Iron-Catalyzed CO_2 Hydrogenation

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A Well-Defined Iron Catalyst for the Reduction of Bicarbonates and Carbon Dioxide to Formates, Alkyl Formates, and Formamides**

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Carbon dioxide is the primary carbon source in the atmosphere and provides the basis for all organic matter on earth. Even though CO_2 is abundant, cheap, and relatively nontoxic compared to the alternative C_1 source carbon monoxide, it is the latter species that is used as a raw material in many bulk-scale chemical processes. One promising approach to overcoming the low reactivity of CO_2[1] is its activation by catalytic hydrogenation to form formic acid or its derivatives.[2] Until now, noble-metal catalysts based on rhodium,[3,4] ruthenium,[5–7] and iridium[8,9] were mostly used for this transformation. Graf and Leitner had already achieved significant turnover numbers (TONs) of 3400 with rhodium phosphine complexes in the early 1990s.[3] Jessop, Ikariya, and Noyori were able to increase the catalyst efficiency by using a Ru^{II} complex in supercritical CO_2 ($scCO_2$).[5,6] Very recently, Nozaki and co-workers used a pincer-type Ir^{III} catalyst for the hydrogenation of CO_2 which gave the highest TON reported so far.[9]

Much less work on the biologically relevant reduction of carbonates and bicarbonates has been reported, and the reported activities of hydrogenation catalysts are significantly lower compared to the reaction of CO_2. For example, Joó and co-workers obtained a TON of 108 with $[\{RuCl_2(mTPPMS)_2\}_2]$ (mTPPMS = *meta*-monosulfonated triphenylphosphine) in aqueous solution.[10]

An important long-standing goal in chemistry is the development of bio-inspired catalysis and the replacement of noble metal based catalysts, that is, ruthenium, iridium, and rhodium, with nonprecious metals, such as iron, zinc, and manganese.[11] In this respect, an iron-based reduction of carbonates and carbon dioxide constitutes a challenging and highly attractive goal.

Despite the recent achievements in iron-catalyzed hydrogenations and transfer hydrogenations,[12] there are only two examples of the homogeneous catalyzed reduction of carbon dioxide. Evans and Newell reported a catalyst system derived from $[HFe_3(CO)_{11}]^-$ for the synthesis of methyl formate.[13] However, the product is only formed with a very low TOF ($0.06\,h^{-1}$) and turnover number (up to 6). Jessop and co-workers demonstrated by high-throughput screening that the combination of $Fe(OAc)_2$ or $FeCl_3$ with bidentate phosphines created active catalysts for the reduction of carbon dioxide. Although formic acid was formed under optimized conditions ($FeCl_3$/1,2-bisdicyclohexylphosphinoethane) with an improved catalyst turnover number of 113, the reaction proceeded only in the presence 0.5 equivalents of the expensive base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 100 bar total pressure.[14] Moreover, a large excess of carbon dioxide was used in both reports, and consequently no yields based on CO_2 or amine are given.

Therefore, the need still exists to develop an efficient iron catalyst for the hydrogenation of CO_2 and carbonates. Based on our previous studies on the ruthenium-catalyzed hydrogenation of carbonate and bicarbonate,[15] we describe herein for the first time an active iron catalyst system which can be used for the reduction of both carbon dioxide and bicarbonates to give formates, alkyl formates, and formamides. Central to the success of this work is the combination of the iron source $Fe(BF_4)_2\cdot 6\,H_2O$ (**1**) and the tetradentate ligand $P(CH_2CH_2PPh_2)_3$ (PP_3) which form defined iron hydride complexes $[FeH(PP_3)]BF_4$ (**2**) and $[FeH(H_2)(PP_3)]BF_4$ (**6**) under the reaction conditions.

In our initial approach we tested different iron precursors and various nitrogen- and phosphine-containing ligands for the hydrogenation of sodium bicarbonate to sodium formate. Selected results of this investigation are shown in Table 1. To the best of our knowledge, the use of any homogeneous iron catalyst in this reaction has not been described before. Commercially available mono-, bi- as well as tridentate ligands—for example, different derivatives of triphos [1,1-bis(2-diphenylphosphinoethyl)phenylphosphine (triphos 1), 1,1,1-tris(diphenylphosphino)methane (triphos 2), 1,1,1-tris-(diphenylphosphinomethyl)ethane (triphos 3)], bisdiphenylphosphinomethane (dppm), 1,2-bisdiphenylphosphinoethane (dppe), triphenylphosphine, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos), tris[2-(dimethylamino)ethyl]-amine (Me_6TREN), and tris(2-aminoethyl)amine (TAEA)—showed no activity at all (Table 1, entries 1–5). Also, no activity was observed when blank experiments were per-

