CO_2 Hydrogenation

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A Process for the Synthesis of Formic Acid by CO_2 Hydrogenation: Thermodynamic Aspects and the Role of CO**

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The industrial usage of CO_2 has gained increasing attention over the last few years.[1] In the absence of renewable sources of reducing agents such as hydrogen, it has become clear that this usage will not contribute to CO_2 abatement. There remains, however, the possibility of utilizing CO_2 as an economical C_1 building block. The homogeneously catalyzed hydrogenation of CO_2 to formic acid (FA) has been extensively studied in this context and has been reviewed a number of times.[2] Unfortunately, this attractive reaction has not yet found industrial application, owing to two main drawbacks:

- A simple and efficient recycling concept for the precious-metal catalysts has not yet been developed.[3]
- The presence of a base (in most work NEt_3) is needed to shift the unfavorable equilibrium of the CO_2 hydrogenation. The economic separation of formic acid from the resulting salts is, however, not trivial.[4]

BASF, with a yearly capacity of 230000 tons world market leader in formic acid production, has been interested in overcoming these limitations. We have developed a multiphase liquid–liquid process which combines an efficient recycling of the active catalyst with the isolation of formic acid. This process uses a carefully matched combination of solvent, amine, and catalyst and exploits the properties and phase behavior of these components.[5]

This process is outlined in Figure 1 and can be divided into three steps: 1) hydrogenation, 2) catalyst extraction, and 3) product separation. The process is based on the key observation that formic acid trihexylamine ($NHex_3$) salts are not miscible with the free amine and can be cleaved thermally to give pure formic acid and the amine under relatively mild conditions (150 °C, 150 mbar). $NHex_3{\cdot}FA$ salts can be dissolved in polar solvents such as diols, thus forming a two-phase system with the free amine ($NHex_3$ is not miscible with most diols). The CO_2 hydrogenation can, therefore, be carried out in a two-phase liquid–liquid system (diol/$[NHex_3{\cdot}HCOOH]$—$NHex_3$) using liphophilic ruthenium complexes such as $[Ru(H)_2(PnBu_3)_4]$, which preferably dissolve in the free amine. After the reaction, the phases are separated and the amine phase, containing most of the active catalyst, is recycled back to the hydrogenation step. The product phase, which contains trace amounts of the catalyst, is extracted with the free amine obtained in the thermal separation step. The amine from the catalyst extraction is also recycled back to the hydrogenation step. After the extraction, the product phase is free of catalyst. The formic acid can then be separated from the high-boiling diol and amine by distillation. The solvent is recycled directly to the hydrogenation step, whereas the amine is used for catalyst extraction, leading to closed loops for the solvent, the catalyst, and the amine.

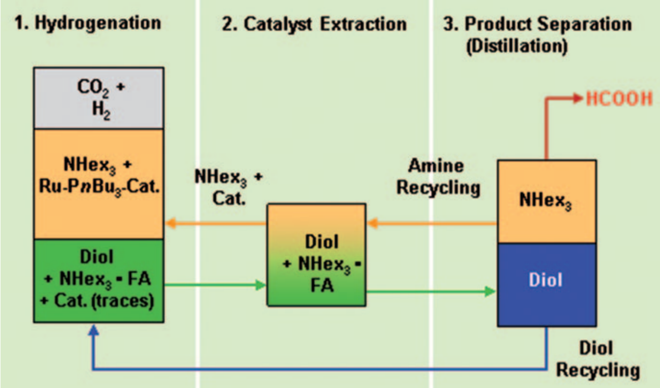

Figure 1. Process Concept.

We have studied this system in detail, in particular the crucial thermodynamic role of the solvent. We have also carried out spectroscopic investigations on species present in the reaction mixture. This work has led to new insights into this reaction, which are reported herein.

Although the hydrogenation of CO_2 to formic acid is exothermic, the reaction is strongly endergonic [Eq. (1)].[2b] In the presence of a base such as ammonia, exothermic protonation of the base by formic acid delivers enough energy to make the reaction exergonic [Eq. (2)].[2b] Approximately 44–50 kJ per mole formic acid are needed to obtain an exergonic reaction.

$$\begin{aligned}&CO_2\,(g) + H_2\,(g) \rightarrow HCOOH\,(l)\\&\Delta G^0 = 32.9\,\text{kJ mol}^{-1},\ \Delta H^0 = -31.2\,\text{kJ mol}^{-1},\\&\Delta S^0 = -215\,\text{J K}^{-1}\,\text{mol}^{-1}\end{aligned}\tag{1}$$

$$\begin{aligned}&CO_2\,(g) + H_2\,(g) + NH_3\,(aq) \rightarrow HCO_2^-\,(aq) + NH_4^+\,(aq)\\&\Delta G^0 = -9.5\,\text{kJ mol}^{-1},\ \Delta H^0 = -84.3\,\text{kJ mol}^{-1},\\&\Delta S^0 = -250\,\text{J K mol}^{-1}\end{aligned}\tag{2}$$

