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Homogeneous Catalysis

# Catalytic Disproportionation of Formic Acid to Generate Methanol**

*Alexander J. M. Miller,* D. Michael Heinekey, James M. Mayer, and Karen I. Goldberg**

The decomposition of formic acid almost always proceeds by dehydrogenation to produce $H_2$ and $CO_2$ [Eq. (1)] or by dehydration to produce CO and $H_2O$ [Eq. (2)].[1] In rare cases, disproportionation to produce formaldehyde [Eq. (3)] has been observed—with low selectivity on metal oxides above 200 °C.[2]

$$HCO_2H(aq) \rightarrow CO_2(g) + H_2(g) \qquad \Delta G^{\circ}_{298} = -9.2\ \text{kcal mol}^{-1} \tag{1}$$

$$HCO_2H(aq) \rightarrow CO(g) + H_2O(aq) \qquad \Delta G^{\circ}_{298} = -3.7\ \text{kcal mol}^{-1} \tag{2}$$

$$2\,HCO_2H(aq) \rightarrow H_2CO(aq) + H_2O(aq) + CO_2(g) \qquad \Delta G^{\circ}_{298} = -11.9\ \text{kcal mol}^{-1} \tag{3}$$

In 1911, Sabatier and Mailhe reported that some dimethoxymethane was produced upon thermolysis of $HCO_2H$ over $ThO_2$, thereby providing indirect evidence for a methanol-producing pathway [Eq. (4)].[3] There is great interest in the

$$3\,HCO_2H(aq) \rightarrow CH_3OH(aq) + H_2O(aq) + 2\,CO_2(g) \qquad \Delta G^{\circ}_{298} = -23.5\ \text{kcal mol}^{-1} \tag{4}$$

facile interconversion of various C1 chemicals, so it is remarkable that one hundred years have passed without further reports on the decomposition mode shown in Equation (4). Catalytic transformations of $C_1$ feedstocks (natural gas ($CH_4$) and synthesis gas ($CO/H_2$) derived from various sources) are a key foundation of the chemical industry.[4] $HCO_2H$ is produced on large scale (ca. 700000 tons/year) using these traditional fossil fuel feedstocks.[5] Alternative, renewable routes to $HCO_2H$ are being developed, with $CO_2$ or biomass as starting points.[6,7] New transformations of formic acid are needed to ignite and promote development of renewable $C_1$ chemistry; conversion to methanol represents a renewable route to a major commodity chemical and high energy density fuel.[8]

We report herein that a molecular iridium species catalyzes the disproportionation of formic acid to methanol, water, and $CO_2$ [Eq. (4)]. The present study represents, to our knowledge, the first well-defined example of such a reaction mode of formic acid. The reaction occurs in acidic aqueous solution, without the need for any organic solvent or added hydrogen. The net reaction is formally a transfer hydrogenation, with $HCO_2H$ acting as hydrogen source and substrate simultaneously. This fundamental $C_1$ reaction poses a number of interesting mechanistic questions and may have ramifications in the conversion of $CO_2$ to fuels and chemicals. Hydrogenation of formic acid to methanol directly is very unusual (generally an alkyl formate intermediate must be produced);[9] disproportionation of formic acid raises the possibility of direct formation of methanol. We have started to map the scope and mechanism of this simple, yet essentially unrecognized reaction. While dehydrogenation of $HCO_2H$ occurs simultaneously, we have shown that the catalyst activity and the selectivity to methanol can be tuned by changing reaction conditions.

