Stepping stones in CO$_2$ utilization
Towards process development of oxalic and glycolic acid monomers
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Wer A sagt, der muss nicht B sagen.
Er kann auch erkennen, dass A falsch war.

- Berthold Brecht -
A new way to make oxalic acid from CO$_2$ and alkali formates
Chapter V  

A new way to make oxalic acid from CO$_2$ and alkali formates

Abstract  Conversion of CO$_2$ to valuable chemicals such as polymers via the electrochemical reduction of CO$_2$ to formate followed by the formate to oxalate coupling reaction (FOCR) is an interesting concept to replace fossil feedstocks with renewable ones. Yet, the activation of CO$_2$ is challenging and energy-intensive and today the production of one oxalate molecule first requires the reduction of two CO$_2$ molecules. Recently we confirmed the crucial role of the reactive carbonite intermediate in the FOCR. Due to its high reactivity, this intermediate might also be a strong enough nucleophile to react with CO$_2$ directly. If this is the case, we can form oxalate directly from CO$_2$ and formate and avoid the need for double electrochemical CO$_2$ reduction in oxalate production. In this work, we successfully established the conversion of CO$_2$ (with a theoretical yield of 52%) to oxalate (via the reaction with carbonite), as well as to formate and carbonate. The direct reaction of the reactive carbonite intermediate with CO$_2$ was the dominant pathway for CO$_2$ incorporation in oxalate. For enhancing the CO$_2$ incorporation in oxalate, we found a reaction temperature of 200 °C, stoichiometric amounts of the base, and the presence of CO$_2$ in the supercritical state most suitable. The residence time is strongly depending on the reactor type but should be kept to a minimum to avoid carbonate formation. The presence of high amounts of hydride and supercritical CO$_2$ appeared to also cause the formation of carbonates as a side-product. The carbonate formation increased with higher temperatures and longer reaction times, which suggests a consecutive decomposition of oxalate formed in the reaction.
5.1 Introduction

Oxalic acid is receiving increasing interest as a platform chemical to produce, for example, polymers or ingredients for pharmaceuticals and health care products.\(^1\)–\(^4\) It can be produced from renewable sources including CO\(_2\), CO, formate, ethylene glycol, ethylene, and sugars.\(^5\) As society strives to reduce atmospheric CO\(_2\) levels and find sustainable alternatives to fossil feedstocks, the electrochemical reduction of CO\(_2\) to formate and subsequent carbon-carbon coupling towards oxalate in the formate to oxalate coupling reaction (FOCR) is an interesting carbon capture and utilization (CCU) option. From an economic perspective, CO\(_2\) is an interesting feedstock as it has low or even negative costs and is highly abundant.\(^5\)–\(^9\) Yet many routes leading to valuable products from CO\(_2\) require improvements before becoming commercially viable.\(^10\),\(^11\) The fixation of CO\(_2\) as formate, one of the most promising options for electrochemical CO\(_2\) reduction, is relatively expensive as it requires the investment of two electrons per CO\(_2\) molecule.\(^8\) Hence, it is desirable to reduce the required amount of formate obtained from CO\(_2\) in a process towards a valuable C\(_2\) product.

In the formate coupling reaction towards oxalate, shown in Scheme 5.1, the reactive carbonite di-anion (CO\(_2\)^\(-2\)) is formed by the abstraction of a proton from formate with the use of a superbase. This active intermediate is crucial as it facilitates the carbon-carbon coupling by attacking another formate.\(^12\),\(^13\) The carbonite formation requires the presence of the formate in its molten form and thus reaction temperatures of at least 170 °C when potassium formate is used.\(^13\)

![Scheme 5.1](image_url)

Scheme 5.1 Coupling of two formate molecules to oxalate and hydrogen via the carbonite dianion (CO\(_2\)^\(-2\)) intermediate with the regeneration of the hydride catalyst in the FOCR.

We strive to make use of the strong reactivity of the carbonite dianion and explore its potential of reacting with other electrophilic partners. In our recent perspective paper, we evaluated potential coupling partners for their suitability based on their reactivity, the potential of side reactions, and the attractiveness of the prospective product.\(^14\) We identified CO\(_2\) as the most desirable coupling partner, due to its broad availability and low potential for side reactions. Interestingly, CO\(_2\) has been coupled to oxalate using carbonite before and has been studied extensively in recent years.\(^15\)–\(^33\) However, all those approaches only use CO\(_2\) as a starting material which is reduced to carbonite in a two-step one-electron reduction and subsequently stabilized through the interaction with a metal.\(^25\) This reaction can be facilitated in electrochemical cells,\(^17\),\(^18\),\(^30\)–\(^33\) by organometallic complexes\(^19\)–\(^25\) or by vaporized alkali metals in the gas phase.\(^15\),\(^16\),\(^26\)–\(^29\)

![Scheme 5.2](image_url)

Scheme 5.2 Alternative coupling of formate and CO\(_2\) to oxalate via carbonite dianion (CO\(_2\)^\(-2\)).

Our idea, shown in Scheme 5.2, is different from previous reports as it entails the in-situ production of carbonite by the abstraction of the proton of formate with a superbase which we demonstrated earlier.\(^12\),\(^13\) We aim to provide carbon dioxide in its supercritical state to increase its availability for the reaction with carbonite as a coupling partner.
to form oxalate. As the base cannot be regenerated as in the FOCR, we supplied it in equimolar amounts. The fact that CO₂ has been shown to act as a poison in the FOCR where it reacts with either carbonite or hydride to form formate and oxalate encouraged this work. The goal of this research is to explore the potential of coupling of formate (converted to carbonite by reaction with stoichiometric amounts of hydride base) with CO₂, with proof of principle experiments, investigations into the influence of various process parameters, and proving the mechanism by using isotope labelling studies.

