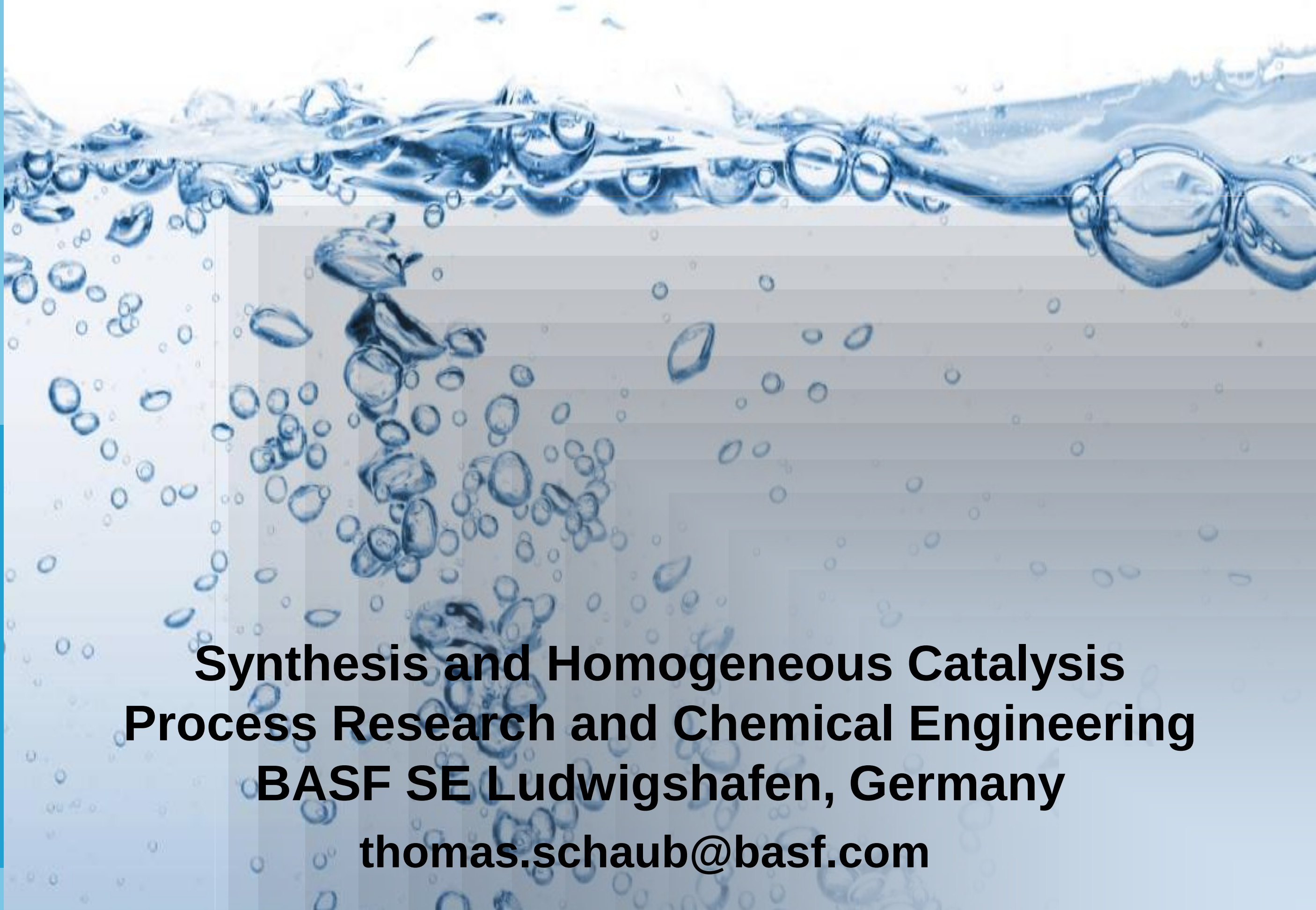
Formic Acid via CO_2-Hydrogenation

Dr. Thomas Schaub



Synthesis and Homogeneous Catalysis
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BASF
The Chemical Company

BASF SE

“Ammonia Lab”

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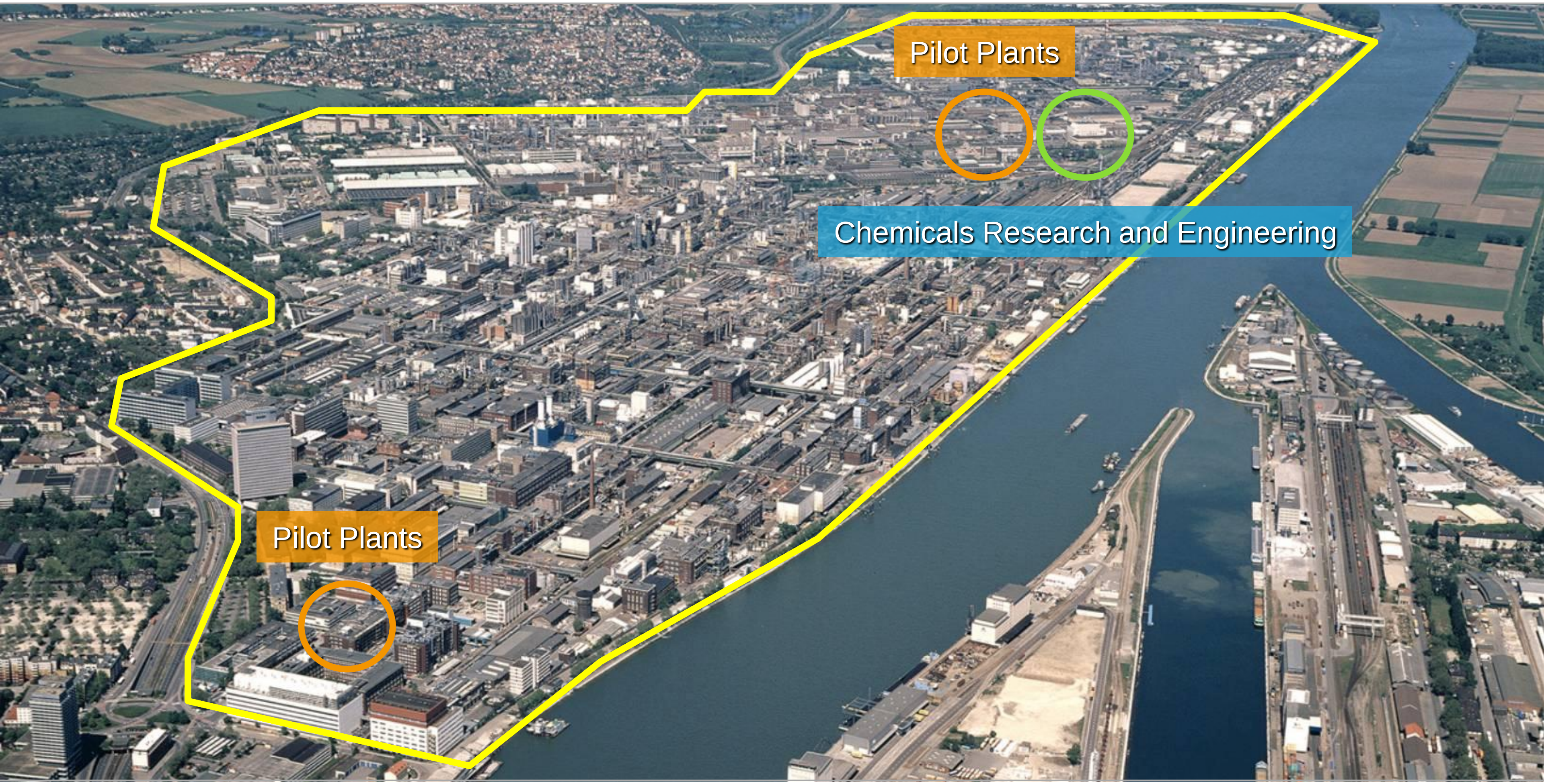

