

Electrochemical Dehydration of Dicarboxylic Acids to Their Cyclic Anhydrides

Johannes Schneider,^[a] Andreas P. Häring,^[a] and Siegfried R. Waldvogel^{1*}[a, b, c]

An intramolecular electrochemical dehydration reaction of dicarboxylic acids to their cyclic anhydrides is presented. This electrolysis allows dicarboxylic acids as naturally abundant, inexpensive, safe, and readily available starting materials to be transformed into carboxylic anhydrides under mild reaction conditions. No conventional dehydration reagent is required. The obtained cyclic anhydrides are highly valuable reagents in organic synthesis, and in this report, we use them in-situ for acylation reactions of amines to synthesize amides. This work is part of the recent progress in electrochemical dehydration,

which – in contrast to electrochemical dehydrogenative reactions for example – is an underexplored field of research. The reaction mechanism was investigated by ¹⁸O isotope labeling, revealing the formation of sulfate by electrochemical oxidation and hydrolysis of the thiocyanate-supporting electrolyte. This transformation is not a classical Kolbe electrolysis, because it is non-decarboxylative, and all carbon atoms of the carboxylic acid starting material are contained in the carboxylic anhydride. In total, 20 examples are shown with NMR yields up to 71 %.

Introduction

Carboxylic anhydrides are highly valuable reagents in organic synthesis, commonly used in acylation reactions of amines for the synthesis of amides.^[1] Amidation reactions like these are of utmost importance in organic synthesis from laboratory to industrial scale,^[2] since amides are among the most common functional groups in medicinal chemistry.^[3] The valorization of carboxylic acids is important because they are naturally abundant, inexpensive, safe, and readily available starting materials.^[4] Due to the reluctant use of fossil feedstock, such valorization must proceed in a renewable manner.^[5] Conventional synthetic approaches to anhydrides require the use of hazardous dehydration reagents, which commonly result in harsh reaction conditions, accompanied by the generation of reagent waste.^[6] Organic electrosynthesis, which is currently experiencing a remarkable renaissance,^[7] offers several advantages that are required for such renewable processes.^[8] Electro-organic reactions are typically carried out under mild reaction

conditions. The use of electricity as inexpensive and universal redox reagent, which should preferably originate from renewable energy sources, prevents the formation of reagent waste.^[9] In 2022, our group reported the first electrochemical synthesis of carboxylic anhydrides directly from carboxylic acids.^[10] In this conceptually new, non-decarboxylative reaction, carboxylic acids are electrochemically dehydrated to their corresponding anhydrides under mild conditions. This finding was rather surprising, since the electrolysis of carboxylic acids, known as the Kolbe electrolysis, had been known and studied already for more than 170 years (Figure 1).^[11] Even more so, it is Herrmann Kolbe's publications from 1848 and 1849 that mark a cornerstone of organic electrosynthesis.^[12] Despite this, an electrochemical dehydration of carboxylic acids had not been reported before. Although electrochemical amide bond formation is a hot topic,^[13] the electrochemical dehydrative electrolysis represents an underexplored field of research, which has only recently received attention.^[14] This is in strong contrast to electrochemical dehydrogenative coupling reactions for example, which have been studied to great extent already.^[15]

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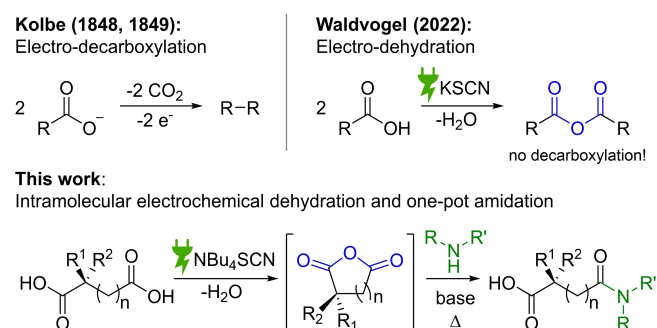


Figure 1. The Kolbe reaction is an electro-decarboxylation, whereas this reaction we reported is a non-decarboxylative dehydrative electrolysis, in which all carbon atoms of the carboxylic acid are preserved in the carboxylic anhydride.

