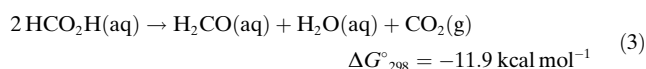
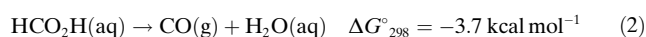


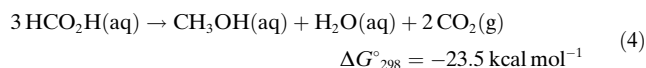
Catalytic Disproportionation of Formic Acid to Generate Methanol**

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The decomposition of formic acid almost always proceeds by dehydrogenation to produce H₂ and CO₂ [Eq. (1)] or by dehydration to produce CO and H₂O [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]



In 1911, Sabatier and Mailhe reported that some dimethoxymethane was produced upon thermolysis of HCO₂H over ThO₂, thereby providing indirect evidence for a methanol-producing pathway [Eq. (4)].^[3] There is great interest in the



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 C₁ feedstocks (natural gas (CH₄) and synthesis gas (CO/H₂) derived from various sources) are a key foundation of the chemical industry.^[4] HCO₂H is produced on large scale (ca. 700 000 tons/year) using these traditional fossil fuel feedstocks.^[5] Alternative, renewable routes to HCO₂H are being developed, with CO₂ or biomass as starting points.^[6,7] New transformations of formic acid are needed to ignite and promote development of renewable C₁ 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 CO₂ [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 HCO₂H acting as hydrogen source and substrate simultaneously. This fundamental C₁ reaction poses a number of interesting mechanistic questions and may have ramifications in the conversion of CO₂ 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 HCO₂H occurs simultaneously, we have shown that the catalyst activity and the selectivity to methanol can be tuned by changing reaction conditions.

Aqueous HCO₂H solutions containing [Cp*Ir(bpy)-(H₂O)](OTf)₂ (**1**, Cp* = pentamethylcyclopentadienyl, bpy = 2,2'-bipyridine)^[10] produced methanol upon heating. This result was surprising, because HCO₂H is commonly used as a source of H₂ in transfer hydrogenation reactions, and **1** is a well-known transfer hydrogenation catalyst, with no prior reports of methanol-producing side reactions.^[11] When HCO₂H (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 HCO₂H esterification) are the only products observed in solution, but roughly 23 % of the HCO₂H 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(H₂O)₃]₂SO₄ 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 HCO₂H was confirmed by the production of ¹³CH₃OH upon heating a solution of H¹³CO₂H in D₂O at 80 °C in the presence of **1** in a sealed NMR tube. In addition to the signal for ¹³CH₃OH, a prominent resonance for ¹³CO₂ (but not for ¹³CO) was observed in

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Table 1: Catalytic disproportionation of aqueous HCO₂H.^[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 ₂ H) ^[b]	156(3)	6.5(1)	16(3)	7(1)
6	1 (12 M HCO ₂ H, 60 °C) ^[b]	70(2)	2.9(1)	3(3)	12(2)
7	1 (3 M HCO ₂ H in D ₂ O) ^[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 ¹³C{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 ($\lambda_{\text{max}} = 730$ nm, Figure S13); this color is characteristic of IrO₂ 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 HCO₂H to H₂ and CO₂.^[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 H₂ and CO₂.

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 HCO₂H/D₂O 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)(O₂CH)]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).

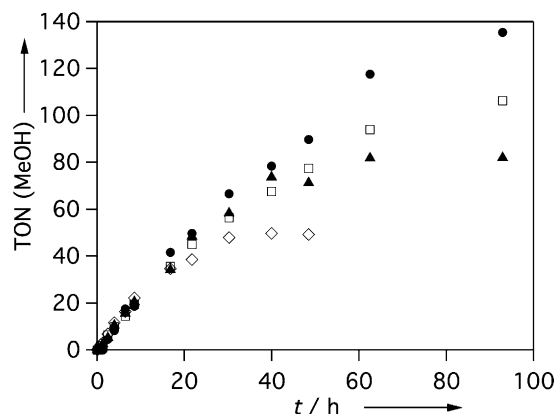


Figure 1. TON for methanol production over time at various concentrations of **1**: 1 mM (◇), 0.5 mM (▲), 0.25 mM (□), and 0.125 mM (●). Conditions: 3 M HCO₂H/D₂O, 80 °C.

