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# Iron-Catalyzed Hydrogenation of Bicarbonates and Carbon Dioxide to Formates

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The catalytic hydrogenation of carbon dioxide and bicarbonate to formate has been explored extensively. The vast majority of the known active catalyst systems are based on precious metals. Herein, we describe an effective, phosphine-free, air- and moisture-tolerant catalyst system based on Knölker's iron complex for the hydrogenation of bicarbonate and carbon dioxide to formate. The catalyst system can hydrogenate bicarbonate at remarkably low hydrogen pressures (1–5 bar).

Carbon dioxide is an attractive $C_1$ source compared to other molecules, such as carbon monoxide, because it is easily and abundantly available, relatively nontoxic, and renewable. However, utilizing carbon dioxide still poses a challenge owing to its thermodynamic stability. In the past decades, the homogeneous catalytic hydrogenation of carbon dioxide and its derivatives has been widely investigated.[1] An overwhelming majority of the catalyst systems known to be active for this reaction is based on precious metals such as rhodium,[2] ruthenium,[3] iridium,[4] and palladium.[5] The relative toxicity, limited availability, and high price of these metals have resulted in a search for alternatives that are more environmentally benign and sustainable. Iron-based catalysts are especially attractive in this context because of the abundant availability of the central metal; however, there have been relatively few studies in the past.

Although several achievements in iron-catalyzed reductions have been made recently,[6] there are only few reports on the iron-catalyzed hydrogenation of carbon dioxide to formic acid or its derivatives. In 2003, Jessop and co-workers reported a combination of $FeCl_3$ or $Fe(OAc)_2$ with bidentate phosphines for the hydrogenation of carbon dioxide to formic acid with turnover number (TON) of up to 113.[7] In 2010, Beller, Laurenczy, and co-workers reported an iron complex [generated in situ from $Fe(BF_4)_2$ and a tetradentate phosphine ligand, $P(CH_2CH_2PPh_2)_3$); ($PP_3$)] capable of the hydrogenation of carbon dioxide and bicarbonates with TON of up to 727.[8] Soon after, the same group developed the most active and productive iron-based catalyst system reported so far. The system, $Fe(BF_4)_2$/tris(2-diphenylphosphine)phenyl)phosphine), can hydrogenate bicarbonate to formate with TON of up to 7546 and carbon dioxide to DMF with TON of up to 5104.[9] Finally, Milstein and co-workers reported an iron–pincer complex, *trans*-[(*t*Bu-PNP)$FeH_2$], capable of reducing carbon dioxide and bicarbonate at remarkably low pressures (initial $H_2$ pressure 6.2 bar) with high TONs.[10]

Although significant progress has been made in the iron-catalyzed hydrogenation of carbon dioxide and bicarbonate, as described above, challenges still remain. All of the mentioned highly active iron catalyst systems contain at least two phosphine donors, which are often air- and moisture-sensitive and tedious to prepare. Therefore, from an environmental as well as a practical standpoint, the development of easily available, air- and moisture-tolerant iron catalysts for this transformation is still highly desirable.

A pioneering work by Guan and Casey in 2007 described a bifunctional catalyst, Knölker's iron complex, as an efficient hydrogen catalyst.[11] Its unique catalytic behavior and easy access have lead to a number of applications in the last 6 years.[12] Although Knölker's iron complex is an active hydrogen catalyst, it is air- and light-sensitive. In sharp contrast, its precursor, the tricarbonyl (cyclopentadienone)iron complex, is air- and moisture-stable but not an active hydrogen catalyst. However, it is capable of generating Knölker's iron complex in situ by selective mono-decarbonylation/protonation. By utilizing this property, several groups have recently successfully applied the tricarbonyl (cyclopentadienone)iron complex or analogues thereof as precatalysts for various redox transformations.[13] As part of our ongoing efforts to explore the catalytic properties of Knölker's iron complex we present here, for the first time, this complex as a highly active catalyst for the hydrogenation of bicarbonate and carbon dioxide to formate.

