RSC Advances

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Cite this: *RSC Advances*, 2013, **3**, 4634

Electrochemical dicarboxylation of conjugated fatty acids as an efficient valorization of carbon dioxide

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Received 9th January 2013,
Accepted 30th January 2013

DOI: 10.1039/c3ra00129f

www.rsc.org/advances

Carbon dioxide was electrochemically incorporated in internal conjugated dienes and the process was optimized to achieve satisfactory yields (>70%) even for less reactive substrates. Reactions were performed galvanostatically in an undivided cell at room temperature with a magnesium or aluminium sacrificial anode. Using an optimized electrosynthetic method for the dicarboxylation of 1,3-cyclohexadiene (optimal electrode material, CO_2 pressure, amount of charge), the effect of molecular configuration and alkyl substitution on the reactivity of conjugated double bonds towards carboxylation was studied. Use of a bubble reactor at atmospheric pressure instead of a higher pressure reactor, and lowering of the current density made it possible to effectively perform the double carboxylation of internal conjugated double bonds in open chains. Conjugated linoleic acid methyl esters were used in this reaction for the first time and by searching for the optimal reaction conditions (solvent, supporting electrolyte, reactant concentration, amount of charge, current density) yields approaching 80% of the corresponding fatty triacid product could be obtained, at current efficiencies over 50%.

Introduction

Carbon dioxide (CO_2) is one of the major contributors to the greenhouse effect and its increasing concentration in the atmosphere requires fast and efficient measures.[1] CO_2 can also be considered as a non-toxic, non-flammable, low-cost and renewable carbon source for the synthesis of organic chemicals.[2] Due to its high thermodynamic stability, harsh reaction conditions are often needed for reactions with CO_2 in traditional organic synthesis. Sodium salicylate synthesis[3] and the hydrogenation of carbon dioxide to methane[4] are examples of industrial processes which require high temperatures to activate CO_2. Research on the chemical fixation of carbon dioxide in organic chemicals is usually limited to rather reactive substrates like epoxides,[5–11] alcohols,[12–14] amines,[12,14,15] terminal alkynes,[16] and butadiene,[17,18] and even then, elevated reaction temperatures and/or complex catalyst systems are required. Organometallic transition metal compounds can be used to activate carbon dioxide by the formation of metal–CO_2 complexes. When using stoichiometric amounts of these transition metals, CO_2 can be incorporated into unsaturated substrates, with electron-rich Ni(0) complexes being the most successful.[19]

Despite the high thermodynamic stability of CO_2, it can easily be activated by a one-electron reduction at an electrode. These electrochemical processes can often be conducted at room temperature since the energy of the electrons is determined by the applied voltage.[2] The electroreduction takes place on a cathode surface, in this way minimizing the need for homogeneous organometallic complexes. On the other hand, these complexes can still be used in catalytic amounts as redox mediator to increase the CO_2 reduction efficiency and influence the product selectivity.[2] Since electricity will be increasingly of sustainable origin in the future, organic electrosynthesis is a promising technology for environmentally friendly chemical processes. A recent review by Frontana-Uribe and colleagues lists an impressive series of such transformations.[20] Electroreduction can be used to transform CO_2 into valuable products. One option is the synthesis of fuels like formic acid, methanol or methane *via* two-, six- and eight-electron reductions, respectively.[2,21,22] This could be a way of storing electric energy from intermittent renewable sources, like solar or wind energy.[23] Another approach, investigated in this work, is the fixation of CO_2 in organic chemicals by means of an energy-efficient one-electron reduction step to produce carboxylic acids, which are important intermediates in the synthesis of polymers and pharmaceuticals. Carbon dioxide has been incorporated in organic compounds such as arylalkenes,[24–31] alkynes,[24,32–38] aromatic ketones,[39–44] halides[45–50] and epoxides.[51–53] The electrochemical carboxylation of conjugated dienes has been investigated in less detail,[24,28,54–60] with only one paper reporting on the use of an acyclic aliphatic internal conjugated

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diene as reactant,[56] and most emphasis being paid to the dicarboxylation of butadiene.[54,55,59,60] Faradaic yields for carboxylating conjugated double bonds are generally poor, despite use of high CO_2 pressures, addition of Ni(0) complexes as redox mediators or use of reaction temperatures below 0 °C to increase CO_2 solubility.[24,55,56] At a CO_2 pressure of 3 MPa, the dicarboxylated product of 1,3-cyclohexadiene was obtained with a current efficiency of only 35%.[55] When using a Ni-*N*,*N*,*N′*,*N′′*,*N′′*-pentamethyldiethylenetriamine (Ni-PMDTA) catalytic system, a product yield of 60% was obtained for the reaction with 1,4-diphenylbutadiene.[24] Even when working at −10 °C a maximum current efficiency of only 26% was reached in the electrocarboxylation of methyl sorbate.[56]

