Supplementary Information

Electrochemical transformation of D,L-glutamic acid into acrylonitrile

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Contents

1.		Additional results	3
	i.	Nitrile formation by electro-oxidative decarboxylation	3
	ii.	Non-Kolbe electrolysis to acrylonitrile	4
2.		Experimental	12
	i.	General procedure	12
	ii.	Procedure of the electro-oxidative decarboxylation	13
		Electro-oxidative decarboxylation of L-glutamic 5-methylester	13
		Electro-oxidative decarboxylation of D,L-glutamic acid	13
	iii.	. Saponification of 3-cyanopropanoic acid methyl ester (CME)	14
	iv.	. Non-Kolbe electrolysis of 3-CP	14
		Variation of current density, Faraday equivalents and substrate concentration	14
		Stability of acrylonitrile in reaction mixture	15
		Stability of acrylonitrile during non-Kolbe electrolysis	15
		Stabilisation of acrylonitrile during non-Kolbe electrolysis	15
		Non-Kolbe electrolysis of acrylonitrile in presence of a bromide source	16
	v.	Nuclear magnetic resonance spectroscopy	17
	vi.	. Materials	18
3.		Literature	19

1. Additional results

i. Nitrile formation by electro-oxidative decarboxylation

In the following, additional information is given that supports our discussion.



Figure S 1: General illustration of the electro-oxidative decarboxylation by *in-situ* generated hypobromite (BrO⁻) that serves as oxidising agent. (WE: working electrode, CE: counter electrode).



Figure S 2: Inorganic solid deposition growing from the CE to the WE during mediated electro-oxidative decarboxylation of 3-CP with NaBr. (Conditions: Pt-Ti; solvent: MeOH-d₄:D₂O (4:1); L-glutamic acid 5-methyl ester: 0.2 M (1 eq.); NaBr: 0.3 M (1.5 eq.); f = 80 mA cm⁻²; T = 0 °C; $F_{eq} = 5.2$).



Figure S 3: Left: Initial substrate solution containing D,L-glutamic acid ($c = 0.2 \text{ mol } L^{-1}$: 0.1030 g, 0.7 mmol, 1 eq.) and ammonium bromide ($c = 0.3 \text{ mol } L^{-1}$: 0.1028 g, 1.05 mmol, 1.5 eq.). A 4:1 mixture of MeOH-d₄ (2.8 mL) and D₂O (0.7 mL) was used as solvent. *Right*: Product solution directly after electrolysis. The sediment was identified as substrate. (Electrolysis conditions: T = 0 °C; electrode pair: Pt-Ti; $F_{eq} = 2$; $j = 80 \text{ mA cm}^{-2}$; stirring).



Figure S 4: ¹H-NMR spectrum of D,L-glutamic acid in the presence of 1 eq. KOH (Spectrum 1). Spectrum 2 describes the product solution after electrolysis in D₂O. 2 eq. of KOH were added after electrolysis. Spectrum 3 visualises the product sample when 2 eq. of KOH were added to the substrate solution and then electrolysis was performed. After electrolysis, 2 more eq. of KOH were added for NMR. Spectrum 4 describes the product 3-CP after work-up obtained by the saponification reaction of CME. Solvent: D₂O. (Electrolysis conditions: D,L-glutamic acid (0.1030 g, 0.7 mmol, 1 eq.); NH₄Br (0.1028 g, 1.05 mmol, 1.5 eq.); $V(D_2O) = 3.5$ mL; sample of spectrum 3: KOH (0.0785 g, 1.4 mmol, 2 eq.); T = 0 °C; electrode pair: Pt-Ti; $F_{eq} = 2$; j = 80 mA cm⁻². Saponification of CME: sample of spectrum 4: CME (0.838 mL, 8 mmol, 1 eq.); KOH (0.4489 g, 8 mmol, 1 eq.); $V(H_2O) = 20$ mL; t = 60 min; T = 60 °C).