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 D₂O (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 HCO₂H concentration. When 3 M HCO₂H solutions (0.25 mM in **1**), with pH value adjusted with HBF₄ 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 2A). The change of the initial HCO₂H 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 HCO₂H) to 62 (12 M HCO₂H; Figure 2A). The selectivity for methanol was not significantly affected by the pH value (Figure 2B), 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 HCO₂H concentration (adjusted to pH 1.4): 0.5 M HCO₂H solutions showed very poor selectivity for methanol (ca. 0.05 %) with selectivity of 10 % seen in 12 M HCO₂H (Figure 2B).

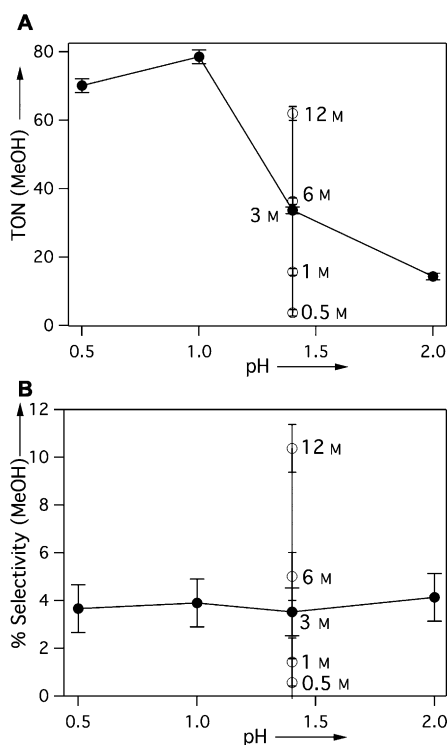
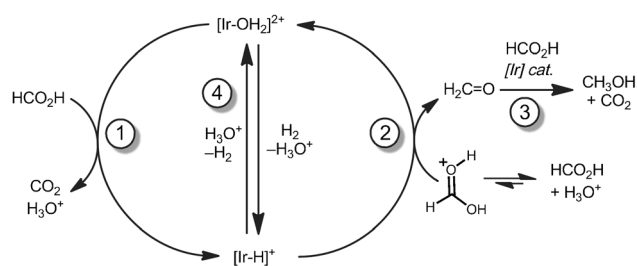


Figure 2. A) TON for methanol production as a function of pH value (3 M HCO₂H, ●) and HCO₂H concentration (○). B) Methanol selectivity as a function of pH value (3 M HCO₂H, ●) and HCO₂H concentration (○). Conditions: **1** (0.25 mM), 80 °C, 24 h; solutions were adjusted to the appropriate pH value by using HBF₄ or NaOH.

We considered three possible intermediates for the multi-step hydrogenation of HCO₂H: CO, CO₂, or formaldehyde. The intermediacy of CO or CO₂ was ruled out by inspection of the isotopic composition of the methanol produced from different reaction mixtures. Conversion of HCO₂H in D₂O solvent formed CH₃OD, CH₂DOD, and CHD₂OD but no CD₃OD (determined by ¹H and ²H NMR spectroscopy, see Figure S6 in the Supporting Information). Conversely, only CDH₂OH (no CH₃OH) was observed when DCO₂D was the substrate in H₂O. 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 HCO₂H 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 HCO₂H solutions, as a higher ratio of HC(OH)₂⁺ to H₃O⁺ 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).

Formaldehyde was shown to be a competent potential intermediate in the reaction.^[19] Heating a 3 M HCO₂H/D₂O



Scheme 1.

solution containing ¹³C-enriched paraformaldehyde and **1** to 60 °C resulted in rapid formation of ¹³CH₃OD and ¹³CH₂DOD. 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 H₂CO is much faster than the observed catalytic rates of HCO₂H disproportionation (Table 1, entry 6 and Table S1, entry 1 in the Supporting Information), consistent with turnover-limiting reduction of protonated HCO₂H.

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 CO₂ by addition of H₂ (Scheme 1, step 4). Under the standard HCO₂H (3 M) conditions, addition of H₂ (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 HCO₂H concentration gave the best selectivity for methanol. Heating concentrated HCO₂H (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 HCO₂H 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 H₂ 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 H₂ and CO₂ 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 C₁ chemistry, one that may eventually play a role in the renewable production of methanol.

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