Homogeneous Catalytic Formic Acid Dehydrogenation in Aqueous Solution using Ruthenium Arene Phosphine Catalysts

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This paper is dedicated to Prof. Dr. Peter Comba on the occasion of his 65th birthday.

Abstract. In this work, we studied catalytic formic acid dehydrogenation with a homogeneous RAPTA type precatalyst in aqueous solution. The effects of an amino group, added in situ to the reaction were evaluated. The initial compound, ([η]-benzylidimethylamine)Ru[PTA(Cl)]2Cl (3), was synthesized and proved to be moderately active for selective formic acid dehydrogenation. The addition of a second equivalent of PTA at the beginning of the reaction significantly improved the catalytic performance. The activation energies for both catalytic systems were assessed via an Arrhenius plot. 1H- and 13C-NMR spectroscopy was used to follow the course of the reaction online and verified complete consumption of substrate. A triplet signal was observed in the hydride region along with its corresponding coupling counterpart in 31P spectra.

Introduction

In 2017, “The Guardian” released an article entitled “Want to fight climate change? Have fewer children”, stating that “…by far the biggest ultimate impact is having one fewer child, which the researchers calculated equated to a reduction of 58.6 tonnes of CO2 for each year of a parent’s life.”[1] As a matter of fact, the world population is continuously growing, and rising living standards become apparent in many societies. Both factors contribute to an ever-increasing demand for energy. Currently, the primary energy sources are fossils fuels, namely coal, gas, and petrol, which release carbon dioxide (CO2) upon their combustion with oxygen. In the earth atmosphere, carbon dioxide acts as a greenhouse gas, contributing to phenomena known as global warming and in further extend, climate change.[3] A possible solution to break this vicious cycle could be to switch to renewable energy sources by harvesting energy from natural occurrences such as wind or sun. One significant disadvantage of solar and aeolian driven energy generation is their fluctuating nature and in most cases incompatibility with a mobile application. A system needs to be put in place to compensate for the gaps in primary production. The electrolysis of water to hydrogen and oxygen allows a simple transition from electrical to chemical energy, in which hydrogen becomes an energy carrier.[13] Fuel cell technology converts hydrogen efficiently on demand back to electrical energy. As of now, no fully satisfying hydrogen storage technology for large-scale application has been developed. Compression and liquefaction of gaseous hydrogen require significant amounts of energy and in both methods are inherently unsafe processes since they involve the handling of highly pressurized containers or liquefied hydrogen.[4]

Chemical storage of hydrogen in the form of liquid organic hydrogen carriers (LOHC)[6] is an attractive solution, offering a range of advantages. Formic acid unites some wanted properties such as a high hydrogen content of 53 g·L−1, equal to a 700 bar pressurized cylinder, inflammable (85% in water), no bioaccumulation, posing, therefore, no environmental risk and is easy to handle since it is a liquid at ambient temperature.[7] The production of formic acid in a sustainable way can be accomplished by CO2 hydrogenation in the presence of appropriate catalysts. Hydrogen delivery from formic acid requires as well a catalyst, providing then hydrogen with an overall storage efficiency of 100%. Both reactions are the two halves of the formic acid/carbon dioxide cycle for reversible hydrogen storage (Figure 1), which is a schematic representation of a hydrogen battery.[8]

Figure 1. The formic acid/carbon dioxide cycle for reversible hydrogen storage[5].

Both, the homogeneous catalytic formic acid dehydrogenation and the carbon dioxide hydrogenation can take place in different solvents, including water, organic solvents, and ionic...
The effect, the solvents exert on chemical reactions is profound, and additives are used to shift reaction equilibria. Suitable transfer hydrogen catalysts comprise numerous platinum group metal complexes with Ru and Ir as a central ion. Often the ligands contain phosphorus, nitrogen donor atoms, or being pincer-type complexes. Recently, Himeda and co-workers reported on a Cp*Ir catalyst with an N-phenylpicolinamide ligand, reaching a TOF of 118,000 h⁻¹ at 60 °C and a constant dehydrogenation rate of 35,000 h⁻¹ over six hours at 50 °C (TON 1,000,000). However, for industrial application, first-row transition metal catalysts are desirable and this for many reasons, but mainly because they are cheap and abundant. Especially for iron catalysts, the recent developments in the field are remarkable. There are recommendable review papers available. Heterogeneous catalysts, heterogenized complexes, nanoparticles, nanostructures have also been proven to be active in the hydrogen storage/delivery in the formic acid/carbon dioxide couple, as reviewed by Himeda et al.