Homogeneous Catalysis Group

5 PhD Chemists and 21 Technicians

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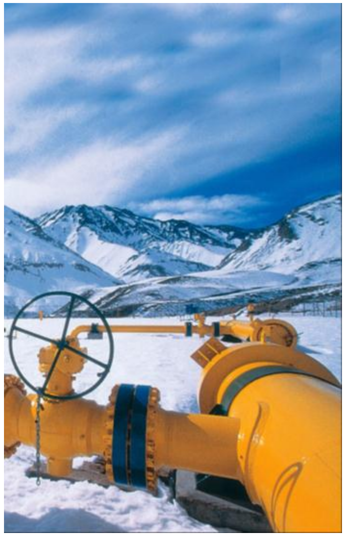
- **Research Areas**
  - Hydroformylation
  - Carbonylation
  - Homogeneous Hydrogenation (*e.g.* Enantioselective Hydrogenation)
  - Olefin Isomerization, Oligomerization, Telomerization
  - C-C-Coupling Chemistry

- **Competences in Homogeneous Catalysis**
  - Catalyst Design and Synthesis
  - Catalyst Recovery and Recycle
  - Computer Assisted Catalyst Design
  - High Throughput Screening

Raw Material Change

Alternatives for Petrochemistry

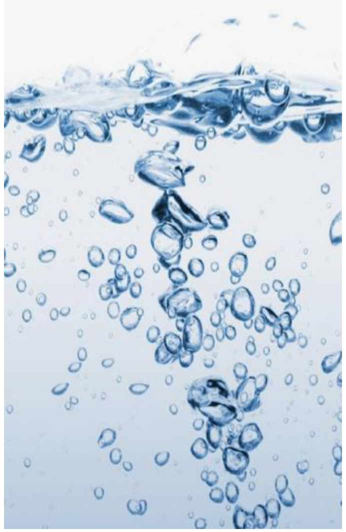
Gas



Coal

Biomass

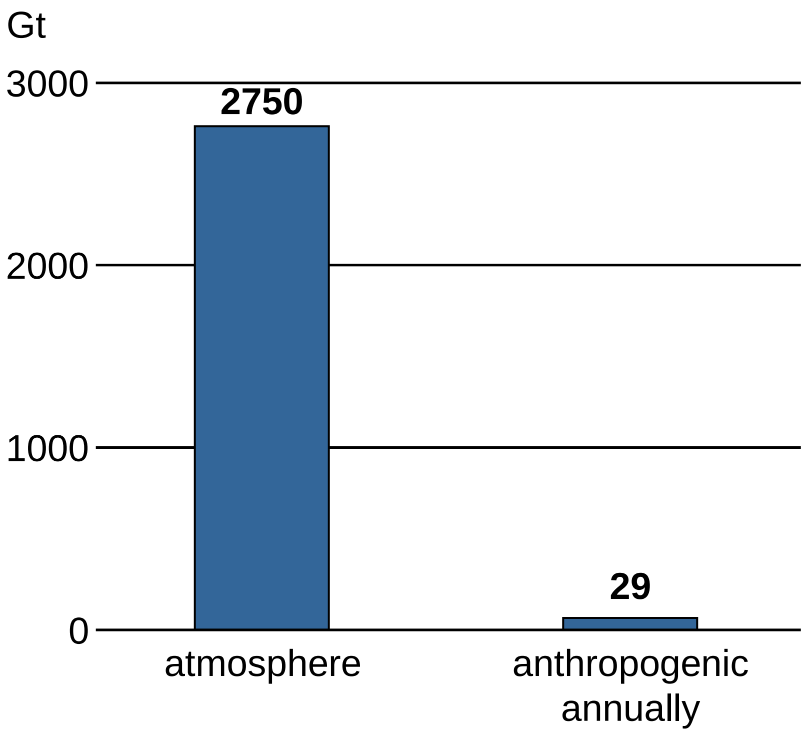
Carbon dioxide



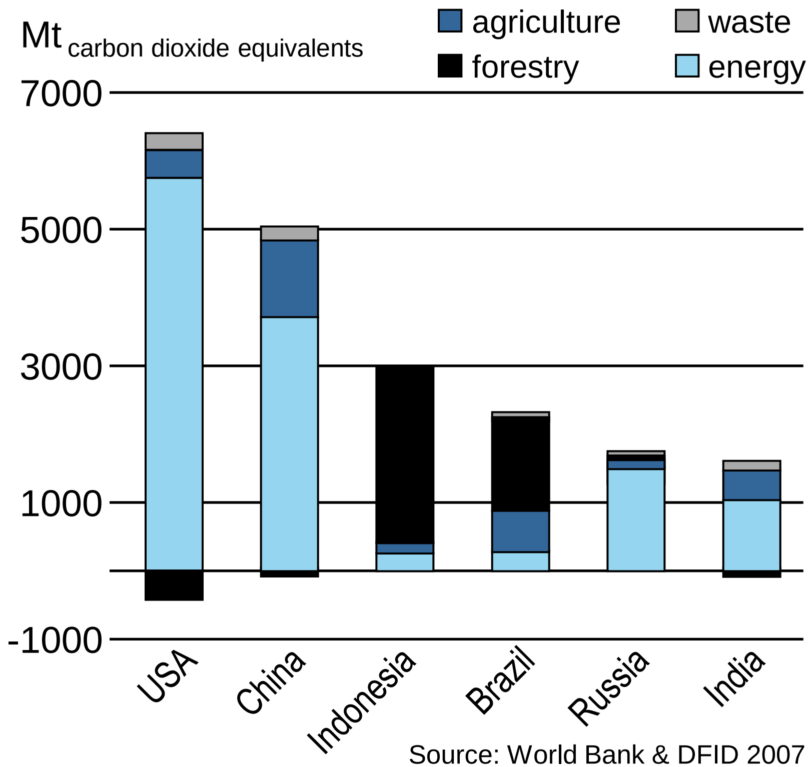
Carbon Dioxide

Availability

Quantity



Producer



Source: World Bank & DFID 2007

Atmospheric carbon dioxide concentration has increased from ~280 ppm in pre-industrial times to 380 ppm today.