This paper reports on a significant improvement of the carboxylation yield of internal conjugated dienes by optimizing electrosynthesis conditions like electrode material, CO_2 pressure and current density. The effect of alkyl substitution and molecular configuration of the conjugated dienes on the susceptibility towards electrocarboxylation is investigated. All reactions were carried out in a simple undivided cell with a sacrificial magnesium or aluminium anode. The electrochemical carboxylation with sacrificial anodes was first introduced by the groups of Périchon[61–63] and Silvestri.[27,64,65] The use of such anodes has both advantages and disadvantages. Advantages are the easy product recuperation of the insoluble metal salts that are formed,[66] and the fact that a high selectivity for dicarboxylation can be obtained, which is a critical problem in systems with a stable anode.[59,60] Disadvantages of sacrificial anodes are the production of salt waste and the gradual consumption of the anode. Using an undivided cell also avoids the high ohmic resistance introduced by a membrane separating the anolyte from the catholyte and reduces the cell manufacturing cost.[67] A particular application field for the dicarboxylation is the modification of renewable resources, such as vegetable and animal oils and fats. In unsaturated fatty acids, the carboxylic group, the double bond(s) and the allylic C–H bonds may be electroactive.[68] Reports have appeared on anodic coupling of fatty acids by decarboxylation,[69] anodic acetoxylation of the double bond,[70] and anodic oxidation of allylic hydrogen atoms to form ketones.[71] However, no research on the cathodic electrocarboxylation of fatty acids has been reported yet.

In this work, a system is developed by which conjugated linoleic acid methyl esters (CLAME, **1g**) can be dicarboxylated with good yields (Scheme 1). The fatty triacids (**2g**) formed in this reaction may have value as emulsifiers in the food and pharmaceutical industries, and in dispersion technologies in general. There are important applications for fatty acids functionalized with a polar group along the chain, with 10- or 12-hydroxystearic acids as examples of compounds widely used in stabilization of pigment dispersions. Both CO_2 and linoleic acid are renewable reactants, no additional catalyst is used and the reactions are performed at atmospheric pressure and room temperature. These factors contribute to make this a clean and environmentally benign process.

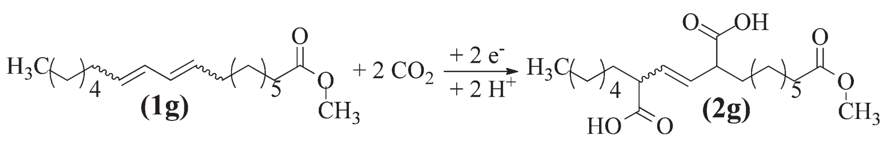
Experimental

Chemicals

The use of dry chemicals is crucial in view of the high water sensitivity of the electrosynthesis procedure. Water causes an oxidative deactivation of the anode material and a cathodic formation of hydrogen and formic acid, thus lowering the current efficiency of the electrochemical process. Tetrabutylammonium bromide (TBABr), tetrabutylammonium iodide (TBAI) and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were purchased from Sigma-Aldrich (⩾99.0%) and dried at 60 °C *in vacuo* for 15 h. *N*,*N*-Dimethylformamide (DMF), acetonitrile (CH_3CN) and tetrahydrofuran (THF) were purchased from Acros Organics (Extra Dry, AcroSeal®) and were used without further purification. A mixture of fatty acids containing 61% conjugated linoleic acid (Nouracid® DE 656) was obtained from Oleon (Oelegem, Belgium). This mixture was methylated with acetyl chloride in dry methanol with a molar ratio methanol/fatty acid of 72 : 1 and acetyl chloride/fatty acid of 6.6 : 1. After continuous stirring for 20 min at 70 °C, a full conversion to the methylated product was obtained. HCl was neutralized with an aqueous solution of $NaHCO_3$. The methyl esters were extracted with ethyl acetate and this organic phase was dried over $MgSO_4$. Ethyl acetate was removed under reduced pressure to obtain a mixture of fatty acid methyl esters containing 61% conjugated linoleic acid methyl esters (CLAME). Other dienes were purchased from Sigma-Aldrich and were used without further purification. The purity of CO_2 was 99.7% (Air Liquide).

Electrosynthesis procedure

Prior to the electrosynthesis, the anode and cathode were cleaned with diluted hydrochloric acid, followed by washing with distilled water and acetone, and then dried with hot air. The electrocarboxylation reactions were performed in a stainless-steel undivided cell with a cylindrical cathode mesh (wet surface area of 10 cm^2) and a central sacrificial anode rod (wet surface area of 4 cm^2). If required, the cell can be pressurized. A schematic picture of this setup is shown in Fig. 1. In a typical experimental procedure, dry solvent (3.5 mL), supporting electrolyte (0.175 mmol) and diene substrate



Scheme 1 Electrocarboxylation of conjugated linoleic acid methyl esters.

