag>Cu>Ni>Ti, which is in agreement with the reduction potential of **1a** at these electrodes: −1.56 V (Ag)≈ca. −1.5 V (Cu)>ca. −2 V (Ni)>ca. −2.5 V (Ti). Owing to the very negative potentials required for the reduction of **1a** at Ni and Ti electrodes, concomitant reduction of CO_2 probably takes place, which resulted in a high consumption of charge and give oxalate, CO and carbonate.[10]

The influence of supporting electrolyte on the electrochemical carboxylation of **1a** was also investigated. The nature of anions and cations especially inorganic halide anions of supporting electrolytes plays important role on the synthesis. Silver has shown specific affinity towards organic halides, especially in the case of bromides and iodides. In fact, though negatively charged at Ag electrode, inorganic halide anions were reported to remain specifically absorbed at Ag electrode in acetonitrile solution in the sequence of $Cl^{-1} \leq Br^{-1} \leq I^{-1}$,[11] which is consistent with many well known halide properties, such as the solubility of the products with silver ions. Adsorption of halide anions at Ag electrode is so strong as to hold also at remarkably negative potentials: ≥−0.8 V (SCE) for bromides and ≥−1.2 V (SCE) for iodides.[12] Adsorption competition between organic halides and inorganic halide anions hinders reduction of organic halides taking place at Ag electrode, which is unfavourable to electrochemical carboxylation reaction. As shown in Table 2 (entries 1, 5–7), in the same tetraethylammonium cation (TEA^+) case, the yield of carboxylic acid increased in order of $Cl^{-1} > BF_4^{-1} > Br^{-1} > I^{-1}$ under the same electrolytic conditions. The nature of cations also had some influence on the yield of carboxylic acid (Table 2, entries 5, 7, 10 and 11). The performance of tetraalkylammonium salts was better than that of imidazole salts. The initial concentration of magnesium ions was too low to stabilize the electrogenerated carboxylate anion since they were generated gradually by electrolytic dissolution of the magnesium metal anode. Hence, tetraalkylammonium cation played an important role in stabilizing carboxylate anion at the initial electrocarboxylation stage. When TEA salt was used as supporting electrolyte, carboxylate anion could be stabilized by forming an ion pair, $\{TEA^+–RCO_2^{-1}\}$, which was helpful to the electrosynthesis.[13]

Table 2
Electrocarboxylation of 3-chloro-2-methylpropene under various synthetic parameters[a]

Entry	E_{app}[b]/V	Cathode	T/°C	Supporting electrolytes	Yield[c]/%
1	−1.6	Ag	20	TEACl	69
2	−1.5	Cu	20	TEACl	52
3	−2	Ni	20	TEACl	45
4	−2.5	Ti	20	TEACl	38
5	−1.6	Ag	20	TEABr	60
6	−1.6	Ag	20	TEAI	50
7	−1.6	Ag	20	$TEABF_4$	62
8	−1.6	Ag	20	TBABr	54
9	−1.6	Ag	20	TBAI	47
10	−1.6	Ag	20	$BMIMBF_4$	38
11	−1.6	Ag	20	BMIMBr	34
12	−1.6	Ag	10	TEACl	77
13	−1.6	Ag	0	TEACl	89

[a] General conditions: 3-chloro-2-methylpropene=0.2 M, Mg as anode, CH_3CN=20 mL, P_{CO2}=1 atm, electricity 2 F mol^{-1}.
[b] Applied potential.
[c] Isolated yield.

Table 3
Electrochemical carboxylation of aliphatic halides (RX) in $CH_3CN–Et_4NCl$[a]

Entry	RX	E_{app}[b]/V	RCO_2H	Yield[c]/%
1	**1a**	−1.6	**2a**	89
2	**1b**	−1.7	**2b**	57
3	**1c**	−1.6	**2b**	68
4	**1d**	−1.8	**2d**	48
5	**1e**	−1.9	**2e**	40
6	**1f**	−2.0	**2f**	22
7	**1g**	−1.3	**2g**	38
8	**1h**	−1.9	**2h**	27
9	**1i**	−1.8	**2i**	24

[a] General conditions: **1a**–**i**=0.2 M, Et_4NCl=0.1 M, CH_3CN=20 mL, Ag cathode, Mg anode, T=0 °C, electricity 2 F mol^{-1}, P_{CO2}=1 atm.
[b] Applied potential.
[c] Isolated yield.