ii. Non-Kolbe electrolysis to acrylonitrile

Kolbe and non-Kolbe electrolysis describe the anodic oxidation of carboxylates. After a first single electron transfer, an instable acyloxy radical is formed. The instability leads to a decarboxylation and a primary alkyl radical is formed. Dimerisation of these primary alkyl radicals results in the Kolbe product (**Scheme S 1**). On the other hand, a further oxidation of the primary alkyl radical can take place, leading to a carbocation. The carbocation can react with nucleophiles like hydroxide ions, alcohols, or water, resulting in the Hofer-Moest product (alcohols or ether). When a β -H-elimination occurs, a vinyl product is formed, which is called non-Kolbe product.^{1, 2}



Scheme S 1: Mechanism of the formation of Kolbe, non-Kolbe and Hofer-Moest products.

Since the formation of the non-Kolbe product proceeds *via* a carbocation intermediate, the product solution of 3-CP electrolysis contains the Hofer-Moest products 3-hydroxypropanenitrile and 3-methoxypropanenitrile (**Figure S 5**). Moreover, also the formation of oligoacrylonitrile was observed.



Figure S 5: ¹H-NMR spectrum of the product solution after applying non-Kolbe electrolysis to 3-CP. The spectrum confirms the formation of acrylonitrile (green box), of the Hofer–Moest products 3-methoxypropanenitrile (grey box) and 3-hydroxypropanenitrile (red box), as well as the formation of oligomers of acrylonitrile (blue box). The substrate 3-CP (purple) is also visible, visualising that the substrate was not fully converted. (Conditions for the electrolysis: 3-CP (0.0347 g, 0.25 mmol, 1 eq.); V(MeOH-d_4) = 3.5 mL; T = 0 °C; electrode pair: C_{gr} -Ti; $F_{eq} = 1$; j = 40 mA cm⁻²; stirring).

In general, two different reactions can yield oligomers, namely the anionic or the radical oligomerisation of acrylonitrile.^{1, 3} To investigate whether an anionic oligomerisation was present at a pH of 8.6, destabilised acrylonitrile was added to the reaction solution consisting of 3-CP (0.071 M) in MeOH-d₄. The solution was stirred for 40 min (typical electrolysis time) at 0 °C and afterwards the reaction mixture was analysed. Nevertheless, the product solution did not show oligomer formation, illustrating that anionic oligomerisation did not take place (**Figure S 6**).



Figure S 6: Stability test of acrylonitrile under electrolysis conditions without the application of a current. The solution was stirred for 40 min, afterwards the ¹H-NMR spectrum was recorded. Acrylonitrile is marked by the green box, while 3-CP is highlighted by the purple box. No oligomer signals are visible. (Conditions: 3-CP (0.0366 g, 0.267 mmol) was dissolved in 3.5 mL MeOH-d₄. Destabilised acrylonitrile (0.256 mmol) was added. The solution was stirred for 40 min at 0 °C.).

The nature of the oligomerisation mechanism was investigated by adding destabilised acrylonitrile to the substrate solution of 3-CP (0.071 M) dissolved in MeOH-d₄ and performing the non-Kolbe electrolysis. As shown in **Figure S 7**, an increasing of the oligomer signals was observed, illustrating the instability of acrylonitrile under electrolysis conditions. According to Schäfer, the radical polymerisation can be initiated by the formed acyloxy radical (**Figure S 8**).¹

The acyloxy radical is not that stable and therefore highly reactive. The free radical polymerisation or oligomerisation takes place until a termination reaction occurs.^{1, 3}



Figure S 7: Electrochemical stability of acrylonitrile, when non-Kolbe electrolysis conditions are applied. Spectrum a) (1) describes the product sample after electrolysis of 3-CP without additional acrylonitrile. Spectrum b) (2) describes the product sample after electrolysis of 3-CP in presence of destabilised acrylonitrile. Oligomer peak increased, verifying the electrochemical instability of acrylonitrile. (a) + b): 3-CP (0.0366 g, 0.267 mmol, 1 eq.); V(MeOH-d_4) = 3.5 mL; T = 0 °C; electrode pair: C_{gr} -Ti; $F_{eg} = 0.93$; j = 40 mA cm⁻²; stirring; b): 0.2 mL destabilised acrylonitrile were added to the sample).