Source: BGR 2009

CO_2 as a C1-Building Block

Present Use

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CO_2 from anthropogenic sources

110 MT p.a. = 0.4 % presently used by industry

- Urea 70 MT
- Inorganic carbonates 30 MT
- Methanol 6 MT

29 GT p.a.

Source: US Department of Energy

CO_2 as a C1-Building Block

Cost

CO_2 from anthropogenic sources

29 GT p.a.

But: > 140 MT p.a. CO_2 emitted while producing these compounds!

⇨Net CO_2-production

Source: US Department of Energy

CO_2 as a C1-Building Block

Reactivity

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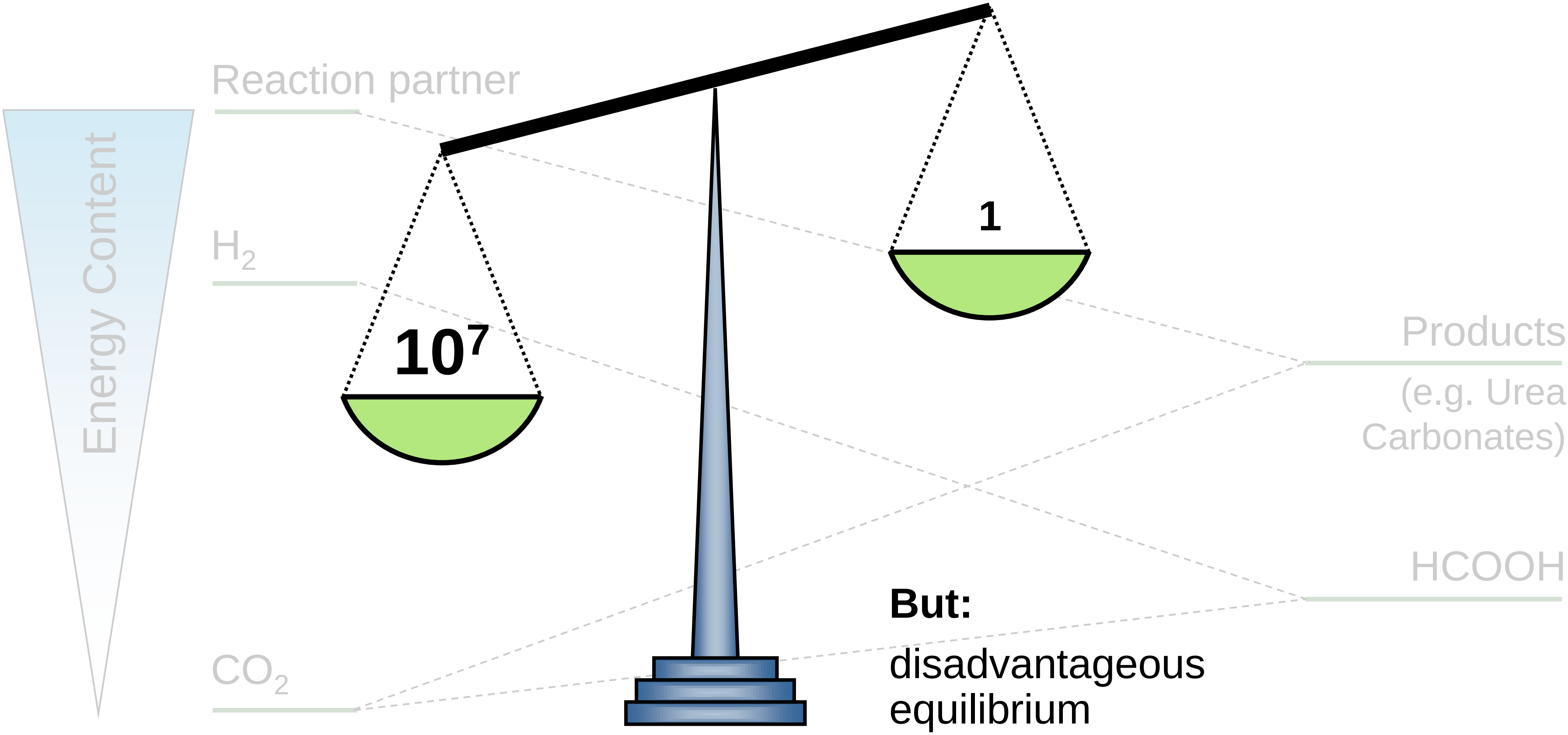
Very stable molecule: $\Delta H_0 \sim -400\ kJmol^{-1}$

→ Energetic reaction partners necessary (*e.g.* H_2, NH_3, epoxides)



But:

disadvantageous equilibrium

CO_2 Hydrogenation

Background

$$CO_2 + H_2 + NR_3 \xrightarrow{\text{cat.}} HCOOH{\cdot}NR_3$$

- CO_2-hydrogenation with homogeneous catalysts in the presence of bases such as amines has been known for decades

  Selected reviews:

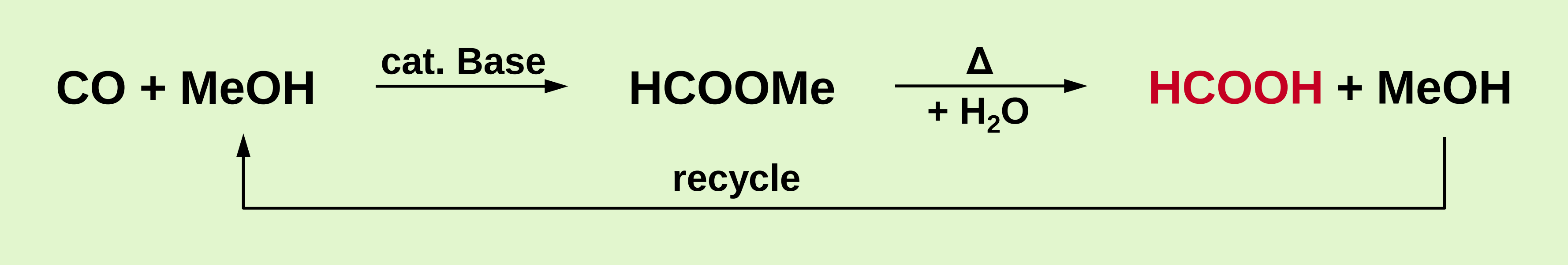
  W. Leitner, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2207-2221;
  P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1995**, *95*. 259-272
  P. G. Jessop, F. Joó, C. C. Tai, *Coord. Chem. Rev.* **2004**, *248*, 2425-2442
  P. G. Jessop, in *The Handbook of Homogeneous Hydrogenation*, Vol. 1 (Eds: J. G. De Vries, C. J. Elsevier), WILEY-VCH, Weinheim, **2007**, pp. 489-51
  T. Sakakura, J. C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365-2387

