Sacrificial anode-free electrosynthesis of α -hydroxy acids via electrocatalytic coupling of carbon dioxide to aromatic alcohols

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ABSTRACT

Electrocarboxylation of organic compounds using CO₂ is a promising approach towards a sustainable low-carbon society, but it is desirable to avoid the use of conventional sacrificial anodes in terms of green chemistry. Here, we report a novel electrocarboxylation methodology operating in a simple undivided cell with a non-sacrificial anode, at which tetramethylpiperidine-

1-oxyl (TEMPO)-mediated alcohol oxidation takes place. Aromatic alcohols can be oxidized with high efficiency to ketones or aldehydes at the anode in the presence of a small amount of water, and then converted to α -hydroxy acids in yields of up to 61 % by coupling with CO₂ at the cathode. The electrocarboxylation mechanism comprising electron and proton transfers at the cathode is discussed along with experiments using various cathode materials. Electron and proton transfers are influenced by the hydrogen adsorption energy of the cathode material, which plays an important role in the electrocarboxylation efficiency.

INTRODUCTION

The chemical incorporation of carbon dioxide (CO₂) into organic molecules can offer opportunities to use CO₂ as a C1 building block in organic synthesis. Carboxylation provides a direct route to valuable organic chemicals by making C-C bonds through the coupling of CO₂ with organic molecules. However, CO₂ is highly thermodynamically stable; a typical carboxylation process demands harsh reaction conditions with high temperature and high pressure, often generating environmentally harmful metal salts as waste.¹⁻⁵ An electrochemical route for carboxylation, i.e. electrocarboxylation, can be free from these issues by using electrons as a redox reagent instead of wasteful chemical reagents.⁶⁻⁸ Electron transfers from the electrode to CO₂ or unsaturated organic substrates, such as ketones, aldehydes, or olefins, can readily produce reactive radicals, which enables an efficient carboxylation even under mild conditions such as room temperature and atmospheric CO₂ pressure. Moreover, the electrocarboxylation process can use environmentally benign materials as the electrodes for the electron transfer process. Therefore,

electrocarboxylation using CO₂ is highly promising in organic synthesis from the viewpoint of CO₂ valorization towards a low-carbon economy.

Al or Mg dissolution has been conventionally adopted as a balancing anodic reaction for the electrocarboxylation at the cathode.^{9–11} The use of sacrificial anodes ensures high yield and stability of the carboxylated products.¹² However, a gradual consumption of electrode materials hampers a continuous electrocarboxylation process, lowers the product purity and generates stoichiometric amounts of metal ions, which presents a serious drawback in terms of green chemistry. In this regard, for a reliable and sustainable electrosynthesis of carboxylic acids, it is desirable that the sacrificial anode should be replaced by an inert anode. Recently, several studies on the sacrificial anode-free electrocarboxylation have been reported.¹³ Matthessen, De Vos et al. reported an electrocarboxylation methodology for dienes utilizing divergent paired electrosynthesis, using a graphite anode and a Ni cathode; however, the yield in such a process is theoretically limited to 50%, since half of the diene is reduced and half is oxidized.¹⁴ This process involves a simultaneous cathodic carboxylation and anodic acetoxylation of conjugated dienes. Senboku, Hara et al. reported a convergent paired electrocarboxylation by using a quasi-divided cell with a Pt wire anode and a Pt plate cathode.¹⁵ At the anode, dimethylformamide (DMF) is decomposed into the *N*-methyl-*N*-formyliminium ion, which is coupled with benzyl halides and CO₂ at the cathode to produce *N*-methyl-*N*-acyloxymethylformamides, together with a chloride salt. These studies show that exploring anode reactions that could be compatible with the electrocarboxylation is a key factor in the success of the sacrificial anode-free process.

In this work, we devised a novel electrocarboxylation methodology without the use of sacrificial anodes, operating in a simple undivided cell. As shown in Scheme 1, in our system,

tetramethylpiperidine-1-oxyl (TEMPO) -mediated alcohol oxidation was adopted for the anode reaction instead of the dissolution of Mg or Al.

Scheme 1. Electrosynthesis of α -hydroxy acids via electrocatalytic coupling of alcohols and CO_2 without the use of sacrificial anodes.