Ruthenium-arene complexes equipped with 1,3,5-triaza-7-phosphatricyclo-[3.3.1.1]decane ligand (PTA), commonly known as RAPTA, became famous for their cytostatic properties. Particularly well known are RAPTA-C (cymene) and RAPTA-T. The compound depicted in Figure 2 was initially studied by Dyson et al. in 2006 upon its cytotoxicity. Besides their cytostatic properties, it was discovered that η₆-arene-ruthenium(II) complexes, among them RAPTA and related structures, own catalytic properties for several types of reactions, including transfer hydrogenation.

![Figure 2. RAPTA type precatyslat 3.](image)

Herein, we investigated a catalytic system for formic acid dehydrogenation in aqueous media with [(η₆-benzylidimethylamine)Ru(PTA)Cl₂]Cl (3) as a precatyslat, which is synthesized from dimeric [(η₆-benzylidimethylamine)RuCl₂]Cl₂ (2) and one equivalent of PTA per central Ru atom. The dimethylated amino group connects via a single CH₂ linker to the arene. The amino group introduces a range of new possibilities and features to the molecule compared to purely aliphatic aromatics. In the first place, the solubility in aqueous media is considerably increased but also from a mechanistic point of view, the in acidic media positively charged trialkylammonium functionality, offers interesting options. An important aspect when selecting this arene was that the amino group could help coordinate substrate molecules via hydrogen bonding and also stabilize intermediates during the dehydrogenation process through its charge via an outer-sphere mechanism.

It should be mentioned that the linker measures only one carbon atom to prevent the amino moiety from interacting directly with the central ruthenium atom via its lone pair. The PTA, on the other hand, provides steric protection by its bulky cage-like structure, and the phosphine donates electron density towards the center to render it less prone to reduction by formic acid or dihydrogen. Also, PTA increases the solubility in aqueous media, especially in a protonated state in an acidic milieu.

Results and Discussion

Compound 3 was synthesized, characterized by NMR and mass spectroscopy and subsequently studied to explore the potential towards formic acid dehydrogenation. The catalytic activity was assessed by dehydrogenating a defined amount of formic acid and following the process with two orthogonal techniques. During dehydrogenation, formic acid releases hydrogen and carbon dioxide in equal amounts, causing a pressure increase in a closed tube, which can, when recorded over time, be correlated with the reaction progress. The complex, which is added to the water-substrate mixture is considered as a precatalyst and undergoes ligand exchange of labile chloride ligands to become the catalytically active species, as was described by Guan et al. for the similar complex [(η₆-cymene)Ir(2,2'-biimidazolone)Cl]Cl. At the end of the reaction, pressure increase levels off and finally stops. The increase of pressure in a closed vessel can be correlated with the progress of the reaction since the two only products from FA dehydrogenation are carbon dioxide and hydrogen (Figure S2, Supporting Information). The kinetic curves shown in Figure 3 were obtained when dehydrogenating FA under constant conditions except for the temperature (70–100 °C).

![Figure 3. Conversion of FA (dehydrogenation) vs. time; [(η₆-benzylidimethylamine)Ru(PTA)Cl₂]⁺ to CO₂ and H₂ at 70–100 °C; 222 mg FA in 1778 mg water and catalyst load 0.0165 m](image)
showed signs of degradation and the catalytic activity broke in. From the formation of black debris and metallic depositions on the walls of the tube was deduced that reduction of the central Ru\(^{II}\) atom is the most plausible cause for inactivation and further reasoned that a second PTA could provide improved compound stability.