Based on our previous work on the hydrogenation of aldehydes and ketones catalyzed by Knölker's iron complex,[14] we started by investigating the hydrogenation of sodium bicarbonate using in situ-generated catalysts. Initially, iron complex **1a** was selected as precatalyst for this investigation, and the results are listed in Table 1. As expected the reaction did not show any conversion in the absence of iron catalyst (entry 1). The desired product, sodium formate, was formed with a TON of 26 in the presence of complex **1a** (entry 2). To further improve the reaction, we evaluated the influence of critical reaction parameters such as solvent, temperature, and hydrogen pressure. The highest activity in a survey of several solvents was achieved when using ethanol as co-solvent (TON of 447;

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**Table 1.** Iron-catalyzed hydrogenation of sodium bicarbonate to sodium formate.[a]

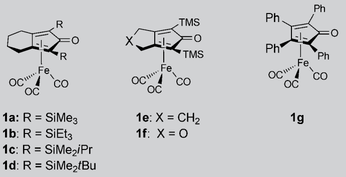
$$NaHCO_3 + H_2 \xrightarrow[\text{conditions}]{0.1\text{ mol\% }\mathbf{1a}} NaOOCH + H_2O$$

| Entry | Solvent | $T$ [°C] | $p(H_2)$[b] [bar] | Yield[c] [%] | TON[d] |
|---|---|---|---|---|---|
| 1 | THF/$H_2O$ | 120 | 30 | 0 | 0 |
| 2 | THF/$H_2O$ | 120 | 30 | 2.6 | 26 |
| 3 | *i*PrOH/$H_2O$ | 120 | 30 | 10.5 | 105 |
| 4 | MeOH/$H_2O$ | 120 | 30 | 1.3 | 13 |
| 5 | EtOH/$H_2O$ | 120 | 30 | 44.7 | 447 |
| 6 | EtOH/$H_2O$ | 100 | 30 | 0 | 0 |
| 7 | EtOH/$H_2O$ | 140 | 30 | 0.2 | 2 |
| 8 | EtOH/$H_2O$ | 120 | 1 | 4.7 | 47 |
| 9 | EtOH/$H_2O$ | 120 | 2 | 10.4 | 104 |
| 10 | EtOH/$H_2O$ | 120 | 5 | 16.3 | 163 |
| 11 | EtOH/$H_2O$ | 120 | 10 | 22.9 | 229 |
| 12 | EtOH/$H_2O$ | 120 | 20 | 38.2 | 382 |
| 13 | EtOH/$H_2O$ | 120 | 40 | 39.4 | 394 |
| 14 | EtOH/$H_2O$ | 120 | 60 | 31.8 | 318 |
| 15 | EtOH/$H_2O$ | 120 | 80 | 33.8 | 338 |
| 16 | EtOH/$H_2O$ | 120 | 100 | 32.5 | 325 |

[a] Reaction conditions: $NaHCO_3$ (3 mol), Fe complex (0.003 mol). [b] Pressure at RT. [c] Determined by $^1H$ NMR analysis using DMF as an internal standard. [d] Mol of sodium formate per mol of catalyst.

**Table 2.** Variation of iron complexes of **1b–g** for hydrogenation of sodium bicarbonate to sodium formate.[a]

$$NaHCO_3 + H_2 \xrightarrow[\substack{H_2\text{ (30 bar), EtOH/}H_2O\\ 120\ ^{\circ}C,\ 24h}]{0.1\text{ mol\% Fe catalyst}} NaOOCH + H_2O$$



**1a:** R = $SiMe_3$
**1b**: R = $SiEt_3$
**1c**: R = $SiMe_2$*i*Pr
**1d**: R = $SiMe_2$*t*Bu

**1e**: X = $CH_2$
**1f**: X = O

**1g**

| Entry | Fe catalyst | Yield[b] [%] | TON[c] |
|---|---|---|---|
| 1 | **1 a** | 44.7 | 447 |
| 2 | **1 b** | 33.5 | 335 |
| 3 | **1 c** | 35.4 | 354 |
| 4 | **1 d** | 12.2 | 122 |
| 5 | **1 e** | 23.2 | 232 |
| 6 | **1 f** | 4.7 | 47 |
| 7 | **1 g** | 0 | 0 |