Figure S 8: Based on the instability of acrylonitrile under electrolysis conditions, we propose a radical pathway for oligomerisation. A possible initiator for the radical oligomerisation reaction can be the formed acyloxy radical which reacts with already formed acrylonitrile. The oligomerisation reaction proceeds until a termination reaction occurs.

It was found that also the applied current density has an impact on the oligomer formation. Decreasing the current density resulted in an increasing of the oligomer signals (**Figure S 9**).



Figure S 9: Comparison of the ¹H-NMR spectra with focus on the oligomer peaks. The samples were obtained from the non-Kolbe electrolysis of 3-CP at current densities of 20 (red) and 40 mA cm⁻². Conditions of electrolysis: C_{gr} -Ti; solvent: MeOH-d₄; 3-CP: 0.071 M; F_{eq} = 1.0; stirring; T = 0 °C.

Based on this, it becomes clear that the formed acrylonitrile must be stabilised. So, we tested the impact of different inhibitors or retarders for radical polymerisation reactions such as phenothiazine (PTZ), monomethyl ether hydroquinone (MEHQ) or the combination of MEHQ and oxygen (**Figure S 10**; **Figure S 11**). The combination of MEHQ and oxygen was investigated as they show a synergistic inhibition effect in retarding a polymerisation.⁴⁻⁶

Using PTZ showed no enhanced stabilisation effect on acrylonitrile (**Figure S 10**; **Figure S 11**, spectrum 1 vs. 2). This is explainable by the fact that PTZ is electrochemically instable and gets oxidised at the anode.⁷



Figure S 10: Impact of the inhibitor or retarder on the acrylonitrile formation illustrated by yield (Y) and selectivity (S) achieved. Superscript *c* stands for acrylonitrile. Furthermore, the carbon balance (C.B.) and the substrate conversion (X) are shown. (3-CP ($c_{sub} = 0.076 \text{ mol } L^{-1}$: 0.0366 g, 0.267 mmol) was dissolved in 3.5 mL MeOH-d₄. 0.09 equivalents (eq.) of the inhibitor PTZ or retarder MEHQ, based on the amount of substrate, were added to the substrate solution. When oxygen was used, it was passed continuously through the solution with a 20 min pre-run and shut off after electrolysis was complete. Further reaction conditions: T = 0 °C; electrode pair: C_{gr} -Ti; $F_{eq} = 0.93$; $j = 40 \text{ mA cm}^{-2}$; internal standard for ¹H-NMR: 1,3,5-trioxane).



Figure S 11: Impact of the retarder/inhibitor on the oligomer formation visualised by stacked ¹H-NMR spectra. (3-CP ($c_{sub} = 0.076 \text{ mol } L^{-1}$: 0.0366 g, 0.267 mmol) was dissolved in 3.5 mL MeOH-d₄. 0.09 eq. of the inhibitor PTZ or retarder MEHQ, based on the amount of substrate, were added to the substrate solution. When oxygen was used, it was passed continuously through the solution with a 20 min pre-run and shut off after electrolysis was complete. Further reaction conditions: T = 0 °C; electrode pair: C_{gr} -Ti; $F_{eq} = 0.93$; $j = 40 \text{ mA cm}^{-2}$; internal standard for ¹H-NMR: 1,3,5-trioxane).

Application of MEHQ increased the yield by around 3% while the selectivity of acrylonitrile formation increased by 7% compared to the inhibitor free experiment. The best performance was achieved by using the combination of oxygen and MEHQ. The selectivity was increased to 44% (\pm 6%), while the oligomer formation was reduced (**Figure S 11**, spectrum 1 *vs.* 4).

