Due to the growing interest in dimethoxymethane (DMM) as formaldehyde synthon and fuel additive, new and more efficient routes toward the formaldehyde analog are being investigated. One approach is the reductive transformation of carbon dioxide using a ruthenium phosphine catalyst and a Lewis acid additive in methanol. In the present work, we investigated the underlying reaction network, consisting of several intermediates, equilibria and side products, through in situ IR spectroscopy. We determined rate constants and activation parameters for the hydrogenation steps. Their temperature-dependent differences can be used to influence the product selectivity in this catalysis. To favor DMM formation, the acetalization equilibrium and especially the amount of water formed were identified as promising optimization opportunities. Simulation of concentration profiles on the basis of the proposed kinetic model enables the prediction of experimental product distributions for various reaction parameters, demonstrating the power of reaction network analysis for process optimization.

Introduction

In recent years, the industrial use of carbon dioxide as a renewable resource has gained increasing interest. This can be partially attributed to the role of CO₂ as a greenhouse gas and the growing awareness of its associated connection to anthropogenic climate change.¹ To meet this urgent challenge for present and future generations, academia and the chemical industry are exploring the possibilities of CO₂ utilization through various novel approaches.²⁻⁵ A promising target for the realization of the resulting circular approach is formaldehyde as it is an important building block with high demand in various chemical value chains and additionally offers the potential as hydrogen storage medium.⁶ Currently, formaldehyde is produced from methanol in an atom-inefficient process on a multimillion ton scale every year.⁷ Therefore, a sustainable solution based on carbon dioxide would be highly desirable. In addition to formaldehyde itself, its analogs are considered important to overcome the unfavorable thermodynamics of reducing CO₂ to formaldehyde because they are less susceptible for reduction to methanol.⁸⁻¹⁰ One compound with high potential is the dimethyl acetal, dimethoxymethane (DMM), which can be converted to formaldehyde or used as formaldehyde synthon.¹¹ Further, it is an essential precursor for oxymethylene ethers, that are currently discussed as renewable fuels and fuel additives.¹² Utilizing a homogeneous catalytic system for the reduction of carbon dioxide to DMM could present one possibility to realize this challenging transformation. The first homogeneous system that achieved a selective conversion of carbon dioxide to DMM consisted of a transition metal catalyst and a Lewis acidic co-catalyst together with hydrogen gas in alcoholic solvents.¹³ For this hydrogenation, ruthenium complexes bearing a triphos-type tridentate and tripodal phosphine ligand have proven to be particularly active (Scheme 1). The Lewis acid is needed to facilitate the esterification and acetalization steps. Through the use of multivariate analysis, process parameters could be optimized to reach a turnover number (TON) of 3874.¹⁴ In addition, the only other compound observed was methyl formate (MF), an intermediate in the reaction sequence, which can be further converted to DMM.¹⁵

Previous studies focused on structural and electronic modifications of the catalyst, like interchanging the transition metal center,¹⁶ varying the coordinating phosphorus moiety,¹⁷ or introducing different hetero-atoms in the apex position of the triphos ligand.¹⁸ Furthermore, it was reported that formic acid can be employed as starting compound for the synthesis of DMM under the same catalytic conditions.¹⁹ In addition, the ruthenium triphos formate complex has been identified as an active catalytic species and catalyst deactivation pathways can

Acknowledgements

This work was supported by the German Science Foundation (DFG) within the Research Training Group 1664 "Green Chemistry: Optimized Catalytic Processes and High-Value Products from Renewable Resources" (GRK 1664). The routine use of NMR in the compound identification was supported by the Helmholtz Institute Ulm. Partial financial support by the DFG (DFG-SPP 1767) and the Federal Ministry of Education and Research (BMBF, 03SF0510A) is also gratefully acknowledged.