Considering the enormous importance of dehydration reactions in organic synthesis,^[1] electrochemical dehydrations could offer many new interesting reactivities to explore, which will help to eliminate commonly accepted limits and myths about synthetic electrochemistry.^[16]

In this report, we further developed the electrochemical dehydration of dicarboxylic acids for the synthesis of cyclic carboxylic anhydrides. The obtained anhydrides were used in-situ for acylation reactions of amines to synthesize amides that contain an ω -carboxylic acid side chain, which allows for further functionalization.

Results and Discussion

To optimize the reaction, the conditions shown in Table 1 were applied to the test reaction depicted in Figure 2, in which succinic acid is electrochemically dehydrated to succinic anhydride. The yields were determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. It is known from our initial publication that the highest yields are obtained with thiocyanates as supporting electrolytes,^[10] hence NBu₄SCN was chosen as supporting electrolyte in this work, which offers higher solubility with dicarboxylic acids compared with KSCN. The standard reaction conditions (Table 1, entry 1) gave succinic anhydride in 70% yield. Using only 2.4 *F* resulted in a decreased yield of 45% (entry 2). Increasing the amount of applied charge to 3.0 *F* or 3.3 *F* led to 69% (entry 3) and 66% (entry 4), respectively. A current density of 30 mA cm⁻² or 60 mA cm⁻² gave 58% (entry 5) and 59% (entry 6) yield, respectively. An even higher current density of 70 mA cm⁻² combined with a higher amount of applied charge of 3.0 *F* resulted in 64% yield (entry 7). Next, other electrode materials were tested. For glassy carbon as anode material (entry 8), 50% yield was found and for graphite as anode material (entry 9), 50% yield was observed as well. Using BDD (boron-doped diamond)^[17] as metal-free electrode material for both anode and cathode resulted in only 16% yield (entry 10). This underlines the importance of the counter reaction in electro-organic synthesis and optimization.^[18] Based on these results, all further reactions were carried out using BDD as anode material and stainless steel as cathode material. The reaction should be carried out at room temperature because cooling it to 0 °C gave 58% yield (entry 11) and heating it to 60 °C gave 55% yield (entry 12). Diluting the electrolyte to 0.3 mol L⁻¹ succinic acid gave 44% yield (entry 13), while carrying out the reaction at 0.5 mol L⁻¹ resulted in 59% yield (entry 14). Using 0.3 equiv. NBu₄SCN instead of 0.5 equiv. resulted in a lower yield of 31% (entry 15). This could be because thiocyanates can undergo other electrochemical oxidation reactions which do not contribute to electrochemical dehydration.^[19] Increasing it to 1.0 equiv. or 1.5 equiv. gave 71% (entry 16) and 70% (entry 17), respectively. Using the ionic liquids 1-ethyl-3-methylimidazolium thiocyanate (EMIMSCN) or 1-butyl-3-methylimidazolium thiocyanate (BMIMSCN) instead of NBu₄SCN as supporting electrolyte resulted in 36% and 19% yield, respectively (entries 18 and 19). Replacing NBu₄SCN with NH₄SCN (1.0 equiv.) gave only 3%

#	Deviation from standard conditions depicted in Figure 2	NMR yield ^[a]
1	none	70
2	2.4 <i>F</i>	45
3	3.0 <i>F</i>	69
4	3.3 <i>F</i>	66
5	30 mA cm ⁻²	58
6	60 mA cm ⁻²	59
7	70 mA cm ⁻² , 3.0 <i>F</i>	64
8	glassy carbon stainless steel	50
9	graphite stainless steel	50 ^[b]
10	BDD BDD	16
11	0 °C	58
12	60 °C	55
13	1.5 mmol SM, c(SM) = 0.3 mol L ⁻¹	44
14	2.5 mmol SM, c(SM) = 0.5 mol L ⁻¹	59
15	0.3 equiv. NBu ₄ SCN	31
16	1.0 equiv. NBu ₄ SCN	71
17	1.5 equiv. NBu ₄ SCN	70
18	no NBu ₄ SCN, 0.5 equiv. EMIMSCN	36
19	no NBu ₄ SCN, 0.5 equiv. BMIMSCN	19
20	no NBu ₄ SCN, 1.0 equiv. NH ₄ SCN	3 ^[c]
21	no NBu ₄ SCN	0 ^[d]
22	no electricity	0

