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Electrochemical synthesis of carboxylic acids from alkenes using various nickel-organic mediators: CO_2 as C1-synthon[†]

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Direct and mediated electrochemical reductive coupling reactions between alkenes and CO_2 have been studied using an undivided electrochemical cell. Propene and 1-butene were used to study the behavior of monoenes. Propene, in the absence of a mediator, yielded two main products: 2-methyl-butanedioic acid and 3-butenoic acid; from 1-butene, mainly ethenyl-succinic acid and 3-pentenoic acid were generated. As a conjugated diene, 1,3-butadiene was investigated intensively. In the absence of a mediator, 1,3-butadiene was mainly dicarboxylated to give the 1,2- (2-ethenyl-succinic acid) and 1,4-addition product (3-hexene-1,6-dioic acid) and various higher coupling products. Using an NiN3 mediator the reaction between 1,3-butadiene and CO_2 resulted in a preferred generation of the 1,4-addition product: 3-hexene-1,6-dioic acid. Experiments with a Ni-(cyclam) mediator resulted in an increased concomitant generation of a monocarboxylation product: 3-pentenoic acid. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: electrochemistry; reduction; carbon dioxide; synthesis; catalysis; nickel; carboxylic acids

1 INTRODUCTION

In the recent past, increasing numbers of working groups have shown an interest in utilization of CO_2 as C1-synthon in electrochemical synthesis[1–13] because it is a low cost, non-toxic and always available basic compound. In contrast to classical chemical reactions, where CO_2 shows a very low reaction activity, electrochemistry provides the possibility of an easy cathodic activation to a CO_2 radical anion $[CO_2^{\cdot}]^-$ at a potential of -2.21 V vs standard calomel electrode (SCE) in dry DMF.[14] This reactive species can react with weakly activated hydrocarbons like dienes and alkenes to give carboxylic acids. CO_2 can be reduced directly (Fig. 1) at the cathode or indirectly using the Ni(II)/Ni(0) system. The Ni(II)-organic mediator system is reduced to Ni(0) at the cathode. The Ni(0) complex itself reduces CO_2 or the alkene to give carboxylic acids. After the reaction Ni(II) is reduced again at the cathode so that the reaction cycle is closed (Fig. 2). The various Ni(II)-organic mediators used are listed in Table 1.

2 EXPERIMENTAL

All experiments were carried out in a laboratory

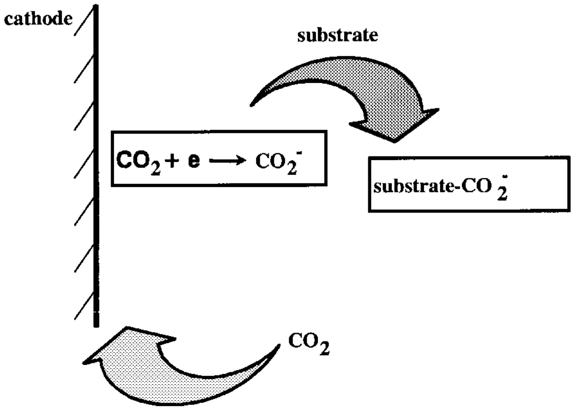

Figure 1 Direct cathodic reduction of carbon dioxide.

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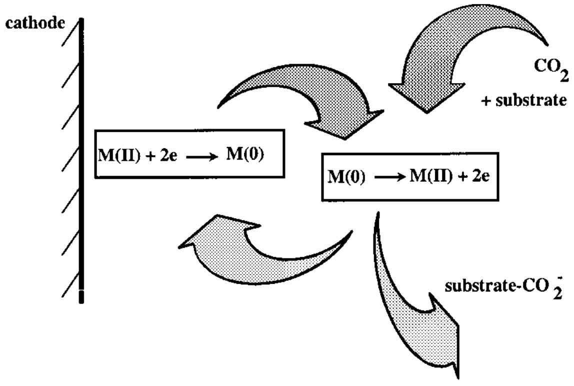


Figure 2 Indirect (mediated) electroreduction of carbon dioxide.