Supporting Information

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.202100437

Scheme 1. Reductive transformation of carbon dioxide to dimethoxymethane (DMM) and methyl formate (MF) homogeneously catalyzed by a ruthenium triphos complex (X=C–CH₂,N) and a Lewis acid additive.
be suppressed by addition of formic acid and monodentate phosphine ligands, thus contributing to catalyst recycling.\textsuperscript{[13,15]}

Even though catalyst modification, reaction parameter optimization as well as recyclability studies were conducted to dramatically increase turnover numbers and selectivities, the kinetic parameters of the reaction network are not well investigated. First advances in this direction mainly focused on methanol production and compared the complexes used\textsuperscript{[16]} or investigated only a part of the entire cascade.\textsuperscript{[13]} We envisioned that more detailed studies on the reaction network may provide crucial insights that can further contribute to the optimization of this promising process and its potential industrial realization.

**Results and Discussion**

Taking into account previous reports, we started to define a reaction network incorporating all relevant reaction steps for the reduction of carbon dioxide to DMM (Scheme 2). Because the autoclave used in this investigation has a non-negligible gas volume, the transitions of CO\textsubscript{2} and H\textsubscript{2} between the gas and the liquid phase were defined as pre-equilibria. With temperature-dependent Henry’s law constants from solubility studies of carbon dioxide\textsuperscript{[16]} and hydrogen\textsuperscript{[13]} in methanol at hand, starting concentrations could be calculated from the applied pressure, and only one reaction rate constant for each gas-to-liquid transition had to be determined. A mass-transfer limitation of the reaction was ruled out since even after a reaction time of 60 hours significant amounts of dissolved CO\textsubscript{2} were observed. Furthermore, analysis of the CO\textsubscript{2} solution-to-gas transfer kinetics with fixed equilibrium constants \(k_0\) resulted in reaction rate constants of \(\approx 0.1\ \text{s}^{-1}\). A similar rate can be assumed for H\textsubscript{2} and thus a rate of 0.1 s\textsuperscript{-1} was applied for the rate constants \(k_3\) and \(k_6\) in all analyses.

For the reduction of dissolved CO\textsubscript{2}, several aspects had to be considered. Although formic acid is the most likely product of the first reduction step, neither formic acid nor formate salts were directly observed in any of our reactions. It can be assumed for H\textsubscript{2} production and compared the complexes used\textsuperscript{[16]} or investigated only a part of the entire cascade.\textsuperscript{[13]} We envisioned that more detailed studies on the reaction network may provide crucial insights that can further contribute to the optimization of this promising process and its potential industrial realization.

Two steps to be combined as one. The reverse reaction was considered in our reaction network because ester hydrolysis\textsuperscript{[18]} as well as the decomposition of formic acid to hydrogen and carbon dioxide gas\textsuperscript{[15,12]} have already been reported in literature. The reversibility of CO\textsubscript{2} reduction and the following esterification was confirmed in a separate experiment, in which MF was employed as substrate instead of CO\textsubscript{2} at 60 bar H\textsubscript{2} and otherwise identical catalytic conditions with CO\textsubscript{2} formation being observed via in situ IR spectroscopy (peak at 2341 cm\textsuperscript{-1}, for detailed documentation see the SI).

In theoretical studies on CO\textsubscript{2} hydrogenation without a Lewis acid co-catalyst, it was shown that the reduction of formic acid to methanol is an energetically favorable pathway toward methanol.\textsuperscript{[20]} Therefore, we concluded that methoxymethanol (MM) is the most plausible product for the reduction of MF, which is further supported by the presence of MM in NMR data of reports on CO\textsubscript{2} conversion to DMM.\textsuperscript{[21]} Subsequently, MM reacts with MeOH to DMM and H\textsubscript{2}O under Lewis acid catalysis. This acetalization equilibrium is shifted toward DMM, because MeOH is employed as solvent and is thus present in high concentration. The equilibrium constant \(K_{eq}\) for this acetalization was reported to be temperature-independent,\textsuperscript{[21]} and the rates of this equilibrium can be reasonably estimated to be several orders of magnitude higher than for the reductive steps, as MM concentrations were below the limit of detection in our experiments. The reaction rate constant \(k_{DMM}\) was obtained from in situ IR-spectroscopic measurements at 60.0 °C with DMM in methanol-d\textsubscript{4} in the presence of the Lewis acid Al(OTf)\textsubscript{3}. Constant \(k_{DMM}\) can be calculated from the reaction rate constants and the values were used in all analyses (experimental details of the estimation can be found in the SI).

