Homogeneous catalytic reduction of CO₂ in aqueous medium

PhD thesis

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Debrecen, 2002


**Introduction, aims**

The homogeneous catalytic hydrogenation of CO\textsubscript{2} has recently become an intensively studied field of chemical research. The fact that the environmental problems have become of greater importance makes the study of this topic even more urgent. The large-scale use of CO\textsubscript{2} – as a raw material of chemical industry – would reduce the strain of the environment, and the use of aqueous medium may open the door for the development of environmentally friendly technologies. This way the chemical processes using toxic or other solvent that can be treated only with difficulties could be replaced.

[1]

In our research group we develop, prepare, and study transition metal complexes suitable for the homogeneous catalytic hydrogenation of various substrates. I studied the catalytic effect of Ru, Rh and Ir complexes with PTA and TPPMS ligands on the reaction of CO\textsubscript{2} and H\textsubscript{2}. My thesis is based on the work with [RuCl\textsubscript{2}(TPPMS)\textsubscript{2}] and its derivatives.

Although we can find more and more publications on the hydrogenation of CO\textsubscript{2}, the number of reactions in aqueous medium is rather small and the conversions achieved are also small. Therefore I aimed at the development and characterisation of aqueous systems suitable for the catalytic hydrogenation of CO\textsubscript{2}. 

2
Methods applied

Some of the reactions were carried out in a pressure proof (up to 12 bars) glass tube reactor equipped with a septum and a gas-inlet valve. Further experiments were performed in a pressure-proof cuvette (up to 40 bars) and by in situ NMR techniques (up to 100 bars).

The detection and separation of formic acid and formates from the other molecules present in the reaction mixture was carried out by HPLC. The instrument consisted of a Waters 501 HPLC pump, a SUPELCOGEL® 610H styrene-divinylbenzene based ion-exchange column and a Waters 490E UV/VIS detector.

The spectrophotometric measurements were performed in a home made pressure proof cuvette. The spectra were recorded on a Hitachi U2000 instrument, the data collection was carried out by computer while the data processing was done with U2000 and Excel 97 softwares.

A Chrom 5 instrument was used for the gas chromatographic measurements with a column of 10% Carbowax + 3.5% KOH 80/100 Chromosorb.

The NMR measurements at atmospheric pressure were performed on an analogue, Bruker AM360 instrument, while the high pressure measurements with a digital Bruker DRX 400 device.

The infrared spectra were recorded on a PE Paragon 1000 PC instrument in KBr pastilles.
Results

The new scientific results of my work are as follows

1. $[\text{RuCl}_2(\text{TPPMS})_2]$ was found to catalyze the hydrogenation of CO$_2$ in aqueous solution.

Performing the reaction in acidic medium there is only physically dissolved CO$_2$ present in the solution. In a typical reaction where the concentration of the catalyst was $2,5 \cdot 10^{-3}$ mol/dm$^3$, at 10 bar pressure (the ratio of CO$_2$ and H$_2$ was 3:7) formic acid was formed. The turnover frequency was 0,3 h$^{-1}$.

![Meta-sulphonatophenyl-diphenylphosphine (TPPMS)](image)

Figure 1
Meta-sulphonatophenyl-diphenylphosphine (TPPMS)
2. It was found, that the rate of the reaction of CO₂ and H₂ depends on the pH of the medium: the reduction of the HCO₃⁻ is the fastest.

In the mechanistic interpretations published in the literature – even in aqueous systems – CO₂ molecule is included as the reactive species. Of course this is possible – especially in organic solvents – however it seems from our study that out of the three species formed in the reaction of CO₂ and water (i.e. solvated CO₂, HCO₃⁻, CO₃²⁻) HCO₃⁻ rapidly reacts - at least relatively to the other two.

This fact explains the earlier experimental observations [2] that the presence of a small amount of water has favourable effect on the rate of the hydrogenation of CO₂ even in organic solvents.

<table>
<thead>
<tr>
<th></th>
<th>T (°C)</th>
<th>T (h)</th>
<th>cₖₐₜ (mol/dm³)</th>
<th>TOF (1/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (aq)</td>
<td>50</td>
<td>4</td>
<td>2·10⁻³</td>
<td>0,3</td>
</tr>
<tr>
<td>0,3M Na₂CO₃</td>
<td>50</td>
<td>4</td>
<td>2·10⁻³</td>
<td>0,5</td>
</tr>
<tr>
<td>0,3M NaHCO₃</td>
<td>50</td>
<td>1</td>
<td>1·10⁻³</td>
<td>54</td>
</tr>
</tbody>
</table>

Table 1.

The rate of the reduction of CO₂, CO₃²⁻ and HCO₃⁻ under similar conditions

3. Nitrogen-containing organic bases facilitate the process by reacting with the product formic acid, and/or by forming catalytically more active metal complexes.
Earlier studies on reactions catalyzed by Rh and Ru TPPTS (trisulphonatophenyl-phosphine) complexes found, that the presence of some amine is necessary for the formation of formic acid and its derivatives.

In the case of the reactions catalyzed by \([\text{RuCl}_2(\text{TPPMS})_2]\) the reaction rate is also increased by amines though their presence is not essential.

The use of quinoline resulted in the most significantly increased rate of the reaction. The turnover frequency changed from 54 to 66 in case of the use of 40 µl quinoline under the same conditions.