After oxidation of the alcohols, the resulting ketones or aldehydes can migrate to the cathode, where they are carboxylated to the corresponding α -hydroxycarboxylic acids by coupling with dissolved CO_2 . This paired, convergent process results in the following net reaction:

2 moles of electrons per mole of alcohol are supplied to the anode in the alcohol oxidation and used in the electrocarboxylation at the cathode. TEMPO is an efficient and versatile redox mediator for the selective oxidation of primary and secondary alcohols to aldehydes and ketones,^{16–18} thus the use of TEMPO should allow the consecutive reactions from alcohols to α -hydroxy acids with high efficiency. Furthermore, the resulting α -hydroxy acids could be used as valuable precursors for pharmaceuticals, cosmetics and biodegradable polymers.^{19–21} Therefore, it can be expected that the use of the TEMPO-mediated alcohol oxidation as the anodic reaction would be an effective

way to realize a sacrificial anode-free electrocarboxylation for producing valuable organic chemicals using CO₂.

RESULTS AND DISCUSSION

Since our electrocarboxylation process starts with the TEMPO-mediated alcohol oxidation at the anode, we first carried out some experiments to optimize the concentrations of TEMPO and water and the amount of charge applied, which all influence the alcohol conversion, using 1-phenylethanol (1a) as a model substrate (Scheme 2).

Scheme 2. Electrocarboxylation of 1-phenylethanol^a.

^aYield and selectivity were determined by GC-FID analysis after a silylation with BSTFA-TMCS (99:1), using ECN values. See Supporting Information for details.

All reactions were performed in our own home-made reactor (Fig. S1-Sn and S2-Sn) equipped with a glassy carbon (GC) plate anode and a nickel (Ni) foil cathode by applying 7 mA cm⁻² of current density for 2 F mol_{alcohol}⁻¹ of charge. 7 mA cm⁻² proved the optimal current density in an initial screening for the best carboxylate yield, and was therefore used in subsequent reactions (Fig S6-Sn). CO₂ pressure was maintained at 5 bar during the reaction. Acetonitrile was used as solvent and tetraethylammonium acetate (TEAAc) as electrolyte. This acetate anion conveniently provides the basicity required for efficient alcohol oxidation by aiding in the deprotonation of the alcohol substrate¹⁷. As shown in Fig. 1(a) and (b), the presence of TEMPO together with water is essential for the oxidation of 1-phenylethanol (1a) at the anode.

Figure 1. Effects of (a) TEMPO concentration, (b) water concentration, and (c) applied charge on the carboxylate yield starting from 1-phenylethanol.

This is likely because water mediates the proton transfer from the alcohol to TEMPO during the oxidation reaction. Accordingly, the alcohol conversion and carboxylate yield were quite low at low concentrations of TEMPO and water. Upon increasing the TEMPO and water concentration to 0.01 M and 0.03 M, respectively, the alcohol conversion increased to about 70 %, and the carboxylate, viz. 2-phenyllactate (1b) was obtained in near 30 % yield. However, further addition of TEMPO decreased the alcohol conversion as well as the carboxylate yield due to the direct reduction of oxo-ammonium species at the cathode, hampering the alcohol oxidation. Adding more water also decreased the carboxylate yield and selectivity by causing side reactions at the cathode. It is widely accepted that the protonation of ketyl intermediates by trace water causes the formation of dimer 1c by pinacol coupling of two protonated ketyls instead of the coupling with CO₂.^{22,23} Moreover, at higher water concentrations, the hydrogen evolution reaction (HER) is also likely to occur at the cathode, in competition with the electrocarboxylation. Upon increasing the applied charge up to 3 F mol_{alcohol}⁻¹ with the optimized TEMPO and water concentrations, the carboxylate (1b) yield increased to 36 %, with a selectivity of 41 % , as alcohol conversion increased. However, applying an excess charge of more than 3 F mol_{alcohol}⁻¹ decreased the carboxylate yield as well as

the alcohol conversion (Fig. 1(c)). This is because the alcohol is depleted when higher excess charge is applied, leading to decarboxylation of the carboxylate back into alcohol (1a) and CO₂ at the anode instead of the alcohol oxidation. Although some side products were observed, almost 40 % of carboxylate yield (1b) could be obtained by optimizing the experimental parameters.

To expand the substrate scope, we additionally examined the electrocarboxylation of benzyl alcohol (2a) and benzhydrol (3a) to respectively mandelic acid and benzylic acid (Scheme 3).