5.2 Results and Discussion

In our previous work, we showed that CO₂ acted as a poison on the formate coupling reaction when supplied as a gas. We then however did use catalytic and not equimolar amounts of a base catalyst. At low loadings, the base might have been consumed in a reaction with the gaseous CO₂ as indicated in Scheme 5.2. Hence, we believe it would be possible to supply CO₂ also in gaseous form. However, it is difficult to make enough CO₂ available in the short reaction times for the reaction between formate and carbonite in the classical formate to oxalate formation. The limited mixing between the gas and liquid, when CO₂ is supplied as gas, would favour the reaction between two formates rather than the attack of carbonite on CO₂. To supply a large excess of CO₂ relative to formate we decided to supply the CO₂ in liquid or supercritical form. We used a glass-lined pressurized reactor which we filled in a glove box with an equimolar mixture of potassium formate and potassium hydride. We chose potassium formate because of its low melting point and the higher production rate of formate from CO₂ in electrochemical reactors with potassium ions. Further details on the exact reaction procedures can be found in the supplementary information.

5.2.1 Proof-of-principle in equimolar formate and hydride mixtures

We chose reaction conditions, shown in Table 5.1, based on our work with superbases for which we have shown the presence of carbonite in an equimolar mixture of formate and hydride. In the control reactions without formate, we used the same molar amount of hydride (equimolar to formate) as in other reactions. We performed four types of reactions:

1) The intended reaction of formate, hydride, and CO₂ (FHC)
2) The positive control reaction of formate coupling with hydride in nitrogen atmosphere (FOCR)
3) Control reactions between CO₂ + hydride (COH)
4) Control reactions between CO₂ + formate (COF)

After the reaction, the mass balance of solids was used as a first indication for the successful incorporation of CO₂. We used Eq. S1 to calculate the mass change, shown in Figure 5.1A, after the reaction relative to the introduced solids formate and hydrides. After measuring the weight increase, we added water to the obtained solids to react the remaining hydride with water to form hydrogen and hydroxide. Whilst adding the water, we measured the volume of evolving hydrogen. From the hydrogen volume, we calculated the consumption of hydride shown in Figure 5.1B using Eq. S2. To identify and quantify the obtained reaction products, we used an IR cell for analysis of liquids and calculated the carbon balances based on the introduced formate and hydride as shown in Figures 1C and 1D using Eq. S8.
Table 5.1 Reaction conditions used during the formate/hydride + CO$_2$ (FHC) reaction study with base settings and an expanded range of values adopted from our earlier work with superbases as catalysts.\textsuperscript{13}

<table>
<thead>
<tr>
<th>Variable</th>
<th>Set value\textsuperscript{13}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>200 °C</td>
</tr>
<tr>
<td>Heating rate</td>
<td>10 °C/min</td>
</tr>
<tr>
<td>Reaction time</td>
<td>15 min</td>
</tr>
<tr>
<td>CO$_2$ Pressure</td>
<td>120 bar</td>
</tr>
<tr>
<td>CO$_2$ volume</td>
<td>100 mL (gas at 55 bar)</td>
</tr>
<tr>
<td>Hydride: Formate molar ratio</td>
<td>1:1</td>
</tr>
<tr>
<td>Reactant mass (equimolar Formate + Hydride mixture)</td>
<td>200 mg</td>
</tr>
<tr>
<td>Reactor volume</td>
<td>70 mL</td>
</tr>
</tbody>
</table>

In the desired alternative reaction system (FHC) with formate, CO$_2$ and hydride present, we observed the largest mass increase of 25 wt. % relative to the introduced formate (Figure 5.1A). During the reaction, 96 % of the added hydride was consumed and the carbon content measured via IR increased 47 % in FHC. This suggests that 0.47 of available CO$_2$ molecules were fixated per hydride molecule. However, we did not only obtain the desired reaction product oxalate. Figure 5.1C shows, that most carbons were present in the form of formate (81 %) followed by oxalate (46 %) and carbonate (19 %). Especially the high carbonate content was surprising as we never observed the formation of carbonate from formate at temperatures lower than 400 °C or in the presence of catalytic amounts of hydrides. The only changes in these reaction conditions compared to our previous work were the use of equimolar amounts of hydride and the presence of excess amounts of supercritical CO$_2$. The low conversion of formate, high carbonate content, and high consumption of hydride might indicate the occurrence of another, not anticipated, competing reaction triggered by the supercritical CO$_2$ which causes the consumption of the hydride catalyst.

The importance of hydride for this competing reaction is shown by the COF control reaction. For the mixture of formate and CO$_2$, COF, we did not observe any change of mass as shown in Figure 5.1A. The IR analysis of COF (Figure 5.1C) shows that formate remained unreacted and no carbon was lost during the heating. For the positive control reaction between formate and hydride (FOCR), we observed a weight loss of 1% as shown in Figure 5.1A. This was expected due to the production of some hydrogen during this reaction. For the FOCR at hydride loadings below 5 wt.% relative to formate, we could show high reaction speeds and full formate conversion, which we reported recently.\textsuperscript{13} This indicates that in the FOCR the hydrides are regenerated. Yet, in the present FOCR experiments with equimolar hydride loadings, up to 48% of the added hydride was consumed in the FOCR. The product analysis (Figure 5.1C) of the FOCR with equimolar amounts of hydride shows that oxalate formation (77.4 % of all carbon) via the pathway illustrated in Figure 5.2A, is still dominant. Even though enough hydride was present, 4% of the formate remained unreacted. Like the FHC, we detect carbonate (7.6% of all carbon) and lose 11% of the carbon introduced as formate. As the decrease in the carbon balance is bigger than the weight loss, also the formation of insoluble (potentially elemental) carbon might be possible. Like gaseous carbon compounds, non-soluble carbon compounds cannot be quantified in the IR method and thus lead to a reduction in the overall carbon balance. The formation of carbonate and loss of carbon in the FOCR with equimolar amounts of hydride indicates that high amounts of hydride lead...
to decomposition reactions even in the absence of CO$_2$, yet only half as much hydride was consumed and less carbonate was produced compared to the FHC.