  C. Federsel, R. Jackstell, M. Beller, *Angew. Chem.* **2010**, *122*, 6392-6395

- To date, no industrial process has been realized

Formic Acid

State of the Art

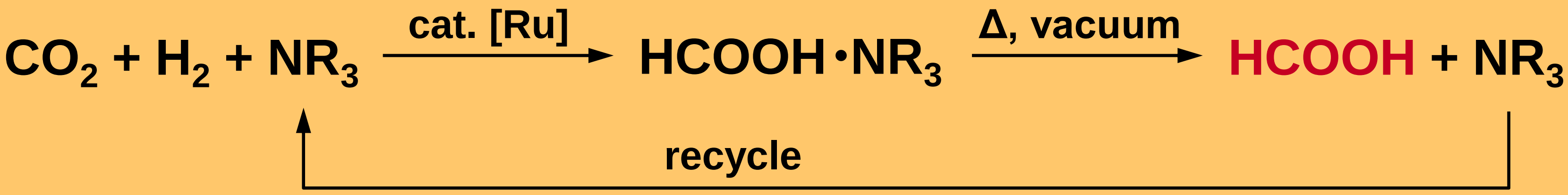


$$CO + MeOH \xrightarrow{\text{cat. Base}} HCOOMe \xrightarrow[+ H_2O]{\Delta} HCOOH + MeOH$$

- Leading technologies based on hydrolysis of methyl formate
- Methyl formate obtained by base catalyzed carbonylation of methanol
- BASF global market leader (230 kT p.a.)

Formic Acid *via* CO_2 Hydrogenation

BASF Concept

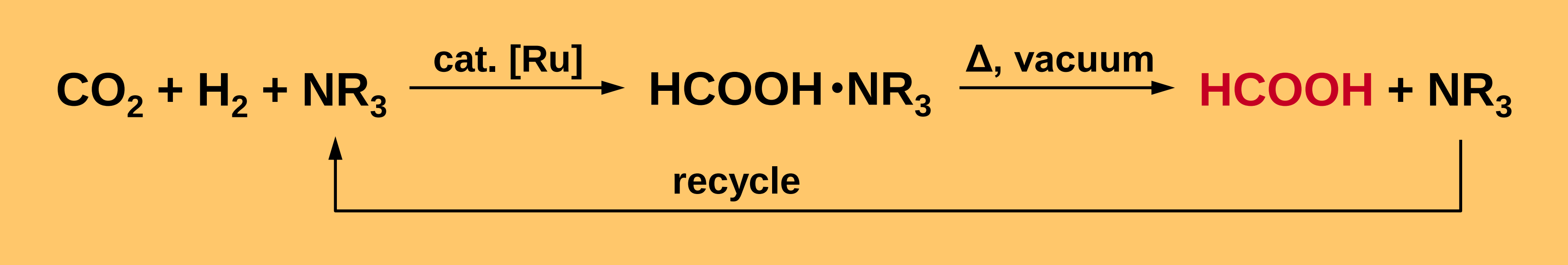


$$CO_2 + H_2 + NR_3 \xrightarrow{\text{cat. [Ru]}} HCOOH \cdot NR_3 \xrightarrow{\Delta\text{, vacuum}} HCOOH + NR_3$$

- Thermal cleavage of formic acid (FA) adducts with trialkylamines such as $NHex_3$ (THA) can be used for efficient formic acid separation
- Use of solubility and phase behavior makes efficient catalyst recycle possible

Formic Acid *via* CO_2 Hydrogenation

Experimental Observations



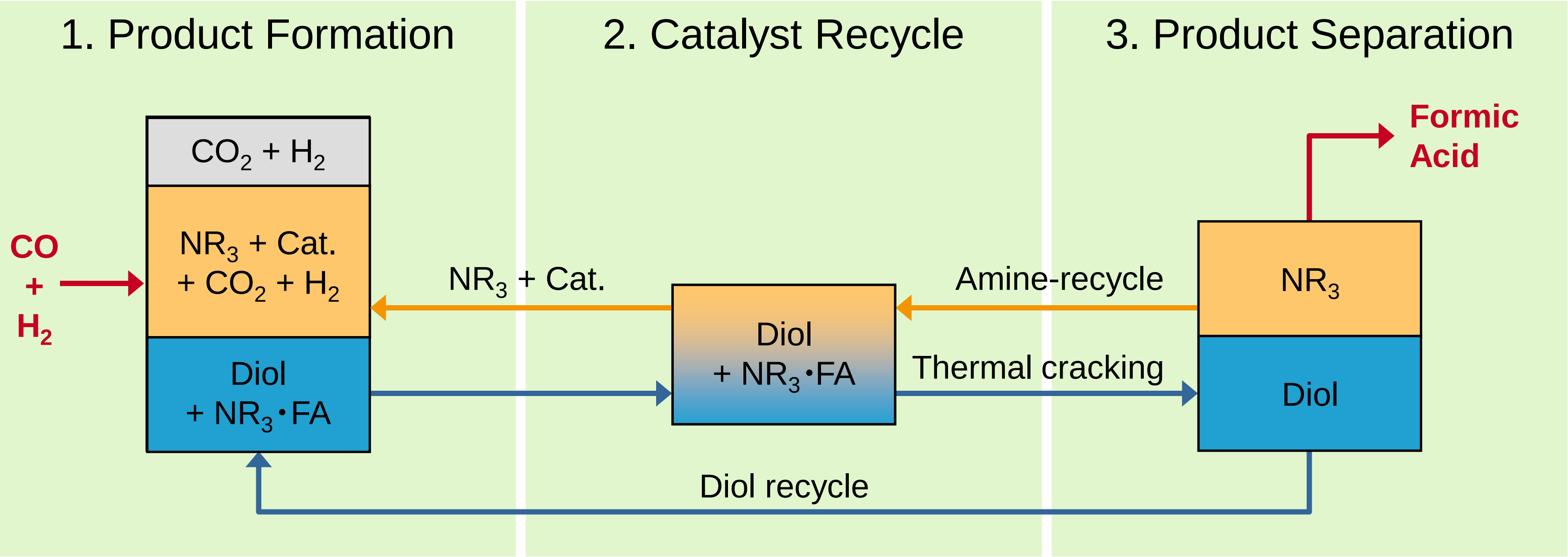
$$CO_2 + H_2 + NR_3 \xrightarrow{\text{cat. [Ru]}} HCOOH \cdot NR_3 \xrightarrow{\Delta,\ \text{vacuum}} HCOOH + NR_3$$

recycle

- Long chain trialkylamines are immiscible with polar solvents such as diols
- Formic acid salts of these amines, however, are soluble in diols
- Hydrogenation can be carried out in this liquid-liquid system with lipophilic ruthenium catalysts
- Catalyst traces can be removed from raw product using amine from thermal product separation