glass cell of 50 ml volume equipped with a tantalum ring cathode and a magnesium rod sacrificial anode (diameter: 10 mm) centered in the middle of the ring cathode (Fig. 3). The electrolyte consisted of 40 ml dried DMF (dried over calcium hydride) and 100 mg *n*-tetrabutylammonium tetrafluoroborate as conducting salt. CO_2 and the gaseous alkenes were bubbled through the solution using medical cannulas. The gas flows (1 ml min^{-1} CO_2, 2 ml min^{-1} alkene) were controlled by an MKS® gas flow controller. In experiments that included mediators 50 mg of the nickel compound was added additionally. A constant current of 50 mA was applied to the electrodes in all experiments at $T = 20$ °C. After each experiment, 250 mg Na_2CO_3 and 2.5 ml CH_3I for full esterification of the generated carboxylic acids was added to the reaction solution, which was stirred overnight. Afterwards the solution was mixed with 10–20 ml 0.1 M HCl and was three times extracted with 50 ml diethyl ether each. Then the ether phase was re-extracted with 50 ml of water for the removal of the conducting salt. The ether phase was reduced to 2–3 ml by evaporation and was directly injected in a Hewlett Packard® G1800A GC/MS for analysis (HP-5 column; length: 25 m; inner diameter, 0.2 mm; layer thickness: 0.33 μm).

Table 1 The Ni(II)-organic mediators

Short name	IUPAC name
NiN3	2,4,4-trimethyl-1,5,9-triazacyclododecence nickel(II) tetrafluoroborate
Ni(homo)	bishomopiperazine nickel(II) tetrafluoroborate
Ni(cyclam)	1,4,8,11-tetraazacyclotetradecane nickel(II) bromide

3 RESULTS

3.1 Coupling of 1,3-butadiene and CO_2

The first experiment on the reductive coupling of CO_2 and 1,3-butadiene was done in a direct way. CO_2 and butadiene were bubbled through the solution and the current was turned on after 10 min. The electrolyte consisted only of DMF and conducting salt. In Fig. 4 the gas-chromatic (GC) spectrum of the reaction products is shown. From the literature the reduction potential of CO_2 is -2.21 V vs SCE, the reduction potential of 1,3-butadiene is -2.6 V vs SCE.[12] Therefore, it was to be expected that CO_2 would be cathodically reduced before butadiene, so that the product spectrum shown in Scheme 1 is probable. In the GC spectrum (Fig. 4) two peaks of the isomeric forms (*Z*-/*E*-) of 3-pentenoic acid (**1**, 7.33 min, 7.44 min, yield: 7.7%) are present, whereas 4-pentenoic acid (**2**) is absent. 2-Ethenyl-succinic acid (**3**, 13.25 min, yield: 4.8%) and *cis*-/*trans*-3-hexene-1,6-dioic acid (**4**, 15.06 min, 15.25 min, yield: 16.4%) were generated as expected. Various dimerization and condensation products are observed between 18 and 21 min.

The next experiment was conducted under the same conditions, with 50 mg Ni(cyclam) as electroreductive mediator. A significant increase in the

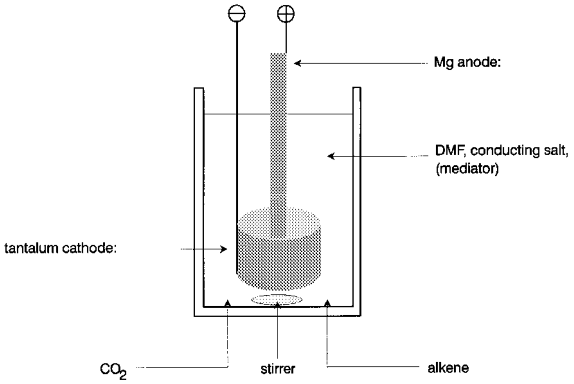


Figure 3 Experimental device for the coupling of alkenes and carbon dioxide.