Regarding the over-reduction to MeOH, two pathways can be considered as plausible: Either formaldehyde is hydrogenated after formation from MM, or MM directly undergoes a reductive cleavage. However, formaldehyde and MM concentrations could not be monitored with our setup and we decided to simplify the reaction network and to treat this transformation as one step with a single effective reaction rate constant \(k_7\).

In all experiments conducted for this investigation, the catalytic system consisting of [Ru(N-Triphos\textsuperscript{20}(tmml)] for the hydrogenation and Al(OTf)\textsubscript{3} for the acetalization as well as the esterification was employed due to its high performance in previous studies.\textsuperscript{[16–18]} To ensure comparability, the amount of hydrogenation catalyst, Lewis acid additive as well as the reaction mixture volume were kept constant at \(n_{CO}_2=4.5\ \text{μmol}, n_{add}=18\ \text{μmol},\) and \(V=6.0\ \text{mL}\). Due to the technical pressure limit of 69 bar of the ReactIR probe, that was used for reaction monitoring, the sum of partial pressures was kept at a maximum 65 bar. Hence, partial pressures of carbon dioxide \(p_{CO}_2\) and hydrogen \(p_{H}_2\) of 10 and 55 bar, respectively, were applied.

The reaction progress of the most pronounced vibrational peaks of CO\textsubscript{2}, MF and DMM were monitored by in situ IR spectroscopy, a typical profile is shown in Figure 1 for an experiment at 72.6 °C. As CO\textsubscript{2} is reduced (Figure 1a, d), the intermediate MF is formed (Figure 1b, e), which passes a maximum after 12 hours and then declines as it is in turn...
hydrogenated. DMM is generated after a small induction period (Figure 1c, f) reaching its highest concentration after 42 hours and decreases very slowly afterwards. In separate hydrogenation experiments with DMM as substrate, 60 bar H$_2$, three equivalents of water, and otherwise identical catalytic conditions, the half-life $t_{1/2}$ of DMM was determined to be 16 h at 83.7 °C, 39 h at 77.1 °C, 114 h at 67.1 °C, and 241 h at 60.0 °C, indicating that DMM is moderately stable under the applied reductive conditions (for detailed documentation see the SI).

For calibration and data analysis, the second derivatives of the IR spectra (Figure 1d–f) were used because they are less susceptible to self-absorption phenomena of the IR-probe and minor fluctuations of external conditions, such as small changes in ambient temperature due to day-night cycles or refill of the detectors cooling agent.$^{[22]}$

The concentration courses of MF and DMM (Figure 2a–d) were analyzed with the free network simulation software COPASI$^{[23]}$ to gain access to the rate constants $k_1$, $k_{-1}$, $k_2$, and $k_3$ of the hydrogenation steps (for detailed information see the SI). Recorded CO$_2$ concentrations were not used for analysis because the monitored peak is located in a wavenumber range of high self-absorption of the IR probe, resulting in a nonlinear relation between the concentration and the measured signal. Instead, the initial concentrations calculated from Henry’s law constants were used to account for gaseous and dissolved CO$_2$ in the network.

