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**Highly efficient dehydrogenation of formic acid in aqueous solution
catalysed by an easily available water-soluble iridium(III) dihydride.**

G. Papp,^{a*}G. Ölveti,^b H. Horváth,^a Á. Kathó^b and F. Joó^{a,b*}

^a Hungarian Academy of Sciences, Research Group of Homogeneous Catalysis and Reaction Mechanisms, P.O.Box 400, Debrecen, H-4002 Hungary

^bUniversity of Debrecen, Department of Physical Chemistry, P.O.Box 400, Debrecen, H-4002 Hungary

Corresponding authors:

Gábor Papp, e-mail: papp.gabor@science.unideb.hu

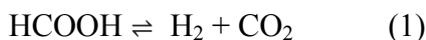
Ferenc Joó, e-mail: joo.ferenc@science.unideb.hu

Abstract

The new water-soluble *cis-mer*-[IrH₂Cl(*mtp*ppms)₃] (*mtp*ppms = monosulfonated triphenylphosphine) was employed as catalyst for selective decomposition of formic acid to H₂ + CO₂ in aqueous solutions at T=30-100°C. The easily synthesized compound showed high catalytic activity (up to TOF=298 000 h⁻¹) and could be reused several times with no loss of activity (total TON=67 650). A sharp maximum in the reaction rate was observed at pH=3.75; its coincidence with the pK_a of formic acid shows that both H⁺ or HCOOH and HCOO⁻ play important role in the reaction mechanism.

Introduction

Formic acid (FA) is regarded as a potential hydrogen storage material since its selective dehydrogenation yields a 1:1 mixture of H₂ and CO₂ (eq. 1). Hydrogen can be used for generation of electricity in fuel cells where it combines with O₂ and produces water as the sole product with no harm to the environment. Ideally, FA can be produced by hydrogenation of CO₂ using hydrogen from renewable sources such as e.g. from water via photochemical water splitting, and this allows carbon neutral utilization of renewable H₂.[§] However, hydrogen generation should be highly selective in order to prevent formation of CO (eq. 2) and to avoid poisoning the fuel cell electrodes.



Selective dehydrogenation of formic acid has been in the focus of intensive research¹ and was achieved by both heterogeneous² and homogeneous catalysis. High catalytic activities were observed with soluble complexes of ruthenium,³ rhodium⁴ and iridium⁵ and many of these catalysts proved active for long periods of time leading to extremely high turnover numbers (TON=total number of catalytic cycles for one molecule of catalyst). Catalysts based on abundant and cheap metals such as Fe⁶ and Ni⁷ have also been discovered. For practical applications it is important to avoid the use of any additives such as (volatile) amines or organic co-solvents.

Iridium complexes play a prominent role in catalytic dehydrogenation of FA.⁵ Himeda and coworkers investigated a family of Ir-complexes with various hydroxybipyridine and hydroxybipyrimidine⁸ as well as with variousazole and imidazoline⁹ ligands. For example, with [Cp*Ir(H₂O)L]²⁺ (Cp*=pentamethylcyclopentadienyl, L=6-(4,5-Dihydro-1H-imidazol-2-yl)pyrimidine-2,4-diol) the rate of H₂ generation (TOF=TON/reaction time) was 322 000 h⁻¹,¹⁰ while with the [Cp*Ir(4DHBP)(H₂O)][SO₄] catalyst (4DHBP=4,4'-dihydroxy-

2,2'-bipyridine) the pressure reached as high as 123 MPa.⁸ Another important achievement was made by Li and coworkers, who reported unprecedentedly active catalysts based on Ir(I) and *N,N'*-diimine ligands. For example, the [Cp*IrCl(2,2'-bi-1,4,5,6-tetrahydropyrimidine)]Cl complex showed an initial TOF of 487 500 h⁻¹ at 90°C (the highest presently known) and a TON of 2 400 000 (at 80°C).¹¹ Both the Himeda and Li groups found a maximum in FA dehydrogenation rate at about pH 3.7 corresponding to the pK_a of HCOOH in water.¹⁰⁻¹¹ Nozaki et al reported the use of an Ir-PNP complex as an efficient catalyst for dehydrogenation of FA in the presence of base.¹²