Figure 4. Arrhenius plot to determine the \(E_a\) of the catalyst 3; the necessary kinetic data was derived from pressure vs. time curves; only the linear part of the curves was taken into consideration for the extraction of kinetic data.

In 2004, Kaitó et al. reported on a water-soluble (\(\eta^6\)-arene)ruthenium(II)-phosphine complexes (arenes are benzene and \(p\)-cymene) and their catalytic activity in hydrogen carbonate hydrogenation in aqueous solution.\(^{[26]}\) Of particular interest to us was the described mode of catalyst formation, which was accomplished by in-situ combination of the dinuclear metal precursor and the desired amount of PTA in the reaction vessel. Among other mutually catalytically active species, they suggest \([[\eta^6\text{-arene}]\text{Ru(PTA)}_2\text{H}]^+\) as intermediate structure. A structurally related compound, \([\eta^6\text{-p-cymene}]\text{Ru(PTA)}_2\text{Cl}]\text{BPh}_4\) was described by Peruzzini et al. in 2008.\(^{[29]}\) Accordingly, we combined the precatalyst 3 in water with one equivalent PTA, added substrate and started the reaction. First, we observed a color change from shades of red to an orange-yellow solution, then an increased catalytic activity.

The curves in Figure 5 were obtained under the same experimental conditions as outlined for Figure 3. The dehydrogenation progresses significantly faster in with the modified catalyst, therefore the time axis is no longer in logarithmic scale.

The activation energy was assessed by an Arrhenius plot (Figure 6) and the apparent activation energy \((E_a)\) was determined to be \(88.67 \pm 4\text{ kJ} \cdot \text{mol}^{-1}\), a value lower than the one of the initial compound and thus providing a possible explanation for the increased activity at equal temperatures.

The second technique, real-time NMR spectroscopy, enabled us to observe the reaction progress on a molecular level at all times. For this purpose, the reaction occurred in sealed medium pressure sapphire tubes within the NMR instrument. Figure 7 shows the proton spectrum of \(^{13}\text{C}\) labeled formic acid dehydrogenation by the in-situ generated catalyst. Formic acid appears as a doublet (7.75 and 8.30 ppm, \(J = 218.8\text{ Hz}\)) since the carbon-13 induced splitting occurs almost quantitatively, while the small peak in the center (\(\delta = 8.03\text{ ppm}\)) results from unlabeled formic acid. Between spectrum 5 and 6, all formic acid is dehydrogenated. Meanwhile, in the \(^{13}\text{C}\) NMR, a carbon dioxide peak is emerging at \(\delta = 125.1\text{ ppm}\) (see Figure S1, Supporting Information).
1H NMR measurements ensured that the catalyst is capable of completely consuming all formic acid, an important aspect when using pressure measurements to follow the reaction to completion.

Transition metal hydrides are crucial intermediates in many catalytic cycles, especially when transfer hydrogenation, hydrogen evolution or hydrogenation is observed. For this reason, we examined our compound towards metal hydrides and identified a triplet in the hydride region at $–11.91$ ppm ($J = 40.2$ Hz, Figure 8). The next logical step was to look for a corresponding nucleus, which was coupling with the hydride. n $^{31}$P spectra, a doublet at $\delta = –23.68$ (Figure 9) featured an almost identical coupling constant ($J = 39.2$ Hz). The two signals are not only linked by their almost identical coupling constant but also phosphorus decoupled measurement caused the triplet in the hydride region to collapse into a singlet signal (Figure S3 A/B, Supporting Information). Likewise, $^{31}$P($^1$H) scans afforded a singlet in the $^{31}$P NMR spectrum at the same place as the doublet appeared before (Figure S3 C/D, Supporting Information). These findings serve as confirmation for a first coordination sphere where phosphorus and one hydride are present.