SM: starting material (dicarboxylic acid). BDD: boron-doped diamond. EMIMSCN: 1-ethyl-3-methylimidazolium thiocyanate. BMIMSCN: 1-butyl-3-methylimidazolium thiocyanate. [a] The yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b] The upper terminal voltage limit of the power supply was reached during electrolysis, nonetheless 2.7 *F* were fully applied. [c] The reaction had to be stopped after 2.1 *F* because of the formation of a precipitate inside of the electrolysis cell, which resulted in blocking of the electrodes. [d] The electrolysis can't be carried out without NBu₄SCN, because the upper terminal voltage limit of the power supply is reached, demonstrating that the thiocyanate supporting electrolyte is indispensable for the reaction.

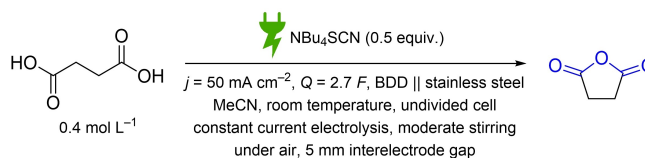


Figure 2. The standard reaction conditions of the test reaction: electrochemical dehydrative reaction of succinic acid to succinic anhydride. More details about the experimental setup can be found in the Supporting Information.

yield (entry 20), and the electrolysis had to be stopped after 2.1 *F* because of the formation of a precipitate inside of the electrolysis cell, which resulted in blocking of the electrodes.

Without any supporting electrolyte (entry 21), the electrolysis cannot be carried out, because the high ohmic resistivity of the electrolyte causes the upper terminal voltage of the power supply to be reached. This demonstrates that the thiocyanate supporting electrolyte is essential for the reaction. Without the application of any electric current, no traces of anhydride product were found (entry 22).

Scope

The anhydrides shown in Figure 3 were obtained from the corresponding commercially available dicarboxylic acids by electrochemical dehydration according to the reaction conditions shown in Figure 2. The yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Succinic anhydride **1** was found in 71% yield, 2-methylsuccinic anhydride **2** in 56% yield, and 2,2-dimethylsuccinic anhydride **3** in 66% yield. Phenylsuccinic anhydride **4** was obtained in 16% yield, and maleic anhydride **5** was found only in traces. *cis*-Cyclopentane-1,2-dicarboxylic anhydride **6** was obtained in 62% yield, and *cis*-cyclohexane-1,2-dicarboxylic anhydride **7** in 57% yield. *cis*-4-Cyclohexene-1,2-dicarboxylic anhydride **8** was observed in 17% yield. The low yields for substrates **5** and **8** could be the result of side reactions of the double bond. (+)-Camphoric anhydride **9** was found in 67% yield, and *cis*-norbornene-*endo*-2,3-carboxylic anhydride **10** was found in 60%. For glutaric anhydride **11**, a yield of 59% was achieved, and 2,2-dimethylglutaric anhydride **12** was observed