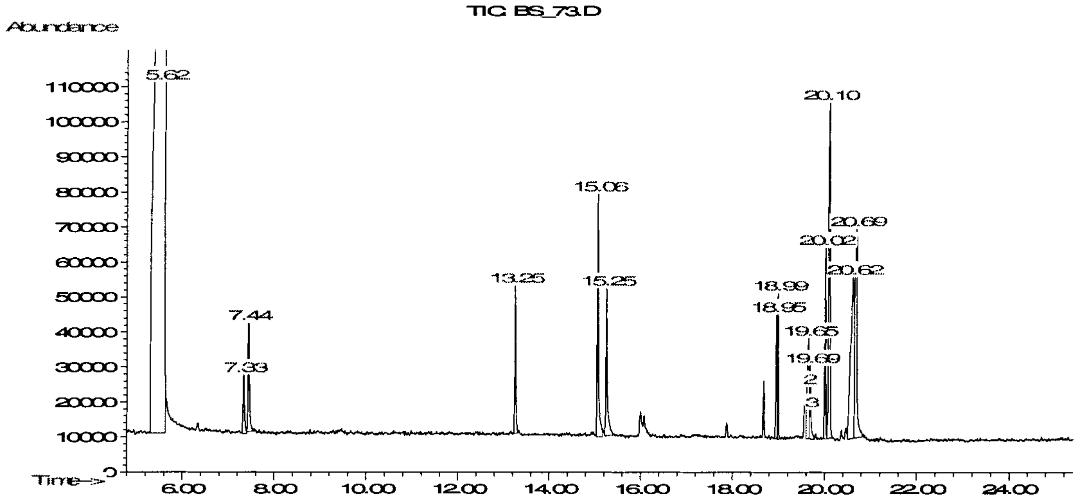
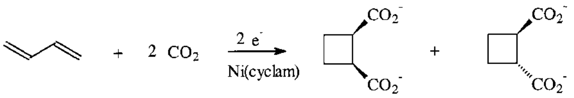


Figure 4 Product contribution for the direct electroreductive coupling of 1,3-butadiene and CO_2. 5.62: solvent, DMF; 7.33: 3-pentenoic acid; 7.44: 3-pentenoic acid (isomer); 13.25: 2-ethenyl-succinic acid; 15.06: *cis*-3-hexene-1,6-dioic acid; 15.25: *trans*-3-hexene-1,6-dioic acid; 18–21: higher coupling products.

production of 3-pentenoic acid compared with the reaction run without mediator could be observed (yield: 28.6%). An overall observation is that the generation of the short-chained mono- and di-carboxylic acids is increased (yields: 30.7% and 30.6% respectively) compared with the higher coupling products. Small amounts of 4-pentenoic acid appeared (yield: 2.1%). Additionally, *cis*- and *trans*-1,2-cyclobutanedicarboxylic acid could be identified (**5, 6**):



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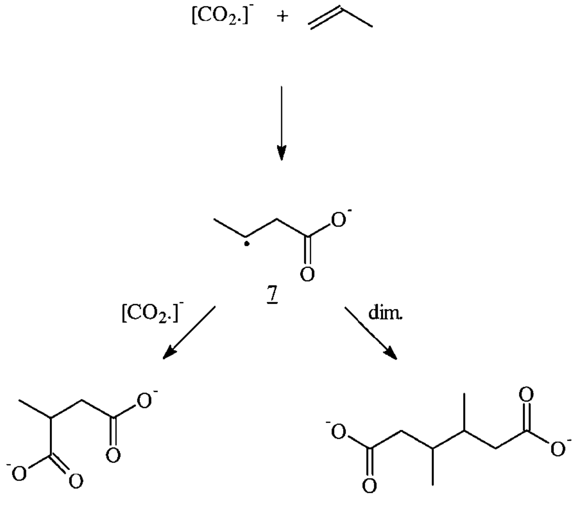
The reaction between CO_2 and butadiene using Ni(homo) as mediator led to the result that the generation of higher coupling products is completely suppressed. Only 3-pentenoic acid (yield: 44.9%), 4-pentenoic acid (yield: 3.3%), 2-ethyl-succinic acid (yield: 9.4%) and 3-hexene-1,6-dioic acid (yield: 29.5%) are generated.

The use of the NiN3 mediator led to a highly selective generation of 3-hexene-1,6-dioic acid (Fig. 5). No higher coupling products could be observed; even the generation of the monocarboxylic acids is suppressed. The yields of 4-pentenoic acid, 2-ethenyl-succinic acid and 3-hexene-1,6-dioic acid are 1.75%, 8.0% and 80.5% respectively.