As the combination of MEHQ and oxygen showed reduced oligomer formation, the next step focused on the increase of the acrylonitrile yield by increasing the amount of current passed through the cell in the presence of MEHQ and oxygen. This should increase the conversion of 3-CP and if the oligomer formation can be suppressed the yield acrylonitrile should be increased. As expected, increasing the Faraday equivalents (F_{eq}) increased the conversion of 3-CP, but the yield of acrylonitrile as well as the carbon balance (C.B.) decreased (**Figure S 12**). This visualises that increasing the yield of acrylonitrile at high conversion rates was not successful.



Figure S 12: Impact of the applied Faraday equivalents (F_{eq}) on product formation in the presence of 0.09 eq. MEHQ and oxygen, visualised in terms of yield (Y) and selectivity (S) measured. Superscript *c* stands for acrylonitrile. Furthermore, the carbon balance (C.B.), the substrate conversion (X), and the current efficiency (C.E.) are shown. (3-CP ($c_{sub} = 0.076 \text{ mol L}^{-1}$: 0.0366 g, 0.267 mmol) was dissolved in 3.5 mL MeOH-d₄. 0.09 eq. of the retarder MEHQ, based on the amount of substrate, were added to the substrate solution. Oxygen was passed continuously through the solution with a 20 min pre-run and shut off after electrolysis was complete. Further reaction conditions: T = 0 °C; electrode pair: C_{gr} -Ti; $F_{eq} = 0.93$, 1.86 or 2.79; $j = 40 \text{ mA cm}^{-2}$; internal standard for ¹H-NMR: 1,3,5-trioxane).

Figure S 13 shows the effect of the amount of current passed through the cell when no inhibitor or retarder was used by highlighting the intensity of the oligomer signals. Increasing the amount of electricity led to an increase of the oligomer signal intensities.



Figure S 13: Effect of the amount of electricity passed through the cell on the formation of oligoacrylonitrile. Oligomer formation is an undesired side reaction in the non-Kolbe electrolysis of 3-CP. Stacked ¹H-NMR spectra are shown, whereby 1,3,5-trioxane was used as internal standard. Electrolysis conditions: C_{gr} -Ti; solvent: MeOH-d₄; 3-CP: 0.071 M; stirring; T = 0 °C.

A similar trend was observed before, as the variation of F_{eq} in the presence of MEHQ and oxygen was studied. Trials to reduce the probability for a bimolecular reaction by adding foreign anions such as tetrabutylammonium perchlorate were not successful as under the used conditions a precipitation occurred (**Figure S 14**). The sediment was also present after electrolysis and contained unconverted substrate (**Figure S 15**). The formation of the sediment made the analytics difficult and therefore this was not further investigated.



Figure S 14: Solubility test of tetrabutylammonium perchlorate with and without the presence of 3-CP.



Figure S 15: ¹H-NMR spectrum of the sediment after non-Kolbe electrolysis of 3-CP when tetrabutylammonium perchlorate was used as additive to reduce the amount of surface radicals during electrolysis. The sediment displays beside the presence of unconverted 3-CP. Electrolysis conditions: C_{gr} -Ti; solvent: MeOH-d₄; 3-CP: 0.071 M; F_{eq} = 4.76; stirring; T = 0 °C.

The one-pot synthesis of acrylonitrile was not successful, as the presence of bromide anions inhibited the conversion of 3-CP. A suggestion why 3-CP was not converted in the presence of bromide anions is visualised in **Figure S 16**.



Figure S 16: Explanation for the observation why acrylonitrile was not formed in the presence of bromide. a) Oxidation of bromide to hypobromite is favoured and the formed BrO⁻ blocks the active surface. Therefore, 3-CP cannot be oxidised and thus cannot be converted into acrylonitrile. b) Without the presence of bromide, 3-CP can cover the electrode surface, where it is oxidised to acrylonitrile.