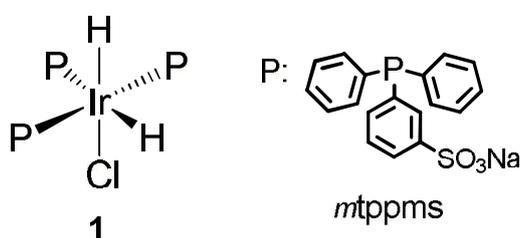
Homogeneous catalysis of dehydrogenation of FA by several Pt(II), Ru(II), Rh(I), Ir(I), and Ir(III) complexes in refluxing acetic acid was first reported by Coffey in 1967.¹³ The most active catalysts were [IrH₃(PPh₃)₃] (TOF=8890 h⁻¹, TON>11 000) and [IrH₂Cl(PPh₃)₃] (TOF=1187 h⁻¹). Despite these findings, no other studies of tertiary monophosphine complexes of Ir(I) or Ir(III) have been reported for FA dehydrogenation.

In the course of our research on aqueous organometallic catalysis¹⁴ and on chemical hydrogen storage¹⁵ we have discovered that the easily synthesized water-soluble *cis-mer*-[IrH₂Cl(*mtp*ppms)₃] (**1**) (*mtp*ppms=monosulfonated triphenylphosphine Na-salt or 3-diphenylphosphinobenzenesulfonic acid Na-salt) catalyzed the dehydrogenation of aqueous FA with exceedingly high activity and selectivity in the 30-100°C temperature range. The catalyst is stable for prolonged use and pressures up to 140 bar (H₂+CO₂) can be produced in short reaction times. Details are described below.

Results and discussion

cis-mer-[IrH₂Cl(*mtp*ppms)₃] (**1**) was obtained as a pale yellow solid in the reaction of IrCl₃×3H₂O and excess *mtp*ppms in refluxing ethanol. The complex was characterized by elemental analysis and its structure was assigned on the basis of ¹H-, ¹³C-, and ³¹P-NMR, ESI-

MS and IR spectroscopies. (For details see ESI.) Specifically, $^1\text{H-NMR}$ showed two triplets of doublets in the hydride region at $\delta = -27.71$ ppm and $\delta = -11.10$ ppm, while the ^{31}P NMR spectrum showed a doublet at $\delta = 8.21$ ppm and a triplet at $\delta = -0.76$ ppm with the appropriate coupling constants (Fig. S1-S3). Terminal hydride stretching frequencies in the IR spectrum were observed at 2249 and 2145 cm^{-1} (Fig. S4). These features are in accord with the suggested *cis-mer* configuration. A related complex, $[\text{IrH}_2\text{Cl}(\text{PPh}_3)_3]$ (water-insoluble) was first synthesized by Vaska,¹⁶ and the effect of the *mtppps* vs PPh_3 ligand is shown by the $\nu(\text{Ir-H})$ values which are larger by 34 and 35 cm^{-1} , respectively, than those reported for $[\text{IrH}_2\text{Cl}(\text{PPh}_3)_3]$. **1** is freely soluble in methanol, water and in aqueous FA solutions, poorly soluble in ethanol and insoluble in apolar organic solvents.



Scheme 1. *cis-mer*- $[\text{IrH}_2\text{Cl}(\text{mtppps})_3]$ (**1**)

cis-mer- $[\text{IrH}_2\text{Cl}(\text{mtppps})_3]$ (**1**) catalysed the dehydrogenation of aqueous FA selectively to $\text{H}_2 + \text{CO}_2 = 1:1$ with high activity (the reaction mixtures contained 0.098-0.500 M HCOONa). Gas chromatographic measurements showed the CO content of the resulting gas < 10 ppm allowing the use of the produced H_2 in fuel cells. Gas evolution could be conveniently followed in the 30-70°C temperature range by using a thermostated gas burette. The reactions started with no induction period and proceeded with a steady rate (Fig. 1) until 100% decomposition of FA (established by HPLC); the final solutions contained only the unchanged HCOONa . Initial turnover frequencies of 437-17813 h^{-1} were determined in this temperature range (Fig. S5) and an Arrhenius-plot of these data yielded an apparent activation

energy, $E_a=79.6$ kJ/mol (Fig. S6), in good agreement with the 72.1 kJ/mol determined by Li et al¹¹ for a tetrahydropyrimidine-ligated Ir catalyst which points to a similar rate determining step in the reaction mechanism, probably the C-H bond rupture in FA.