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Table 1: Catalytic hydrogenation of bicarbonate to formate.

$$HCO_3^- + H_2 \xrightarrow[\text{MeOH}]{\text{Fe cat.}} HCO_2^- + H_2O$$

Entry[a]	Catalyst	Yield [%][b]	TON[c]
1	$Fe(BF_4)_2$/triphos 1	0	–
2	$Fe(BF_4)_2$/triphos 2	0	–
3	$Fe(BF_4)_2$/triphos 3	0	–
4	$Fe(BF_4)_2/Me_6TREN$	0	-
5	$Fe(BF_4)_2$/TAEA	0	–
6	$Fe(BF_4)_2/PP_3$	88	610
7[d]	$Fe(BF_4)_2/PP_3$	12	83
8[e]	$Fe(BF_4)_2/PP_3$	11	76
9[f]	$Fe(BF_4)_2/PP_3$	16	112
10[g]	$Fe(BF_4)_2/PP_3$	52	360
11	$[\{RuCl_2(benzene)\}_2]/PP_3$	90	624
12	$[HFe_3(CO)_{11}]^-/PP_3$	0	–
13	$[Fe(acac)_3]$[h]$/PP_3$	25	173
14	$FeCl_2/PP_3$	10	69

[a] Reaction conditions: 80 °C, 60 bar H_2 at room temperature, 20 h, 0.685 mmol catalyst per liter of solvent. [b] Yield based on ^1H NMR signals of sodium formate, with THF used as an internal standard. [c] Turnover number = moles of sodium formate per mole of catalyst. [d] 60 °C. [e] 100 °C. [f] 30 bar H_2. [g] 90 bar H_2. [h] acac = acetylacetanoate.

formed without catalyst or ligand (see the Supporting Information for an extended version of Table 1). However, the hydrogenation proceeded smoothly with a catalyst formed in situ from $Fe(BF_4)_2{\cdot}6\,H_2O$ and the tetraphos ligand (PP_3). In the presence of only 0.14 mol% of this catalyst at 80 °C, sodium formate was formed in an excellent yield of 88% with a high turnover number (610; Table 1, entry 6). Noncationic iron salts as well as iron carbonyl complexes led to no or significantly lower activity (Table 1, entries 12–14). Interestingly, the analogous ruthenium complex generated from $[\{RuCl_2(benzene)\}_2]$ does not give better results (Table 1, entry 11).

Next, we were curious whether this catalyst could be applied to the hydrogenation of CO_2 to form esters and amides. Indeed, methyl formate was formed in high yield (56%) and a TON of 585, which is two orders of magnitude higher than the previous best result with iron catalysts (Table 2, entries 1–3).[13] In addition to methyl formate, dimethylformamide was obtained in high yield (75%) with a TON of 727 (Table 2, entry 4), which is again comparable to known Ru, Ir, and Rh systems.[16] Furthermore, *N*-formylpiperidine was formed in 41% yield with a TON of 373 (Table 2, entry 5).

Table 2: Catalytic hydrogenation of carbon dioxide.

$$CO_2 + H_2 \xrightarrow[\text{MeOH, base}]{\text{Fe cat.}} HCO_2H\text{-base} \xrightarrow{ROH\,/\,NHR'_2} HCO_2R\,/\,HCONR'_2$$

Entry[a]	Product	P_{H_2/CO_2}[b] [bar]	Yield[c] [%]	TON
1	HCO_2Me	60/30	56	292
2[d]	HCO_2Me	60/30	14	585
3[e]	HCO_2Me	60/30	47	245
4	DMF	60/30	75	727
5	$C_6H_{11}NO$	60/30	41	373

[a] Reaction conditions: 100 °C, 20 h, 2 mL NEt_3 for alkyl formates, 0.025 mol amine for formamides. [b] Pressure at room temperature. [c] Yield was determined by GC analysis (mole of product per mole of base) (NEt_3 was used for formation of alkyl formates, and the corresponding secondary amine in the case of formamides). [d] 16 mL NEt_3. [e] $[FeH(H_2)PP_3]BF_4$ (**6**) used.

