Electrochemical Conversion of Carboxylic Acids to Terminal Alkenes Enabled by Dialkyl Phosphate Electrolyte

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Abstract

Electrochemical regioselective conversion of carboxylic acids to terminal alkenes through dehydrogenative decarboxylation was developed. Mechanistic studies suggested that the reaction proceeds through oxidative decarboxylation of carboxylic acids to give the corresponding primary carbocation intermediates followed by deprotonation. It was implied that when using a supporting electrolyte with high donor number anion, such as dialkyl phosphate, the isomerization of the primary carbocation intermediates was suppressed to cause higher selectivity to terminal alkenes.

Keywords: Electrochemical conversion; Dialkyl phosphates; Carboxylic acids; Dehydrodecarboxylation; Terminal alkenes

1. Introduction

Electrochemical conversion of carboxylic acids *via* decarboxylation has long been studied since the Kolbe electrolysis reported in 1847 (Figure 1a).^{1, 2} In this reaction, carboxylic acids are anodically oxidized and decarboxylated to generate alkyl radicals, which subsequently dimerize to form long-chain alkanes. Meanwhile, the Non-Kolbe processes, which utilize carboxylic acids as a carbocation source, have also attracted much attention (Figure 1b).^{3, 4, 5} Among them, the Hofer-Moest reaction, which is the reaction of a nucleophile with a carbocation intermediate produced by electrolytic anodic oxidation of a carboxylic acid, has been extensively studied (Figure 1b, upper route).⁶⁻⁸ In contrast, there is still room for development of a method to generate alkenes, especially terminal one, an important building block in synthetic chemistry, by deprotonation from the carbocation intermediate (Figure 1b, lower route).^{9, 10} Owing to the growing demand for producing value-added chemicals from renewable sources, ^{3, 11-14} the conversion of carboxylic acids, which are readily available from waste oils or fats, to terminal alkenes has been of great interest. However, regioselective electrochemical conversion of primary carboxylic acids to terminal alkenes is still challenging due to the facile isomerization of highly reactive primary carbocations to the relatively stable secondary ones (Figure 1b, lower route). For example, Baran and coworkers recently reported that the ratio of terminal to internal alkenes was approximately 1/1 for the electrolysis of a primary carboxylic acid employing an alternating polarity strategy.⁹

Controlling the reactivity of the carbocation intermediate is the key to achieving the high regioselectivity for the conversion of carboxylic acids to terminal alkenes. Our strategy to tackle this challenge is to employ a supporting electrolyte anion with high Lewis basicity which can interact with and stabilize the highly active primary carbocation intermediate, and thus, can suppress the isomerization. It is known that the constituent ions of the supporting electrolyte, which are added to improve the conductivity of the reaction solution, have a significant impact on reaction selectivity. The effect of supporting electrolytes has well been studied for hydrogen evolution reaction^{15, 16}, CO₂ electroreduction, and so on.¹⁷⁻¹⁹ In these reactions, an appropriate choice of electrolyte cations (e.g. alkali metal cations) can improve faradic efficiency and regulate the product selectivity.²⁰ In organic synthesis, supporting electrolytes play important roles on mass transfer²¹⁻²³ and

intermediate stabilization,²³⁻²⁵ by which reaction selectivity can be controlled. Herein, we successfully achieved the electrolytic conversion of carboxylic acids to terminal alkenes with high regioselectivity using tetramethylammonium dibutyl phosphate as the supporting electrolyte (Figure 1c). Mechanistic studies suggested that the isomerization of the resulting primary carbocation was suppressed by highly electron-donating phosphate anion likely through non-covalent interaction without trapping the carbocation intermediates, leading to the conversion of carboxylic acids to terminal alkenes with high selectivity (Figure 1c).