In the control reaction with CO$_2$ and hydride, COH, we used the same amount of hydride as in other experiments (1:1 versus formate) but in the COH no formate was added. We based the carbon balance and mass balance on the theoretical carbon capture from the introduced hydride. The solid mass in this experiment increased by 8 wt.% (if the same amount of formate was present as in other experiments, Figure 5.1A). After the reaction, 32% of hydride was consumed (Figure 5.1B). Interestingly, we did not get any formate or oxalate but only carbonate was obtained after the reaction in COH. Whilst trace amounts of formate and oxalate were visible in the IR spectra, they lay below the quantification limit. The carbon balance in Figure 5.1C shows that 6.3% of the originally introduced hydride was converted with CO$_2$ to carbonate. Based on the presence of trace amounts of formate and oxalate we propose, that the CO$_2$ was fixated as formate which reacted to oxalate as illustrated in Figures 2B and 2C. We prove the occurrence of this reaction below. Subsequently, the oxalate decomposed to carbonate and CO$_2$ or CO and insoluble (elemental) carbon in the presence of large amounts of hydride. This decomposition could also explain the discrepancy between fixed carbon and hydride consumption in the FHC reaction.

From these first experiments, we conclude that hydrides facilitated the fixation of CO$_2$ as oxalate but their presence in high concentrations also appears to facilitate decomposition towards carbonate, CO$_2$ and CO or insoluble solids. With excess amounts of supercritical CO$_2$ these decomposition reactions and hydride consumption appear to increase even further. Our recent literature overview of formate coupling reactions includes all decomposition reactions for formate and oxalate.$^{14}$ Gorski et al. proposed two mechanisms for the carbonate formation from either formate or oxalate as shown in Scheme 5.4.$^{38}$ In both cases, carbonate is formed in a reaction between a metal oxide and CO$_2$ but the formation of metal oxide from formate and oxalate differ. Formate requires a two-step activation: First, formate decomposes to metal hydride and CO$_2$. In a second step, carbonite is formed in the reaction of the hydride and another formate as in the FOCR. They suggested that the carbonite can then decompose to a metal oxide and carbon monoxide in the absence of CO$_2$ and formate. If formate or CO$_2$ were present, oxalate would be formed instead. The oxalate activation starts with the decomposition of oxalate to carbonite and CO$_2$. This is followed by the decomposition of carbonite to metal oxide and CO in absence of CO$_2$ (and formate). These mechanisms don’t explain the increase of carbonate formation with higher hydride loadings. The increased carbonate formation in the presence of supercritical CO$_2$ increased the CO$_2$ concentrations in the system. This makes the formation of oxalate from carbonite more likely over the decomposition of carbonite to metal oxide and CO which, according to Gorski et al. requires the absence of CO$_2$. Hence, in-depth investigations into the decomposition pathways of formate and oxalate and the involvement of superbase and CO$_2$ are part of future work.
In both decomposition reactions carbonate is formed from metal oxide and CO$_2$ as in step I. The decomposition of formate starts with step II where formate decomposes to metal hydride and CO$_2$. For the reaction to develop towards carbonate formation, the CO$_2$ is removed and another formate is introduced in step III. In step IV, carbonite is formed by the abstraction of hydrogen from formate by the newly formed hydride in the absence of CO$_2$. The carbonite decomposes in absence of CO$_2$ and formate to metal oxide and CO in step V. After the reintroduction of CO$_2$, the metal oxide reacts to carbonate in step I. Oxalate decomposition is initiated by its disproportionation to carbonite and CO$_2$ as in step VI. Metal oxide and CO are formed in step VII by decomposition of the carbonite in absence of CO$_2$ and formate.

5.2.2 Temperature, reaction time, hydride loading and CO$_2$ pressure

In the next step, we altered the reaction time and temperature, the hydride loading and the CO$_2$ pressure to investigate their effects on the reaction towards oxalate formation. The effects of these experiments are shown in Figure 5.1D. We increased the reaction time from 15 to 120 minutes whilst keeping all other parameters the same as those in Table 5.1. With increased reaction time, the overall carbon incorporation reduced by 20 % from 47 % to 27 % (Figure 5.1D). Simultaneously, the carbonate content increased from 18 to 22 %. This might indicate that carbonate is formed from oxalate or formate over time and that the decomposition coincides with the formation of gaseous or non-soluble carbon species which are not detected in the analysis of the dissolved products. This makes the carbon incorporation appear lower, as some initially fixated carbon is released again into the gas phase or as a non-soluble carbon species.

An increase in reaction temperature from 200 to 250 °C increase the carbon fixation by 5 % from 47 to 52 % (Figure 5.1D). However, the increase of carbonate from 18 to 41 % leads to an overall decrease in oxalate yield from 46 to 30 %. As this indicated that higher temperatures benefit the decomposition of the desired oxalate, we attempted to reduce the reaction temperature. Temperatures below the melting point of formate only lead to the formation of carbonate analogous to the COH system where only CO$_2$ and hydride are present.