The temperature appeared to be a crucial factor for the electrochemical carboxylation of **1a**. The solubility of CO_2 in CH_3CN was increased with the decrease of temperature, indicating that low temperature favours the reaction. Under an atmospheric pressure of CO_2, the yield of carboxylic acid **2a** increased from 69% (entry 1) to 89% (entry 13) when the electrolysis temperature was changed from 20 °C to 0 °C.

2.3. Electrocarboxylation of other aliphatic halides

To test the applicability of this electrochemical carboxylation, the investigation was extended to other aliphatic halides **1b**–**i**. The results of these electrolyses under optimized conditions (Table 2, entry 13) are reported in Table 3. In all cases, the corresponding carboxylic acid was obtained. The best yield was obtained with **1a**, while the moderate yields were achieved with **1b**–**i**. The electrocarboxylation yields of aliphatic halides decreased with the negative shift of applied potentials, since the concomitant reduction of CO_2 may take place, which resulted in a high consumption of charge and decrease of electrocarboxylation yield. When the electrochemical carboxylation was carried out using **1g** as a substrate, the electron-withdrawing group may significantly weaken the nucleophilicity of carbanion, the corresponding carboxylic acid **2g** was only obtained in 38% yield.

3. Conclusion

In conclusion, we have demonstrated a simple and efficient electrochemical route with silver cathode for electrocarboxylation of aliphatic halides. We have shown that various conditions, such as the nature of the electrode, the supporting electrolyte and the temperature, can affect the yield of carboxylic acid. Under the optimized condition, aliphatic halides **1a**–**i** were electrochemically reduced in the presence of CO_2 to the corresponding carboxylic acids in moderate to good yields (22–89%).

Cyclic voltammograms and electrolysis data of 3-chloro-2-methylpropene (**1a**) in CH_3CN at different electrodes showed significant electrocatalytic effect of the silver electrode towards the reductive carboxylation of aliphatic halides. Compared with the electrochemical methods reported in the literatures,[5,6] this electrochemical route appears to be more simple and more efficient for electrocarboxylation of aliphatic halides.

4. Experimental

4.1. General

^1H NMR and ^{13}C NMR spectra were recorded on AVANCE 500 (500 MHz) spectrometer in $CDCl_3$ with Me_4Si as an internal standard. Mass spectra were obtained on a 5973N spectrometer connected with a HP 6890 gas chromatograph. Cyclic voltammograms were measured with CHI660 electrochemical analyzer (CHI, USA). Silver (Ag), copper (Cu), nickel (Ni) and titanium (Ti) electrodes (d=2 mm) were used as working electrodes, respectively. The counter electrode and the reference electrode were a platinum wire and Ag–AgI–0.1 M n-Bu$_4$NI in DMF, respectively.

Acetonitrile (CH_3CN) was kept over 4 Å molecular sieves. Tetraethylammonium chloride (Et_4NCl) and tetraethylammonium tetrafluoroborate (Et_4NBF_4) were prepared according to the literature.[14] 1-Butyl-3-methyl imidazolium tetrafluoroborate ($BMIMBF_4$) and 1-butyl-3-methyl imidazolium bromide were prepared according to the literature.[15] Other reagents were used as received.

4.2. General procedure for electrochemical carboxylation of aliphatic halides

Controlled-potential electrolysis was carried out at −1.6 V in a mixture of **1a** (0.2 M) and Et_4NCl (0.1 M) in 20 mL dry MeCN under a slow stream of CO_2 in a one compartment electrochemical cell equipped with a metallic ring cathode and a sacrificial Mg anode until 2 F mol^{-1} of charge was passed. After electrolysis, the solvent was evaporated off under reduced pressure and the residual was acidified with 2 mol L^{-1} aqueous hydrochloric acid and extracted with (25×4 mL) diethyl ether. The extracts were mixed with a saturated aqueous solution of $NaHCO_3$. After separation of ether and aqueous phases, the latter was acidified with 2 mol L^{-1} hydrochloric acid and the carboxylic acid was extracted with (25×4 mL) diethyl ether. Then, the organic layer was treated with saturated aqueous NaCl, and dried with $MgSO_4$. After evaporation of ether, an almost pure 3-methyl-3-butenoic acid was obtained.