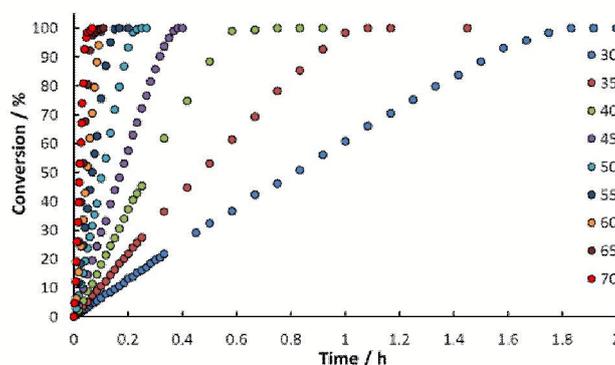


Figure 1. Catalytic dehydrogenation of formic acid catalysed by *cis-mer*-[IrH₂Cl(*mtppps*)₃] (1) at various temperatures. $n_{\text{Ir}} = 4.9 \times 10^{-6}$ mol; $n_{\text{HCOOH}} = 3.58 \times 10^{-3}$ mol; $n_{\text{HCOONa}} = 4.9 \times 10^{-4}$ mol; $V = 5.0$ mL.

The rate of FA dehydrogenation varied linearly with catalyst concentration (Fig. S7) and showed saturation with increasing FA concentration (Fig. S8). Addition of *mtppps* decreased the reaction rate exponentially (Fig. S9). Variation of the pH of the reaction mixture in the 2.0-8.5 range led to a sharp maximum of the rate at pH=3.75 (Fig. 2). Similar pH effect was observed by Himeda and Li, too.¹⁰⁻¹¹ Figure 2 also shows the molar distribution of HCOOH and HCOO⁻ as a function of pH (calculated with $pK_a=3.797$ at 60°C¹⁷). At the rate maximum HCOOH and HCOO⁻ are present in equal concentrations showing that both formate anion and undissociated HCOOH and/or H⁺ play important role in the reaction.

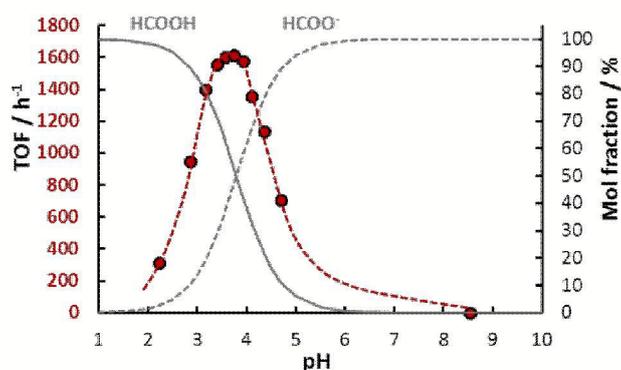


Figure 2. Effect of pH on FA dehydrogenation catalysed by **1** (red dots; $n_{\text{Ir}} = 9.9 \times 10^{-6}$ mol; $n_{\text{HCOOH} + \text{HCOONa}} = 1.00 \times 10^{-3}$ mol; $V = 5.0$ mL; $T = 60^\circ\text{C}$), and the calculated molar distribution of HCOOH (full line) and HCOO⁻ (broken line), respectively.

Catalysis of FA dehydrogenation by **1** was also studied in a 100 mL Parr-reactor by following the resulting increase in pressure. Time course of FA dehydrogenation is shown on Fig S10. After 12 min, HPLC determination showed full conversion of FA to H₂ and CO₂ resulting in 70.9 bar total pressure in the reactor, meaning that the reaction proceeded with a TOF = 298 000 h⁻¹. Accordingly, *cis-mer*-[IrH₂Cl(*m*tppms)₃] is one of the most active catalysts for FA dehydrogenation, together with the catalysts reported by Himeda et al.¹⁰ (TOF = 332 000 h⁻¹) and by Li et al.¹¹ (TOF = 487 500 h⁻¹). The final pressures were proportional to the HCOOH concentration and a pressure of 140 bar was observed after 100% conversion of 0.25 mol FA (Fig. S11). However, with increasing [HCOOH] (but constant [HCOONa]) the reaction rate decreased considerably (Fig. S12), accompanied by a (calculated) pH changed from 2.9 to 2.4. In agreement with the data of Figure 2, this pH change accounts fully for the observed decrease of the reaction rate (Fig. S13) and, consequently, no self-inhibition by HCOOH should be considered.