Scheme 3. Electrocarboxylation of benzyl alcohol and benzhydrol^a.

^aYield and selectivity were determined by GC-FID analysis after a silylation with BSTFA-TMCS (99:1), using ECN values. See Supporting Information for details.

Mandelic acid can be polymerized to polymandelide, a biodegradable polyester with styrene-like properties²¹, while benzylic acid is the starting points for the preparation of various glycolate pharmaceuticals such as Flutropium²⁴. The carboxylate yield and selectivity for benzyl alcohol were much lower than those for 1-phenylethanol. The highest carboxylate (2b) yield was only 15 %, with a selectivity of 16 %, when 3 F mol_{alcohol}⁻¹ of charge was applied, while the dimer (2c) yield was 43 %, which is significantly higher than for 1-phenylethanol under the same conditions (27 %). It seems that benzaldehyde is more prone to undergo side reactions, such as the pinacol coupling, compared to acetophenone due to its higher reactivity. In addition, it was observed that small amounts of benzoic acid (10 %) could be formed as a side product. Since water content is very low, overoxidation of benzyl alcohol to significant amounts of benzoic acid at the anode seems unlikely.²⁵ Therefore we propose that the local alkaline environment near the cathode

surface leads to the formation of benzoic acid via the Canizzaro disproportionation of benzaldehyde (Scheme S1-Sn).^{26,27} On the other hand, no side products were observed in the electrocarboxylation of benzhydrol, as it is likely too sterically hindered to undergo dimerization. Accordingly, the carboxylate yield from benzhydrol was much higher than from 1-phenylethanol and benzyl alcohol. We could obtain 59 % of carboxylate (3b) yield with 74 % of carboxylate selectivity by applying 3 F mol_{alcohol}⁻¹ of charge. However, an excess charge of more than 3 F mol_{alcohol}⁻¹ also decreased the carboxylate (3b) yield while reducing alcohol conversion, probably due to the decarboxylation of the product 3b into the starting alcohol (3a) and CO₂.

Next, we investigated the effect of cathode materials on the carboxylate yield from 1-phenylethanol, benzyl alcohol, and benzhydrol. Considering the possible involvement of water in the side reactions at the cathode, we selected zinc (Zn), tin (Sn), molybdenum (Mo), and tantalum (Ta) foils as cathode materials in addition to Ni, based on the hydrogen adsorption energies of these metals. According to the volcano plots in hydrogen electrocatalysis, Zn and Sn have weak metal-hydrogen (M-H) bond strengths, while Mo and Ta have strong M-H bonds, and Ni has intermediate M-H bonds.^{28,29} Fig. 2(a) shows the summarized carboxylate yields from 1-phenylethanol, benzyl alcohol, and benzhydrol using Zn, Sn, Ni, Mo, and Ta cathodes, when 2 F mol_{alcohol}⁻¹ of charge was applied.

Figure 2. (a) Carboxylate yields with various cathode materials and (b) the highest carboxylate yields for substrates 1-phenylethanol, benzyl alcohol, and benzhydrol.

For the electrocarboxylation of 1-phenylethanol, the carboxylate yield varied greatly depending on the cathode materials. Zn and Sn cathodes exhibited a very low carboxylate yield of less than 10 %, but Ni, Mo, and Ta cathodes gave higher carboxylate yields in the range of 30 %. In addition, it was observed that acetophenone concentration in the product mixture was significantly higher in reactions with Zn and Sn cathodes than with Ni, Mo and Ta cathodes (Table S5-Sn). This almost 3-4 times larger amount of acetophenone at Zn and Sn is likely due to an increased formation of protonated ketyl radicals at these electrode surfaces, followed by a disproportionation reaction between two protonated ketyl radicals to 1-phenylethanol and acetophenone, a reaction specific for ketones. In the case of benzyl alcohol, although the difference in the carboxylate yield between the cathode materials was not very large because of the generally low carboxylate yield, a similar trend was observed. Zn and Sn cathodes produced lower carboxylate yield than Ni, Mo and Ta