Aqueous $HCO_2H$ solutions containing $[Cp^*Ir(bpy)(H_2O)](OTf)_2$ (**1**, Cp* = pentamethylcyclopentadienyl, bpy = 2,2′-bipyridine)[10] produced methanol upon heating. This result was surprising, because $HCO_2H$ is commonly used as a source of $H_2$ in transfer hydrogenation reactions, and **1** is a well-known transfer hydrogenation catalyst, with no prior reports of methanol-producing side reactions.[11] When $HCO_2H$ (3 M, 2 mL, pH 1.4) containing **1** (0.5 μmol, 0.25 mM, 0.008 mol %) was heated at 80 °C for 24 h in a sealed vessel, 17 μmol of methanol were produced (analyzed by $^1H$ NMR spectroscopy), which corresponds to 34 turnovers (TON) and a turnover frequency (TOF) of 1.4 $h^{-1}$ (Table 1, entry 3). Methanol and methyl formate (produced by $HCO_2H$ esterification) are the only products observed in solution, but roughly 23 % of the $HCO_2H$ had been consumed at this time, indicating 4 % selectivity for methanol.[12] 1:2 mixtures of $[Cp^*Ir(Cl)_2]_2$ and bpy gave similar results (Table 1, entry 2). The bipyridyl ligand is important, as neither $[Cp^*Ir(Cl)_2]_2$ (Table 1, entry 1) nor $[Cp^*Ir(H_2O)_3]SO_4$ without bpy produced any detectable methanol. Formic acid was consumed with these Ir species, however, and the pressure in sealed reaction vessels rose, thereby implying that Equations (1) and/or (2) are catalyzed in lieu of Equation (4).

That the methanol originates from $HCO_2H$ was confirmed by the production of $^{13}CH_3OH$ upon heating a solution of $H^{13}CO_2H$ in $D_2O$ at 80 °C in the presence of **1** in a sealed NMR tube. In addition to the signal for $^{13}CH_3OH$, a prominent resonance for $^{13}CO_2$ (but not for $^{13}CO$) was observed in

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[*] Prof. A. J. M. Miller,[+] Prof. D. M. Heinekey, Prof. J. M. Mayer, Prof. K. I. Goldberg
Department of Chemistry
University of Washington
Seattle, WA 98195-1700 (USA)
E-mail: ajmm@email.unc.edu
goldberg@chem.washington.edu

[+] Current address: Department of Chemistry
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599-3290 (USA)

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***Table 1:*** Catalytic disproportionation of aqueous $HCO_2H$.[a]

| Entry | Catalyst (conditions) | TON | TOF [$h^{-1}$] | Conversion [%] | MeOH selectivity [%] |
|---|---|---|---|---|---|
| 1 | $[Cp^*Ir(Cl)_2]_2$ | 0 | 0 | 16(3) | 0 |
| 2 | $[Cp^*Ir(Cl)_2]_2$ + 2 bpy | 33(1) | 1.4(1) | 20(3) | 4(1) |
| 3 | **1** | 34(1) | 1.4(1) | 23(3) | 4(1) |
| 4 | **1** (pH 0.5) | 70(2) | 2.9(1) | 48(3) | 4(1) |
| 5 | **1** (12 M $HCO_2H$)[b] | 156(3) | 6.5(1) | 16(3) | 7(1) |
| 6 | **1** (12 M $HCO_2H$, 60 °C)[b] | 70(2) | 2.9(1) | 3(3) | 12(2) |
| 7 | **1** (3 M $HCO_2H$ in $D_2O$)[c] | 54(9) | 2.6(2) | 12(3) | 11(2) |

[a] Conditions (unless noted): formic acid (3 M, pH 1.4), Ir catalyst (0.25 mM, 0.0083 mol%, 83 ppm), 80 °C, 24 h. Average of at least two runs, with estimated uncertainty in parentheses. Full details available in the Supporting Information. [b] Ir catalyst (0.25 mM, 0.002 mol%, 20 ppm). [c] Values from NMR data.

the $^{13}C\{^1H\}$ NMR spectrum; this result is consistent with a competition between Equation (1) and Equation (4).[13,14]