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Many trialkylamines form formic acid rich liquid salts, which are not miscible with the free amine.[3k] In these salts, only one equivalent of formic acid is deprotonated, whereas the excess (with respect to the amine) is presumably coordinated through hydrogen bonding. Addition of formic acid to $NHex_3$, for example, yields a liquid salt with a constant ratio of amine to formic acid of 1:1.5 that is not miscible with the amine.[6]

We carried out most CO_2 hydrogenation experiments with $[Ru(H)_2(PnBu_3)_4]$ as the catalyst.[6] When using $NHex_3$ as the only reactant or solvent, we were unable to observe the formation of formic acid in any case under widely varying conditions. Addition of small amounts of water or alcohols, as reported by Jessop, Noyori et al.,[7] did not lead to significant improvement. Furthermore, the protocol of Fachinetti et al.,[3k] in which small amounts of formic acid salts were added as initiator in the NEt_3 system, was not successful in the case of $NHex_3$ as the sole solvent.

To understand this behavior, we studied the $NHex_3{\cdot}FA$ salt formation by calorimetry. We found that the reaction enthalpy for the reaction of formic acid with $NHex_3$ is only $-28.1\ kJ\,mol^{-1}$ [Eq. (3)]. It appears that the CO_2 hydrogenation is thermodynamically not feasible in pure $NHex_3$ because too little reaction enthalpy is delivered by amine protonation [calculated by the combination of the value given in the literature and our own measurements; Eq. (4)].

$$1.5\,HCOOH + NHex_3 \rightarrow [HNHex_3][HCOO\cdot 0.5\,HCOOH] \quad \Delta H^0 = -28.1\ kJ\,mol^{-1}\ \text{(per mol FA)}^{[6]} \qquad (3)$$

$$1.5\,CO_2 + 1.5\,H_2 + NHex_3 \rightarrow [HNHex_3][HCOO\cdot 0.5\,HCOOH] \quad \Delta H^0 = -59.3\ kJ\,mol^{-1}\ \text{(per mol FA)}^{[6,2b]} \qquad (4)$$

This picture changes when polar solvents such as diols are used. The 1:1 formic acid salts are formed when formic acid is added to a stirred two-phase liquid–liquid mixture of $NHex_3$ and the diol. The salt then dissolves in the diol. Significantly more reaction enthalpy is delivered per mole FA than in the solvent-free system [Eq. (5)]

$$HCOOH + NHex_3 \rightarrow [HNHex_3][HCOO]\ \text{(in 2-methyl-1,3-propanediol)} \quad \Delta H^0 = -43\ kJ\,mol^{-1}\ \text{(per mol FA)}^{[5]} \qquad (5)$$

Addition of the $[HNHex_3][HCOO{\cdot}0.5\ HCOOH]$ salt to a stirred mixture of $NHex_3$ and 2-methyl-1,3-propanediol is also exothermic, most probably due to complete deprotonation of FA to the 1:1 salt, which is then found in the diol [Eq. (6)]. Owing to this solvent effect, the overall CO_2 hydrogenation is more exothermic (ca. $-77\ kJ\,mol^{-1}$) and energetically in the range of the CO_2 hydrogenation in the presence of NH_3 [Eq. (7)]. It appears that this reaction enthalpy is sufficient to shift the reaction to an exergonic process.

$$[HNHex_3][HCOO\cdot 0.5\,HCOOH] + 0.5\,NHex_3 \rightarrow [HNHex_3][HCOO]\ \text{(in 2-methyl-1,3-propanediol)} \quad \Delta H^0 = -17.7\ kJ\,mol^{-1}\ \text{(per mol FA)}^{[5]} \qquad (6)$$

$$CO_2 + H_2 + NHex_3 \rightarrow [HNHex_3][HCOO]\ \text{(in 2-methyl-1,3-propanediol)} \quad \Delta H^0 = -77\ kJ\,mol^{-1}\ \text{(per mol FA)}^{[5,1b]} \qquad (7)$$

Presumably, the OH-containing solvent stabilizes the formate anion by hydrogen bonding, a role similar to that of the formic acid in the $NHex_3{\cdot}1.5\ HCOOH$ salts. This leads to an equilibrium concentration of formic acid in the product phase for the hydrogenation, owing to insufficient hydrogen bonding beyond this concentration. This concentration can be determined by calorimetry. It is found at the point of maximum heat formation during addition of formic acid to the reaction system and can be easily recognized, as less energy is obtained upon addition of further formic acid. Equilibrium concentrations were measured in this manner for diols of interest (Table 1). Molar ratios of FA/diol in the range of about 1:3 were consistently obtained.