As expected, the calculated reaction rate constants $k_1$, $k_{-1}$, $k_2$, and $k_3$ increase with temperature (Figure 2e), with the rates $k_1$ for the reduction of CO$_2$ being the lowest. This implies that reduction and esterification of CO$_2$ is the rate-determining step in this network. In addition, the equilibrium lies on the CO$_2$ side as the rates $k_{-1}$ for the reversed reaction are higher (Figure 2e). Initially, high concentrations of CO$_2$ and MeOH are present in solution, leading to a fast initial increase of MF since its reaction rate is not yet significantly influenced by the reverse step. As the reaction proceeds, the overall CO$_2$ concentration decreases, and an increasing amount of H$_2$O is formed. Consequently, the concentration of MF decreases as the rates for the reverse reaction to CO$_2$ as well as the hydrogenation to MM increase.

Interestingly, the rate constants $k_3$ for the hydrogenation of MM are the highest of the three reductive steps, rendering the stability of DMM under the applied conditions strongly dependent on its equilibrium with MM. Considering the reaction pathways starting from MF, it is obvious that the reaction toward DMM is not feasible without a large excess of alcoholic solvent as otherwise the reduction to the methanol oxidation state is strongly favored due to the lack of acetalization.

The reaction progress plots resulting from the determined rate constants listed in Figure 2e are in very good agreement with the experimental values (Figure 2a–d), supporting the established model of the reaction network (Scheme 2) and the obtained kinetic data.

To determine the activation parameters for the investigated ruthenium-catalyzed reduction steps, the Eyring-Polanyi-Equation was used. By plotting the natural logarithm of the reaction rate constant divided by the temperature $\ln(k/T)$ versus the
reciprocal temperature \( T^{-1} \), the enthalpy of activation \( \Delta H^* \) was calculated from the slope and the entropy of activation \( \Delta S^* \) from the y-intercept of the linear fit (Figure 2f–h). For the determined reaction rate constants (Figure 2e, entries 1–4), the plots exhibit a good linear dependency. A higher variance in the Eyring plot for \( k_3 \) and the resulting higher errors of the activation parameters led us to further evaluate the hydrogenation experiments with DMM as substrate (see the SI). If the approximation of our model, that rates for acetalization equilibria are much higher than for hydrogenation steps, is correct and if no further significant decay pathways for DMM exist, the rate for DMM consumption under hydrogenation conditions should correspond to \( k_3 \). These calculated data points (Figure 2e, entries 5–8) fit in well with the Eyring analysis for the reduction of MM (Figure 2h) and even reduce variance, thus confirming the validity of the presented model and approximations made therein. All activation parameters determined from the depicted Eyring plots are within the typical range of transition metal-catalyzed hydrogenation reactions and are listed in Table 1.

With the reaction temperature ranging from 60 to 100 °C in the present and previous studies,[8–9,11] the Gibbs free energy of activation \( \Delta G^* \) is given for elevated temperatures of 333 K, 353 K and 373 K. For the herein investigated catalytic system, the enthalpy of activation increases from \( \Delta H_1^* \) to \( \Delta H_2^* \) to \( \Delta H_3^* \), ranging from 64.3 kJ · mol\(^{-1}\) to 113.0 kJ · mol\(^{-1}\). In the same order, the entropy of activation becomes larger and even positive for the reduction of MM. The first two reduction steps are less favorable at higher temperatures, though this effect is less pronounced for the hydrogenation of MF. In contrast, the reduction to MeOH is favored at higher temperatures. At 333 K, \( \Delta G^* \) for the second and the third step are the same within the margin of error and 10 kJ · mol\(^{-1}\) lower than for the first step. At elevated temperatures, the differences become more pro-
nounced and the reductive transformation of MM to MeOH has its lowest activation barrier, resulting in greater MeOH yields. The observed trends for the activation parameters match very well with experimental data, where synthesis of MF is carried out at lower temperatures, while DMM is synthesized at higher temperatures and for MeOH synthesis the highest temperatures are applied. Nevertheless, it has to be noted that the determined absolute values for \( \Delta G^\ddagger \) of the hydrogenation steps seem to disfavor DMM formation. This, however, is contrasted by the fact that acetalization rate constants are several orders of magnitude greater (10^{-1} vs. 10^{-6}-10^{-8}, see Figure 2e), which is an initial constraint for our model. To obtain significant amounts of DMM under these conditions, it has to be ensured that the equilibrium with MM stays in favor of DMM. For this purpose, high MeOH and low H concentration. 