2. Experimental

i. General procedure

The experiments were performed in a 5 mL vial. The electrochemically active surface was limited to 1 cm². WE and CE were fixed to a 3D printed lid that had two slits. The electrolysis experiments were performed under amperostatic control using a *Metrohm* Autolab B.V. PGSTAT302N Potentiostat/Galvanostat. A general visualisation of the setup is shown by **Figure S 17**.



Figure S 17: General illustration of the electrochemical cell used for the electrolysis experiments.

The time of electrolysis was calculated using **Equation 1**. If the current efficiency is reduced due to undesired side reactions, multiple equivalents of charge $(1 < F_{eq})$ with regard to the amount of substrate must be applied to achieve full conversion.

$$\frac{n \cdot F \cdot z}{I} \cdot F_{eq} \tag{1}$$

I: Applied current [A]

t =

- t: Time [s]
- *z*: Theoretical amounts of electrons to convert one substrate molecule into the desired product [-]
- F: Faraday constant [96485.33 C mol⁻¹]
- ^{*F*}_{*eq*}: Faraday equivalents [-]

ii. Procedure of the electro-oxidative decarboxylation

Electro-oxidative decarboxylation of L-glutamic 5-methylester

L-Glutamic 5-methylester (1 eq.) and the respective bromide salt (1.5 eq.) were dissolved in 3.5 mL of MeOH-d₄:D₂O (4:1) by using an ultrasonic bath. The general concentration of L-glutamic 5-methylester was 0.2 mol L⁻¹ and 0.3 mol L⁻¹ for the mediator salt.

The electrochemical cell was prepared according to the aforesaid procedure and located in an ice bath during electrolysis. A current density of 80 mA cm⁻² was applied. Platinum and titanium were used as electrodes. If the reaction solution was stirred during electrolysis, 500 rpm were used. As mediator NaBr and NH₄Br were tested. The duration of electrolysis was calculated using **Equation 1**, whereby *z* was 4. F_{eq} between 5.2 and 2.0 were tested.

When sodium bromide was used as mediator, an inorganic solid formation at the CE was observed. With ammonium bromide, this was not the case. The product solution after electrolysis was usually orange (**Figure S 18**). The product of the electro-oxidative decarboxylation of L-glutamic 5-methylester yielded 3-cyanopropanoic acid methyl ester (CME).

CME: ¹H-NMR (400 MHz, MeOH-d₄) δ 3.75 (s, 3H), 2.81 – 2.69 (m, 4H).



Figure S 18: Exemplary picture of the product solution directly after synthesis. In this case the product solution of the conversion of L-glutamic 5-methylester to 3-cyanopropanoic acid methyl ester (CME) is shown.

Electro-oxidative decarboxylation of D,L-glutamic acid

D,L-glutamic acid (1 eq.) and ammonium bromide (1.5 eq.) were dissolved in 3.5 mL D₂O using an ultrasonic bath. The final concentration of D,L-glutamic acid was 0.2 mol L⁻¹ and 0.3 mol L⁻¹ for the mediator salt. For the second approach, 2 eq. of KOH were added to the substrate mixture. The electrochemical cell was prepared according to the aforesaid procedure and located in an ice bath (0 °C) during electrolysis. A current density of 80 mA cm⁻² was applied. Platinum and titanium were used as electrodes, the reaction mixture was stirred with 500 rpm and 2 F_{eq} were utilised. The duration of electrolysis was calculated using **Equation 1**, whereby *z* was 4.

An orange discoloration was observed at the platinum electrode, while gas evolution was present at the CE. When no KOH was added to the substrate mixture, a suspension was formed after the electrochemical cell was located in the ice bath, which turned into a yellow/orange solution by electrolysis. If KOH was added to the substrate mixture, no suspension was formed after the cell was placed in the ice bath. The product solution was orange. After electrolysis 2 eq. of KOH were added to product mixture to obtain potassium 3-cyanopropanoate (3-CP).