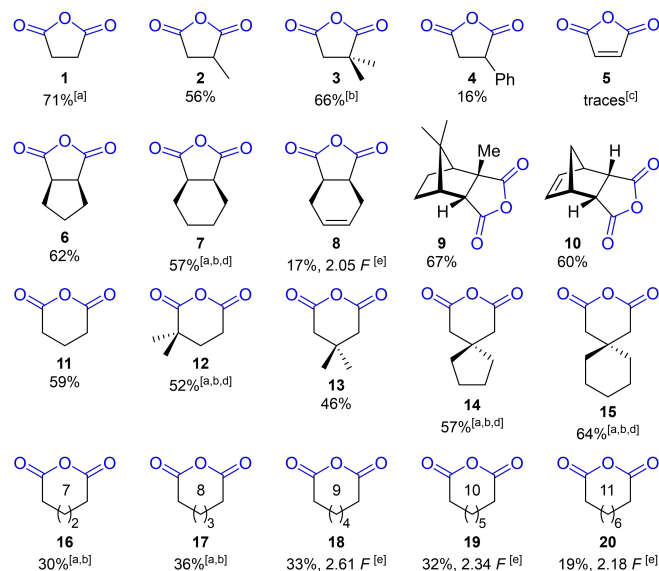


Figure 3. Anhydride scope. The electrolysis conditions of Figure 2 were applied as standard reaction conditions. The yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [a] 1.0 equiv. NBu_4SCN . [b] 3.0 F. [c] The upper terminal voltage limit of the power supply was reached during electrolysis, but 2.7 F of charge were fully applied. [d] $\text{MeCN}/\text{isobutyronitrile}$ 2:1 (vol%). [e] The electrolysis had to be stopped after the mentioned amount of applied charge because of the formation of a precipitate inside of the electrolysis cell, which resulted in blocking of the electrodes.

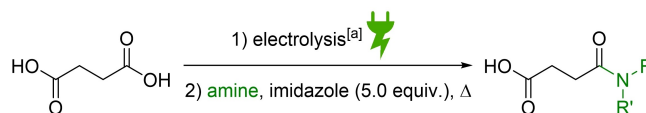


Figure 4. Amidation test reaction. [a] electrolysis reaction conditions: MeCN , succinic acid (0.4 mol L^{-1}), NBu_4SCN (1.0 equiv.) constant current electrolysis, current density $j = 50 \text{ mA cm}^{-2}$, amount of applied charge $Q = 3.0 \text{ F}$, BDD || stainless steel, 5 mm interelectrode gap, under air, moderate stirring. More details can be found in the Supporting Information.

in 52% yield, while 3,3-dimethylglutaric anhydride **13** was found in 46%. 1,1-Cyclopentanediacetic anhydride **14** was found in 57% yield, and 1,1-cyclohexanediacetic anhydride **15** in 64%. For adipic anhydride **16**, pimelic anhydride **17**, suberic anhydride **18**, azelaic anhydride **19**, and sebacic anhydride **20**, yields of 30%, 36%, 33%, 32%, and 19% were obtained, respectively. The yield for substrates **17** to **20** likely decrease because of increasing ring size of the anhydride product. For some substrates in Figure 3, the formation of a precipitate is observed, which could be caused by side reactions of the thiocyanate supporting electrolyte.^[19]

Amide Synthesis

The cyclic carboxylic anhydrides which are obtained by electrolysis were used in-situ for amidation reactions, as depicted in Figure 4. The atom economy of acylation reactions with cyclic anhydrides is beneficial because the reaction product contains a ω -carboxylic acid side chain, which allows for further functionalization, and no reagent waste from the cyclic anhydride is generated during the acylation reaction. To optimize the reaction conditions, benzylamine and morpholine were tested as amines, as shown in Table 2. The yields for benzylamine were higher than the yields for morpholine in all

Table 2. Optimization of the amidation test reaction.

#	Deviation from standard conditions depicted in Figure 4	NMR yield ^[a]
1	benzylamine (5.0 equiv.), no imidazole	68
2	benzylamine (5.0 equiv.)	71
3	benzylamine (5.0 equiv.), no imidazole, DMAP (0.05 equiv.)	73
4	benzylamine (5.0 equiv.), DMAP (0.05 equiv.)	72
5	morpholine (5.0 equiv.), no imidazole	36
6	morpholine (5.0 equiv.)	31
7	morpholine (5.0 equiv.), no imidazole, DMAP (0.05 equiv.)	38
8	morpholine (5.0 equiv.), DMAP (0.05 equiv.)	32

DMAP: 4-(dimethylamino)pyridine. [a] The amide yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. More details can be found in the Supporting Information.