Initial observations indicate that the formic acid disproportionation is homogeneously catalyzed.[15] Under the reaction conditions described here, no films or particles were deposited from the clear, yellow solutions. Addition of a mercury drop to a vigorously stirred reaction had no impact on the amount of MeOH produced. There was no induction period, with methanol forming steadily once the reaction temperature was reached (Figure S9 in the Supporting Information). Under other conditions, such as high concentrations of Ir catalyst (> 10 mM) or prolonged heating at 100 °C, reaction mixtures turned dark blue-purple ($\lambda_{max}$ = 730 nm, Figure S13); this color is characteristic of $IrO_2$ nanoparticles.[16] Notably, the blue solids that remained after removal of volatiles were essentially inactive towards methanol production, and instead acted as highly active catalysts for the dehydrogenation of $HCO_2H$ to $H_2$ and $CO_2$.[13]

Catalyst decomposition is further indicated by recycle experiments at 80 and 100 °C. At 80 °C, the catalyst was fairly robust and could be recycled four times with only approximately 30 % loss of activity for methanol production (Figure S14 in the Supporting Information). In contrast, at 100 °C, 95 % loss of methanol production activity was observed over four cycles (and the reaction mixture became turbid purple-blue). Together, these observations are consistent with homogeneous catalyst **1** acting as the only catalyst for methanol production, whereas both **1** and its decomposition products catalyze the transformation to $H_2$ and $CO_2$.

Intrigued by the unprecedented homogeneous formic acid disproportionation reaction, we set out to understand catalyst speciation and other salient features of the mechanism to improve the selectivity to methanol. $^1H$ NMR spectroscopic studies revealed that dissolving precatalyst **1** in 3 M $HCO_2H/D_2O$ causes rapid conversion at ambient temperature to a mixture of deuteride [Cp*Ir(bpy)D]OTf (**2**)[10] and another species in an approximately 9:1 ratio. Electrospray ionization mass spectrometry under the same conditions featured ion peaks for deuteride **2** (*m*/*z* 486.2, Figure S22 in the Supporting Information) and identified the minor species as the formate complex [Cp*Ir(bpy)($O_2CH$)]OTf (**3**, *m*/*z* 529.1). When catalytic reactions at 80 °C (concentration of **1**: 1 mM) were periodically cooled to room temperature and monitored by NMR spectroscopy, **2** and **3** remained unchanged for over 8 h before being gradually replaced by new, unidentified species over 48 h (Figure S5 in the Supporting Information). Methanol was observed as soon as 15 min after initiating heating, and its production increased steadily for over 8 h before it slowed until halting after 48 h, coincident with decomposition of the catalyst species **2** and **3** (Figure 1).

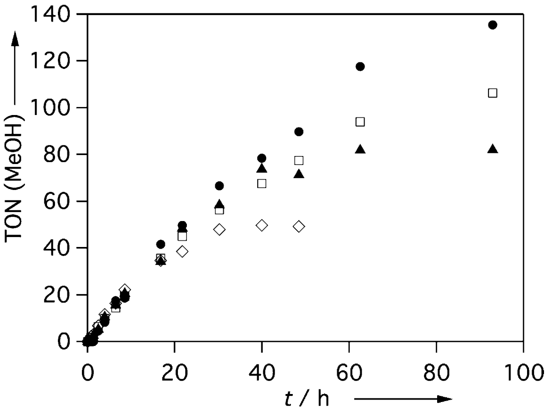


***Figure 1.*** TON for methanol production over time at various concentrations of **1**: 1 mM (◇), 0.5 mM (▲), 0.25 mM (□), and 0.125 mM (●). Conditions: 3 M $HCO_2H/D_2O$, 80 °C.