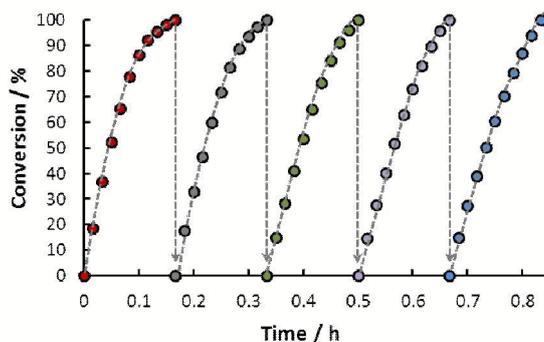


Figure 3. Repeated use of the same solution of **1** for catalysis of FA dehydrogenation ($n_{\text{Ir}} = 9.8 \times 10^{-6}$ mol; $n_{\text{HCOONa}} = 5 \times 10^{-2}$ mol; $n_{\text{HCOOH}} = 1.33 \times 10^{-1}$ mol/cycle; $V = 20.0$ mL; $T = 100^\circ\text{C}$).

Repeated use of the catalyst is demonstrated by Figure 3. In these experiments a new batch of FA was added to the reaction mixture after the previous one was dehydrogenated with full conversion. At 100°C , 80-81 bar pressure was produced in each cycle; these conditions did not lead to decomposition of the catalyst as shown by the constant initial TOFs ($121\,000 \pm 6100\text{ h}^{-1}$) in the five subsequent cycles. Furthermore, in a closed system 8.81×10^{-8} mol **1** dehydrogenated 5.94×10^{-2} mol FA (total TON 674 000) in 40 h at 115°C , demonstrating the long-term stability of *cis-mer*- $[\text{IrH}_2\text{Cl}(\text{mtpms})_3]$ (see ESI for details).

Conclusion

We reported here that *cis-mer*- $[\text{IrH}_2\text{Cl}(\text{mtpms})_3]$ (**1**) is an exceedingly active catalyst ($\text{TOF} = 298\,000\text{ h}^{-1}$ at 100°C) for selective dehydrogenation of aqueous formic acid to H_2 and CO_2 in the presence of small amounts of HCOONa . The highly water-soluble complex is easily synthesized from $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ and monosulfonated triphenylphosphine. Final pressures up to 140 bar were achieved in short reaction times and the high catalyst activity did not change in five consecutive cycles. These findings encourage further studies on the use of **1** and related complexes in chemical hydrogen storage.

Acknowledgement

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Notes and references

§Distinction should be made between the use of formic acid as a replenishable fuel (H_2 source) and as a hydrogen storage material in a hydrogen battery. While in both devices H_2 is generated by dehydrogenation of FA, a hydrogen battery also requires hydrogenation of CO_2 back to formic acid in the same device. Presently available methods¹⁸ for additive-free hydrogenation of CO_2 to $HCOOH$ are either slow, and/or yield low $HCOOH$ concentrations and/or require organic solvents. Therefore the known hydrogen batteries use aqueous solutions of formate salts^{15,19} (instead of $HCOOH$) or other hydrogen storage materials.²⁰

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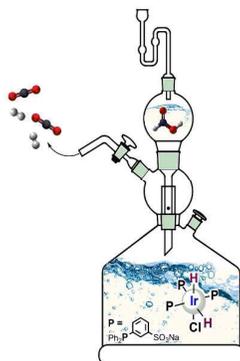
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Highly efficient dehydrogenation of formic acid in aqueous solution catalysed by an easily available water-soluble iridium(III) dihydride

Gábor Papp, Gábor Ölveti, Henrietta Horváth, Ágnes Kathó, and Ferenc Joó



Water-soluble *cis-mer*-[IrH₂Cl(*mtp*ppms)₃] selectively dehydrogenated formic acid with TOF 298000 h⁻¹, final pressure of 140 bar, and a TON_{max} of 674 000.