2. Results and discussion

2.1. Effect of supporting electrolyte

We first investigated supporting electrolyte effect on electrolysis of 6-phenylhexanoic acid (**1a**) to 5-phenyl-1-pentene (**2a**) using a graphite anode and a platinum plate cathode. When using tetrabutylammonium dibutyl phosphate (${}^{n}Bu_{4}N^{+}({}^{n}BuO)_{2}PO_{2}^{-}$) as the electrolyte, **2a** and its internal isomers **2a'** were obtained in 5% and 1% yields, respectively (Table 1, entry 1). Commonly utilized supporting electrolytes, such as ${}^{n}Bu_{4}N^{+}BF_{4}^{-}$ or ${}^{n}Bu_{4}N^{+}TfO^{-}$ resulted in higher yields of alkenes; however, the internal isomers are formed in higher selectivity in these cases (Table 1, entry 2 and 3). Moreover, the use of tetramethylammonium dibutyl phosphate (Me₄N⁺({}^{n}BuO)_{2}PO_{2}^{-}), which has a cation smaller than ${}^{n}Bu_{4}N^{+}({}^{n}BuO)_{2}PO_{2}^{-}$, gave 30% and 6% yields of **2a** and **2a'**, respectively; thus, the terminal to internal ratio of the alkene products reached to 5/1, much higher than the ratio reported by Baran and coworkers⁹ (Table 1, entry 4). Further investigation on the effect of alkyl chain length of dialkyl phosphate anions (diethylphosphate or didecyl phosphate) for the reaction revealed that the terminal to internal ratios are almost constant (approximately 5/1 to 7/1, Table 1, entries 4–6). The phosphate moiety plays an essential role: the use of tetramethylammonium diphenylphosphate (Me₄N⁺(PhO)_2PO_{2}^{-}) as the electrolyte resulted in the drastic decrease of substrate conversion and alkene yields (Table 1, entry 7). Changing the concentration of the supporting electrolyte resulted in no significant difference in product yield and terminal to internal ratio (Table 1, compare entry 4 with entries 8 and 9).

The effect of solvent was also significant (Table S1). The reaction in DCM solvent afforded almost the same yield of **2a** (27%) and **2a'** (5%) as in DCM/acetone mixed solvent. But the conductivity in DCM solvent was lower and recorded even higher cell voltages than the mixed solvents. On the other hand, when acetone was employed as the solvent, **2a** and **2a'** were formed in 11% and 6% yields, respectively. The reaction in MeCN gave **2a** and **2a'** in only 4% and 3% yields, respectively. Furthermore, a lower amount of 2,4,6-collidine resulted in a slightly lower yield of **2a** (Table S2). When tetramethylammonium hydroxide (Me₄N⁺OH⁻) was used as a base, which is employed in the Baran's system, **2a** was obtained in 20% yield. Even under 2,4,6-collidine or Me₄N⁺OH⁻-free conditions, **2a** was still obtained in 23% yield. We also carried out the electrolysis under potentiostatic conditions; however, the yield of **2a** did not improve (Table S3).

Ph	С(+)	Pt(-)	+ internal isome	ers of 2a	
1a		2a	2a'		
Entry	Supporting electrolyte	Concentration (M)	1a conv. $(\%)^b$	Yield $(\%)^b$	
				2a	2a'
1	$^{n}Bu_{4}N^{+}(^{n}BuO)_{2}PO_{2}^{-}$	0.10	27	5	1
2	$^{n}\mathrm{Bu}_{4}\mathrm{N}^{+}\mathrm{BF}_{4}^{-}$	0.10	70	5	15
3	$^{n}Bu_{4}N^{+}TfO^{-}$	0.10	68	10	17
4	$Me_4N^+(^nBuO)_2PO_2^-$	0.10	75	30	6
5	$Me_4N^+(EtO)_2PO_2^-$	0.10	52	24	5
6	$Me_4N^+({^nC_{10}H_{21}O})_2PO_2^-$	0.10	74	20	3
7	$Me_4N^+(PhO)_2PO_2^-$	0.10	2	2	1
8	$Me_4N^+(^nBuO)_2PO_2^-$	0.05	62	24	7
9	$Me_4N^+(^nBuO)_2PO_2^-$	0.20	76	23	6

Table 1. Electrolysis of 6	-phenvlhexanoic acid ((1a) with various	supporting electrolytes ^{<i>a</i>}

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^{*a*}Reaction conditions: **1a** (0.12 mmol, 0.02 M), 2,4,6-collidine (0.18 mmol, 0.03 M), supporting electrolyte (0.60 mmol, 0.1 M), DCM/acetone (5.5/0.5 mL), undivided cell with graphite anode and plated platinum cathode. Reactions were performed under constant current conditions (3.0 mA) for total charge of 1.8 F/mol at room temperature under N₂ (1 atm). ^{*b*}Determined by ¹H NMR analysis.