With catalytic amounts of hydride (5 wt.%) in the presence of supercritical CO$_2$ and molten formate at 200 °C, the results after 15 minutes of reaction were closest to those of the COF experiments. There was no weight change, and the carbon balance was 98 %. All hydrides were consumed and only a small amount of formate was converted to oxalate (7 % of carbon balance). In this reaction, we did observe the formation of carbonate but only in small amounts (2% of carbon balance). We assume the hydrides were quickly consumed in a reaction with CO$_2$ and then no further reactions took place.
The reduction of CO$_2$ pressure below its condensation points of 55 bar at room temperature leads to a drastic reduction in the amount of CO$_2$ added to the reaction due to its lower density as a gas. Effectively we exchanged the nitrogen atmosphere in the FOCR with a CO$_2$ atmosphere. The results resembled those of the FOCR with the only difference that less carbonate was produced. The distribution of products was well within the error bars of the FOCR reaction. Only traces of the CO$_2$ appeared to be available for the reaction and did not reduce the hydride content enough to prevent its catalytic effect in the FOCR. In an attempt to distinguish the influence of overall lower CO$_2$ amounts and their presence as gas and not as a supercritical fluid, we performed a reaction in which we kept adding CO$_2$ to compensate for its lower density as a gas. Again, we did not increase the carbon incorporation which indicates that gaseous CO$_2$ is much less available for a reaction with hydride or carbonite compared to supercritical CO$_2$.

Figure 5.1 Results in Figure A) show the increase in weight, based on the initial formate mass for the intended reaction of equimolar mixtures of formate and hydride with an excess of supercritical CO$_2$ (FHC), the positive control reaction of formate with equimolar amounts of hydride (FOCR), control reactions between supercritical CO$_2$ + hydride (COH), and the control reactions between CO$_2$ + formate (COF) all performed at 200 °C. The hydride consumption in Figure B) during FHC, COH and FOCR was calculated from the hydrogen evolution from the product upon addition of water. Figure C) shows the carbon balance relative to the introduced formate. Figure D) Shows the effects of changing reaction time from 15 to 120 minutes, temperature from 200 to 250 °C, catalyst loading from equimolar to 5 wt.% and CO$_2$ pressure from above 100 to 50 bar (gaseous instead of supercritical) whilst keeping other parameters as in FHC. The column on the left is equivalent to the FHC reaction in Figure C) for the middle column the reaction time was increased to 120 minutes, for the right column, the reaction temperature was increased to 250 °C.

As FHC and COH show, formate and oxalate can only be produced in the presence of molten formate and hydride and not from CO$_2$ and hydride alone. Additionally, CO$_2$ must be present as a liquid or in the supercritical form to react with hydride towards formate and oxalate in the formate melt. If hydride is only added in catalytic amounts as shown in Figure 5.1D, it is quickly consumed in a reaction with formate. In the FHC, higher temperatures and longer reaction times benefit the decomposition towards carbonate.
and non-soluble or gaseous carbon products.

5.2.3 Mechanistic proof via isotope labelling

In the FHC, oxalate can be formed from only formate or captured CO₂ and formate via three pathways illustrated in Figure 5.2. From the product analysis alone, it is yet unclear if CO₂ is captured by carbonite to form oxalate as shown in Figure 5.2D. Alternatively, as shown in Figure 5.2C, CO₂ can also react with hydride to form formate which then undergoes the FOCR. This stepwise reaction requires the proximity of two hydride molecules: in the first step hydride molecule is consumed in the fixation of CO₂. In a second step, another hydride is required to drive the formate coupling reaction, however, this hydride is recovered and therefore of catalytic nature. Whilst the formation of oxalate from two formates is a catalytic process (Figure 5.2A), the formation of oxalate from CO₂ requires equimolar amounts of formates and hydride.

Figure 5.2 Three fundamental pathways for oxalate production are consisting of either A) without or B), C) and D) with the involvement of CO₂. A) Oxalate and hydrogen can be formed by traditional formate to oxalate coupling (FOCR) from two formates catalysed by hydride via the carbonite intermediate in the formate melt. CO₂ can dissolve in the formate melt and react towards oxalate in two ways. B) Two formates can be formed from CO₂ in a reaction between CO₂ and Hydride. One of these two formates is activated to carbonite and react with the other formate to oxalate in a FOCR reaction as in A). C) It can react with hydride to form formate which can subsequently react towards oxalate in a FOCR reaction. D) Alternatively, CO₂ can be attacked by the reactive carbonite intermediate formed from the reaction of formate with hydride to form oxalate directly in a stoichiometric reaction.
To gain further insight into the mechanism, we used isotope labelling and introduced $^{13}\text{C}$-labeled formate in FHC. For the reaction between formate and CO$_2$, various pathways are possible in the labelled system as shown in Scheme 5.5. Labelled formate can be activated via pathway I by hydride to form hydrogen and labelled carbonite dianion ($^{13}\text{CO}_2^-$) which can react either via pathway II to form $^{13}\text{C}-^{13}\text{C}$-oxalate in a carbonite (from formate) – formate coupling reaction or via pathway III where it forms $^{12}\text{C}-^{13}\text{C}$-oxalate in an attack on unlabelled CO$_2$. Formate can also be formed in-situ from CO$_2$ and hydride directly as shown in pathway IV. This reaction leads to $^{12}\text{C}$-formate and via a pathway I to $^{13}\text{C}$ carbonite. Subsequently, $^{12}\text{C}-^{13}\text{C}$-oxalate is formed by the reaction of this unlabelled carbonite with (labelled) formate (pathway II). Finally, the unlabelled carbonite ($^{12}\text{CO}_2^-$) can alternatively react with unlabelled CO$_2$ to form $^{12}\text{C}-^{12}\text{C}$-oxalate via pathway III.

