A prolific catalyst for dehydrogenation of neat formic acid

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Formic acid is a promising energy carrier for on-demand hydrogen generation. Because the reverse reaction is also feasible, formic acid is a form of stored hydrogen. Here we present a robust, reusable iridium catalyst that enables hydrogen gas release from neat formic acid. This catalysis works under mild conditions in the presence of air, is highly selective and affords millions of turnovers. While many catalysts exist for both formic acid dehydrogenation and carbon dioxide reduction, solutions to date on hydrogen gas release rely on volatile components that reduce the weight content of stored hydrogen and/or introduce fuel cell poisons. These are avoided here. The catalyst utilizes an interesting chemical mechanism, which is described on the basis of kinetic and synthetic experiments.
Many strategies for the conversion of solar energy into chemical bonds involve electrocatalytic (or photocatalytic) cleavage of water to form hydrogen and oxygen. The reducing equivalent, H₂, is thus an energy carrier because it can be re-oxidized, either by combustion to give heat or catalytically in a fuel cell to give electricity. There is a disabling problem with large-scale utilization of hydrogen as a fuel, since it is a gas under ambient conditions, thus limiting its volume-energy density (0.013 MJ l⁻¹). As a result, physical methods-based hydrogen storage technologies (compression, cryogenic liquefaction, adsorption) involve low capacity, high costs or safety issues. Therefore, the discovery of highly weight-efficient strategies for on-demand hydrogen release from hydrogen-rich liquids has value. Formic acid (HCO₂H, FA, 7.5 MJ l⁻¹) is a hydrogen carrier, owing to its ability to release hydrogen under mild conditions with only CO₂ as a by-product, which can then be recycled, in principle, to give a carbon-neutral fuel cycle.

To date, many efficient heterogeneous and homogeneous catalysts for FA dehydrogenation have been developed. Heterogeneous catalysts have advantages of separability and reusability, while homogeneous catalysts are generally more efficient. The best turnover numbers (TONs) achieved in homogeneous catalysis are (1) > 1 M, by a catalyst system composed of [RuCl₂(benzene)]₂, the ligand diphenylphosphinoethane and a FA/Et₃N adduct as substrate developed by Bodden et al. and (2) 983,642, by a system composed of an iron pincer complex and LiBF₄ developed by Bielinski et al. The highest turnover frequency achieved is 728,000 h⁻¹ by an iridium catalyst developed by Hull et al. Supplementary Table 1 has a more complete comparison of homogeneous catalysts for this reaction. In heterogeneous catalysis, the highest TOF achieved is 7,256 h⁻¹, by palladium nanoparticles immobilized on carbon nanospheres developed by Zhu et al. Also, homogeneous catalysts generally are more selective, producing less carbon monoxide, a common byproduct of FA dehydrogenation. This is essential, because CO is a fuel cell catalyst poison. Still, no known system is stable and reactive through multiple uses, air and water tolerant, selective against CO formation, and functions in neat FA liquid. Each of these is critical to achieving a usable hydrogen generation system based on FA. Herein we report an iridium-based catalytic system that meets all of these criteria.

**Results**

**Reactivity in FA dehydrogenation.** Complex 1, which is easily prepared from known materials (Fig. 1), decomposes FA (500 µl, 12.7 mmol) with NaO₂CH co-catalyst (5 mol%) at 50 p.p.m. loading and 90 °C, resulting in the production of 386 ml of gas (62% conversion; TON = 12,530) after 13 h. The mass balance of FA condenses as a liquid in the reactor out of reach of the catalyst (vide infra). The rate of the reaction is constant through ca. 20% of conversion before it accelerates as FA disappears.

![Synthesis and structure of catalyst precursor cation 1.](image)

Figure 1 | Synthesis and structure of catalyst precursor cation 1. Ellipsoids are drawn at the 50% probability level.
Mechanistic studies. Equally remarkable as the reactivity of this new catalytic system is the unique, two-metal mechanism through which it operates. We used three approaches to gain insight into this mechanism: stoichiometric model reactions, reaction kinetics and isotope labelling studies. Figures 3 and 4 present a sketch of a possible mechanism for our system.

Species 1 is a catalyst precursor from which an active catalyst is generated. To determine the nature of this active species, we conducted stoichiometric reactions of 1 (Fig. 3). Species 1 loses its cyclooctadiene ligand as cyclooctene in a solution of either H₂ or buffered FA and dimerizes to form 2. Complex 2 has analogy to \( [(P-N)\text{Ir}(CH_2Cl_2)(H)](\mu^2-H_2)]^2+ \) characterized by Paltauf\(^2\) (P-N = SimplePHOX). In buffered FA conditions, 2 is then converted to a formate-bridged species 3a. While this species is observable by NMR, it is not amenable to isolation in our hands. By contrast, its acetate homologue (3b) yielded to crystallization, which enabled determination of its structure (Fig. 3). Species 3a is relevant in catalysis: we observe it by NMR as the minor form of the working catalyst. We see a second, major resting species by NMR, which has a spectrum consistent with structure 4, featuring three differentiated metal hydride groups. The NMR spectra of intermediates are shown in Supplementary Figs 7–11, which are further analysed in Supplementary Discussion.