Potassium 3-cyanopropanoate (3-CP): ¹H NMF – 2.47 (m, 2H).

iii. <u>Saponification of 3-cyanopropanoic acid methyl ester (CME)</u>

KOH (1 eq.) was transferred into a flask containing 20 mL of water. The solution was heated up to 60 °C under stirring. Subsequently, commercial CME (1 eq.) was added to the warm KOH solution. This mixture was stirred at 60 °C for 60 min. Then, water was removed under reduced pressure to yield a colorless product. The solid was dissolved in methanol and molecular sieve (3 Å) was added. This was filtered after 2 h and methanol was removed under reduced pressure. A colourless product was obtained with an average yield of 82% (\pm 3%) (**Figure S 19**). The purity was determined by ¹H-NMR using 1,3,5-trioxane as internal standard. The measurements verified a purity >99%. This product was used as substrate for the non-Kolbe electrolysis.

Potassium 3-cyanopropanoate (3-CP): 1 H-NMR (400 MHz, D₂O) δ 2.67 – 2.59 (m, 2H), 2.57 – 2.47 (m, 2H).



Figure S 19: Product obtained from the saponification of CME.

iv. Non-Kolbe electrolysis of 3-CP

Variation of current density, Faraday equivalents and substrate concentration

Based on a first experiment, the current density, Faraday equivalents and substrate concentration were varied later. In the following, the conditions of the first experiment will be described.

3-CP (1 eq.) was weighed into a 5 mL vial and dissolved in 3.5 mL MeOH-d₄. The final concentration of 3-CP was 0.071 mol L⁻¹. As electrode pair, graphite and platinum were used, with graphite as anode. The electrochemical cell was prepared according to the general scheme and placed in an ice bath afterwards. For the non-Kolbe electrolysis *z* is 2. A current density of 40 mA cm⁻² and 1 F_{eq} were applied. During electrolysis, the reaction mixture was stirred (500 rpm). In general, gas evolution was observed at both electrodes. The product solution was clear and colourless.

Variation of the current density was performed between 20 and 50 mA cm⁻² in 10 mA cm⁻² steps. The impact of 1.0, 2.0, 2.5 and 3.0 Faraday equivalents on the non-Kolbe electrolysis of 3-CP were tested. The substrate concentration was varied between 0.009 and 0.142 M. The concentration was doubled by experiment starting with 0.009 M. In these experiments, all other conditions were as in the first experiment to see the impact of variation.

Acrylonitrile: ¹H-NMR (400 MHz, MeOH-d₄) δ 6.27 (dd, J = 17.8, 1.0 Hz, 1H), 6.15 (dd, J = 11.8, 1.0 Hz, 1H), 5.86 (dd, J = 17.8, 11.8 Hz, 1H).

Stability of acrylonitrile in reaction mixture

3-CP (0.0366 g, 0.267 mmol, 1 eq.) was dissolved in 3.5 mL MeOH-d₄ that results in a final concentration of 0.076 M. The pH of the solution was 8.6. Acrylonitrile (0.256 mmol) was destabilised by filtration over basic aluminium oxide. The reaction mixture was placed into an ice bath and was stirred (500 rpm) for 40 min (equal to electrolysis duration). After this, the reaction mixture was analysed *via* ¹H-NMR. No oligomer signals were observed.

Stability of acrylonitrile during non-Kolbe electrolysis

3-CP (0.0366 g, 0.267 mmol, 1 eq.) was dissolved in 3.5 mL MeOH-d₄ that results in a final concentration of 0.076 M. In a second experiment, destabilised acrylonitrile (0.2 mL) was added to the 3-CP solution. The electrochemical cell was prepared according to the general procedure. As electrode pair, graphite and platinum were used. The electrolysis cell was placed in an ice bath, followed by a cooling period of 20 min. Then the electrolysis was started using 0.93 F_{eq} and a current density of 40 mA cm⁻². The duration of electrolysis was calculated using z = 2. The product solutions were clear and colourless. Oligomer formation was observed in both cases, but more strongly in the approach with additional 0.2 mL of acrylonitrile.