2.2. Substrate scope

Next, the substrate scope was examined. Aliphatic primary carboxylic acids (**1b** and **1c**) with different chain length gave terminal alkenes as the major products (Table 2, entries 1 and 2). Moreover, ester group was tolerated under the electrolysis conditions (**1d**, Table 2, entry 3). Notably, when 4-phenylbutyric acid (**1e**) was used as the substrate, allylbenzene was obtained as the main product in 16% yield and the more stable conjugated

alkene, β -methyl styrene, remained as the minor (Table 2, entry 4). The electrolysis of 2-methylhexadecanoic acid (**1f**), which generates secondary cation intermediate, afforded the corresponding internal alkenes as the major products (Table 2, entry 5). The electrolysis of a tertiary carboxylic acid (**1g**) that affords an inherently stable carbocation, gave the corresponding terminal alkene in a higher yield than using primary or secondary carboxylic acids as the substrate (Table 2, entry 6). For carboxylic acids having carboxyl group on benzylic position (**1h**-**1j**), the corresponding alkenes together with the alcohol side products were obtained (Table 2, entries 7–9). Considering the reactions were carried out under N₂ atmosphere, the alcohol products were formed by the reaction of the benzylic carbocation intermediates with water contained in the reaction system (e.g., electrode, electrolyte. etc.). Actually, when the electrolysis of **1i** and **1j** was carried out in the presence of molecular sieves 3A, the yield of the alkene product increased while that of the alcohol side product decreased, supporting the hydroxy group was derived from water (Table S4). Moreover, in the case of **1i** and **1j**, further dehydrogenation of the alkene products to biphenyl or naphthalene did not occur.

Table 2. Substrate scope^{*a*}



^aReaction conditions: Substrate (0.12 mmol, 0.02 M), 2,4,6-collidine (0.18 mmol, 0.03 M), $Me_4N^+(^{B}BuO)_2PO_2^-$ (0.60 mmol, 0.1 M), DCM/acetone (5.5/0.5 mL), undivided cell with graphite anode and plated platinum cathode. Reactions were performed under constant current conditions (3.0 mA) for total charge of 1.8 F/mol at room temperature under N₂ (1 atm). ^bDetermined by ¹H NMR analysis. ^cDetermined by GC analysis.

2.3. Mechanistic studies

To verify whether the present electrolysis proceeds through the carbocation intermediate, the following control experiment was carried out. When the electrolysis of 3-hydroxy-1-adamantane carboxylic acid was conducted under the conditions shown in Figure 2, the corresponding Grob fragmentation product $2\mathbf{k}$ was formed in 7% yield, supporting the formation of carbocation intermediate during the electrolysis.^{8,9}



Figure 2. Electrolysis of 3-hydroxyadamantane-1-carboxylic acid. ^{*a*}Reaction condition: **1k** (0.12 mmol, 0.02 M), 2,4,6-collidine (0.18 mmol, 0.03 M), $Me_4N^+(^{n}BuO)_2PO_2^-$ (0.60 mmol, 0.1 M), DCM/acetone (5.5/0.5 mL), undivided cell with graphite anode and plated platinum cathode. Reaction was performed under constant current condition (1.0 mA) for 1.8 F/mol to 3-hydroxyadamantane-1-carboxylic acid. Yield was determined by NMR analysis.