Kinetic isotope effect data indicate that both the C–H and O–H groups of FA are involved in (or before) the rate-determining transition state. Table 2 summarizes the reaction rates for four selectively labelled FA isotopologues. The combined isotope effect (\( k_{\text{CHOH}}/k_{\text{CDOD}} = 6.5(2) \)) is comparable to the product of the average separate C–H and O–H isotope effects (6.5(4)). This is consistent with a mechanism by which bonds to proton and hydride are transformed in a single kinetically relevant step. Hydrogen loss from 4 involves protonation of an iridium hydride (which comes from FA’s C–H group) by a FA group. Further, we observe that in a sample of FA–(O)–\( \delta_1 \) NMR reveals H-D gas as the catalytic product (Supplementary Fig. 12 and Supplementary Discussion). A small portion of H₂ is formed in the process of catalyst initiation, but none is detected during catalysis. This indicates that there is separation of proton and hydride groups throughout the mechanism and refutes the possibility of an iridium dihydride species in the mechanism, because such a species would be likely to enable proton/hydride scrambling via reversible reductive elimination of dihydrogen. This observation also shows that the reaction is irreversible at ambient pressure, so we assign the isotope effects as kinetic.

Eyring analysis reveals activation parameters of \( \Delta H_\text{T} = +29.0(3) \text{ kcal mol}^{-1} \) and \( \Delta S_\text{T} = +16(1) \text{ eu} \) \( \Delta H_\text{T} = 121(12) \text{ kJ mol}^{-1} \); \( \Delta S_\text{T} = +67(4) \text{ J mol}^{-1} \text{ K}^{-1} \) (Supplementary Fig. 13). This strongly favourable entropy of activation is consistent with the release of at least one gaseous product in the rate-determining transition state. We expect that this is H₂ release in the conversion of 4 to 6 because of the strong isotope effects.

The observed rate law for FA dehydrogenation has rate ~ \( [\text{Ir}]^{1}\text{[base]}^{0.2}[\text{FA}]^{-1} \), which is based on the slopes of double logarithmic plots (Supplementary Figs 14–18) recorded both in neat FA and dilute in tetraglyme solution (Table 3). This rate law requires that two sites of the catalyst are activated by a...
single equivalent of formate, thus causing half-order dependence on base. We propose a possible catalytic cycle in Fig. 4. After the first equivalent of H₂ is lost in the conversion of 4 to 6, a second equivalent forms from the iridium hydride on the complementary metal centre. We propose that the latter is more rapid than the former, and that the single equivalent of formate enables both by opening a formate bridge in dimer 3a. The rate law also has [Ir] first order, which indicates a dimeric iridium species that does not dissociate once formed. Inverse order in [FA] implies inhibition, but the origins of this inhibition are unclear. Acid is known to favour closure of carboxylate bridges in ruthenium species similar to ours⁴⁴, which enables several opportunities for FA inhibition in our mechanism. Moreover, FA has potential roles in the conversion of 4 and as solvent. We are currently studying this complex system of interactions.

Discussion

We show here a new catalytic system for the repeated conversion of FA to CO₂ and hydrogen. This has translation potential because it is the first known homogeneous system, to the best of our knowledge, to operate in neat FA, thus enabling far greater weight content of H₂ release than any other known catalyst for FA dehydrogenation. Moreover, it is the highest turnover system, because, in part, it can be re-used directly with FA substrate that is not rigorously purified or dried. We further propose a mechanism to account for kinetic, thermochemical, stoichiometric and labelling data that we have collected for the catalytic reaction. More detailed mechanistic studies, including computational investigation and ligand variation, are currently under way.

Methods

Synthesis of complex 1. General experimental information and characterization details can be found in the Supplementary Methods. In the drybox under nitrogen, 2-((di-t-butylphosphino)methyl)pyridine⁴⁵ (105.3 mg, 0.44 mmol) was dissolved in a dry vial in 5 ml of dry dichloromethane. In another vial containing a Teflon stir bar, chloro(1,5-cyclooctadiene)iridium(I) dimer (149.0 mg, 0.22 mmol) and sodium...
Triflate (130 mg, 0.75 mmol) were suspended in 10 ml of dry dichloromethane. The suspension was stirred vigorously and then the phosphinepyridine solution was added slowly dropwise. The phosphinepyridine vial was rinsed with 5 ml of dichloromethane and the iridium precatalyst are dissolved in either FA or tetraglyme solvent. The reaction flask is then heated in an oil bath to 86 °C. Gas production is observed. The reaction mixture is heated for ca. 15 min to allow the temperature to equilibrate. The volume of gas produced over time is recorded. Some portion of the liquid FA vapours and re-condenses in the head space of the flask and gas evacuation tube, which prevents complete conversion.

Dehydrogenation procedures. The dehydrogenation of FA can generally be performed by preparing a stock solution of the catalysts. In the drybox, formate and the base are dissolved in dry dichloromethane. Tetrahydrofuran (130 mg, 0.75 mmol) was dissolved in 0.6 ml dichloromethane–neat and the vial was left in a desiccator for 1 week. A crystal suitable for X-ray diffraction was isolated from the vial (Supplementary Data 2). Although the crystal of 3b is stable for days, the pure crystal of 3b re-dissolved in dichloromethane–d$_2$ appears to be in equilibrium with 2 and potentially any other form of the iridium complex. NMR spectra of complex 3b are shown in Supplementary Figs 24–27.

Supplementary Information for full details.
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Author contributions
J.J.A.C., Z.L. and T.J.W. conceived and designed the experiments, analysed the data, and wrote the paper. J.J.A.C., Z.L., E.A.K. and N.J.T. executed the experiments.

Additional information
Accession codes: The X-ray crystallographic coordinates for the structures reported in this Article have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC #1415049 (1) and #1415050 (3b).

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