Methanol formation and formic acid consumption both exhibited a first-order dependence on the concentration of Ir catalyst at early reaction times (Figures S7 and S8 in the Supporting Information). Interestingly, catalyst deactivation was dependent on the concentration of Ir complex, with lower concentrations of **1** leading to longer catalyst lifetimes (Figure 1). Higher TON values were therefore achieved at lower catalyst loadings. At 0.0313 mM **1** (ca. 10 ppm), the TON was 200 after 120 h. The selectivity for methanol was significantly higher in $D_2O$ (Table 1, entry 7). Reaction (1) may be slowed relative to reaction (4) owing to a large kinetic isotope effect of Ir–H protonolysis.[17]

The reaction is strongly influenced by both pH value and $HCO_2H$ concentration. When 3 M $HCO_2H$ solutions (0.25 mM in **1**), with pH value adjusted with $HBF_4$ or NaOH, were heated to 80 °C for 24 h, the TON varied from only 14 turnovers at pH 2 to 70 or more below pH 1 (Figure 2 A). The change of the initial $HCO_2H$ concentration from 0.5–12 M (while maintaining pH 1.4) resulted in a similar, roughly 15-fold increase in TON, from 4 (0.5 M $HCO_2H$) to 62 (12 M $HCO_2H$; Figure 2 A). The selectivity for methanol was not significantly affected by the pH value (Figure 2 B), thus suggesting that reactions (1) and (4) respond similarly to changes of the pH value. However, selectivity for methanol was markedly improved upon increasing the initial $HCO_2H$ concentration (adjusted to pH 1.4): 0.5 M $HCO_2H$ solutions showed very poor selectivity for methanol (ca. 0.05 %) with selectivity of 10 % seen in 12 M $HCO_2H$ (Figure 2 B).

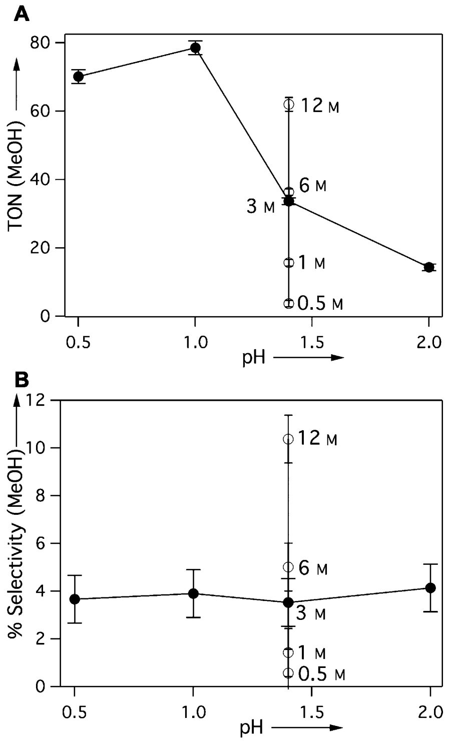
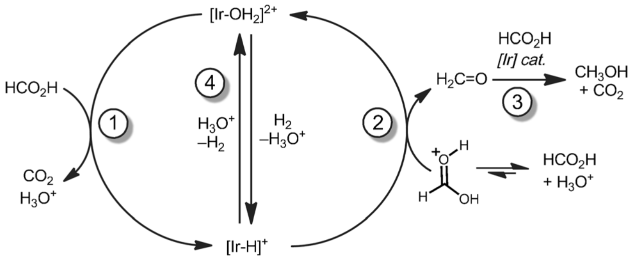


***Figure 2.*** A) TON for methanol production as a function of pH value (3 M $HCO_2H$, ●) and $HCO_2H$ concentration (○). B) Methanol selectivity as a function of pH value (3 M $HCO_2H$, ●) and $HCO_2H$ concentration (○). Conditions: **1** (0.25 mM), 80 °C, 24 h; solutions were adjusted to the appropriate pH value by using $HBF_4$ or NaOH.