![Scheme 5.5 Potential reaction pathways for oxalate formation in a system with $^{13}\text{C}$-Formate and $^{13}\text{CO}_2$. Overall, four steps I-IV can be combined to lead to three different outcomes. Step I is the activation of formate to carbonite via the abstraction of a proton and subsequent hydrogen formation by the metal hydride. The reactive carbonite can undergo a reaction with another formate via step II to form oxalate by attacking a CO$_2$ molecule via step III. Formate can also be formed in-situ from CO$_2$ and hydride via step IV. This unlabelled formate can react to oxalate via carbonite by the normal FOCR or by reaction with CO2.](image)

After the reaction, we dissolved the sample in water and analysed it in the IR cell for liquid samples. The introduction of $^{13}$C carbon atoms (higher mass) causes the shift of the vibrational modes in IR spectra towards lower frequencies. 39–41 Our region of interest was in the frequency range from 1200 cm$^{-1}$ to 1450 cm$^{-1}$ due to the absence of overlapping water peaks. For $^{12}$C-$^{13}$C-oxalate this region contains one peak at 1308 cm$^{-1}$ representing the alternating symmetric C=O stretch. First, we measured standards of $^{12}$C-$^{13}$C-oxalate, $^{12}$C-formate, and $^{13}$C-formate. Yet no standard of $^{13}$C-$^{12}$C-oxalate, or $^{13}$C-$^{13}$C-oxalate was available. To overcome this problem, we used a DFT approach to calculate the expected frequency for $^{13}$C labelled oxalate. We proved the approach with formate for which standards were available and calculated the shift caused by isotope labelling as shown in Table 5.2.

From the frequency changes and the position for the $^{12}$C-$^{12}$C-oxalate standard, we could calculate the expected peak position of labelled oxalates.

For formate, we observed two vibrational modes in the region of interest: the symmetric stretch of C=O in the formate molecule at 1351 cm$^{-1}$ and the rotation around the
carbon-hydrogen bond at 1330 cm\(^{-1}\). The effect of the mass change was relatively big (21 cm\(^{-1}\)) for the symmetric stretch, as the carbon is involved in a translational movement. For the rotational mode, the shift was relatively small (3 cm\(^{-1}\)) as the translational movement of the carbon is small and therefore the change in mass has a lower effect. We conclude that our approach is valid given the close resemblance between the calculated and measured frequency difference.

Table 5.2 Measured IR frequencies for \(^{12}\)C and \(^{13}\)C formate and calculated shift in the energy of the vibrations expressed as frequency shift from DFT calculations

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Measured frequency (cm(^{-1}))</th>
<th>(\Delta E)(_{\text{measured}}) (cm(^{-1}))</th>
<th>(\Delta E)(_{\text{calculated}}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation around C-H bond</td>
<td>1382 (^{12})C-Formate</td>
<td>1380 (^{13})C-Formate</td>
<td>3 (^{12})C-Formate</td>
</tr>
<tr>
<td>Symmetric C=O stretch</td>
<td>1351 (^{12})C-Formate</td>
<td>1330 (^{13})C-Formate</td>
<td>21 (^{12})C-Formate</td>
</tr>
</tbody>
</table>

The frequency of the alternating symmetric C=O stretch of oxalate decreases with the substitution by heavier carbon atoms. With our DFT approach, we calculated an expected frequency drop by 13 wavenumbers for a single and a further 8 wavenumbers for a full substitution (Table 5.3). Hence this approach allows a clear distinction between \(^{12}\)C-\(^{12}\)C-oxalate, \(^{13}\)C-\(^{12}\)C-oxalate and \(^{13}\)C-\(^{13}\)C-oxalate using IR spectroscopy. As we are observing the same vibrational mode for all isotopes, this method can also be used to estimate their relative quantities. This requires using the Lambert-Beer-Law and a well-defined environment with a defined sample thickness.

Table 5.3 Measured IR frequencies for unlabelled potassium oxalate and calculated shift in the energy of the vibrations expressed as frequency shift from DFT calculations

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Measured frequency (cm(^{-1}))</th>
<th>Calculated frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alternating Symmetric C=O stretch</td>
<td>1308 cm(^{-1}) (^{12})C-(^{12})C-Oxalate</td>
<td>1295 cm(^{-1}) (^{13})C-(^{12})C-Oxalate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1287 cm(^{-1}) (^{13})C-(^{13})C-Oxalate</td>
</tr>
</tbody>
</table>