4. It was observed, that the presence of CO\(_2\) in the gas phase – in the range of 1-10 bar - reduces the reaction rate of the hydrogenation of NaHCO\(_3\).

![Image of graph showing the effect of CO\(_2\) on the rate of the HCO\(_3^-\)-hydrogenation](image)

The effect of CO\(_2\) on the rate of the HCO\(_3^-\)-hydrogenation (\(t=4\)h, 6 bar H\(_2\), 50°C, Ru:P = 1:4, \(c_{\text{NaHCO}_3} = 0.2\)M, \(c_{\text{kat}} = 2\times10^{-3}\)M)
Figure 2 shows that in presence of 6 bar hydrogen the increase in the partial pressure of CO₂ causes slower production of formic acid.

5. It was found, that the [RuCl₂(TPPMS)₂] catalyst is able to hydrogenate CaCO₃ in aqueous suspension under CO₂ pressure with formation of Ca(HCOO)₂.

![Figure 3. Formate concentration as a function of time, during the hydrogenation of CaCO₃](image)

(p= 10 bar, CO₂ : H₂ = 2:8, T= 50°C, 50 mg CaCO₃ suspended in 10 ml water, 9,7 mg [RuCl₂(TPPMS)₂], 8 mg TPPMS)
In the first phase of the reaction the rate is high, but then it decreases strongly. The formate concentration at the end of the fast period corresponds to the initial amount of CaCO₃.

6. It was observed that the product formate inhibits the reaction during the hydrogenation of the CaCO₃.

To investigate this effect more closely, different amounts of Na-formate was added to the reaction mixtures before hydrogenation.

![Graph showing formate-inhibition during hydrogenation of CaCO₃](image-url)

**Figure 4.**
Formate-inhibition during hydrogenation of CaCO₃
(t=1h, T=50°C, 10 bar H₂, cₐₐ₃=10⁻³ mol/dm³, Ru/P= 1:4.)
Figure 4 shows that the presence of formate reduces the reaction rate radically.

In the same experimental sequence of the hydrogenation of NaHCO₃ – using 0,3 M NaHCO₃ solution instead of 50 mg CaCO₃ – no product inhibition was found.

7. It was established that the distribution of the hydrido-complexes in the reaction of [RuCl₂(TPPMS)₂] and H₂ depends not only on the pH but also on the pressure of hydrogen.

![Visible spectra of the hydrido-complexes formed from [RuCl₂(TPPMS)₂] at different H₂ pressures (cₐ₀= 10⁻³ mol/dm³, Ru/P=1:4, T= 25 °C, Δt= 20 min)](image)

Figure 5.
It is known from the literature that [RuCl₂(TPPMS)₂] in aqueous solution, at atmospheric H₂ pressure results in various hydrido-complexes depending on the pH. [3]

It was shown by medium pressure visible spectrophotometric, as well as by \(^1\)H, \(^{13}\)C and \(^{31}\)P NMR studies, that there are new hydrido species in the reaction mixture whose structure is different from the ones known before. Clarification of the exact molecular structures needs further investigations.

8. The [Ru(HCO₃)₂(TPPMS)₂] complex was identified and characterised, and the procedure of its preparation was developed.

The reaction of [RuCl₂(TPPMS)₂] and NaHCO₃ gives a yellow flaky - hard to filter - precipitate. The solid complex is dark purple when dried, but becomes immediately bright yellow when contacts water. The process is reversible.

The precipitate dissolves under hydrogen and its reaction gives formic acid in the homogeneous solution.

The molecular composition of the complex is calculated upon data of \(^{13}\)C, \(^{31}\)P NMR and elemental analysis.

9. A possible mechanism of hydrogenation of NaHCO₃ solution was suggested:
The first step leading towards the catalytic cycle is the formation of the bicarbonato-complex mentioned above, which - under hydrogen - forms the dihydrido-complex [RuH₂(TPPMS)₄].

According to the mechanism illustrated in Figure 6, there is no need of amines or other organic bases in the catalytic cycle.

All the molecular species of this proposed mechanism – except [RuH(HCO₃)(TPPMS)₄] – are or have been previously characterized.

Figure 6.
Proposed mechanism of the hydrogenation of NaHCO₃ in aqueous solution
List of publications

Articles in connection with this Thesis:


J. Elek, L. Nádasdi, G. Papp, G. Laurenczy, and F. Joó: Homogeneous hydrogenation of carbon dioxide in aqueous solution

**Conferences, oral presentations, posters:**


*J. Elek, J. Kovács, F. Joó:* Homogeneous Catalytic Hydrogenation of Carbon Dioxide in Aqueous Solutions


F. Joó, G. Papp, J. Kovács, A.Cs. Bényei, J. Elek, L. Nádasdi, G. Laurenczy:
Formation and catalytic activity of hydrido-ruthenium(II) complexes with meta- and para-monosulfonated triphenylphosphine ligands (Poster)
Hungarian COST Chemistry Day, Budapest, 2000

G. Papp, F. Joó, J. Kovács, J. Elek:
Selectivity as the fundamental principle of green chemistry. The Ru-catalyzed hydrogenation of unsaturated aldehydes (invited lecture)

F. Joó, L. Nádasdi, G. Papp, J. Elek, G. Laurenczy:
Selective hydrogenations catalyzed by water-soluble ruthenium-phosphine complexes
References