Stabilisation of acrylonitrile during non-Kolbe electrolysis Impact of the inhibitor or retarder

3-CP (0.0366 g, 0.267 mmol, 1 eq.) and the respective inhibitor (PTZ (0.0050 g, 0.0249 mmol, 0.09 eq.)) or retarder (MEHQ (0.0031 g, 0.0249 mmol, 0.09 eq.)) were dissolved in 3.5 mL MeOH-d₄. The electrochemical cell was prepared according to the general procedure. As electrode pair, graphite and platinum were used. The electrolysis cell was placed in an ice bath, followed by a cooling period of 20 min. When oxygen was used, the gas was passed through the solution, which was started during the cooling period and shut off after electrolysis was completed. The adjusted setup when oxygen was utilised is shown in **Figure S 20**. The electrolysis *z* is 2. During electrolysis, the solutions were stirred (500 rpm). Using PTZ, the reaction solution turned blue by starting the electrolysis. After electrolysis, a dark red product solution was present, which could indicate the presence of phenothiazone-3, an oxidation product of PTZ.⁸ The product solution of the entry with MEHQ as retarder was slightly yellow, while the combination of MEHQ and oxygen resulted in a greyish product solution.



Figure S 20: Electrochemical cell, when oxygen was passed through the cell.

Impact of the applied Faraday equivalents on the non-Kolbe electrolysis in the presence of oxygen and MEHQ

3-CP (0.0366 g, 0.267 mmol, 1 eq.) and MEHQ (0.0031 g, 0.0249 mmol, 0.09 eq.)) were dissolved in 3.5 mL MeOH-d₄. The electrochemical cell was prepared according to the general procedure. As electrode pair, graphite and platinum were used. The electrolysis cell was placed in an ice bath, followed by a cooling period of 20 min. Oxygen was passed through the solution, which was started during the cooling period and shut off after electrolysis was completed. The electrolysis was performed using 0.93, 1.86 or 2.79 F_{eq} and a current density of 40 mA cm⁻². For the non-Kolbe electrolysis *z* is 2. During electrolysis, the solutions were stirred (500 rpm). The product solution produced with 0.93 F_{eq} was greyish. Using 1.86 or 2.79 F_{eq} resulted in a slightly yellow product solution.

Non-Kolbe electrolysis of acrylonitrile in presence of a bromide source

3-CP (0.0093 g, 0.068 mmol, 1 eq.), KOH (0.0038 g, 0.068 mmol, 1 eq.) and ammonium bromide (0.0100 g, 0.1017 mmol, 1.5 eq.) were dissolved in 3.5 mL MeOH-d₄. The electrochemical cell was prepared according to the general procedure. As electrode pair, graphite and platinum were used. The electrolysis cell was placed in an ice bath, followed by a cooling period of 20 min. Then the electrolysis was started using 0.93 F_{eq} (first experiment) or 2.79 F_{eq} (second experiment) and a current density of 40 mA cm⁻². The duration of electrolysis was calculated using z = 2. During electrolysis, the solutions were stirred (500 rpm). The product solutions were clear and colourless. No acrylonitrile formation was observed in both experiments. The non-Kolbe electrolysis of 3-CP in the presence of NH₄Br resulted in a yellow product solution, indicating the presence of BrO⁻ (Figure S 21).⁹



Figure S 21: Product solution after electrolysis of 3-CP in the presence of NH₄Br. 3-CP ($c_{sub} = 0.019 \text{ mol } L^{-1}$: 0.0093 g, 0.068 mmol) was dissolved in 3.5 mL MeOH-d₄. Further reaction conditions: T = 0 °C; electrode pair: C_{gr}-Ti; $F_{eq} = 2.76$; $j = 40 \text{ mA cm}^{-2}$; stirring).