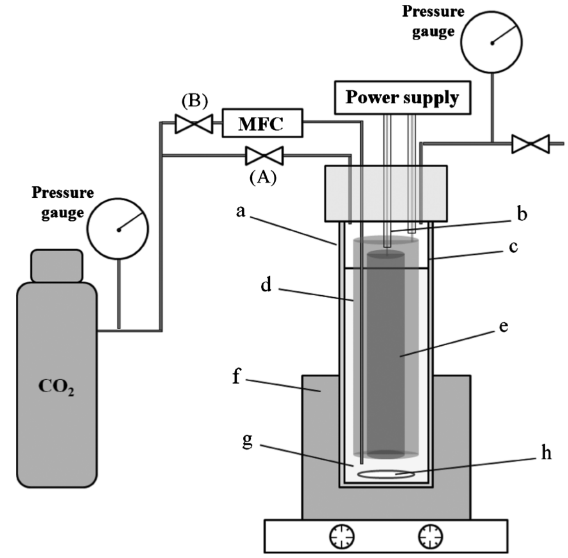


Fig. 1 Schematic representation of the experimental setup used for electrocarboxylation reactions. (A) pressure reactor mode; (B) bubble reactor mode; (a) high-pressure stainless-steel cell; (b) PTFE tubing; (c) PTFE liner; (d) cylindrical cathode; (e) rod-shaped anode; (f) cell holder; (g) sample solution; (h) magnetic stirrer.

were added to the cell. This reaction mixture was flushed with CO_2 for 5 min to remove all dissolved oxygen. Afterwards, CO_2 was charged into the cell to the desired pressure (setup A) or continuous bubbling was maintained during the whole electrosynthesis using a mass flow controller (MFC) (setup B). The galvanostatic electroreduction was carried out under continuous stirring at room temperature, using a dc regulated power supply TS3022S (Thurlby Thandar Instruments, UK). After the desired amount of charge was supplied the solvent was distilled at reduced pressure, the residue was acidified with dilute hydrochloric acid (2 M), and the free acids were extracted with ethyl acetate (2 × 3 mL). The organic phase was washed with distilled water and dried over anhydrous $MgSO_4$. After evaporation of the extraction solvent, a yellow viscous liquid was obtained, containing the product.

Characterization of products

After electrosynthesis, the acid products were methylated using acetyl chloride in dry methanol as described earlier. The products were identified by ^1H NMR and mass spectra. ^1H NMR spectra were recorded on an AVANCE 300 (300 MHz, Bruker, Germany) spectrometer in $CDCl_3$ with Me_4Si as an internal standard. Mass spectra were obtained on a 5973-N spectrometer connected with an HP 6890 gas chromatograph (Agilent, USA) with an apolar HP-5 column.

2-Cyclohexene-1,4-dicarboxylic acid dimethyl ester (methylated 2a). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.58–1.72 (m, 4H, $-CH_2-$), 3.11–3.19 (m, 2H, $>CH(-COOCH_3)$), 3.68 (s, 6H, $-COOCH_3$), 5.42–5.54 (m, 2H, $-CH=$); GC–MS (*m*/*z*, %): 198 (M^+, 0.8), 166 (47.2), 139 (27.6), 123 (2.4), 107 (31.7), 79 (100.0), 67 (4.8), 59 (16.3).

8-Methyl-4-carboxymethyl-3,7-nonadienoic acid dimethyl ester (methylated 2b). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.56 (s, 6H, $-CH_3$), 2.04–2.18 (m, 4H, $-CH_2-$), 3.02–3.06 (d ,2H, $-CH_2(-CH=)(-COOCH_3)$), 3.06 (s, 2H, $-CH_2(-C\leqslant)(-COOCH_3)$), 3.68 (s, 6H, $-COOCH_3$) 5.31–5.62 (m, 2H, $-CH=$); GC–MS (*m*/*z*, %): 254 (M^+, 0.8), 239 (0.8), 222 (8.9), 207 (8.9), 194 (16.3), 180 (16.3), 166 (35.8), 134 (8.9), 121 (13.0), 107 (8.9), 93 (5.7), 85 (13.0), 73 (100.0), 59 (9.8), 41 (16.3).

4,8,12-Trimethyl-5-carboxy-3,7,11-tridecatrienoic acid dimethyl ester (methylated 2c). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.57 (s, 6H, $(CH_3)_2{>}C=$), 1.61–1.73 (m, 6H, $CH_3-C\leqslant$), 2.02–2.19 (m, 6H, $-CH_2-$), 3.05 (d, 2H, $-CH_2(-COOCH_3)$), 3.18 (t, 1H, $>CH(-COOCH_3)$), 3.68 (s, 6H, $-COOCH_3$), 5.31–5.61 (m, 3H, $-CH=$); GC–MS (*m*/*z*, %): 322 (M^+, 4.1), 290 (6.5), 262 (35.0), 247 (9.8), 235 (10.6), 219 (35.8), 207 (48.8), 175 (61.8), 159 (30.9), 147 (43.1), 135 (59.3), 121 (93.5), 107 (65.0), 93 (45.5), 81 (100.0), 69 (77.2), 55 (69.9), 41 (78.9).

8,12-Dimethyl-4-carboxymethyl-3,7,11-tridecatrienoic acid dimethyl ester (methylated 2d). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.57 (s, 6H, $(CH_3)_2 > C=$), 1.63 (s, 3H, $CH_3-C\leqslant$), 2.02–2.19 (m, 8H, $-CH_2-$), 3.03–3.07 (d ,2H, $-CH_2(-CH=)(-COOCH_3)$), 3.07 (s, 2H, $-CH_2(-C\leqslant)(-COOCH_3)$), 3.68 (s, 6H, $-COOCH_3$), 5.31–5.61 (m, 3H, $-CH=$); GC–MS (*m*/*z*, %): 322 (M^+, 4.1), 290 (6.5), 262 (35.0), 247 (9.8), 235 (10.6), 219 (35.8), 207 (48.8), 175 (61.8), 159 (30.9), 147 (43.1), 135 (59.3), 121 (93.5), 107 (65.0), 93 (45.5), 81 (100.0), 69 (77.2), 55 (69.9), 41 (78.9).