3.2 Coupling of propene and 1-butene with CO_2

The reaction between propene and a CO_2 radical anion is expected to give first a butanoic acid radical anion (**7**). To that reactive species another CO_2 radical anion can be added to give methyl-succinic acid (**8**) or a dimerization can occur to give 3,4-dimethyl-hexanedioic acid (**9**):



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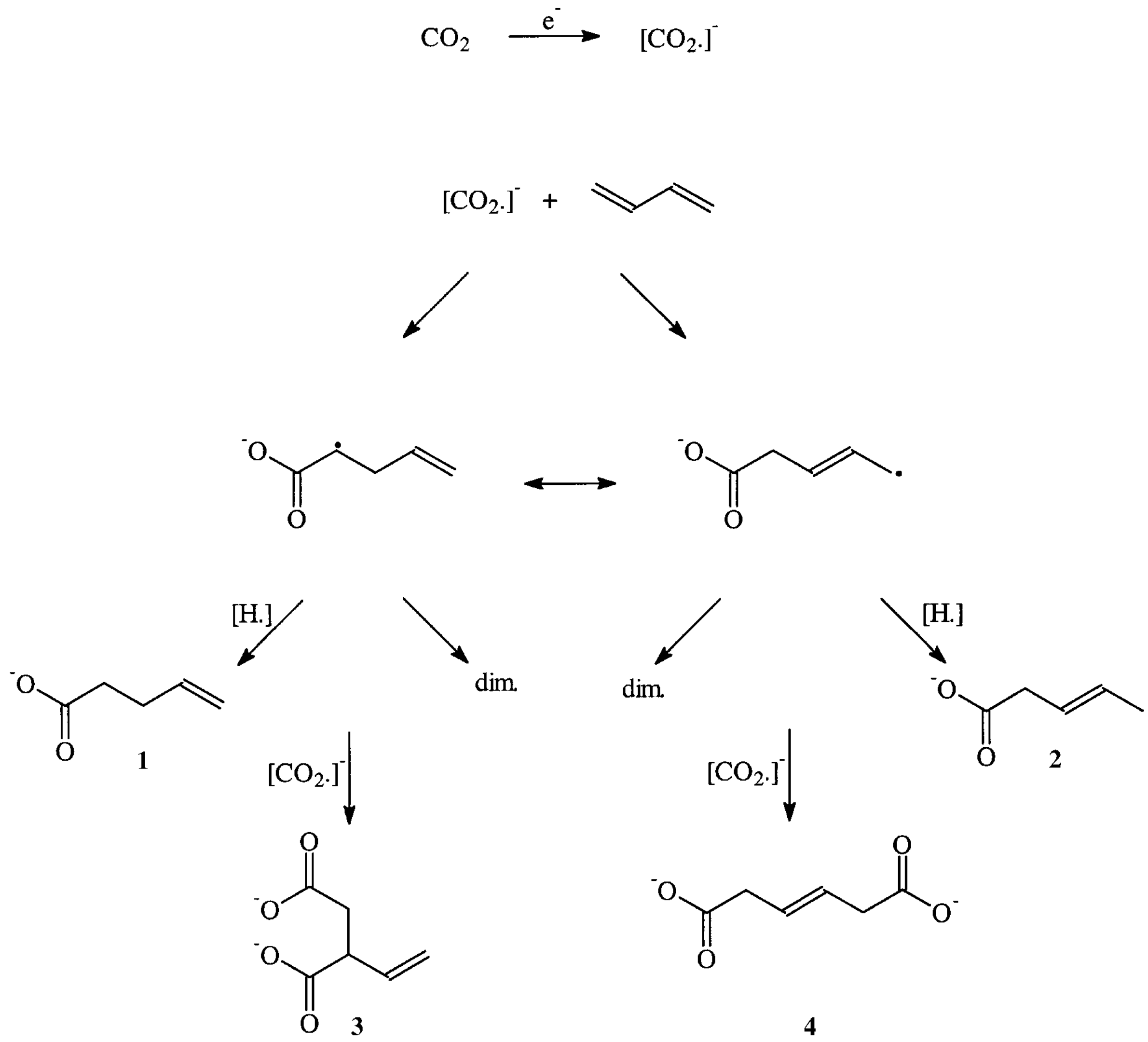
The direct cathodic coupling between propene and CO_2 gave as main products 2-methyl-succinic acid



Scheme 1

(**8**) with a yield of 49% and, unexpectedly, 3-butenoic acid (**10**) with a yield of 38.5%:

10

The mechanism of this reaction is still unrevealed. On the one hand, there is the possibility of a CO_2 insertion in a C—H bond; on the other hand, it could be added to the double bond followed by a hydrogen radical abstraction in position 4.