Formic Acid *via* CO_2 Hydrogenation

Process Concept



Formic Acid *via* CO_2 Hydrogenation

Catalytically Important Species

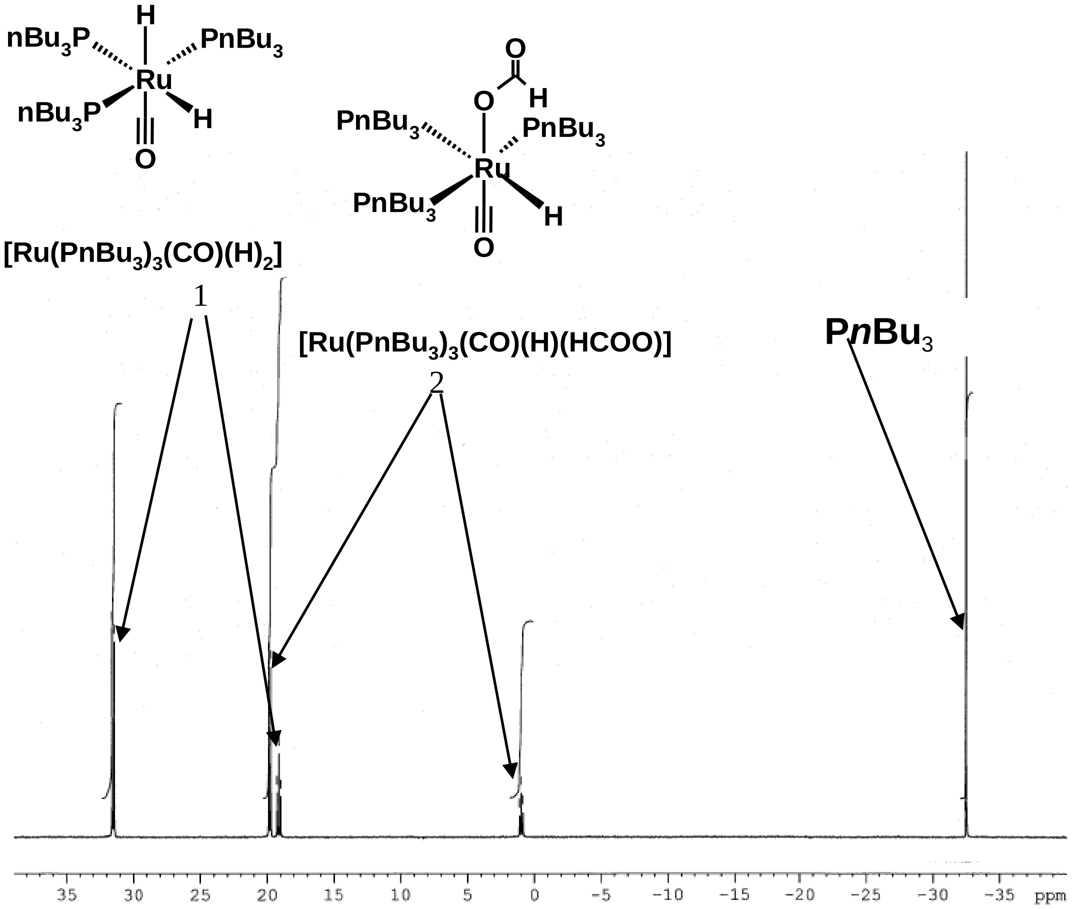
$$\mathrm{Ru(PnBu_3)_4(H)_2 + HCOOH} \xrightarrow[\substack{\text{Toluene or THF}\\ -\mathrm{H_2O},\ -\ \mathrm{PnBu_3}}]{\text{rt}} \begin{array}{c}\mathrm{Ru(PnBu_3)_3(CO)(H)_2}\\ \text{(1)}\\ +\\ \mathrm{Ru(PnBu_3)_3(CO)(H)(HCOO)}\\ \text{(2)}\end{array}$$

- Characterized by ^{1}H-, ^{31}P-NMR and HRMS (ESI) spectroscopy
- ν*CO* (1) 1917 cm^{-1}, ν*CO* (2) 1908 cm^{-1}
- Compound (2) could only be characterized by in solution, as it decomposes to (1) *via* loss of CO_2 upon evaporation of solvent

Spectroscopic data for (1): Shirakawa et al *J. Am. Chem. Soc.* **2004**, *126*, 13614-13615

Formic Acid *via* CO_2 Hydrogenation

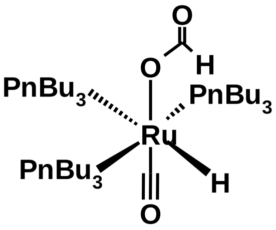
^{31}P-NMR



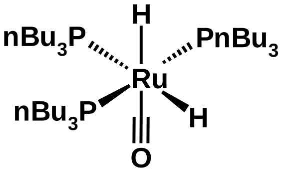
$[Ru(PnBu_3)_4(H)_2]$ (20 mg, 0.02 mmol) was dissolved in Tol-d_8 (1 g).
One drop of formic acid was added at room temperature.

Formic Acid *via* CO_2 Hydrogenation

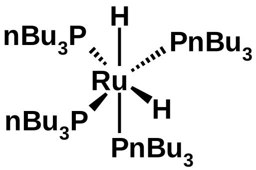
^{1}H-NMR



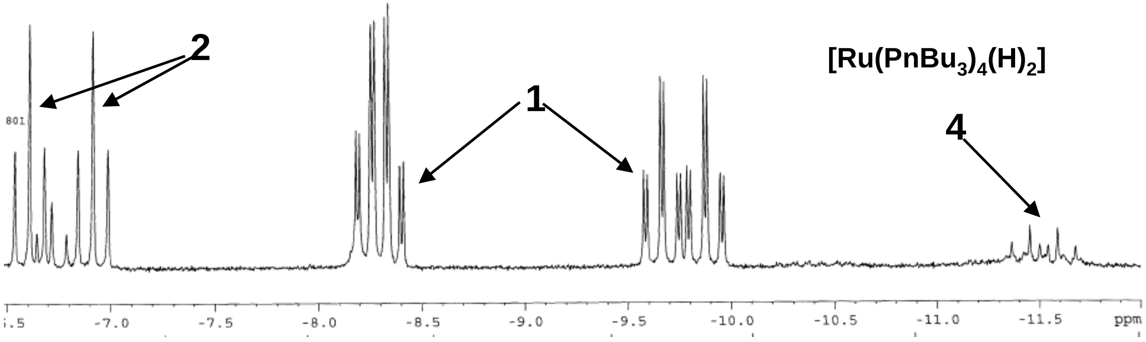
$[Ru(PnBu_3)_3(CO)(H)(HCOO)]$



$[Ru(PnBu_3)_3(CO)(H)_2]$



$[Ru(PnBu_3)_4(H)_2]$



$[Ru(PnBu_3)_4(H)_2]$ (20 mg, 0.02 mmol) was dissolved in Tol-d_8 (1 g). One drop of formic acid was added at room temperature.