Conclusions

We synthesized and evaluated a RAPTA-type compound towards its catalytic properties for selective formic acid dehydrogenation. The compound proved to be active, but the overall performance was below our expectations. The activity became significantly improved when introducing a second PTA in-situ, obtaining the mutually active structure ($\eta^6$-benzylidimethylamine)Ru(PTA)$_2$H$^{2+}$, on which was reported earlier. The activation energies for both systems were determined, and NMR spectroscopy was employed to confirm the complete dehydrogenation of formic acid in the reaction mixture.

Experimental Section

Materials: Solvents and chemicals were purchased from commercial suppliers and used without further purification. RuCl$_3$(H$_2$O)$_4$ (Ru: 40–43%) was obtained from Precious Metals Online (PMO Pty Ltd). All solvents had at least HPLC grade (for synthesis) or analytical grade (p.a.).

Instruments: Microwave syntheses were carried out with a Biotage Initiator 2.0 microwave synthesizer (400 W) in 20 mL microwave vials and equipped with magnetic stirring bars. NMR experiments were performed with a Bruker AV-400 (5 mm) for verification of the synthesized precatalysts while the kinetic measurements were recorded with a Bruker AVIII-400 in 10 mm medium pressure sapphire tubes. MestReNova 11.0.2 was used for spectra analysis and evaluation.

Synthesis of 1-(Cyclohexa-2,5-dien-1-yl)-N,N-dimethylmethanammonium Chloride (1): A Birch reduction of N,N-dimethyl-1-phenylmethanamine (11.7 mL; density = 0.9; 10.5 g, 0.1147 mmol) with lithium afforded 1-(cyclohexa-2,5-dien-1-yl)-N,N-dimethylmethanammonium chloride as white crystalline powder (61% yield). $^1$H NMR (400 MHz, deuterium oxide): $\delta = 5.96$ (s, 1 H), 5.71 (s, 2 H), 3.60 (s, 2 H), 2.77 (s, 6 H), 2.71 (d, $J = 8.7$ Hz, 2 H) ppm.

Synthesis of [(η6-Benzylidimethylamine)RuCl$_2$(PTA)$_2$Cl] (2): RuCl$_3$(H$_2$O)$_4$ (300 mg, 1.147 mmol) was dissolved in a mixture of isobutanol, water, and acetone (6:2:2.2 mL) in a 20 mL microwave tube, and 1 (3.155 mmol, 548 mg, excess 2.75) was added. Stirring with nitrogen did not result in higher yields. The sample was placed in a microwave oven and heated up to 145 °C for 5 min. After cooling to 0 °C, the product was collected by filtration as dark red crystals and washed with methanol, pentane and diethyl ether. The crystals were dissolved in water/MeOH (80:20), filtered through celite to remove traces of unreacted metal. Finally, the filtrate was evaporated to obtain 323 mg of a bright red crystalline substance (yield 82%). $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta = 10.77$ (s, 1 H), 6.39–5.92 (m, 5 H), 4.07 (s, 2 H), 2.83 (s, 6 H) ppm.

Synthesis of [(η6-Benzylidimethylamine)Ru(PTA)$_2$(Cl)$_2$]Cl (3): The dinuclear compound 2 (150 mg, 0.216 mmol) was dissolved in water (15 mL, previously degassed by bubbling N2 through for 15 min) and warmed to 90 °C in a nitrogen atmosphere. One equivalent of PTA (68.6 mg, respectively to Ru atoms) was added. An immediate color change was observed. After keeping the reaction mixture at the same
temperature for 10 more min, the water was evaporated and the compound collected, washed consecutively with 2-propanol, ether, and dried in vacuo. The compound was isolated in 71 \% yield (155 mg) \textsuperscript{1}H NMR (400 MHz, deuterium oxide): $\delta = 6.11$–5.78 (m, 5 H), 4.54 (s, 6 H), 4.27 (s, 6 H), 4.11 (s, 2 H), 2.93 (s, 6 H). \textsuperscript{3}P NMR (162 MHz, deuterium oxide): $\delta = -29.95$ ppm.

Supporting Information (see footnote on the first page of this article):

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