1-Methyl-4-isopropyl-2-cyclohexene-1,4-dicarboxylic acid methyl ester (methylated 2e). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.99–1.03 (d, 6 H, $(CH_3)_2{>}C-$), 1.45 (s, 3H, $-CH_3$), 1.54–1.76 (m, 4H, $-CH_2-$), 2.03–2.28 (m, 1H, $-CH(<(CH_3)_2)$), 3.67 (s, 6H, $-COOCH_3$), 5.40–5.54 (m, 2H, $-CH=$); GC–MS (*m*/*z*, %): 254 (M^+, 0.8), 222 (13.8), 194 (100.0), 179 (26.8), 162 (13.8), 147 (17.1), 135 (53.6), 119 (15.4), 107 (13.8), 93 (46.3), 77 (13.0), 59 (9.7), 43 (13.8).

2,5-Dimethyl-3-hexenedioic acid dimethyl ester (methylated 2f). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.26 (d, 6H, $-CH_3$), 3.12–3.18 (m, 2H, $>CH(-COOCH_3)$), 3.68 (s, 6H, $-COOCH_3$), 5.63–5.66 (m, 2H, $-CH=$); GC–MS (*m*/*z*, %): 200 (M^+, 10.5), 168 (22.8), 141 (56.9), 125 (18.7), 109 (22.8), 85 (100.0), 67 (17.1), 59 (32.5), 41 (16.3).

9,12-Carboxy-10-octadecenoic acid trimethyl ester (methylated 2g). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, 3H, $-CH_3$), 1.11–1.43 (m, 12H, $-CH_2-$), 1.43–1.55 (m, 4H, $-CH_2(-CH_2CH<)$), 1.55–1.67 (m, 2H, $-CH_2(-CH_2COOCH_3)$), 1.67–1.79 (m, 4H, $-CH_2(-CH<)$), 2.30 (t, 2H, $-CH_2(-COOCH_3)$), 2.95–3.00 (m, 2H, $>CH(-COOCH_3)$), 3.67 (s, 9H, $-COOCH_3$), 5.50–5.54 (m, 2H, $-CH=$).

Results and discussion

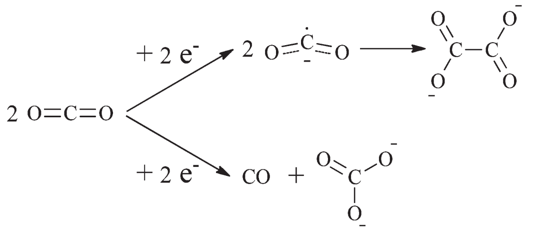
Electrocarboxylation of 1,3-cyclohexadiene

In order to evaluate the relative reactivity of various diene types, one first needs to establish the optimal reaction conditions for a reference compound. 1,3-Cyclohexadiene (**1a**) was chosen as a model compound for a short optimization of the electrosynthesis parameters. The choice of electrode material is of great importance in the electrocarboxylation

Table 1 Electrocarboxylation of 1,3-cyclohexadiene: influence of various reaction parameters[a]

Entry	Cathode	$p\mathrm{CO_2}$ (bar)	Q^b (F mol^{-1})	Yield^c (%)	η^d (%)
1	Ta	5	3.0	18	12
2	Pt	5	3.0	28	19
3	Cu	5	3.0	63	42
4	SS	5	3.0	88	58
5	Ni	5	3.0	96	64
6[e]	Ni	5	3.0	79	52
7	Ni	3	3.0	89	60
8	Ni	10	3.0	85	57
9	Ni	20	3.0	57	38
10	Ni	5	2.0	79	79
11	Ni	5	2.5	93	75
12	Ni	5	4.0	99	49

[a] Solvent: DMF; supporting electrolyte: TBABr (0.05 mol dm^{-3}); anode: Mg; reactant concentration: 0.2 mol dm^{-3}; current density: 10 mA cm^{-2}. [b] Amount of charge. [c] Yield calculated based on initial amount of 1,3-cyclohexadiene. [d] Current efficiency. [e] Anode: Al.



Scheme 2 Cathodic formation of oxalate, carbon monoxide and carbonate.[58]