The underlying absorbance in the raw IR signal with no clear peak in the region of interest stems from contributions of water and carbonate in the solution as also shown in Figure 5.S1. To obtain the pure IR signal of the formate and oxalate species, we subtracted the contributions of water and carbonate by using standards. Only the contributions to the absorbance from formate and oxalate remain, as shown in Figure 5.3. As no standards for the three isotopes were available, we could only estimate their relative quantities based on the peak areas which we calculated using a Gaussian fit. The resulting curves closely represent the measured data as shown in Figure 5.3. We identified \(^{13}\)C-formate with peaks at 1329 cm\(^{-1}\) and \(^{12}\)C-formate at 1351 cm\(^{-1}\). From the integrated peak areas, we conclude that \(^{13}\)C-formate makes up 87.5% whilst the \(^{12}\)C-formate originating from the reaction of CO\(_2\) with KH makes up 12.5% of the total formate. The three oxalate species can be identified at 1287 cm\(^{-1}\) for the \(^{13}\)C-\(^{13}\)C-oxalate originating from traditional formate coupling, 1295 cm\(^{-1}\) for \(^{12}\)C-\(^{13}\)C-oxalate from the coupling of formate with CO\(_2\) and 1308 cm\(^{-1}\) for \(^{12}\)C-\(^{12}\)C-oxalate purely based on incorporated CO\(_2\). In our reaction system, \(^{13}\)C-\(^{13}\)C-oxalate is dominant and contributes to 72 % whilst mixed-origin \(^{12}\)C-\(^{13}\)C-oxalate makes up 27.5% of the formate. Only 0.5% is \(^{12}\)C-\(^{12}\)C-oxalate, which originates exclusively from incorporated CO\(_2\).

From the comparison of the relative distributions of formate and oxalate isotopes, we conclude that both pathways, the direct CO\(_2\) incorporation via the nucleophilic attack of carbonite and the formation of formate from CO\(_2\) as an intermediate, are present. Also, the presence of traditional formate coupling between \(^{12}\)C-formate from CO\(_2\) and \(^{13}\)C-formate
is likely as we see a clear presence of formate coupling between two $^{12}$C-formates and there is no reason why $^{13}$C and $^{12}$C formates should exhibit varying reactivities. As $^{12}$C-formate from CO$_2$ is present we can expect its reaction towards oxalate. However, if assuming similar reactivity of both isotopes, we would expect a similar ratio of the isotope ratios for formates and oxalates. However, the ratio of $^{13}$C-formate to $^{12}$C-formate is 7:1 whilst the $^{12}$C-$^{13}$C-oxalate to $^{12}$C-$^{13}$C-oxalate ratio is 3.5:1. The much smaller oxalate isotope ratio indicates a surplus of $^{12}$C-$^{13}$C-oxalate and we hence conclude, that $^{12}$C-$^{13}$C-oxalate is mainly formed by a direct attack of carbonite formed from $^{13}$C-formate. Fully unlabelled $^{13}$C-$^{12}$C-oxalate can be formed by either an attack of carbonite formed from $^{12}$C-formate or coupling of two $^{12}$C-formates. Its low overall presence is an indication of a relatively slower reaction rate of formate formation from CO$_2$ compared to the coupling reaction. If the formate formation was faster, the reaction should lead to at least 1.7% of $^{12}$C-$^{12}$C-oxalate at equal reactivity of the isotopes, yet we only observed 0.5%.

![Figure 5.3 IR spectrum after 15 minutes of FHC reaction when equimolar amounts of $^{13}$C-formate and hydride are used as reactants with an excess of unlabelled supercritical CO$_2$ at 200 °C. The peak areas were fitted for the calculated expected peak positions of the isotopes using a gaussian fit. Both $^{13}$C and $^{12}$C- formate were present as well as all three oxalate isotopes with $^{13}$C-$^{13}$C-oxalate in the highest quantity.]

**5.3 Conclusions**

In conclusion, we report, for the first time, the incorporation of supercritical CO$_2$ in oxalate by reaction with formate at low reaction temperatures of 200 °C using a hydride superbase as a catalyst and co-reactant and reached a maximum theoretical incorporation efficiency of 52%. With isotopic labelling studies, we prove the incorporation of CO$_2$ in the form of formate and oxalate. In the absence of molten formate, the incorporation of CO$_2$ in solid was reduced by 80% and only carbonate was formed. To incorporate large amounts of CO$_2$, it must be provided in its supercritical form in the presence of molten formate and equimolar amounts of hydride. Long reaction times and higher reaction temperatures reduced the CO$_2$ incorporation and increased the decomposition of oxalate to carbonates and non-soluble or gaseous carbon compounds. Whilst we can clearly show that CO$_2$ is
incorporated in the desired oxalate, we cannot exclude the simultaneous presence of a pathway involving first the formation of formate from CO$_2$ followed by the coupling of two formates. The majority of oxalate, 72%, was formed from traditional formate-formate coupling whilst up to 28% originate from the desired reaction of carbonite with CO$_2$ or coupling of formate fixated from CO$_2$. The production of carbonate as a side product contributes to 15% of the overall carbon balance and could not be avoided in our system. Some further in-depth investigations into the decomposition pathways of formate and oxalate and the involvement of superbase and CO$_2$ are part of future work. At larger scales with dedicated reactor designs, we expect an increase in CO$_2$ incorporation when achieving a higher availability of CO$_2$ to react with the reactive carbonite intermediate and potentially avoid decomposition reactions towards carbonate. Other parameters for future optimization include reaction temperature, stirring of the reaction, hydride loading, reaction time, and heating rate. Overall, our results open the door for a new CCU pathway from CO$_2$ to oxalic acid. It allows to increases the obtainable oxalate or oxalic acid amount per electrochemically reduced CO$_2$ significantly. However, the reaction towards oxalate also requires the use of stoichiometric amounts of alkali hydrides. Alkali hydrides are currently produced from the reaction of their alkali metals with hydrogen and are therefore energy-intensive to produce. We still need to deepen the understanding of the reaction between formate, hydride, and CO$_2$ and the crucial reaction parameters to potentially allow for a better and more sustainable process. Moreover, our work will help accelerate the development of new processes starting from CO$_2$-derived formates as carbon sources.
Picture above: Filling reactors for the FOCR in the glovebox
Chapter 5: Supporting information

S5.1 Experimental details

S5.1.1 Reagents

All chemicals (Potassium formate, Potassium oxalate, Potassium hydride, Sodium hydride, CO\textsubscript{2}, \textsuperscript{13}C-labeled Formic acid) were obtained from commercial suppliers (Sigma-Aldrich\textsuperscript{®}), dried, and stored in a dry environment. Otherwise, the chemicals were not further processed.