Especially with regard to absolute concentrations and optimum reaction times can be optimized to improve the accuracy of predictions, especially with regard to absolute concentrations and optimum reaction time. These include investigating and integrating the reaction parameters like catalyst amount and autoclave volume could not be considered for this simulation, the predicted conversion and selectivity of the reaction coincide well with experimental results (TON_{MF,exp} = 745, selectivity: 80% MF after 18 h). Due to the aforementioned approximations, however, the time course of the reaction could not yet be adequately reproduced.

Generally, the presented simulations show the predictive power of a kinetic model for product distribution in ruthenium-catalyzed CO hydrogenation. There are still several factors that can be optimized to improve the accuracy of predictions, especially with regard to absolute concentrations and optimum reaction time. These include investigating and integrating the role of the active catalyst and additive into the model.

**Conclusion**

We report the kinetic and thermodynamic analysis of the reaction network for the reductive transformation of carbon dioxide to dimethoxymethane (DMM) catalyzed by [Ru(N-Triphos)(tmm)] and Al(OTr)₃. The reduction and esterification of CO₂ to methyl formate (MF) was found to be the rate-determining step of this reaction cascade because this step has the lowest reaction rate constants and the highest Gibbs free energies of activation \( \Delta G^\ddagger \) at the investigated temperatures.
Interestingly, the reductive transformation of methoxymethanol (MM) to MeOH shows the highest reaction rate constants and the lowest $\Delta G^\circ$ of the three hydrogenation steps at elevated temperatures. These findings imply that the formation of DMM is strongly dependent on its equilibrium with MM and thus on the amount of H$_2$O in solution. Removal of water was identified as a promising adjustment to further optimize the process regarding DMM yields.

To explore the predictive capabilities of the proposed kinetic model, we simulated reaction profiles with modified process parameters beyond our experimental data. The calculated product distributions showed that by varying temperature and hydrogen pressure the process can be fine-tuned to mainly yield either MF ($60^\circ$C, 90 bar H$_2$), DMM ($80$–$90^\circ$C, 90 bar H$_2$) or MeOH ($>100^\circ$C, 120 bar H$_2$). The results of these simulations are in good agreement with reported experimental values, confirming the validity of our approach. We anticipate that by refining the kinetic model through further investigations into monitoring possible intermediates as well as the nature and role of catalyst and additive, it will be possible to move to even more accurate predictions of product yield, further paving the way for industrial application of this reaction.

**Experimental Section**

Synthesis of the N-Triphos ligand and the respective ruthenium complex is literature known.$^{[27]}$ Detailed documentation of all reactions and their analysis as well as the performed simulations can be found in the supporting information.

**Preparation of reaction mixture for catalysis:** In a flame-dried Schlenk tube and under argon atmosphere, 6.90 mg (9.00 μmol) [Ru(N-Triphos)$_3$(tmm)] and 17.1 mg (36.0 μmol) Al(OTf)$_3$ were suspended in dried and degassed MeOH (12.0 mL) for 1 h. General procedure for hydrogenation experiments: Catalytic investigations were performed using a method previously established by our group.$^{[9,28]}$ Reactions were carried out in a stainless-steel high-pressure autoclave (30 mL total volume) using a glass inset and a stirring bar for mixing. The autoclave was evacuated and flushed with nitrogen three times before the reaction mixture (6.0 mL) was transferred into the glass inset. The ReactIR probe was installed in nitrogen counter-flow, sealing the autoclave. The carbon dioxide gas line was purged with CO$_2$ and the hydrogen gas line was purged with H$_2$ at least seven times. The autoclave was pressurized with CO$_2$ (10 bar) and the CO$_2$ was deposited by cooling the autoclave to −78 °C for 10 min. Then, the autoclave was pressurized with H$_2$ (55 bar). The closed autoclave was allowed to adjust to room temperature for 20 min. The reaction mixture was stirred at the mentioned temperature for the defined time. The