process. Table 1 (entries 1–6) shows the results obtained with different cathodes (Ta, Pt, Cu, stainless steel, Ni) and anodes (Mg, Al) in DMF as the solvent. It has been reported that tantalum in combination with a nickel(0) catalyst has potential for CO_2 incorporation;[69] the high overvoltage for hydrogen formation could be interesting in lowering the water sensitivity of these reactions. Platinum, which easily produces hydrogen from water, was used as reference. However, both Ta and Pt cathodes gave **2a** in very poor yields. Electroreduction of CO_2 in protic non-aqueous media mainly forms carbon monoxide at a Pt or Ni cathode, while a Cu cathode mostly gives hydrocarbons like methane and ethylene, and Fe and Cr cathodes predominantly form oxalic acid.[2] When using these metals as cathodes in the aprotic electrocarboxylation of 1,3-cyclohexadiene the yield increases in the following order: Pt < Cu < stainless steel (Fe/Cr/Ni = 74 : 18 : 8) < Ni. Nickel gives similar CO_2 reduction products as platinum in protic media, but gives excellent diene electrocarboxylation yields in aprotic media. These results show that there is no direct relation between the product selectivities of these cathodes in both types of reaction media. The superior results with nickel suggest that the electrocarboxylation on the cathode surface is not only dependent on the rate of electroreduction of CO_2 itself, but that a mechanism is operative in which dienes are activated towards CO_2 incorporation, with nickel being a superior surface for this process. This is in agreement with literature results where nickel(0) complexes were used to improve the electrocarboxylation of conjugated dienes.[24,54,58] A possible explanation for the beneficial effect is the strong but reversible adsorption of conjugated dienes on nickel.[72] Magnesium as an anode material gave better results than aluminum when working with a CO_2 pressure of 5 bar and at a current density of 10 mA cm^{-2}. Magnesium is more easily oxidized than aluminium, thus requiring a lower cell potential, which, under these reaction conditions, eliminates undesirable redox reactions like decomposition of the supporting electrolyte or solvent. Using a nickel cathode and a magnesium anode seems the best combination to favor dicarboxylation. This result also agrees well with literature where a positive effect of Mg^{2+} ions on the Ni(0)-catalyzed electrochemical incorporation of CO_2 into unsaturated bonds was found.[32] Employing a nickel cathode eliminates the need for an additional metal catalyst, thus simplifying the process.

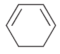
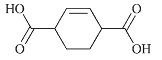
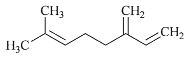
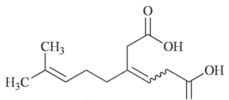
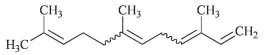
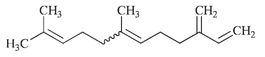
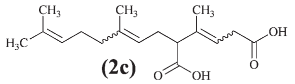
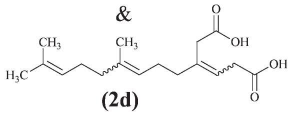
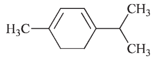
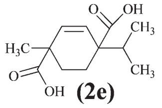
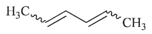
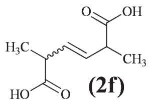
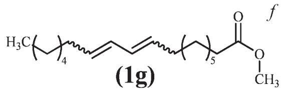
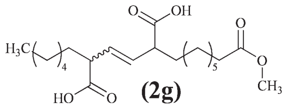
With a nickel cathode and a magnesium anode as the most promising combination, the effect of CO_2 pressure on the carboxylation yield was investigated (Table 1, entries 5, 7–9). The electrosynthesis was carried out under different CO_2 pressures with a constant current density of 10 mA cm^{-2} until an optimum CO_2 pressure of 5 bar was found. When the CO_2 pressure was lowered to 3 bar, a decrease in current efficiency was observed. A possible reason is the lower concentration of dissolved CO_2 at reduced pressures. This gives rise to an increased voltage between cathode and anode when working at a constant current density, which in turn causes the aforementioned side reactions. Increasing the CO_2 pressure to 10 bar and higher also decreased the carboxylation yield. At these elevated pressures there is an increased production of oxalates, carbon monoxide and carbonates (Scheme 2). The corresponding oxalate and carbonate magnesium salts precipitate on the electrode surface during electrosynthesis, and this in turn gradually raises the cell potential.

The electrocarboxylation yield for 1,3-cyclohexadiene was further optimized by passing various amounts of charge through the cell (Table 1, entries 5, 10–12). Dicarboxylation of conjugated dienes is a two-electron reduction, which means that the theoretical charge required is 2 F mol^{-1}. Since the diene concentration decreases as the reaction proceeds, the formation of undesired products like oxalate, carbon monoxide and carbonate gradually increases. Hence raising the amount of charge applied to the system maximizes the yield of desired product, while lowering the current efficiency. An ideal compromise between yield and current efficiency was found when using 2.5 F mol^{-1}.

Electrocarboxylation of various conjugated dienes

Next, the optimized system for 1,3-cyclohexadiene carboxylation was used to examine the effect of molecular configuration and alkyl substitution on CO_2 incorporation into conjugated double bonds of mostly renewable compounds. Besides 1,3-cyclohexadiene (**1a**), myrcene (**1b**), α- and β-farnesene (**1c** + **1d**), α-terpinene (**1e**), 2,4-hexadiene (**1f**) and CLAME (**1g**) were used as substrates. These reactants, their corresponding products and reaction conditions are listed in Table 2. Special attention was paid to the importance of controlling CO_2 pressure and current density in optimizing the dicarboxylation of less reactive conjugated dienes. Before focusing on

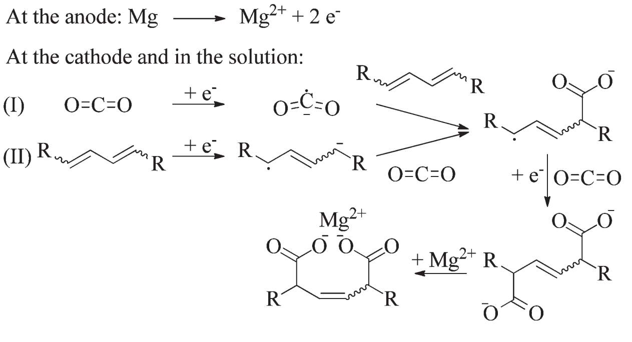
Table 2 Electrocarboxylation of different conjugated dienes: influence of various reaction parameters[a]