Formic Acid *via* CO_2 Hydrogenation

In Situ Characterization of Catalyst Species

- Preformed catalyst

$$Ru(PnBu_3)_4(H)_2 \xrightarrow[\substack{\text{NHex}_3 \\ \text{2-Methyl-1,3-Propandiol}}]{\substack{+\ CO_2\ \text{(20 bar)},\ +\ H_2\ \text{(60 bar)} \\ 50°C,\ 1h}}$$

$Ru(PnBu_3)_3(CO)(H)_2$ (1)

$Ru(PnBu_3)_3(CO)(H)(HCOO)$ (2)
in $NHex_3$

$[HNHex_3][HCOO]$

in 2-Methyl-1,3-Propandiol

- Catalyst formed *in Situ*

$$\begin{array}{c} [Ru(COD)(Cl)_2]_2 \\ + \\ 10\ PnBu_3 \end{array} \xrightarrow[\substack{\text{NHex}_3 \\ \text{2-Methyl-1,3-Propandiol} \\ -\ \text{COD} \\ -\ [HNHex_3][Cl]}]{\substack{+\ CO_2\ \text{(40 bar)},\ +\ H_2\ \text{(40 bar)} \\ 70°C,\ 16h}}$$

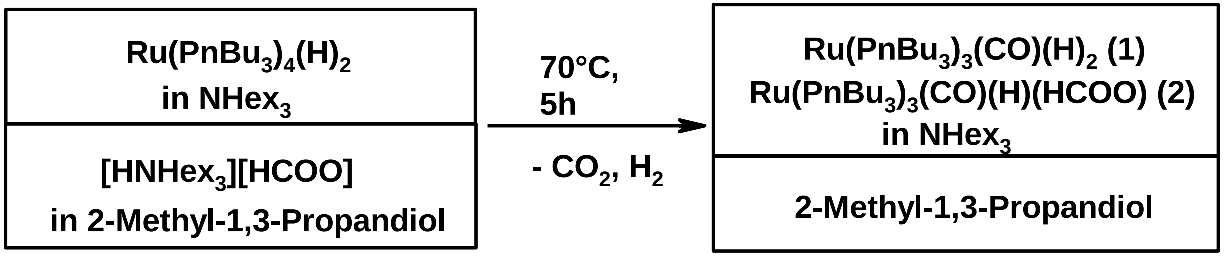
$Ru(PnBu_3)_3(CO)(H)(HCOO)$ (2)
in $NHex_3$

$[HNHex_3][HCOO]$
in 2-Methyl-1,3-Propandiol

Formic Acid *via* CO_2 Hydrogenation

Observations in Reaction Mixtures

- Reverse reaction using preformed catalyst



$Ru(PnBu_3)_4(H)_2$ in $NHex_3$

$[HNHex_3][HCOO]$ in 2-Methyl-1,3-Propandiol

70°C, 5h

$- CO_2, H_2$

$Ru(PnBu_3)_3(CO)(H)_2$ (1)

$Ru(PnBu_3)_3(CO)(H)(HCOO)$ (2)

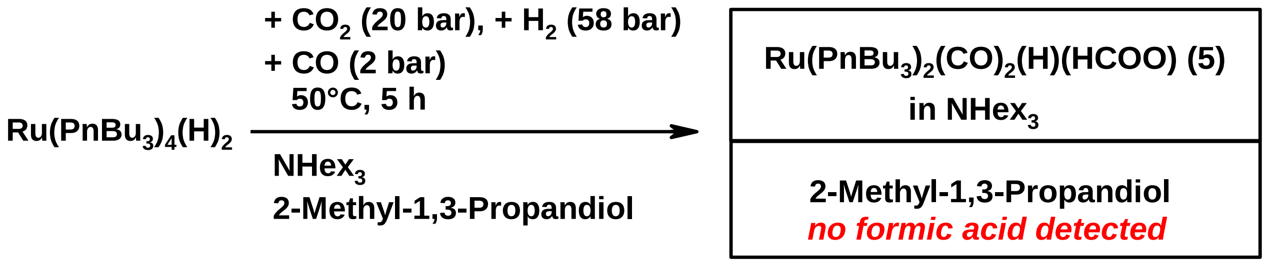
in $NHex_3$

2-Methyl-1,3-Propandiol

Formic Acid *via* CO_2 Hydrogenation

Observations in Reaction Mixtures

- Reaction in the presence of excess CO



$$Ru(PnBu_3)_4(H)_2 \xrightarrow[\text{NHex}_3,\ \text{2-Methyl-1,3-Propandiol}]{+ CO_2\text{ (20 bar)}, + H_2\text{ (58 bar)}, + CO\text{ (2 bar)}, 50°C, 5\text{ h}}$$

$Ru(PnBu_3)_2(CO)_2(H)(HCOO)$ (5) in $NHex_3$

2-Methyl-1,3-Propandiol

no formic acid detected

- Biscarbonyl complex was characterized in solution *via* NMR- and IR-spectroscopy - isolation of the pure compound was impossible due to high boiling amine solvent

  - ^{1H} NMR: hydride triplet at -5.5 ppm (cis-coupling with two equivalent phosphorus atoms); Formate as singlet at 7.9 ppm

  - ^{31}P-NMR: singlet at 26.7 ppm, free phosphine at -32.9 ppm
  - νCO: two equally strong bands at 1952 and 2036 cm^{-1}