Table 1: Equilibrium formic acid concentrations (point of maximum heat formation) in the diol phase determined by calorimetric investigations (Base: $NHex_3$, molar ratio to FA 1:1).

Diol	ΔH_{max} [kJ mol^{-1}]	HCOOH [wt %]	Molar FA/diol ratio
2-methyl-1,3-propanediol	−43	7.5	1:3.3
1,3-propanediol	−40	8.3	1:3.1
1,2-propanediol	−39	8.0	1:3.4
ethanediol	−35.4	8.9	1:3.2

The equilibrium nature of the maximum formic acid concentration observed by calorimetry could be confirmed by running the reverse reaction, the decomposition of excess formic acid, in the form of $[HNex_3][HCOO]$ dissolved in diol, by the active catalyst under the reaction conditions of the CO_2 hydrogenation. The CO_2 hydrogenation itself also yielded the same amount of formic acid by weight. (Table 2).

We were also interested in obtaining information about possible catalytic species in the $NHex_3$/Diol system and, therefore, investigated the hydrogenation using NMR and IR spectroscopy. $[Ru(H)_2(PnBu_3)_4]$ was used as the catalyst owing to its good solubility in $NHex_3$, which is essential for catalyst recycling, its simple one-step synthesis from easily accessible starting materials,[9] and its good activity in the hydrogenation.

Table 2: Comparison of equilibrium formic acid concentrations in 2-methyl-1,3-propanediol, as determined by calorimetry, in the CO_2 hydrogenation and through $[HNHex_3][HCOO]$ decomposition.

	Calorimetry	CO_2 Hydrogenation	Formic acid decomposition
Formic acid [wt %]	7.5	7.5[a]	7.6[b]

[a] 30 bar CO_2, 70 bar H_2, $[Ru(PEt_3)_4(H)_2]$, 50 °C, 1 h.[6] [b] Decomposition of a 8.7% FA solution (starting concentration as $[HNex_3][HCOO]$ dissolved in the diol) under reaction conditions; 26 bar CO_2, 75 bar H_2, $[Ru(PnBu_3)_4(H)_2]$, 50 °C, 2 h.[8]

Ruthenium tetrakis(phosphine) complexes have been investigated for CO_2 hydrogenation in several experimental[7b–d,10] and theoretical studies,[11] and some suggestions have been made concerning active catalyst species. CO as a ligand in active catalyst species has been generally ruled out owing to the strong inhibiting effect when CO is added to the reaction mixtures.[2b,7b,12]

Ruthenium carbonyl complexes, however, can be selectively prepared using the CO_2 hydrogenation conditions. In this case, the formic acid or the ammonium formate acts as the carbonylating agent [Eq. (8)].[13] These complexes were characterized in situ and could also be used for CO_2 hydrogenation.[14]

$$\mathrm{RuCl_3 + 3\,PPh_3 \xrightarrow[NEt_3,\ MeOH]{+\,CO_2/H_2} [Ru(CO)(H)_2(PPh_3)_3] + 3\,[HNEt_3][Cl]} \tag{8}$$

The contradictory results reported in the literature inspired us to investigate the ruthenium species formed under our conditions. In particular, we looked for CO complexes. We found that formic acid itself acts as a mild carbonylating agent when added at room temperature to a solution of $[Ru(H)_2(PnBu_3)_4]$ in THF or toluene [Eq. (9)]. Complex **1** was characterized in solution by ^1H and ^{31}P NMR and HRMS (ESI) spectroscopy, and the results were in accordance with the data given in literature.[15] The ν(CO) signal was detected in the IR spectra as a strong band at 1917 cm^{-1}. Compound **2** could only be characterized in solution, as it decomposes to **1** under elimination of CO_2 when the reaction solution is removed in vacuum [Eq. (10)]. Complex **2** exhibits a doublet of triplets at $\delta = -7.8$ ppm in the ^1H NMR spectrum and a doublet at $\delta = 19.1$ ppm in the ^{31}P NMR spectrum as well as a triplet at $\delta = 1.0$ ppm, in accordance with the proposed structure of **2**. Formic acid was also added to a solution of $[Ru(H)_2(PEt_3)_4]$ in toluene, and the same reaction was observed.[6]