The plausible reaction pathways for the present reaction system are shown in Figure 3. The anodic decarboxylative oxidation of a carboxylic acid generates the corresponding primary carbocation intermediate, which is followed by deprotonation by dialkyl phosphate anions in the electric double layer to give the terminal alkene product (Figure 3, steps 1 and 2). Alternatively, the primary carbocation could isomerize to the thermodynamically more stable secondary one (Figure 3, step 3) and then, selective deprotonation from the terminal position of the secondary carbocation would afford the terminal alkene product (Figure 3, step 4). We think the latter isomerization/deprotonation pathway is less likely since the electrolysis of a secondary carboxylic acid **1f**, that undergoes through the secondary carbocation intermediate, provided internal alkenes as major products (Table 2, entry 5). For the formation of internal alkene side products, there are two possible pathways: (i) deprotonation from the internal position of the secondary carbocation intermediate (Figure 3, step 5), or (ii) isomerization of terminal alkenes (Figure 3, step 6). We think pathway (i) is more likely than (ii) based on the following experiment: the electrolysis of **1a** in the presence of 1-heptadecene resulted in 83% recovery of 1-heptadecene without detection of any internal heptadecenes (Figure 4). For the cathodic reaction, protons generated from the deprotonation steps are reduced to produce molecular hydrogen (Figure 3, step 7). By analyzing gas phase of the reaction, hydrogen gas was indeed detected for the electrolysis of **1a**.



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Figure 4. Electrolysis of 1a in the presence of 1-heptadecene. ^{*a*}Reaction conditions: 1a (0.06 mmol, 0.01 M), 1-heptadecene (0.06 mmol, 0.01 M), 2,4,6-collidine (0.18 mmol, 0.03 M), $Me_4N^+(^nBuO)_2PO_2^-$ (0.60 mmol, 0.1 M), DCM/acetone (5.5/0.5 mL), undivided cell with graphite anode and plated platinum cathode. Reaction was performed under constant current condition (3.0 mA) for 1.8 F/mol to 1a. Yields were determined by GC analysis.

As mentioned above, we attribute the selective formation of terminal alkenes to the suppression of isomerization of the primary carbocation to more stable secondary one (Figure 3, step 3). The following two reasons could be considered for the suppression of isomerization. One is that the primary carbocation is stabilized by a non-covalent interaction between dialkyl phosphate anion and the carbocation in the electric double layer, forming an intimate ion pair (Figure 5a). The other is that the carbocation is trapped by a dialkyl phosphate anion to form a trialkyl phosphate intermediate which then gives the terminal alkene by elimination of the dialkyl phosphoric acid (Figure 5b). The following facts support the route in Figure 5a is more likely. First, in the electrolysis of **1a** using Me₄N⁺($^{n}C_{10}H_{21}O)_{2}PO_{2}^{-}$ as the electrolyte, didecyl (5-phenyl)pentyl phosphate (**3a**) was not detected (Figure 5c). Decene, which could be generated from **3a**, was not observed either (Figure 5c). Furthermore, for the electrolysis of dibutyl (4-phenyl)butyl phosphate (**3b**) in the absence of carboxylic acid, 4-phenylbutene was not detected (Figure 5d). Even in the presence of lauric acid, electrolysis of **3b** did not give 4-phenylbutene while 1-undecene was obtained in 21% yield (Figure 5e).

(a) Via non-covalent interaction



(b) Via trialkyl phosphate intermediate



(c) Reaction of 1a using $Me_4N^+({}^{n}C_{10}H_{21}O)_2PO_2^-$ as the electrolyte