Formic Acid *via* CO_2 Hydrogenation

Observations in Reaction Mixtures

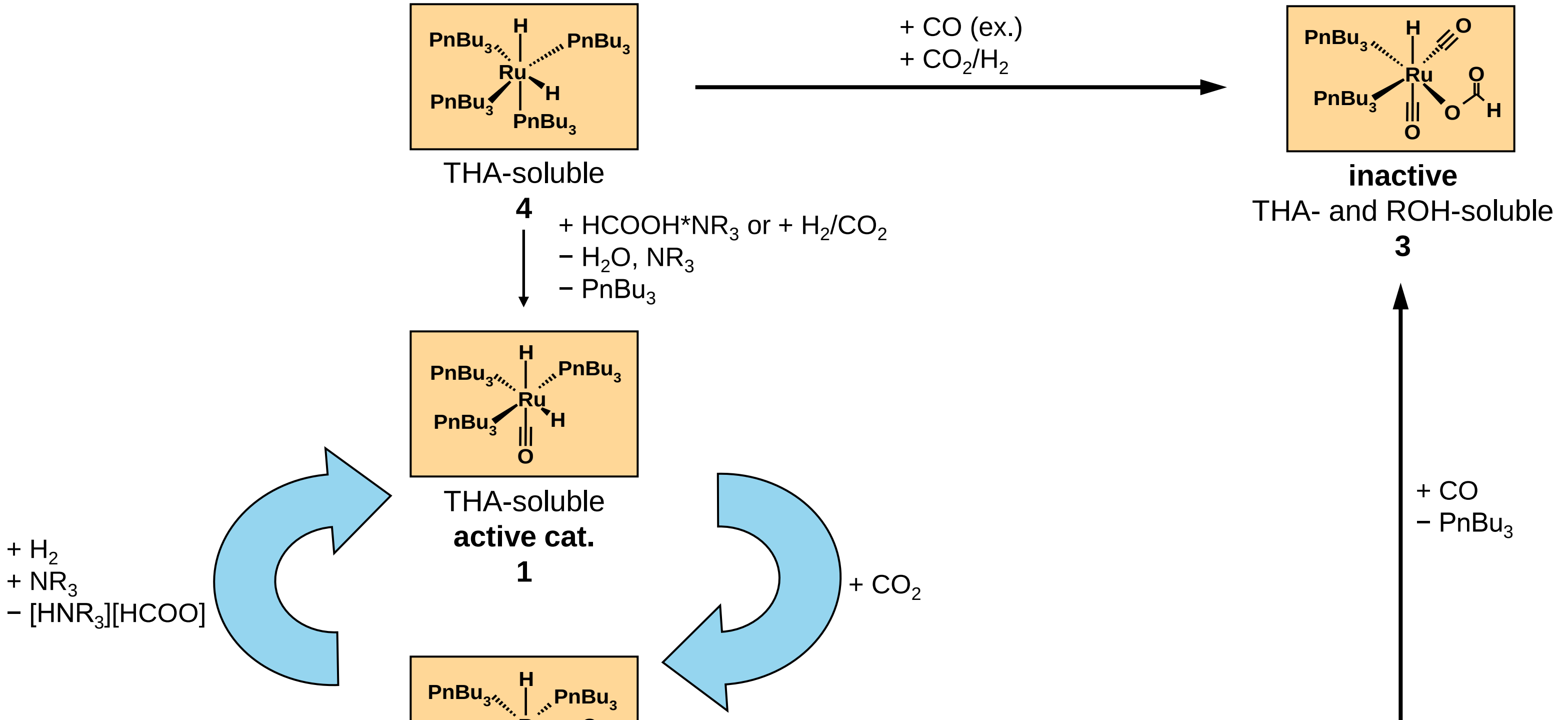
- Reaction in the presence of excess CO but without CO_2

$$\mathrm{Ru(PnBu_3)_4(H)_2} \xrightarrow[\substack{\mathrm{NHex_3} \\ \text{2-Methyl-1,3-Propandiol}}]{\substack{+\ \mathrm{CO/H_2}\ (1{:}1,\ 80\mathrm{bar}) \\ 70°\mathrm{C},\ 1\ \mathrm{h}}} \mathrm{Ru(PnBu_3)_3(CO)(H)_2}\ (1)\ \text{in } \mathrm{NHex_3}$$

- Surprisingly, formate ligand appears to stabilize biscarbonyl complex in presence of excess phosphine ligands

Formic Acid *via* CO_2 Hydrogenation

Overview: Catalytically Important Species



THA-soluble
4

+ CO (ex.)
+ CO_2/H_2

inactive
THA- and ROH-soluble
3

+ $HCOOH*NR_3$ or + H_2/CO_2
− H_2O, NR_3
− $PnBu_3$

THA-soluble
active cat.
1

+ H_2
+ NR_3
− $[HNR_3][HCOO]$

+ CO_2

+ CO
− $PnBu_3$

THA- and ROH-soluble
active cat.
2

Formic Acid *via* CO_2 Hydrogenation

Role of CO

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- Formic acid or NR_3*FA salts act as mild carbonylating agents
- Under the conditions of the catalysis, monocarbonyl complexes are the active species starting from ruthenium tetrakisphosphine complexes
- Complexes characterized using NMR, IR and independent synthesis
- If CO is added, inactive dicarbonyl complexes are formed

⇨ ***Contrary to the opinion in most publications, CO-complexes play a role in CO_2 hydrogenation!***

Formic Acid *via* CO_2 Hydrogenation

Thermodynamics of CO_2-Hydrogenation

- Although the hydrogenation of CO_2 to formic acid is exothermic, the reaction is strongly endergonic

$$CO_2\ (g) + H_2\ (g) \rightarrow HCOOH\ (l)$$

$$\Delta G^0 = 32.9\ \text{kJ/mol};\ \Delta H^0 = -\ 31.2\ \text{kJ/mol},\ \Delta S^0 = -\ 215\text{J/Kmol}$$

- Exothermic protonation of the base by formic acid delivers enough energy to make the reaction exergonic

$$CO_2\ (g) + H_2\ (g) + NH_3\ (aq) \rightarrow HCO_2^-\ (aq) + NH_4^+\ (aq)$$

$$\Delta G^0 = -9.5\ \text{kJ/mol};\ \Delta H^0 = -84.3\ \text{kJ/mol},\ \Delta S^0 = -250\text{J/Kmol}$$

⇨ ca. 40-50 kJ/mol from salt formation necessary to drive reaction

Formic Acid *via* CO_2 Hydrogenation

Thermodynamics of $NHex_3 \cdot HCOOH$ Formation

- Reaction of formic acid with $NHex_3$ studied *via* calorimetry

$$1.5\ HCOOH + NHex_3 \rightarrow [HNHex_3][HCOO \bullet 0.5\ HCOOH]$$

$$\Delta H^0 = -28.1\ \text{kJ/mol (per mol FA)}$$

- Reaction enthalpy can be estimated for CO_2 hydrogenation in pure $NHex_3$

$$1.5\ CO_2 + 1.5\ H_2 + NHex_3 \rightarrow [HNHex_3][HCOO \bullet 0.5\ HCOOH]$$

$$\Delta H0 = -59.3\ \text{kJ/mol (per mol FA)}$$

⇨ **Not enough reaction enthalpy is delivered by amine protonation to make CO_2-hydrogenation thermodynamically feasible in pure $NHex_3$**

Formic Acid *via* CO_2 Hydrogenation

Thermodynamics of Adduct Formation in Diols

- More reaction enthalpy is delivered per mol FA in the presence of diol

  $HCOOH + NHex_3 \rightarrow [HNHex_3][HCOO]$ (in 2-methyl-1,3-propandiol)
  $\Delta H^0 = -43$ kJ/mol (per mol FA)

- Addition of the 1:1.5 salt to a stirred mixture of $NHex_3$ and 2-Methyl-1,3-propandiol is exothermic and also yields the 1:1 salt

  $[HNHex_3][HCOO{\bullet}0.5HCOOH] + 0.5\ NHex_3 \rightarrow [HNHex_3][HCOO]$
  (in 2-methyl-1,3-propandiol)
  $\Delta H^0 = -17.7$ kJ/mol (per mol FA)

Formic Acid *via* CO_2 Hydrogenation

Thermodynamics of CO_2 Hydrogenation in Diols

- CO_2 hydrogenation in the presence of diol is energetically in the range of CO_2 hydrogenation in the presence of NH_3

$CO_2 + H_2 + NHex_3 \rightarrow [HNHex_3][HCOO]$
(in 2-methyl-1,3-propandiol)
$\Delta H^0 = -77$ kJ/mol (per mol FA)

⇨ Solvent effect is what delivers enough reaction enthalpy to make the reaction exergonic under moderate conditions