cathodes, whereas there was no significant difference in the amount of benzoic acid formed between the cathode materials (Table S6-Sn). Surprisingly, Zn and Sn cathodes exhibited much higher carboxylate yields in the electrocarboxylation of benzhydrol. While Zn was the least performant cathode material for the electrocarboxylation of both 1-phenylethanol and benzyl alcohol, it performed at least on par with Sn and Ni and slightly better than Mo and Ta for the electrocarboxylation of benzhydrol. These results show that the M-H energy of cathode materials can have a strong influence on the electrocarboxylation efficiency for each alcohol substrate in the presence of water. As mentioned earlier, the reaction of ketyl radicals with water may be detrimental to the electrocarboxylation by causing side reactions. If the ketyl radicals are protonated without a participation of the cathode, the carboxylate yield should be almost identical, regardless of cathode materials. However, our investigations with various cathode materials revealed that the carboxylate yield varied greatly depending on the cathode materials.

Based on these results, we suggest possible reaction pathways, which involve electron and proton transfers from the cathode in the presence of water, using acetophenone as a model substrate (Scheme 4).

Scheme 4. (a) Electrocarboxylation and (b) side reaction pathways of acetophenone on the cathode in the presence of water.

For the electrocarboxylation with CO_2 (Scheme 4(a)), ketones are first reduced into ketyl radicals *via* one electron transfer from the cathode, and then further transformed and reduced into carboxylates by coupling with CO_2 . Protonation should only take place after the coupling reaction. However, on the cathodes that have a weak M-H energy, ketones could be easily reduced to protonated ketyl radicals through a Langmuir-Hinshelwood step by a proton-coupled electron transfer (PCET) from a surface bound proton,³⁰ as shown in Scheme 2(b). The protonated ketyl radicals are prone to undergo side reactions, such as (iii) pinacol dimer formation, (iv) re-reduction to alcohols and (v) disproportionation to ketone and alcohol via α -hydrogen abstraction, which would be the cause of the limited efficiency of the electrocarboxylation. Benzyl alcohol would undergo almost the same reaction pathways as 1-phenylethanol, except for the disproportionation. Because the amount of benzoic acid formed was almost the same regardless of the cathode material, it seems that the cathode was not directly involved in the Cannizzaro reaction of benzaldehyde. The metals that have a strong M-H energy could be favorable for the electrocarboxylation of 1-phenylethanol and benzyl alcohol by suppressing the reduction reaction *via* PCET. In case of the benzhydrol reaction on the other hand, where reactions (iii) and (v) do

not occur, the reduction reaction *via* PCET might even be the preferred mechanism for an efficient electrocarboxylation, because the PCET is energetically more favorable than a separate electron and proton transfer.³¹ This would be the reason why Zn and Sn cathodes exhibited much higher yields in the electrocarboxylation of benzhydrol, contrary to those obtained with 1-phenylethanol and benzyl alcohol. Finally, the best highest carboxylate yields obtained for 1-phenylethanol, benzyl alcohol, and benzhydrol are summarized in Fig. 2(b). Benzhydrol is the most favorable substrate for the electrocarboxylation using our methodology. Further efforts to minimize the proton and water concentration at the cathode surface, e.g. separating anode and cathode by an ion-exchange membrane, would likely enable achieving higher carboxylate yields with various substrates.

CONCLUSION

In summary, the sacrificial anode-free electrocarboxylation *via* electrocatalytic coupling of aromatic alcohols and CO₂ was developed using the TEMPO-mediated alcohol oxidation as an anode reaction. TEMPO-mediated alcohol oxidation to ketones or aldehydes was facilitated in the presence of a little water, thereby enabling an efficient electrocarboxylation at the cathode. The investigations with various cathode materials demonstrated that the hydrogen adsorption energy of the cathode influences the electron and proton transfer pathway, leading to effects on the carboxylate yield. Under optimized conditions, we could obtain a good α -hydroxy acid yield of up to 61 % in a simple undivided cell using aromatic alcohols as a substrate. The use of a stable and inert anode could advance an industrial implementation of electrocarboxylation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Chemicals and electrode materials, electrolyte, reactor description, electrocarboxylation procedure, reaction analysis, extra results tabulated, cell potentials (PDF)

AUTHOR INFORMATION

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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TABLE OF CONTENTS GRAPHIC

Here, we show the convergent, paired electrosynthesis of aromatic 2-hydroxycarboxylic acids such as mandelic acid from alcohols and CO_2 , avoiding the wasteful use of sacrificial anodes.