As no \textsuperscript{13}C-formate was available for purchase we produced it ourselves from \textsuperscript{13}C-Formic acid and KOH. In this procedure, we slowly added a solution of KOH to the solution of \textsuperscript{13}C-formic acid until the pH was neutral. We subsequently removed the water under vacuum and dried the formate in a vacuum oven at 100 °C for 24 hours.

S5.1.2 Reactor

The reactors of choice from Parr were made from stainless steel, with 70 mL and can withstand pressures as high as 200 bar and temperatures up to 250 °C. To prevent potential reactions with the metal of reactor walls, a borosilicate glass insert was used.

S5.1.3 Reactant preparation

We measured the weight of the solids in the glovebox to avoid the adsorption of water before and after the reaction. The reaction mixture was prepared by a mechanical mixture of the formate and hydride in a dry nitrogen atmosphere. A precise amount of the mixture was then added to the glass reactor inserts in the glovebox. Once the reactor was filled and sealed it was removed from the glovebox.

A pressurizer was used to load the reactors with liquid CO\textsubscript{2}. Utilizing a CO\textsubscript{2} bottle, the reactor was first pressurized with 54 bar. After that, 100 mL of CO\textsubscript{2} at 54 bar were additionally forced into the reactor leading to a final pressure of 65-75 bar. If criticality, indicated by the rapidly rising of pressure readings, was reached earlier, the compression was stopped.

S5.1.4 Reaction procedure

The reactor was then transferred to a Parr parallel autoclave system where it was heated through a heating mantle and pressure was closely monitored. The reaction time was counted from the moment the reactor reached 170°C. The pressure drops or increase was monitored with the pressure gauge of the system.

After the reaction, the reactors were rapidly cooled in an ice bath and the remaining CO\textsubscript{2} was released and purged out with nitrogen. The reactors were transferred back to the glovebox, where they were opened in a nitrogen atmosphere. The obtained solid was first weighed and then homogenized using a mortar. A precise amount of the mixture was then transferred to a glass vial for further volumetric and spectroscopic analysis.

For proof-of-principle reactions, the experience with the traditional formate coupling reaction was used and adapted to the pressurized reactor system. Several experiments,
presented in the main article were performed for which the reaction temperature, time, reactant mass, the ratio of K-Formate and NaH, and CO$_2$ pressure were altered. The heating rate was kept constant. All values used in the experiments are listed in Table 5.S1 below.

**Table 5.S1** Reaction conditions used during the study with base settings based on superbase work and range of values explored in optimization.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Lower value</th>
<th>Base values$^1$</th>
<th>Upper Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>80</td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td>Reaction time (min)</td>
<td>5</td>
<td>15</td>
<td>120</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>50</td>
<td>120</td>
<td>200</td>
</tr>
<tr>
<td>Hydride: Formate ratio</td>
<td>0.05</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Heating Rate (°C / min)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactant mass (mg)</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

**S5.2 Product analysis**

**S5.2.1 Weight-gain measurements during reaction**

The weight of the solids in the reactor before and after the reactions were measured using a fine balance. The weight change was calculated following equation S1.

**S5.2.2 Volumetric quantification of hydride consumption**

\[
Weight\,\,change\,\,(\%) = \frac{Weight\,\,solid\,\,products}{Weight\,\,solid\,\,educts} \times 100\%
\]

Eq. (S1)

The remaining amount of hydride after the reaction was estimated indirectly by measuring the evolving gas volume produced in the vigorous reaction of the hydride with added water. A fraction of the obtained solid was transferred to a sealed vial and water was added in known small amounts. The increase in gas volume was measured with a burette attached to the sealed vial. From the produced gas volume, the molar amount of remaining hydride in the solid product was calculated using the ideal gas law. From the produced moles of hydrogen, the hydride consumption was calculated with equation S2.

**S5.2.3 Qualitative and quantitative IR analysis of the products**

\[
Hydride\,\,consumption(\%) = \frac{Moles\,\,produced\,\,gas\,\,after\,\,reaction}{Moles\,\,added\,\,hydride\,\,before\,\,reaction} \times 100\%
\]

Eq. (S2)

The solution obtained after adding water for the quantification of remaining hydrides in 2) was analyzed in a liquid IR cell. We used a SmartSeal liquid cell from PIKE technologies with CaF$_2$ windows and a cavity thickness of 0.025 mm. The spectra were recorded with a Nicolet iS50R Research FTIR Spectrometer from Thermo Scientific. The cell was flushed with nitrogen gas for 5 - 10 min before measurement. Each sample was scanned thrice in the 400 – 4000 cm$^{-1}$ range to ensure reproducibility. Species present in the solution were both identified and quantified based on the Lambert-Beer-Law. The exact analysis theory, procedure and calculations are described in the supporting information of chapter 3 (S3.2.1 and S3.2.2)
S5.2.4 Labelling experiments and DFT calculations