(d) Reaction of dibutyl (4-phenyl)butyl phosphate (3b) without lauric acid

(e) Reaction of dibutyl (4-phenyl)butyl phosphate (3b) with lauric acid



Figure 5. Possible mechanism to suppress the primary carbocation isomerization by its stabilization. Reaction conditions for (c): **1a** (0.12 mmol, 0.02 M), 2,4,6-collidine (0.18 mmol, 0.03 M), $Me_4N^+({}^nC_{10}H_{21}O)_2PO_2^-$ (0.60 mmol, 0.1 M), DCM/acetone (5.5/0.5 mL), undivided cell with graphite anode and plated platinum cathode. Reaction was performed under constant current conditions (3.0 mA) for total charge of 1.8 F/mol at room temperature under N₂ (1 atm). Yields were determined by GC analysis. Reaction conditions for (d) **3b** (0.05 mmol, 8.3 mM), 2,4,6-collidine (0.18 mmol, 0.03 M), $Me_4N^+({}^nC_{10}H_{21}O)_2PO_2^-$ (0.60 mmol, 0.1 M), DCM/acetone (5.5/0.5 mL), undivided cell with graphite anode and plated platinum cathode. Reaction was performed under constant current conditions (3.0 mA) for total charge of 1.8 F/mol to **3b** at room temperature under N₂ (1 atm). (e) **3b** (0.05 mmol, 8.3 mM), lauric acid (0.12 mmol), 2,4,6-collidine (0.18 mmol, 0.03 M), $Me_4N^+({}^nC_{10}H_{21}O)_2PO_2^-$ (0.60 mmol, 0.1 M), DCM/acetone (5.5/0.5 mL), undivided cell with graphite anode and plated platinum cathode. Reaction was performed under constant current conditions (3.0 mA) for total charge of 1.8 F/mol to **3b** at room temperature under N₂ (1 atm). (e) **3b** (0.05 mmol, 8.3 mM), lauric acid (0.12 mmol), 2,4,6-collidine (0.18 mmol, 0.03 M), $Me_4N^+({}^nC_{10}H_{21}O)_2PO_2^-$ (0.60 mmol, 0.1 M), DCM/acetone (5.5/0.5 mL), undivided cell with graphite anode and plated platinum cathode. Reaction was performed under constant current conditions (3.0 mA) for total charge of 1.8 F/mol to **3b** at room temperature under N₂ (1 atm). (e) **3b** (0.05 mmol, 0.1 M), DCM/acetone (5.5/0.5 mL), undivided cell with graphite anode and plated platinum cathode. Reaction was performed under constant current conditions (3.0 mA) for total charge of 1.8 F/mol to **3b** at room temperature under N₂ (1 atm). The stabilization of the primary carbocation is considered to be in close relation with the Lewis basicity of the electrolyte anion, that is, the higher the Lewis basicity of the anion, the more stable the primary carbocation, and thus, the higher the terminal selectivity. Accordingly, we investigated the correlation between the Lewis basicity of the supporting electrolyte and the terminal regioselectivity of the alkene product. The Gutmann's donor number (DN) was used as a quantitative measure of Lewis basicity.^{26, 27} We performed electrolysis with the addition of supporting electrolytes composed of various cation-anion combinations. Figure 6 shows the terminal regioselectivity of the alkene products (= 2a/(2a+2a')) plotted against the donor number of various electrolyte anions (see also Table S5). From this graph, a positive correlation was found between the DN values and the terminal regioselectivity. This further supports our hypothesis that the carbocation intermediates are stabilized by non-covalent interactions, and which is the key for the high regioselectivity achieved in the present study.²⁸



Figure 6. Relationship between donor numbers and the alkene product regioselectivity. Reaction conditions: Substrate (0.12 mmol, 0.02 M), 2,4,6-collidine (0.18 mmol, 0.03 M), supporting electrolyte (0.60 mmol, 0.1 M), DCM/acetone (5.5/0.5 mL), undivided cell with graphite anode and plated platinum cathode. Reactions were performed under constant current conditions (3.0 mA) for total charge of 1.8 F/mol at room temperature under N₂ (1 atm). Yields were determined by GC analysis.

3. Conclusion

In summary, the electrochemical conversion of primary carboxylic acids to terminal alkenes was achieved in high selectivity by employing $Me_4N^+(^nBuO)_2PO_2^-$ as the supporting electrolyte. Mechanistic studies suggested that the high donor number of the dialkyl phosphate anion can stabilize the primary carbocation intermediate likely via the non-covalent interaction, which suppressed its isomerization to the more stable secondary one.

Following the direct deprotonation from the primary carbocation, the corresponding terminal alkene product was produced in a regioselective manner.

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28. At this stage, we cannot exclude the possibility that the phosphate anion of the electrolyte deprotonates the primary carbocation intermediate in a much faster rate than the isomerization, thus resulting in the high terminal regioselectivity.