$$\mathrm{[Ru(H)_2(P\mathit{n}Bu_3)_4] + HCOOH \xrightarrow[\begin{array}{c}toluene/THF\\ -H_2O,\ -P\mathit{n}Bu_3\end{array}]{RT} \begin{array}{c}[Ru(CO)(H)_2(P\mathit{n}Bu_3)_3]\\ (\mathbf{1})\\ \\ [Ru(CO)(H)(HCOO)(P\mathit{n}Bu_3)_3]\\ (\mathbf{2})\end{array}} \tag{9}$$

$$\mathrm{\begin{array}{c}[Ru(CO)(H)(HCOO)(P\mathit{n}Bu_3)_3]\\ (\mathbf{2})\end{array} \xrightarrow[-CO_2]{evaporation} \begin{array}{c}[Ru(CO)(H)_2(P\mathit{n}Bu_3)_3]\\ (\mathbf{1})\end{array}} \tag{10}$$

Complexes **1** and **2** were also detected by NMR spectroscopy in the amine phase after one hour of CO_2 hydrogenation in the liquid–liquid system $NHex_3$/2-methyl-1,3-propanediol with $[Ru(H)_2(PnBu_3)_4]$ as the catalyst. In contrast, no ruthenium species was found in the diol phase by NMR spectroscopy [Eq. (11)]. Only under very high catalyst loadings could minor amounts of **2** be detected in the diol phase by NMR spectroscopy (see the Supporting Information)

$$\mathrm{[Ru(H)_2(P\mathit{n}Bu_3)_4] \xrightarrow[\begin{array}{c}NHex_3\\ 2\text{-}methyl\text{-}1,3\text{-}propanediol\end{array}]{\begin{array}{c}+\,CO_2\ (20\ bar),\ +\,H_2\ (60\ bar)\\ 50°C,\ 1h\end{array}} \begin{array}{c}[Ru(CO)(H)_2(P\mathit{n}Bu_3)_3]\ (\mathbf{1})\\ [Ru(CO)(H)(HCOO)(P\mathit{n}Bu_3)_3]\ (\mathbf{2})\\ in\ NHex_3\\ \\ [HNHex_3][HCOO]\\ in\ 2\text{-}methyl\text{-}1,3\text{-}propanediol\end{array}} \tag{11}$$

When using an in situ protocol and starting with a mixture of $[\{RuCl_2(cod)\}_2]$ and $PnBu_3$ (cod = 1,5-cyclooctadienyl), only the ν(CO) signal at 1908 cm^{-1} of **2** was detected in the IR spectrum of the amine phase after 16 h [Eq. (12)]. The same species could also be found in the amine phase when the reverse reaction was performed, that is, the decomposition of $[HNHex_3][HCOO]$ with $[Ru(H)_2(PnBu_3)_4]$ as the catalyst and 2-methyl-1,3-propanediol as the solvent [Eq. (13)].

$$\mathrm{\begin{array}{c}[\{Ru(Cl)_2(cod)\}_2]\\ +\\ 10\ P\mathit{n}Bu_3\end{array} \xrightarrow[\begin{array}{l}NHex_3\\ 2\text{-}methyl\text{-}1,3\text{-}\\ propanediol\\ -\ cod\\ -\ [HNHex_3][Cl]\end{array}]{\begin{array}{c}+\,CO_2\ (40\ bar),\\ +\,H_2\ (40\ bar)\\ 70°C,\ 16h\end{array}} \begin{array}{c}[Ru(CO)(H)(HCOO)(P\mathit{n}Bu_3)_3]\ (\mathbf{2})\\ in\ NHex_3\\ \\ [HNHex_3][HCOO]\\ in\ 2\text{-}methyl\text{-}1,3\text{-}propanediol\end{array}} \tag{12}$$

$$\mathrm{\begin{array}{c}[Ru(H)_2(P\mathit{n}Bu_3)_4]\\ in\ NHex_3\\ \\ [HNHex_3][HCOO]\\ in\ 2\text{-}methyl\text{-}1,3\text{-}propanediol\end{array} \xrightarrow[-CO_2,\ H_2]{70°C,\ 5h} \begin{array}{c}[Ru(CO)(H)_2(P\mathit{n}Bu_3)_3]\ (\mathbf{1})\\ [Ru(CO)(H)(HCOO)(P\mathit{n}Bu_3)_3]\ (\mathbf{2})\\ in\ NHex_3\\ \\ 2\text{-}methyl\text{-}1,3\text{-}propanediol\end{array}} \tag{13}$$

These results clearly show that ruthenium tetrakis(phosphine) complexes form monocarbonyl complexes under the conditions of the CO_2 hydrogenation, during the decomposition of trialkyl ammonium formates to CO_2 and H_2 (the reverse reaction), and when pure formic acid is added in an inert solvent.