Entry	Reactant	Dicarboxylated product	j[b] (mA cm^{-2})	Yield[c] (%)	η[d] (%)
1	 **(1a)**	 **(2a)**	10	96	64
2	 **(1b)**	 **(2b)**	10	93	62
3	 **(1c)** &  **(1d)**	 **(2c)** &  **(2d)**	10	72	48
4	 **(1e)**	 **(2e)**	10	21	14
5	 **(1f)**	 **(2f)**	10	52	34
6[e]			10	28	19
7[e]			5	74	49
8	 **(1g)** [f]	 **(2g)**	10	—	—
9			2	15	10
10[e]			2	46	37

[a] Solvent: DMF; supporting electrolyte: TBABr (0.05 mol dm^{-3}); cathode: Ni; anode: Mg; pCO_2 = 5 bar; reactant concentration: 0.2 mol dm^{-3}. [b] Current density. [c] Yield calculated based on initial amount of conjugated diene. [d] Current efficiency. [e] pCO_2 = 1 atm (10 mL min^{-1}). [f] Representative formula: the starting compound contains the following fatty acid methyl esters: 0.2% C8, 0.1% C10, 0.1% C11:1, 0.1% C12, 1.7% C16, 1.6% C18, 6.5% C18:1, 26.4% C18:2 (non-conjugated), 61.0% C18:2 (conjugated), 0.4% C18:3, 0.2% C22:1, 0.5% C18:1 OH, 1.2% other.

the results, it is relevant to sketch the mechanisms proposed so far for the electrocarboxylation of conjugated dienes.[55,56] There are two different hypotheses on the reduction mechanism as shown in Scheme 3. In one view the cathodic reduction of CO_2 is followed by an addition of the $[CO_2\bullet]^-$ anion radical to the diene (mechanism I). The alternative is the electroreduction of the diene to an allyl radical anion which performs a nucleophilic attack on carbon dioxide (mechanism II).[56] It has been suggested that both mechanisms may be operative simultaneously.[55] Since oxalic acid is formed by the dimerisation of two $[CO_2\bullet]^-$ anion radicals and is observed in all reactions as trace product, it is very likely that at least mechanism I is operative.

1,3-Cyclohexadiene with its fixed cyclic conformation containing two *cis* bonds is overall more susceptible towards CO_2 incorporation than the mixture of 2,4-hexadiene isomers (*E*,*E*/*Z*,*E*/*Z*,*Z* = 35 : 43 : 22) (Table 2, entries 1, 5), even at various CO_2 pressures and current densities (Fig. 2). The greater reactivity of 1,3-cyclohexadiene compared to the 2,4-hexadienes could be explained by a difference in adsorption strength on the cathode surface. It is well known that dienes display a strong adsorption on Ni compared to monoenes.[73] In



Scheme 3 Reaction mechanisms (I) and (II) for the electrochemical dicarboxylation of internal conjugated dienes.[55]

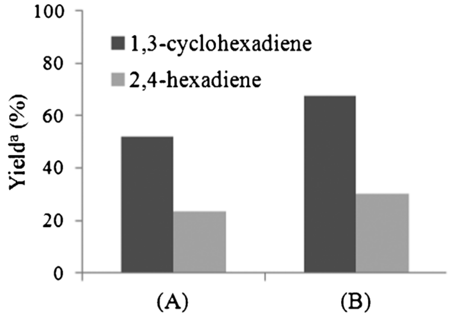


Fig. 2 Competitive reactions of 1,3-cyclohexadiene and 2,4-hexadiene. Solvent: DMF; supporting electrolyte: TBABr (0.05 mol dm^{-3}); cathode: Ni; anode: Mg; diene concentrations: 0.1 mol dm^{-3}; amount of charge: 1 F (mol $diene)^{-1}$; yield calculated based on initial amount of diene. (A) pCO_2 = 5 bar, current density: 10 mA cm^{-2}; (B) pCO_2 = 1 bar, CO_2 flow rate: 10 mL min^{-1}, current density: 5 mA cm^{-2}.

comparison with cyclohexadiene, with its fixed cyclic conformation, the adsorption equilibrium seems less favorable for the linear hexadienes, because the loss of the rotation around the central C–C bond causes a significant decrease in entropy upon adsorption. This line of thought would suggest that dienes undergo the carboxylation according to mechanism II while adsorbed on the surface, either combined or not with mechanism I (Scheme 3). From the changing *E*,*E*/*Z*,*E*/*Z*,*Z* ratio of the remaining hexadiene isomers in the initial phase of the reaction, one calculates that the *E*,*E*-configuration is 1.5 times less reactive than the *Z*,*E*-configuration, which in turn is 1.6 times less reactive than the *Z*,*Z*-configuration. Thus, the diene configuration has a strong stereoelectronic effect on the rate of the dicarboxylation. The competitive reaction of 1,3-cyclohexadiene together with the linear hexadienes shows that the relative reactivity of 1,3-cyclohexadiene *versus* the *E*,*E*/*Z*,*E*/*Z*,*Z*-2,4-hexadiene isomers is 3.5, 2.4 and 1.3 respectively. The fact that 1,3-cyclohexadiene is more reactive even than *Z*,*Z*-2,4-hexadiene proves that besides the configuration of the diene, also the fixed conformation, as in 1,3-cyclohexadiene, increases the reactivity.