experiments. With 5.0 equiv. of benzylamine and without any additional base, an NMR yield of 68% was found (Table 2, entry 1). When using 5.0 equiv. benzylamine with 5.0 equiv. of imidazole, a slightly higher yield of 71% was found (entry 2). Using no additional base, 5.0 equiv. benzylamine, and 0.05 equiv. of DMAP gave 73% yield (entry 3). The reaction which used 5.0 equiv. benzylamine with 5.0 equiv. imidazole and 0.05 equiv. DMAP resulted in a yield of 72% (entry 4). These four experiments were repeated with morpholine instead of benzylamine, which gave 36%, 31%, 38%, and 32% NMR yield, respectively (entries 5–8). To investigate the scalability of this reaction, a 10-fold scale-up of entry 3 in Table 2 was carried out (see Supporting Information for details), and an NMR yield of 61% was obtained (isolated yield: 58% from succinic acid over two steps).

Reaction Mechanism

The postulated reaction mechanism is depicted in Figure 5. The thiocyanate anion I is likely anodically oxidized to intermediate II, which acts as an electrophile for carboxylate III. The resulting species IV is an active ester and reacts subsequently with another carboxylate. The tetrahedral intermediate V is formed, from which hypothiocyanite VI is eliminated, resulting in the formation of carboxylic anhydride VII. Hypothiocyanite VI can be oxidized further in analogous steps from VIII to cyanosulfite XI, resulting in one more equivalent of anhydride being generated. Cyanosulfite XI can be oxidized further as well in steps from XII to cyanosulfate XV. The mechanism presented here represents a simplified picture, as hypothiocyanite species VI is known to undergo various hydrolysis, comproportionation, and disproportionation reactions.^[20] By ¹⁸O isotope labeling of the dicarboxylic acid, sulfate was unequivocally detected within the mixture upon electrolysis, providing strong evidence for the

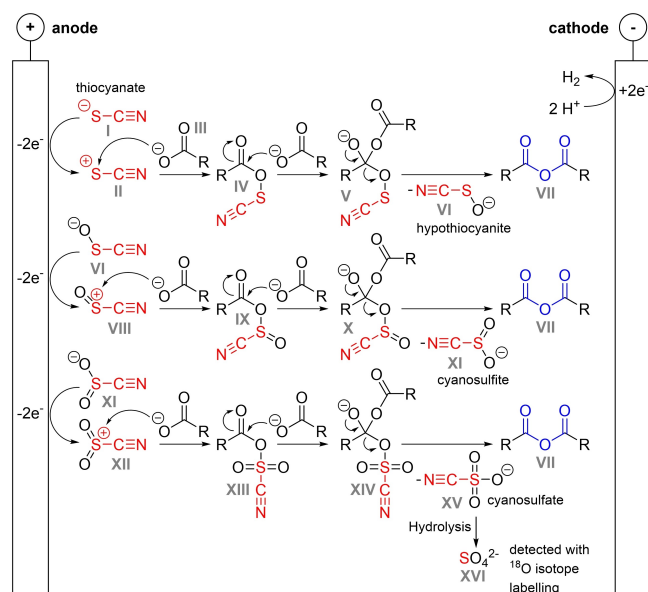


Figure 5. Proposed reaction mechanism.