Formic acid esters based on ethanol or propanol were obtained in lower yields compared to those based on methanol: 16% yield, TON 167 for ethanol; 9% yield, 94 TON for propanol. Darensbourg and Ovalles observed that methanol competes effectively with H_2 for a binding site on the metal.[17] Similar to the trend for alkyl formates, diethylformamide was obtained in lower yield than DMF (28% yield and TON of 255). In agreement with previously published results, the presence of base in the reaction is significant:[1,6] no product is formed without the addition of base.

Iron(II) hydridophosphine complexes have been intensively investigated in organometallic chemistry, and several complexes have already been prepared.[18] However, few catalytic applications are currently known and elucidated. Thus, we tried to determine the reaction mechanism in more detail by using in situ high-pressure NMR spectroscopy and X-ray analysis. Stirring a mixture of $Fe(BF_4)_2{\cdot}6\,H_2O/PP_3$ with hydrogen (10 bar) in the presence of base in THF resulted in the immediate formation of a solution containing $[FeH(PP_3)]BF_4$ (**2**), which was characterized by X-ray crystallography (Figure 1). When **2** was purged with CO_2 (10 bar) $[FeH(CO_2)(PP_3)]$ **3** was formed, and a broad Fe-CO_2 signal at $\delta = 206.2$ ppm (s) was observed in the ^{13}C NMR spectrum.[19] This signal is also obtained upon reaction of $Fe(BF_4)_2{\cdot}6\,H_2O$ and PP_3 with ^{13}C-enriched formic acid. Subsequent insertion into the Fe−H bond species resulted in the formation of complex $[Fe(HCO_2)(PP_3)]$ **4**, which was characterized by a doublet of quartets at $\delta = 164.5$ ppm ($J(H,C) = 206.9$ Hz and $J(P,C) = 4.9$ Hz) in the ^{13}C NMR spectrum.[20] In addition, the formation of $[Fe(H_2)(HCO_2)(PP_3)]$ **5** is assumed because of a broad doublet at $\delta = 173.07$ ppm $J(H,C) = 204.7$ Hz. The starting complex **2** can be recovered through elimination of

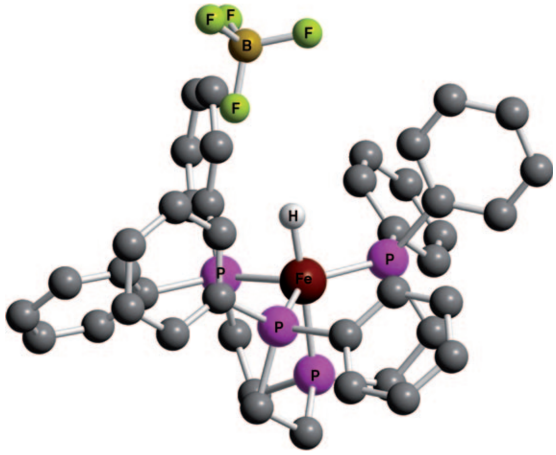
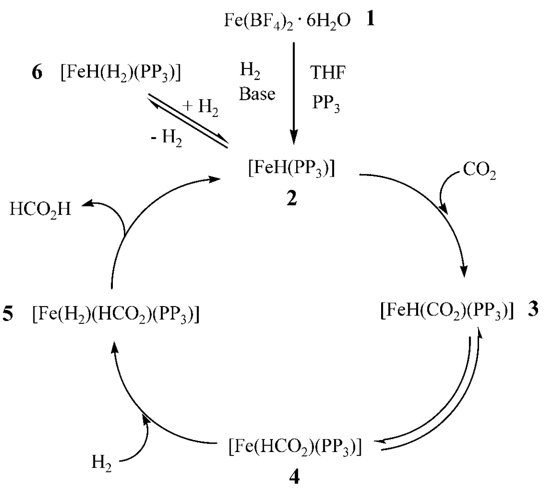


Figure 1. Molecular structure of the salt $[FeH(PP_3)]BF_4$ (**2**) with selected atom labels.