[a] General reaction conditions: $NaHCO_3$ (3 mmol), Fe complex (0.003 mmol), EtOH/$H_2O$ (1.5 mL/3 mL), 120 °C, 30 bar $H_2$. [b] Determined by $^1H$ NMR analysis using DMF as an internal standard. [c] Mol of sodium formate per mol of catalyst. TMS = trimethylsilyl.

**Table 3.** Iron-catalyzed hydrogenation of carbon dioxide.[a]

$$CO_2 + H_2 + NaOH \xrightarrow[\text{EtOH/}H_2O\text{ ,120 }^{\circ}C\text{, 24h}]{0.1\text{ mol\% }\mathbf{1a}} NaOOCH + H_2O$$

| Entry | $p(H_2)$[b] [bar] | $p(CO_2)$[b] [bar] | Yield[c] [%] | TON[d] |
|---|---|---|---|---|
| 1 | 40 | 20 | $<1$ | – |
| 2 | 50 | 10 | $<1$ | – |
| 3 | 60 | 20 | $<1$ | – |
| 4 | 60 | 30 | $<1$ | – |
| 5[e] | 30 | 20 | 30.7 | 307 |

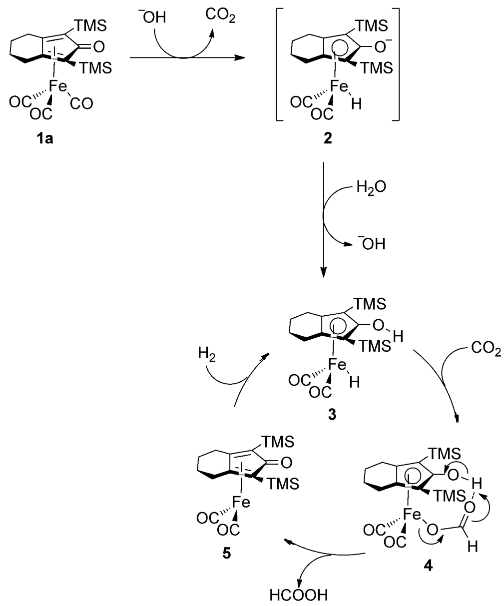
[a] Reaction conditions: NaOH (3 mmol), Fe complex (0.003 mmol), EtOH/$H_2O$ (1.5 mL/3.0 mL) [b] pressure at RT. [c] Determined by NMR analysis using DMF as an internal standard. [d] Mol of sodium formate per mol of catalyst. [e] NaOH (3 mmol) was first transformed to sodium bicarbonate in the presence of $CO_2$, then Fe complex (0.003 mmol) was added to the solution and pressurized to 30 bar hydrogen.

entry 5). The catalyst system also showed temperature-dependence. For example, when the reaction was performed at 100 °C and 140 °C, the TONs dropped to 0 and 2, respectively (entries 6 and 7). Variation of the hydrogen pressure had a significant influence on the activity of the catalyst (entries 8–16). Notably, at low hydrogen pressures (1 to 5 bar) the catalyst system still showed good activities (entries 8–10).

Next, a series of analogues of complex **1 a** were tested for the hydrogenation of sodium bicarbonate to sodium formate. Compared to **1 a**, other iron complexes showed lower activities (Table 2, entries 2–6). Complex **1 g**, bearing a tetraphenyl cyclopentadienone ancillary ligand, did not yield any product at all.