The dicarboxylation yield for myrcene is comparable with the one obtained for 1,3-cyclohexadiene (Table 2, entries 1–2). On one hand, the terminal double bond of myrcene has an increased reactivity towards CO_2 incorporation owing to the absence of steric hindrance at the non-substituted $=CH_2$ groups. On the other hand, the rotational freedom of the conjugated system likely results in a weaker adsorption of myrcene than cyclohexadiene. Farnesene yields less dicarboxylated product than myrcene which is most likely due to the presence of a sterically hindered internal double bond in α-farnesene (**1c**) (entries 2–3). In the reactions of myrcene and farnesene, a small fraction of dimeric products was formed. This is in support of mechanism II with activation of the diene, at least for these two reactants; neither can mechanism II be discarded for other reactions, even if no dimerisation products are formed. The electrocarboxylation of α-terpinene gave poor yields. When this result is compared with that for 1,3-cyclohexadiene it is clear that alkyl substitution on the 1- and 4-positions of the conjugated double bond causes a drastic decrease in carboxylation efficiency (entries 1, 4). Actually, the effect of alkyl substitution is not limited to the steric hindrance around the CO_2 incorporation site but also comprises the electron-donating properties of these alkyl chains, making the double bonds less susceptible to a nucleophilic attack by a $[CO_2\bullet]^-$ anion radical (mechanism I) or for a one-electron reduction (mechanism II).

When CLAME was used as the reactant in these optimized conditions, no carboxylation product was observed at all (Table 2, entry 8). Steric hindrance and the electron-donating characteristics of the long alkyl chains may explain this lack of reactivity. In the reactions of internal dienes like 2,4-hexadiene, α-terpinene and CLAME, when working under a CO_2 pressure of 5 bar and a current density of 10 mA cm^{-2}, there was clear evidence for the precipitation of a magnesium carbonate/oxalate layer on the anode material which caused deactivation. Changing the setup from a pressure reactor to a bubble reactor (Fig. 1), while keeping the same current density, gave even worse results for the dicarboxylation of 2,4-hexadiene (entry 6). At these low CO_2 concentrations, maintaining a current density of 10 mA cm^{-2} required too high cell potentials causing electrolysis of the conducting salt. Working at a lower current density with a CO_2 pressure of 5 bar in the CLAME reaction gave only a minor increase in carboxylation yield (entry 9). A carbonate/oxalate layer was still formed on the anode, drastically increasing the voltage between the electrodes. When both the current density and CO_2 pressure were lowered, a significant increase in carboxylation efficiency was observed for both 2,4-hexadiene and CLAME (entries 7, 10). The rationale is that these less reactive substrates require a longer reaction time, which is obtained by lowering the current density, this way avoiding high cell potentials. Another factor is the easy cathodic formation of oxalates, carbon monoxide and carbonates at elevated CO_2 pressures (Scheme 2). These undesired reactions obviously are even more favored when working with less reactive substrates like 2,4-hexadiene and CLAME. When working at atmospheric CO_2 pressure in a bubble reactor, the formation of these by-products is disfavored so the current efficiency increases and the electrodes remain active during the whole electrosynthesis process. An extra advantage of the bubble reactor setup compared to the pressure reactor setup is the enhanced turbulence facilitating mass transport around the electrodes.

Electrocarboxylation of CLAME

With the aim of further increasing the yield of **2g**, the influence of some key factors on the process has been studied. All further electroreductions are carried out at atmospheric CO_2 pressure with a Ni cathode and a Mg anode.

The effect of different solvents on the electrocarboxylation yield of CLAME was examined. Acceptable yields were obtained when CH_3CN was used as solvent (Table 3, entry 2). The main reason for the increase in yield is the better solubility of CLAME, making the reactive groups more accessible for CO_2 incorporation. Other benefits of this solvent compared to DMF are the larger electrochemical window, the higher CO_2 solubility, the lower viscosity and the limited toxicity. The reaction of CLAME in THF yielded no carboxylation product (entry 3), which is probably due to the narrower

Table 3 Electrocarboxylation of conjugated linoleic acid methyl esters: influence of various reaction parameters[a]

Entry	c^b (mol dm^{-3})	Q^c (F mol^{-1})	j^d (mA cm^{-2})	Yield[e] (%)	η^f (%)
1[g]	0.2	2.5	2	46	37
2	0.2	2.5	2	65	52
3[h]	0.2	2.5	2	—	—
4[i]	0.2	2.5	2	45	36
5[j]	0.2	2.5	2	61	49
6	0.1	2.5	2	49	39
7	0.3	2.5	2	45	36
8	0.2	2.0	2	51	51
9	0.2	3.0	2	71	47
10	0.2	3.0	1	31	21
11	0.2	3.0	3	79	53
12	0.2	3.0	5	32	21