Normal modes describe the possible movements/vibrations of each of the atoms in a system. The normal modes of an isotopically substituted molecule are different from the normal modes of an unsubstituted molecule, leading to different corresponding vibrational frequencies for the substituted atoms. The reduced mass $\mu$ and vibrational energy levels $\nu^e$ are bounded by equation S3 with $\mu$ defined in equation S4. When an atom is replaced by an isotope of a larger mass, $\mu$ increases, leading to a smaller $\nu^e$ and a downshift (or blue shift) in the spectrum of the molecule.\(^{2-4}\)

$$\nu^e = \frac{k}{2\pi \sqrt{\mu}}$$  \hspace{1cm} Eq. (S3)

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$  \hspace{1cm} Eq. (S4)

We used a DFT approach to calculate the expected downshifts of the species caused by the replacement of the carbon atoms of formate or oxalate with $^{13}$C-labelled carbon. We used the Amsterdam Modeling Suite (AMS) which enables the use of density functional calculations of various substances in an array of solvents. The molecules we calculated the IR spectra for include $^{13}$C-Formate and $^{12}$C-Formate ions with a charge of -1.0 which we use as a proof of concept as we were able to measure the real IR-shift for those ions. The ions of interest were $^{12}$C-$^{12}$C-Oxalate, $^{12}$C-$^{13}$C-Oxalate, and $^{13}$C-$^{13}$C-Oxalate with a charge of -2.0. For the model, we use the ADF mode with an LDA XC functional, scalar relativity, DZ as the basis set, large frozen core, and normal numerical quality. To emulate the solvation of the molecules in water, which we use as a solvent for our products’ IR measurements in the liquid cell, we use the COSMO model with Allinger as the default’s solvation radii. From the obtained IR spectra and the peaks in the region of interest, we calculate the shift in frequency using Eq. S5. In table S2 we show the suitability of the approach as the measured and calculated frequency shifts are in agreement for the two IR active vibrational modes of formate.

$$E = \text{Peak frequency}^{12\text{C}-\text{Compound}} - \text{Peak frequency}^{13\text{C}-\text{Compound}}$$  \hspace{1cm} Eq. (S5)

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Measured frequency (cm(^{-1}))</th>
<th>$\Delta E_{\text{measured}}$ (cm(^{-1}))</th>
<th>$\Delta E_{\text{calculated}}$ (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation around C-H bond</td>
<td>$^{12}$C-Formate 1382</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Symmetric C=O stretch</td>
<td>$^{12}$C-Formate 1380</td>
<td>21</td>
<td>21</td>
</tr>
</tbody>
</table>

For oxalate, the frequency of alternating symmetric C=O stretch decreases with the substitution by heavier carbon atoms. We calculated an expected frequency drop by 13 wavenumbers for a single and a further 8 wavenumbers for a full substitution as shown in table S3. Hence this approach allows a clear distinction of $^{12}$C-$^{12}$C, $^{13}$C-$^{12}$C, and $^{13}$C-$^{13}$C oxalate. This makes the signals of oxalate and formate and their isotopes distinguishable.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Measured frequency (cm(^{-1}))</th>
<th>Calculated frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alternating Symmetric C=O stretch</td>
<td>$^{12}$C-$^{12}$C-Oxalate 1308</td>
<td>$^{12}$C-$^{12}$C-Oxalate 1295</td>
</tr>
<tr>
<td></td>
<td>$^{13}$C-$^{12}$C-Oxalate</td>
<td>$^{13}$C-$^{13}$C-Oxalate</td>
</tr>
</tbody>
</table>
S5.2.5 Relative quantification of the isotope-labelled product mixture

As we used an IR cell with a well-defined path length, the absorption of each species can be related to its concentration in the measured solution using the Lambert-Beer Law. In the case of the labelling experiments, we were not able to perform an absolute quantification as this requires measuring a standard solution with a well-defined concentration as a reference. The absorption of each species can be calculated by estimating the area under the respective peaks. In the first step, we subtracted the contribution of water to the peaks using a standard which resulted in the signal shown in figure S1. As the peaks overlap, we performed a Gaussian fit in OriginLabs software for which we obtained a good fit with an \( R^2 \) of 0.9945 which is in close agreement with the adjusted \( R^2 \) of 0.9944.

The obtained areas for the peaks of each species are presented in table S4 below.

![Infrared spectrum of obtained solids](image)

**Figure 5.S1** Infrared spectrum of obtained solids from the reaction of formate, hydride, and CO\(_2\) and standards of labelled and unlabelled potassium formate and potassium oxalate dissolved in water and measured in liquid IR cell. The solid

**Table 5.S4** Details of Gaussian fitting to peaks received in the IR spectrum. R-square: 0.99457 and Adjusted R-square 0.9944

<table>
<thead>
<tr>
<th>Fitted species</th>
<th>(^{13})C,(^{13})C - Oxalate</th>
<th>(^{13})C,(^{12})C - Oxalate</th>
<th>(^{12})C,(^{12})C - Oxalate</th>
<th>(^{13})C - Formate</th>
<th>(^{12})C - Formate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavenumber (cm(^{-1}))</td>
<td>1286.50</td>
<td>1296.23</td>
<td>1309.57</td>
<td>1329.46</td>
<td>1351.62</td>
</tr>
<tr>
<td>Integrated area</td>
<td>1.80 ± 0.04</td>
<td>0.49 ± 0.04</td>
<td>0.0090 ± 0.002</td>
<td>3.93 ± 0.01</td>
<td>0.49 ± 0.01</td>
</tr>
<tr>
<td>Peak width (cm(^{-1}))</td>
<td>11.48 ± 0.27</td>
<td>7.52 ± 0.38</td>
<td>2.94 ± 3.03</td>
<td>10.96 ± 0.05</td>
<td>7.56 ± 0.22</td>
</tr>
</tbody>
</table>

**References**