Having established our optimal reaction conditions for the hydrogenation of sodium bicarbonate, we wondered if this catalyst system could be applied to the hydrogenation of carbon dioxide in the presence of sodium hydroxide (Table 3). A key requirement for this transformation is that Knölker's iron complex is generated in the presence of a large excess of carbon dioxide. Initial studies suggested that this may be problematic. For example, the iron-catalyzed hydrogenation of carbon dioxide in the presence of sodium hydroxide only yielded a trace amount of formate. Considering the Hieber base reaction taking place under basic conditions, we speculate that the pH value of the reaction solution may play an important role for the catalyst system. Indeed, detailed measurements of the pH of the reaction systems confirmed this speculation. For example, the pH value of the hydrogenation of bicarbonate with high activity is close to 8.80; however, the pH value of hydrogenation of carbon dioxide with no activity is around 7.45. Because the in situ generation of Knölker's iron complex by the Hieber base reaction is inhibited by the presence of carbon dioxide, alternatively, sodium hydroxide was first transformed to sodium bicarbonate in the presence of carbon dioxide, then complex **1 a** was added to the solution and pressurized to 30 bar hydrogen. Gratifyingly, a TON of 307 was achieved with this slightly modified procedure.

Based on previous work by the groups of Knölker,[15] Casey,[16] and our own findings, we propose the following mechanism (Scheme 1): Hydroxide adds to one carbon monoxide of the precatalyst **1 a** and the hydride complex **2** is formed with the release of carbon dioxide by a Hieber base reaction. After protonation, Knölker's iron complex **3** is formed and subsequent insertion of carbon dioxide into the Fe–H bond forms the corresponding iron formate complex **4**. Formic acid is liberated from **4** to form the 16-electron iron(0) species **5**, which regenerates Knölker's iron complex **3** by oxidative addition of hydrogen.



**Scheme 1.** Plausible mechanism for the hydrogenation of carbon dioxide catalyzed by complex **1a**.

In conclusion, we describe an effective, phosphine-free, air- and moisture-tolerant iron-based catalyst system for the hydrogenation of bicarbonate and carbon dioxide to formate. Notably, it is capable of hydrogenating bicarbonate under remarkably low hydrogen pressures (1–5 bar). Further studies on the application of this catalytic system to other synthetically interesting substrates are ongoing in our laboratory and will be reported in due course.

## Experimental Section

**General procedure for catalytic hydrogenation of sodium bicarbonate**: First, 20–50 mL solutions of **1a** in ethanol (0.002 M) and $Na_2CO_3$ (1 M) were prepared. A 30 mL autoclave was charged with the catalyst **1a** (0.003 mmol) dissolved in 1.5 mL ethanol and $NaHCO_3$ (3 mmol) dissolved in 3 mL $H_2O$. Once sealed, the autoclave was purged 3 times with hydrogen, then pressurized to 30 bar and heated at 120 °C for 24 h. After reaction, the autoclave was cooled to RT and depressurized. The solvent was evaporated under reduced pressure and the yield was measured through $^1H$ NMR spectroscopy in $D_2O$ with DMF as an internal standard. The results shown in Table 1 and Table 2 were obtained by performing each reaction at least three times to confirm its reproducibility.

**General procedure for catalytic hydrogenation of $CO_2$**: A 30 mL autoclave was charged with NaOH (3 mol) dissolved in 3 mL $H_2O$. The autoclave was pressurized at ambient temperature with $CO_2$ to 20 bar and the solution was stirred at RT for 1 h. After release of $CO_2$, the catalyst **1a** (0.003 mmol) was added to the autoclave. Once sealed, the autoclave was purged 3 times with hydrogen, then pressurized to 30 bar and heated at 120 °C for 24 h. After reaction, the autoclave was cooled to RT and depressurized. The solvent was evaporated under reduced pressure and the yield was analyzed by $^1H$ NMR spectroscopy in $D_2O$ with DMF as an internal standard.

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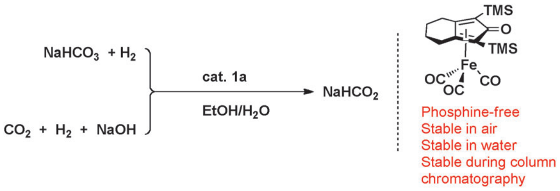

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