Nuclear magnetic resonance spectroscopy ٧.

The ¹H-NMR measurements were performed with a *Bruker Avance* spectrometer (400 MHz) at room temperature. As solvents MeOH-d₄ (δ H: 3.31 ppm) or D₂O (δ H: 4.79 ppm) were used. The sample volume was 0.55 mL and for the quantitative measurements 16 scans were applied in each case, setting the d1 time to 10 s. 1,3,5-Trioxane was applied as internal standard that was added to the sample. For determining the conversion and yield of the products, the following procedure was applied. The compound signals were integrated with respect to the 1,3,5-trioxane signal, which was standardised to 6 protons. Then, for compound x, the quotient of the sum of the integrals and the theoretical number of protons describing compound x by the integrals is calculated (Equation 2). The amount of substance x in the sample volume can be calculated based on Equation 3, while the maximum amount of substance in the sample volume is calculated by Equation 4. The yield respectively to the amount of internal standard can be calculated by Equation 5, based on the aforementioned procedure. The chemical shift δ is expressed in ppm and all coupling constants (J) are stated in Hz.

$$\frac{\sum_{x} I_{x}}{\sum_{C_{Trioxane}} V_{Trioxane} \cdot r_{x}}$$
(2)
(3)

 $n_x =$

$$ne \cdot r_{\frac{X}{IS}}$$
(3)

$$V_{NMR} \cdot \frac{n_{Start}}{V_{End}} \tag{4}$$

 $n_{max} =$

 $r_x =$

ĪS

$$Y^x = -\frac{n_x}{n_{max}} \cdot 100\%$$
(5)

$$r_{\frac{x}{IS}}$$
:

Ratio of the sum of integrals to the number of protons that the sum of integrals theoretically represents [-]



Sum of integrals representing the specific protons of the compound x [-]

Sum of the specific protons of the compound x that the sum of integrals theoretically represents [-]

Concentration of the standard solution of trioxane [mol mL⁻¹]

Volume of the used standard solution of trioxane [mL]

V_{Trioxane}: n_x

 $c_{Trioxane}$.

Amount of substance of compound x, which is in the analysed volume [mol]

n _{max} :	Maximum amount of substance of the compound that could be in the analysed volume [mol]
V _{NMR} :	Used volume of the sample [mL]
n _{Start} :	Amount of substance of the substrate at the beginning [mol]
V _{End} :	Reaction volume after electrolysis [mL]
Y^{x} :	Yield determined by quantitative ${}^1\text{H-NMR}$ for the respective compound [%]

vi. <u>Materials</u>

The chemicals used in this work are listed in **Table S 1** below. They were used without any purification.

Table S 1: List of chemicals used for the experiments.

Chemicals	Purity	Producer
1,3,5-Trioxane	≥ 99%	Sigma-Aldrich
1,4-Dicyanobutane	99%	Acros Organics
4-Methoxyphenol	99%	Sigma-Aldrich
Acrylonitrile	≥ 99%	Sigma-Aldrich
Ammonium bromide	≥99%	Sigma-Aldrich
D_2O	99.95%	Deutero
Graphite foil, 0.4 mm	99.8%	Alfa Aesar
D,L-Glutamic acid		Fluorochem
L-Glutamic acid 5-methyl ester	99%	Alfa Aesar
Methanol-d ₄	99.8%	Deutero
Methyl 3-cynaopropionate	>99.0	Fluorochem
Oxygen	≥99.999	Nippon Gases
Phenothiazine	>98%	TCI
Potassium hydroxide, flake	85%	abcr
Sodium Bromide	≥99.5 %	Sigma-Aldrich
Tetrabutylammonium perchlorate	≥ 99%	Sigma-Aldrich

3. Literature

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