This picture changes when the CO is added to the reaction solution. If 2.5 % CO is present when $[Ru(H)_2(PnBu_3)_4]$ is used as the catalyst, no formic acid is formed. The dicarbonyl complex $[Ru(CO)_2(H)(HCOO)(PnBu_3)_2]$ (**3**) and two equivalents of free $PnBu_3$ are found in the amine phase after the reaction instead of compounds **1** and **2**.

Compound **3** was characterized in solution by NMR and IR spectroscopy, as isolation of the pure compound was impossible owing to the high-boiling amine solvent. The signal of the hydrido ligand was detected in the ^1H NMR spectrum as a triplet at $\delta = -5.5$ ppm (assigned to a *cis* coupling with two equivalent phosphorus atoms) and the formate as a singlet at $\delta = 7.9$ ppm. The ^{31}P NMR spectrum showed a singlet at $\delta = 26.7$ ppm for the $PnBu_3$ ligands and the free phosphine at $\delta = -32.9$ ppm. The ν(CO) signals in the IR spectra could be found as two strong bands of equal intensity at 1952 and 2036 cm^{-1}.

Surprisingly, if an excess of CO (as 1:1 syngas) is added in the absence of CO_2, only the monocarbonyl **1** is formed [Eq. (14)]. Neither **2** nor **3** could be detected by IR and NMR spectroscopy. It appears that the formate ligand stabilizes the dicarbonyl complex **3** in the presence of free phosphine ligands.

$$[Ru(H)_2(PnBu_3)_4] \xrightarrow[\substack{\text{NHex}_3 \\ \text{2-methyl-1,3-propanediol}}]{\substack{\text{+ CO/H}_2\text{ (1:1, 80 bar)} \\ 70°\text{C, 1 h}}} \substack{[Ru(CO)(H)_2(PnBu_3)_3]\ (\mathbf{1}) \\ \text{in NHex}_3} \qquad (14)$$

In summary, we have introduced a new process for hydrogenating CO_2 to formic acid using homogeneous ruthenium catalysts. This process necessitates the use of amines such as $NHex_3$ instead of commonly used NEt_3 to shift the unfavorable equilibrium. Adducts such as $NHex_3$·FA are advantageous as they can be thermally cleaved under relatively mild conditions, thus allowing isolation of the formic acid formed. Calorimetric studies of the interaction of formic acid and such amines have clearly shown that such systems only deliver enough reaction enthalpy to make the CO_2 hydrogenation reaction thermodynamically feasible when it is carried out in the presence of hydrogen-bonding solvents such as diols, which most likely stabilize the FA·amine adduct formed. Participation of the alcohol in the catalytic cycle, as has previously been proposed, may be occurring but is not mandatory. We have also shown that carbonyl complexes are formed in all cases of relevance to CO_2 hydrogenation studied when using highly basic alkylphosphine complexes, such as $[Ru(H)_2(PnBu_3)_4]$ or $[Ru(H)_2(PEt_3)_4]$ as the catalyst. Formic acid and its adducts are excellent carbonylation reagents for such highly electron-rich transition-metal complexes. These results have implications for all previously proposed mechanisms for CO_2 hydrogenation using ruthenium catalysts of this type, which have not incorporated such species.

Experimental Section

$[Ru(PnBu_3)_4(H)_2]$ was prepared according to a modified literature procedure.[9] Calorimetric measurements were performed with a Mettler-Toledo RC1e reaction calorimeter, equipped with a SV01 glass reactor (ca. 1 L). In a typical experiment, the reactor was charged with solvent or the amine and heated to the desired temperature. Reactant was then added using a dosing pump. After the addition was completed, stirring was continued for 30–60 min. The calorimetric measurements yielded heat-flow data, heats of reaction, and heat capacities. In addition to calorimetry, the reactions were simultaneously monitored by on-line IR spectroscopy (Mettler-Toledo ReactIR (TM) equipped with a SiComp (TM) ATR probe).

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[5] The details on the process concept and experimental data are described elsewhere: PCT Application PCT/EP 2010/058208.

[6] Experimental details are given in the Supporting information.

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[8] This maximum concentration in the equilibrium could be reached either in the hydrogenation itself or in the backward reaction for 2-methyl-1,3-propanediol when a 10% mixture of formic acid in the product phase was exposed to the hydrogenation conditions; see the Supporting Information.

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