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**Figure 3.** Simulated concentration time courses for the ruthenium-catalyzed reductive transformation of CO$_2$ for 4.5 μmol [Ru(N-triphos)$_3$(tmm)] and 18 μmol Al(OTf)$_3$, with different process parameters: (a) 90 bar H$_2$, 20 bar CO$_2$, 90°C, 6.0 mL MeOH; (b) 120 bar H$_2$, 20 bar CO$_2$, 120°C, 6.0 mL MeOH; (c) 60 bar H$_2$, 20 bar CO$_2$, 60°C, 6.0 mL MeOH; (d) 90 bar H$_2$, 30 bar CO$_2$, 60°C, MeOH/1,4-dioxane 2:1. Note that the concentration on y-axis is not displayed on the same scale before and after the axis break.
autoclave was cooled to in situ IR spectroscopy: For all hydro-
genation and calibration experiments, Mettler-Toledo ReactIR 15
with the DiComp probe sensor (DST Series 63.6 mm AgX Fiber
Conduit, 1.5 m fiber length, 216 mm probe length) in combination
with a high-pressure adapter (1/2” NPT) and the Mettler-Toledo
software IC IR 7.1 was used. IR Spectra were recorded every 60 s for
at least 24 h (in some cases: then every 120 s) with a resolution of
4 cm⁻¹ and an accumulation of 256 scans. The reaction temperature
inside the autoclave was determined via the built-in temperature
sensor at the ReactIR probe head. For data analysis, the time
courses of the areas of MF (Peak at 1735 cm⁻¹, C=O stretching,
location: 1743–1710 cm⁻¹, baseline: 1765–1690 cm⁻¹) and DMM
(Peak at 923 cm⁻¹; symmetrical O–C–O stretching, location: 940–
914 cm⁻¹, baseline: 940–914 cm⁻¹) were used in combination with
an external calibration model generated by iC Quant software
integrated in iC IR 7.1 to create the concentration time courses.
Starting concentrations of H₂ and CO₂ were calculated from applied
pressures and literature data[16–17,24] on the solubility in MeOH.
NMR Analysis: The concentrations of the reaction mixtures and
calibration solutions were determined by ¹H NMR spectroscopy. A
sample of 50 μL of the respective liquid and 35 μL mesitylene as
internal standard were dissolved in 450 μL DCM-d₅.
Determination of reaction rate constants: The reaction rate
constants were determined using the concentration time courses of
MF and DMM in COPASi files and calculations with used
concentration courses (zip).

Supporting Information
Supplementary data to this article can be found online: Synthetic procedures, characterization data, experimental de-
tails, calibration experiments, Eyring analysis and simulated reaction profiles (PDF); COPASI files and calculations with used
concentration courses (zip).

Author Contributions
M.L. designed and performed the experiments and the reaction
network analysis. All authors contributed to the interpretation
of the data. The manuscript was written through contributions of
all authors. O.T. supervised the project and all authors have
given approval to the final version of the manuscript.

Acknowledgements
Generous financial support by the German Federal Ministry of
Education and Research (BMBF) within the funding initiative
“CO₂Plus – Stoffliche Nutzung von CO₂ zur Verbreitung der
Rohstoffbasis” is gratefully acknowledged. Open access funding
enabled and organized by Projekt DEAL.

Conflict of Interest
The authors declare no conflict of interest.

Keywords: carbon dioxide reduction · homogeneous catalysis ·
IR spectroscopy · kinetic modeling · reaction network analysis

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