We considered three possible intermediates for the multistep hydrogenation of $HCO_2H$: CO, $CO_2$, or formaldehyde. The intermediacy of CO or $CO_2$ was ruled out by inspection of the isotopic composition of the methanol produced from different reaction mixtures. Conversion of $HCO_2H$ in $D_2O$ solvent formed $CH_3OD$, $CH_2DOD$, and $CHD_2OD$ but no $CD_3OD$ (determined by $^1H$ and $^2H$ NMR spectroscopy, see Figure S6 in the Supporting Information). Conversely, only $CDH_2OH$ (no $CH_3OH$) was observed when $DCO_2D$ was the substrate in $H_2O$. These experiments indicate that the existing C–H (or C–D) bond of formic acid is preserved through the reduction; this finding is consistent only with the formaldehyde path. The improved performance at low pH value and high $HCO_2H$ concentration suggests that the species being hydrogenated may be protonated formic acid, $HC(OH)_2^+$. Similar acid-promoted pathways have been invoked for ketone reduction catalyzed by **1**.[10] The improved selectivity would also be consistent with the diminished water content in concentrated $HCO_2H$ solutions, as a higher ratio of $HC(OH)_2^+$ to $H_3O^+$ would disfavor reaction (1).

Scheme 1 lays out a plausible pathway for methanol formation supported by the available data. The Ir–H complex is initially formed (step 1), followed either by protonation (step 4, dehydrogenation)[14,18] or by reduction of protonated formic acid to generate formaldehyde (step 2) and ultimately methanol (step 3).



***Scheme 1.***

Formaldehyde was shown to be a competent potential intermediate in the reaction.[19] Heating a 3 M $HCO_2H/D_2O$ solution containing $^{13}C$-enriched paraformaldehyde and **1** to 60 °C resulted in rapid formation of $^{13}CH_3OD$ and $^{13}CH_2DOD$. This transfer hydrogenation of formaldehyde catalyzed by **1** was found to be quite efficient, with a TOF of approximately 240 $h^{-1}$ at 0.013 mol % catalyst loading, and reached completion at TON > 7000. Thus, the reduction of $H_2CO$ is much faster than the observed catalytic rates of $HCO_2H$ disproportionation (Table 1, entry 6 and Table S1, entry 1 in the Supporting Information), consistent with turnover-limiting reduction of protonated $HCO_2H$.

Scheme 1 implies that improved methanol selectivity should be accessible either by moving to more acidic formic acid solutions, or by suppressing the competing formate decomposition to $CO_2$ by addition of $H_2$ (Scheme 1, step 4). Under the standard $HCO_2H$ (3 M) conditions, addition of $H_2$ (30 atm) significantly improved methanol selectivity from 3.5 to 5.9 % (Figure S4 in the Supporting Information). The combination of low pH value, lower temperature, and high $HCO_2H$ concentration gave the best selectivity for methanol. Heating concentrated $HCO_2H$ (12 M; unadjusted pH 0.4) containing **1** (0.25 mM) at 80 °C for 24 h gave 156 turnovers of methanol at 7 % selectivity (Table 1, entry 5). When carried out at 60 °C, methanol selectivity improved to 12 % (Table 1, entry 6). The latter conditions represent, to our knowledge, the highest reported selectivity for $HCO_2H$ disproportionation.[2]

In summary, we report the first molecular catalyst for the disproportionation of formic acid to methanol, water, and carbon dioxide. The reaction is a novel transformation of formic acid, a difficult substrate for homogeneously catalyzed reduction. Formic acid joins other challenging substrates for which the homogeneous hydrogenation has been recently reported, including carboxylic acids,[20] esters[9] and amides.[21] The formic acid reaction employs a catalyst bearing simple ligands, avoids the use of organic solvents and $H_2$ gas, and features very low catalyst loadings. Future efforts will focus on improving the overall methanol yield by increasing catalyst selectivity and/or recycling the $H_2$ and $CO_2$ byproducts. Thus, one hundred years after Sabatier's initial findings, the presently described reaction [Eq. (4)] represents a new addition to the mature field of $C_1$ chemistry, one that may eventually play a role in the renewable production of methanol.

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