1-Butene showed the same behavior for the direct electroreductive coupling as propene. Besides small amounts of pentanoic acid and oxalic acid, only ethenyl-succicnic acid (yield: 27.5%) and 3-pentenoic acid (yield: 64%) were generated.

4 CONCLUSION

The present work has shown the feasibility of electroreductive carboxylic acid synthesis from petrochemical basic compounds and CO_2. Unsatu-

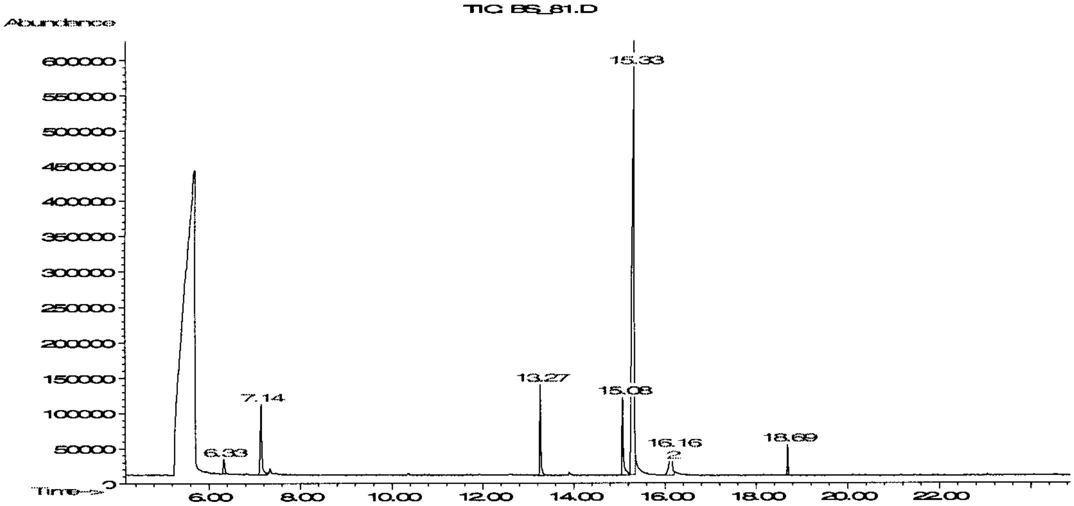


Figure 5 Product contribution for the electroreductive coupling of 1,3-butadiene and CO_2 using NiN3 mediator. 5.67: solvent, DMF; 6.33: 4-pentenoic acid; 7.14: oxalic acid; 13.27: 2-ethenyl-succinic acid; 15.08: *trans*-3-hexene-1,6-dioic acid; 15.33: *cis*-3-hexene-1,6-dioic acid; 16.16: 1,2-cyclobutanedicarboxylic acid; 18.69: conducting salt.

Table 2 Product yields for the reactions

	Yield (%)						
Mediator	3-pentenoic acid	4-pentenoic acid	2-ethenyl-succinic acid	3-hexene-1,6-dioic acid	3-butenoic acid	Methyl-succinic acid	Ethyl succinic acid
Reaction: 1,3-butadience and CO_2							
—	7.7	0	4.8	16.4[a]	—	—	—
NiN3	0	1.75	8.0	80.5	—	—	—
Ni(cyclam)	28.6	2.1	7.8	22.8[a]	—	—	—
Ni(homo)	44.9	3.3	9.4	29.5[a]	—	—	—
Reaction: propene and CO_2							
—	—	—	—	—	38.5	49[b]	—
Reaction: 1-butene and CO_2							
—	64	—	—	—	—	—	27.5[c]

[a] Differences from 100% are higher coupling products and/or oxalic acid.
[b] Difference from 100% is oxalic acid.
[c] Difference from 100% is oxalic acid and pentanoic acid.

rated monocarboxylic acids, like butenoic and pentenoic acid, or unsaturated dicarboxylic acids, like 3-hexene-1,6-dioic acid, are of special interest for the polymer industry. For 1,3-butadiene it was shown that the product spectrum is influenced by nickel-organic mediator compounds. The use of NiN3 suppressed the generation of higher coupling products completely and favored the generation of 3-hexenoic acid with a yield of 80% (Table 2).

The goal of future investigations is the selective coupling of CO_2 to monenes and the elucidation of reaction mechanisms.

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