formic acid. Reaction of complex **2** with hydrogen led to Bianchini's complex $[FeH(H_2)(PP_3)]$ (**6**), which may act as a reservoir of the active catalyst.[20] This complex was identified by ^{1}H NMR spectroscopy by comparison with literature data, with signals observed for dihydrogen (s, 2H) at $\delta = -7.56$ ppm and a hydride (m, 1H) at $\delta = -12.47$ ppm with an AM_2Q spin system of the PP_3 phosphorus atoms ($J(HP_A) = 45.1$ Hz, $J(HP_M) = 58.2$ Hz, $J(HP_Q) = 15.2$ Hz).[20] Complex **2** can also be recovered from **6** by loss of hydrogen at elevated temperatures. Indeed, we demonstrated that complex **6** (yellow) loses H_2 at higher temperature (>60 °C) to give orange crystals of $[FeH(PP_3)]$ (**2**). During the reaction the ^{31}P NMR spectrum exhibited only two singlets at $\delta = 89.9$ ppm (3P) and $\delta = 173.6$ ppm (1P), which is indicative of a fully coordinated PP_3 ligand. On the basis of our studies, the catalytic cycle shown in Scheme 1 is proposed.



Scheme 1. Proposed catalytic cycle for the hydrogenation of CO_2 using $Fe(BF_4)_2{\cdot}6\,H_2O/PP_3$.

In conclusion, we have developed an active and general iron catalyst that is capable of hydrogenating CO_2 to alkyl formates and formamides in good yields and TONs. Although highly active catalysts based on precious metals are known, the present study is of interest in relation to bio-inspired catalysts. For the first time the reduction of readily available bicarbonates to formates in the presence of an iron catalyst has also been demonstrated. This reaction could be an important step in the benign use of carbon dioxide as a hydrogen storage material. Notably, the catalytic cycle has been elucidated in detail by medium-pressure NMR studies (typically 10–100 bar) and X-ray analysis. This study will hopefully lead to the development of improved iron catalysts in the near future.

Experimental Section

Formation of sodium formate: Dissolving $[Fe(BF_4)_2]{\cdot}6\,H_2O$ (9.25 mg, 2.74×10^{-5} mol) and tetraphos $P(CH_2CH_2PPh_2)_3$ (1 equiv) in MeOH (40 mL) led to the immediate formation of a purple solution. $NaHCO_3$ (1.6 g, 0.0190 mol) was placed in a autoclave (100 mL) and the preformed catalyst solution then added. The autoclave was deoxygenated and then filled with 60 bar H_2 at room temperature. The reaction mixture was stirred (400 rpm) for 20 h at 80 °C. After the reaction time, the autoclave was cooled with ice water and the pressure was slowly released. The solution was fully evaporated in a rotary evaporator and the formate content (pale yellow color) was determined by ^{1}H NMR spectroscopy in D_2O with THF used as an internal standard and a relaxation time of 20 s. Each reaction was carried out at least twice to confirm reproducibility.

Formation of alkyl formates: The synthesis of alkyl formates was performed in a similar way as the synthesis of sodium formate, except that the corresponding alcohol (20 mL) was used and NEt_3 (2 mL) was added to the catalyst solution. CO_2 (30 bar) and H_2 (60 bar) were added at room temperature to the solution and the reaction mixture was stirred at 100 °C for 20 h. The product was analyzed by GC [a HP 6890N instrument with a 30 m HP5 column, internal diameter 0.32 mm, 0.25 μm film, N_2 carrier gas, inlet temperature: 270 °C, injection volume: 1 μL, split ratio: 50:1, flow rate (mL min^{-1}): 0.6 (until 20 min) then in 0.5 mL min^{-1} steps to 2.1, T (°C): 35 (until 20 min) then in 20 °C min^{-1} steps to 295 (17 min), detector temperature: 300 °C, H_2 flow: 30 mL min^{-1}, air flow: 300 mL min^{-1}, makeup flow: 25 mL min^{-1}] with diglyme used as an internal standard. The yields are expressed as the ratio of moles of product per mole of NEt_3 used.

Formation of formamides: The synthesis of formamides was performed in a similar way as the synthesis of sodium formate, except that MeOH (20 mL) was used together with the corresponding amine (dimethylamine, diethylamine, piperidine; 0.025 mol). CO_2 (30 bar) and H_2 (60 bar) were added at room temperature to the solution and the reaction mixture was stirred at 100 °C for 20 h. The product was analyzed by GC (see previous paragraph for the specifications) with diglyme used as an internal standard. The yields are expressed as the ratio of moles of product per mole of amine (dimethylamine, diethylamine, piperidine) used.

In situ NMR experiments were performed in sealed high-pressure sapphire NMR tubes (ca. 10 mL) in a DRX 400 (Bruker) spectrometer with $[D_8]$THF used as the solvent.

The defined complex, $[FeH(H_2)(PP_3)]BF_4$ (**6**), was synthesized according to the literature.[20a]

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