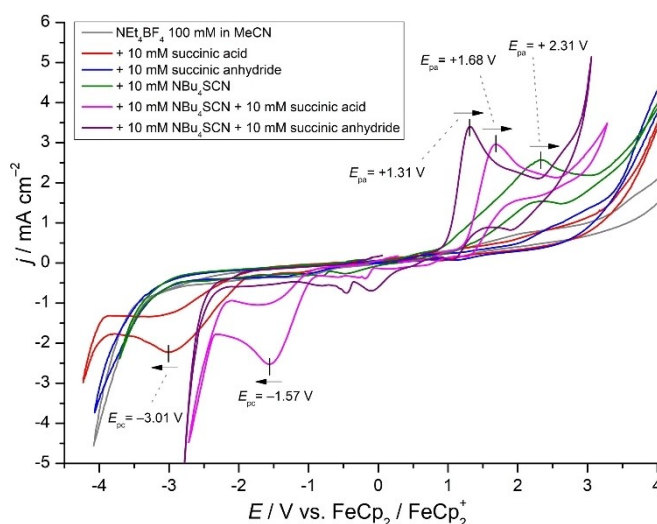


Figure 6. Cyclic voltammetry (CV) measurements. Working electrode: boron-doped diamond (BDD, circular electrode with diameter 2 mm), counter electrode: Pt wire, reference electrode: Ag/AgCl in EtOH/saturated LiCl; Sweep rate: 0.1 V/s. One cycle was measured for each sample starting from 0 V to towards anodic current, then towards cathodic current, and back to 0 V. All CV measurements were carried out under argon atmosphere. Each CV measurement was referenced against ferrocene.

mechanism proposed here. Most likely sulfate XVI is formed from XV by hydrolysis. At the cathode, hydrogen evolution reaction occurs and H₂ was detected by gas chromatography (see Supporting Information). This reaction is not a Kolbe electrolysis, but instead it is a non-decarboxylative electrochemical dehydration reaction. This is another example of the dual role of a supporting electrolyte as reagent and enabler of conductivity.^[21]

CV Measurements

Cyclic voltammetry (CV) measurements are depicted in Figure 6. For succinic acid and succinic anhydride, no anodic current peak is observed. The solution of NBu₄SCN shows an anodic current peak at +2.31 V. Notably, this peak shifts towards +1.68 V for NBu₄SCN mixed with succinic acid, and to +1.31 V in solution of NBu₄SCN with succinic anhydride. This observation indicates that there could be formation of a species which facilitates electron transfer. Succinic anhydride does not show a cathodic current peak and neither does NBu₄SCN. Succinic acid shows a cathodic current peak at –3.01 V, and the cathodic current peak for succinic acid mixed with NBu₄SCN shifts towards –1.57 V.

Conclusions

A method for the electrochemical dehydration of dicarboxylic acids to their cyclic carboxylic anhydrides was established. In this reaction, two carboxylic acid moieties are electrochemically dehydrated to their cyclic anhydride. This method allows

conversion of naturally abundant, inexpensive, safe, and readily available dicarboxylic acids as starting into anhydrides as highly valuable compounds. The cyclic anhydrides obtained by electrolysis were employed in-situ for amide synthesis. The mechanism of the reaction was investigated by mass spectrometry, cyclic voltammetry, and isotope labeling, revealing the anodic oxidation and hydrolysis of the thiocyanate supporting electrolyte as driving force for the dehydration. This reaction is not a classical Kolbe electrolysis, because it is a non-decarboxylative, and all carbon atoms of the dicarboxylic acid starting material are conserved in the cyclic anhydride. This work is part of the recent progress in the underexplored field of electrochemical dehydration reactions. Considering the importance of dehydration reactions in organic synthesis, electrochemical dehydrations could offer many new avenues to explore. This will open-up fields wherein electrosynthesis was not previously considered as future technology.

Supporting Information

Detailed information on general procedures, reaction optimization, and mechanistic studies can be found in the Supporting Information. The authors have cited additional references within the Supporting Information.^[22]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: electrolysis · anhydrides · carboxylic acids · dehydrative reaction · green chemistry

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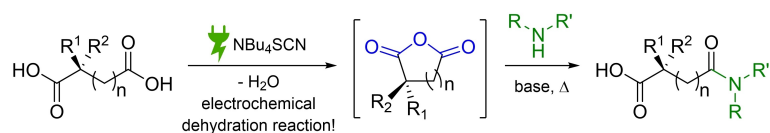
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RESEARCH ARTICLE



An electrochemical dehydrative reaction of dicarboxylic acids to their cyclic anhydrides is presented. The electrochemically generated anhydrides can be directly employed for

amidation reactions. The mechanism of the reaction was investigated by ¹⁸O isotope labeling, revealing the formation of sulfate during electrolysis.

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