Formic Acid *via* CO_2 Hydrogenation

Solvent Effect

- OH-containing solvent is presumably stabilizing the formate anion *via* hydrogen bridging
  - similar to the role of the formic acid in the $NHex_3 \bullet 1.5\ HCOOH$
- Equilibrium concentration of formic acid in the product phase obtained during hydrogenation due to insufficient hydrogen-bonding beyond this concentration
- This concentration can be determined by calorimetry and is found at the point of maximum heat formation
  - this can be easily recognized, as less energy is obtained when adding formic acid beyond this concentration due to insufficient deprotonation

Formic Acid *via* CO_2 Hydrogenation

Overview: Thermodynamics

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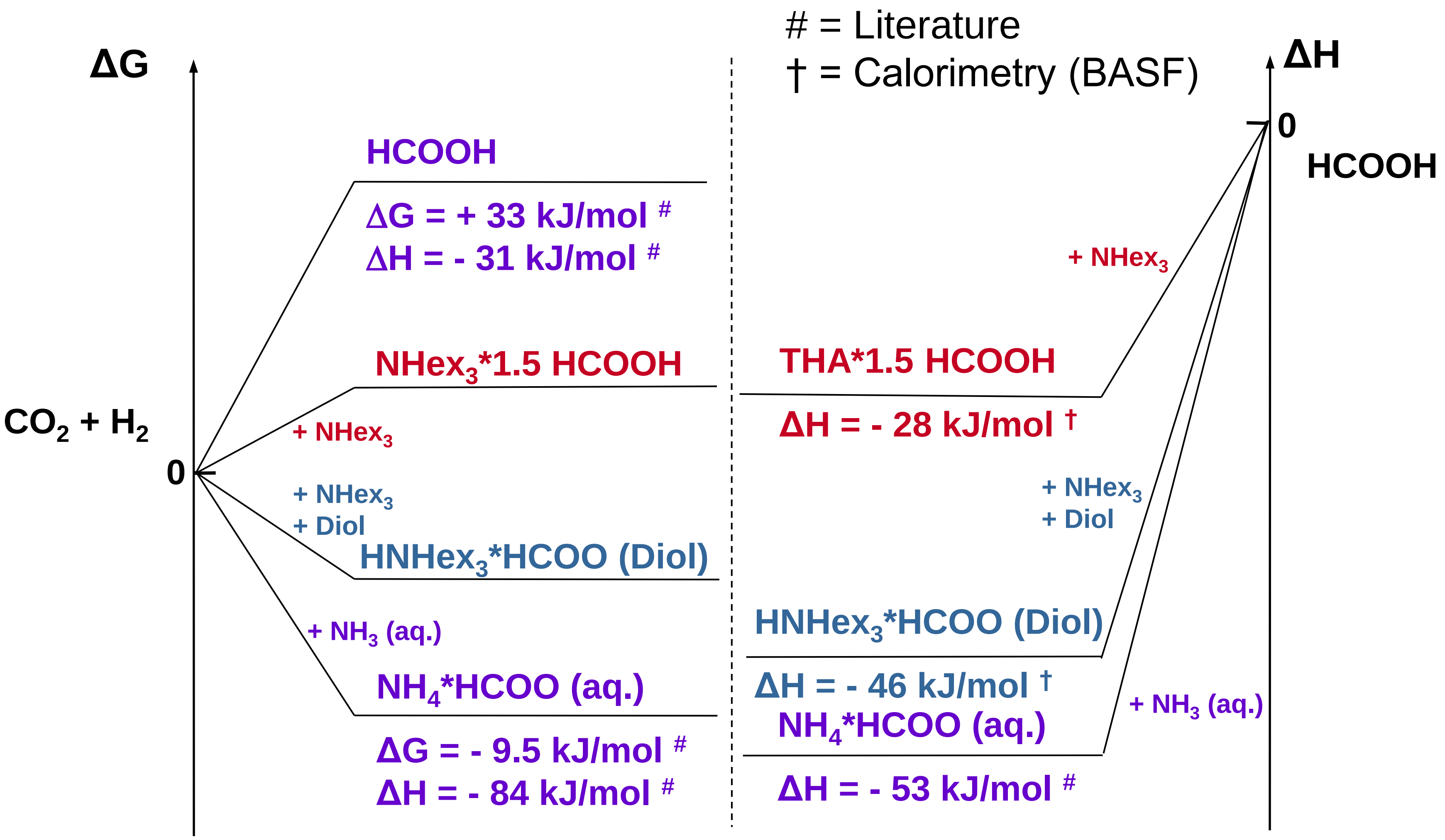

\# = Literature
† = Calorimetry (BASF)

ΔG

$CO_2 + H_2$

0

HCOOH

ΔG = + 33 kJ/mol #
ΔH = - 31 kJ/mol #

$NHex_3$*1.5 HCOOH

+ $NHex_3$

+ $NHex_3$
+ Diol

$HNHex_3$*HCOO (Diol)

+ NH_3 (aq.)

NH_4*HCOO (aq.)

ΔG = - 9.5 kJ/mol #
ΔH = - 84 kJ/mol #

ΔH

0

HCOOH

+ $NHex_3$

THA*1.5 HCOOH

ΔH = - 28 kJ/mol †

+ $NHex_3$
+ Diol

$HNHex_3$*HCOO (Diol)

ΔH = - 46 kJ/mol †

NH_4*HCOO (aq.)

+ NH_3 (aq.)

ΔH = - 53 kJ/mol #

Formic Acid *via* CO_2 Hydrogenation

Thermodynamics

- CO_2 hydrogenation only delivers enough energy for the formation of the monoadduct of formic acid with trihexylamine (THA)
- The monoadduct, however, is only stable in the presence of hydrogen bonds to protic solvents

⇨ ***The real reason for the "alcohol effect" discussed in the literature***

Formic Acid *via* CO_2 Hydrogenation

Summary

- A new process for hydrogenating CO_2 to formic acid has been introduced
- Process is based on the observation that $NHex_3$, unlike the commonly used NEt_3, can be thermally cleaved under relatively mild conditions
- Solubility properties and phase behavior of system components can be exploited in order to efficiently recycle catalyst species
- Calorimetric studies of the interaction of formic acid and amines have shown that systems studied only deliver enough reaction enthalpy to make the CO_2-hydrogenation reaction thermodynamically feasible when carried out in the presence of hydrogen-bridging solvents such as diols
- Participation of the alcohol in the catalytic cycle as has previously been proposed may be occurring, but is not mandatory
- Carbonyl complexes are formed in all cases of relevance to CO_2-hydrogenation when using highly basic alkylphosphine complexes such as $Ru(PnBu_3)_4(H)_2$ or $Ru(PEt_3)_4(H)_2$ as catalyst
- Formic acid and its' adducts are excellent carbonylation reagents for such highly electron rich transition metal complexes.
- This has implications for previously proposed mechanisms for CO_2-hydrogenation using ruthenium catalysts of this type, which have usually not incorporated such species.

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Thank you for your kind attention!

Acknowledgements:
Dr. Armin Bader