[a] Solvent: CH_3CN; supporting electrolyte: TBABr (0.05 mol dm^{-3}); cathode: Ni; anode: Mg; pCO_2 = 1 atm (10 mL min^{-1}). [b] CLAME concentration. [c] Amount of charge. [d] Current density. [e] Yield calculated based on initial amount of CLAME. [f] Current efficiency. [g] DMF as solvent. [h] THF as solvent. [i] TBAI as supporting electrolyte. [j] $TBAPF_6$ as supporting electrolyte.

electrochemical window of this solvent. Room temperature ionic liquids (RTILs) like 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide and 1-butyl-3-methylimidazolium tetrafluoroborate were used as solvent. Working with RTILs as solvent in the dicarboxylation of internal conjugated dienes gave no product, although these solvents can be very useful when starting from activated olefins.[25] The main downside of ionic liquids is their high viscosity which easily causes diffusion-limited reactions. To by-pass this problem, increased temperatures up to 50 °C were used, which lowered the CO_2 solubility and in turn gave increased cell potentials when working with less reactive substrates like CLAME. Because of this increased cell potential, some decomposition of the ionic liquid was observed. A more general disadvantage when employing RTILs in electrocarboxylation reactions with sacrificial anodes is the cumbersome isolation of the product salts due to the non-volatile nature of these solvents.[25,44,46,52]

The electrosynthesis was performed with TBAI, $TBAPF_6$ and TBABr as supporting electrolytes. Tetrabutylammonium was chosen as a cation for its high redox stability. As shown in Table 3 (entries 2, 4 and 5) the yield of **2g** is influenced by the nature of the anion. The total yield decreases in the following order: TBABr $>$ $TBAPF_6$ $\gg$ TBAI.

An optimal CLAME concentration was found at 0.2 mol dm^{-3}. When the electroreduction was conducted with a lower concentration, the yield decreased due to the formation of by-products like oxalates, carbon monoxide and carbonates and the electrochemical decomposition of the supporting electrolyte. Working at a higher concentration also resulted in a decrease of carboxylation efficiency through the precipitation of product salts between cathode and anode leading to an increased cell voltage and a less successful electrosynthesis (Table 3, entries 2, 6 and 7). The results show that using the optimal substrate concentration under well-defined reaction conditions is of great importance.

By varying the amount of charge passed through the cell, the yield and current efficiency of **2g** formation were examined (Table 3, entries 2, 8 and 9). As mentioned before, the practical amount of charge should be higher than the theoretical charge of 2 F mol^{-1}. In this electrocarboxylation reaction of CLAME, the optimal balance between yield and current efficiency was found when using 3 F mol^{-1}.

It seems that the carboxylation yield is very dependent on the current density that is applied (Table 3, entries 9–12). Here also an optimum can be found for the present reaction conditions. When using an optimal current density of 3 mA cm^{-2}, a yield of $\sim$80% and a current efficiency above 50% were reached. Lowering the current density to 1 mA cm^{-2} decreases the cell potential to values below what is needed for the electrocarboxylation. Increasing the current density to 5 mA cm^{-2} increases the voltage between the electrodes leading to undesired reactions.

To emphasize the major advance in comparison with earlier studies, 2,4-hexadiene and CLAME were subjected to the most efficient electrocarboxylation method published until now for conjugated dienes, developed by the group of Jiang.[55] When using that method, 2,4-hexadiene was dicarboxylated with a current efficiency of only 21%, while with CLAME, no dicarboxylation product was observed at all. While Jiang's method is suitable for sterically unhindered dienes, like 1,3-butadiene, or dienes activated by aromatics, like 1,4-diphenylbutadiene, it is not adapted to aliphatic internal conjugated dienes. As a result of the method proposed herein, it is now possible to efficiently carboxylate 2,4-hexadiene and conjugated linoleic acid methyl esters with current efficiencies of 49 and 53%, respectively.

Conclusions

Electroreductive synthesis allows the production of new and complex organic molecules through redox-umpolung of an electroactive group, thus turning an electron-deficient electrophile into an electron-rich nucleophile. This synthetic strategy uses electrons as clean reagents to generate reactive species under mild conditions in contrast with traditional organic chemistry where dangerous and polluting redox agents or high reaction temperatures are required for activation of CO_2.[20] A very simple and efficient electrochemical route for the dicarboxylation of conjugated linoleic acid methyl esters has been developed. Ni as cathode, Mg as anode, CH_3CN as solvent and TBABr as supporting electrolyte were found to be the best experimental parameters for this reaction. A yield of 79% could be achieved at room temperature by supplying 3 F mol^{-1} at 3 mA cm^{-2} to a 0.2 mol dm^{-3} concentration of CLAME, while bubbling CO_2 at atmospheric pressure through the reaction mixture. With both reactants being from renewable sources, no additional catalyst being used and mild reaction conditions being employed, this process agrees well with the principles of green chemistry.

Acknowledgements

This research is funded by the Industrieel Onderzoeksfonds KU Leuven (project IKP/10/005). Dirk De Vos is grateful to KULeuven for support through the Metusalem grant CASAS, and in the frame of IAP 7 Supramolecular Chemistry and Catalysis. The authors are grateful to Oleon for donating the conjugated linoleic acids.

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