4.2.1. *3-Methyl-3-butenoic acid (**2a**)*

GC–MS (m/z, %) 100 (M$^+$, 89), 82 (19), 72 (51), 60 (28), 55 (67), 41 (64), 28 (100), 14 (2); ^{1}H NMR ($CDCl_3$) δ 9.36 (s, 1H), 4.95 (s, 1H), 4.89 (s, 1H), 3.07 (s, 2H), 1.83 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 177.35, 137.92, 115.32, 43.06, 22.37.

4.2.2. *3-Butenoic acid (**2b**)*

GC–MS (m/z, %) 86 (M$^+$, 8), 58 (5), 44 (5), 41 (15), 38 (3), 32 (19), 28 (100), 14 (3); ^{1}H NMR ($CDCl_3$) δ 10.71(s, 1H), 6.00–5.80 (m, 1H), 5.20 (dd, J=12, 1.5 Hz, 2H), 3.15 (d, J=6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 178.17, 129.46, 119.11, 38.78.

4.2.3. *Butanoic acid (**2d**)*

GC–MS (m/z, %) 88 (M$^+$, 3), 73 (35), 60 (100), 45 (13), 42 (16), 39 (10), 28 (20), 15 (2); ^{1}H NMR ($CDCl_3$) δ 11.65 (s, 1H), 2.32 (t, J=7.2 Hz, 2H), 1.69–1.62 (m, 2H), 0.96 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 180.44, 35.96, 18.12, 13.53.

4.2.4. *Pentanoic acid (**2e**)*

GC–MS (m/z, %) 102 (M$^+$, 1), 87 (3), 73 (29), 60 (100), 55 (10), 41 (15), 28 (87), 14 (2); ^{1}H NMR ($CDCl_3$) δ 11.83 (s, 1H), 2.36 (t, J=7.2 Hz, 2H), 1.66–1.60 (m, 2H), 1.42–1.34 (m, 2H), 0.93 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 180.48, 33.80, 26.71, 22.15, 13.63.

4.2.5. *3-Methylbutanoic acid (**2f**)*

GC–MS (m/z, %) 102 (M$^+$, 1), 87 (20), 74 (2), 69 (5), 60 (100), 43 (31), 28 (26), 18 (4); ^{1}H NMR ($CDCl_3$) δ, 9.77 (s, 1H), 2.22 (d, J=6 Hz, 2H), 2.12–2.06 (m, 1H), 0.97 (d, J=6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 179.62, 43.14, 25.41, 22.62, 22.30.

4.2.6. *Ethyl malonic acid (**2g**)*

GC–MS (m/z, %) 132 (M$^+$, 1), 114 (5), 105 (60), 87 (100), 60 (24), 43 (35), 28 (27), 15 (3); ^{1}H NMR δ 8.99 (s, 1H), 4.14 (q, J=7.2 Hz, 2H), 3.54 (s, 2H), 1.30 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 171.23, 166.90, 61.95, 40.83, 13.93.

4.2.7. *Heptanoic acid (**2h**)*

GC–MS (m/z, %) 130 (M$^+$, 1), 113 (2), 101 (9), 87 (28), 73 (56), 60 (100), 43 (25), 28 (15); ^{1}H NMR ($CDCl_3$) δ 10.52 (s, 1H), 2.32 (t, J=7.7 Hz, 2H), 1.62–1.56 (m, 2H), 1.33–1.23 (m, 6H), 0.86 (t, J=7.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 180.54, 34.13, 31.46, 28.72, 24.74, 22.73, 14.01.

4.2.8. *Cyclohexaneacetic acid (**2i**)*

GC–MS (m/z, %) 142 (M$^+$, 7), 124 (2), 99 (6), 83 (90), 60 (100), 53 (10), 41 (32), 28 (29); ^{1}H NMR ($CDCl_3$) δ 11.16 (s, 1H), 2.20 (d, J=6.9 Hz, 2H), 1.85–1.60 (m, 6H), 1.38–1.10 (m, 3H), 1.08–0.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 179.77, 41.93, 34.65, 32.95, 26.08, 25.98.

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