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ARTICLE TYPE

Catalytic hydrogen production from paraformaldehyde and water with an organoiridium complex†

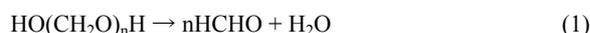
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Paraformaldehyde decomposed using an organoiridium complex (**1**, $[\text{Ir}^{\text{III}}(\text{Cp}^*)(4\text{-}(1\text{H-pyrazol-1-yl-}\kappa\text{N}^2)\text{benzoic acid-}\kappa\text{C}^3)(\text{H}_2\text{O})_2]\text{SO}_4$) as a catalyst in water to produce H_2 and CO_2 in a 2:1 molar ratio at room temperature. The catalytic cycle is composed of the reduction of **1** by paraformaldehyde under basic conditions to produce formic acid and the hydride complex, which reacts with proton to produce H_2 . Formic acid further decomposed to H_2 and CO_2 with **1**.

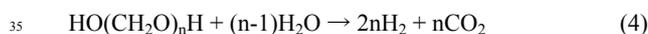
Paraformaldehyde is the polymerisation product of formaldehyde with a molecular formula of $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ ($n = 8 - 100$).¹ Paraformaldehyde forms slowly in aqueous formaldehyde solutions as a white precipitate. Formalin actually contains very little monomeric formaldehyde; most of which forms short chains of polyformaldehyde.² Paraformaldehyde has been reported to be synthesised by electrocatalytic reduction of CO_2 and water.³⁻⁵ Paraformaldehyde can be depolymerised to formaldehyde [eqn (1)] that is subsequently hydrated to form a geminal diol, i.e., methanediol [eqn (2)] in water under basic conditions.^{6,7} Formic



acid, which is the two-electron oxidation product of formaldehyde, has been regarded as a liquid H_2 carrier because of efficient generation of H_2 from HCOOH [eqn (3)] with an



appropriate catalyst under normal pressure at ambient temperature.⁸⁻¹⁴ If H_2 can be generated from paraformaldehyde (eqn (4)), paraformaldehyde would be regarded as a convenient



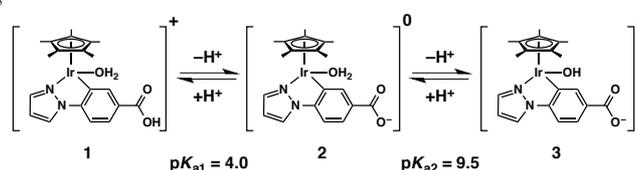
solid H_2 carrier, which has a higher energy density (6.7%) than HCOOH (4.4%). Prechtl and coworkers recently reported selective hydrogen production from paraformaldehyde and formaldehyde using a Ru catalyst ($[(\text{Ru}(p\text{-cymene}))_2(\mu\text{-Cl})_2\text{Cl}_2]$).¹⁵ However, a relatively high temperature (95°C) was required for the efficient hydrogen production from paraformaldehyde.¹⁵ To the best of our knowledge, this is the only example of hydrogen production from paraformaldehyde.

We report herein the catalytic decomposition of paraformaldehyde to H_2 and CO_2 (eqn (4)) with a water-soluble

iridium aqua complex $[\text{Ir}^{\text{III}}(\text{Cp}^*)(4\text{-}(1\text{H-pyrazol-1-yl-}\kappa\text{N}^2)\text{benzoic acid-}\kappa\text{C}^3)(\text{H}_2\text{O})_2]\text{SO}_4$ (**1**)₂SO₄ at room temperature.

Synthesis and characterisation of **1** were performed as reported previously (see ESI).^{14,16} The carboxylic acid form **1** is deprotonated to give the carboxylate form **2** with $\text{p}K_{\text{a}} = 4.0$ and the aqua ligand of **2** is further deprotonated to the hydroxo complex (**3**) as shown in Scheme 1.^{14,16} Under N_2 atmosphere at pH 11 in the presence of a catalytic amount of **2**, paraformaldehyde decomposed to produce H_2 and CO_2 with 2:1 molar ratio as shown in Fig. 1 as expected from eqn (4). The turnover number (TON) based on the Ir catalyst ($5.0 \mu\text{M}$) at 14 h was 21 at 298 K. When the catalyst concentration was decreased to be one-fifth, i.e., $1.0 \mu\text{M}$, TON remains almost unchanged (24) at 298 K as shown in Fig. S1a in ESI. The TON increased to be 51 at 333 K as shown in Fig. S1b. The detailed experimental procedure is described in the Experimental section in ESI.

It should be noted that **1** is converted to **3** at pH 11 (Scheme 1). The rate of production of H_2 decreases with decreasing pH as shown in Fig. 2. No production of H_2 from paraformaldehyde



Scheme 1 Deprotonation equilibrium of **1** to **2** and **3**.

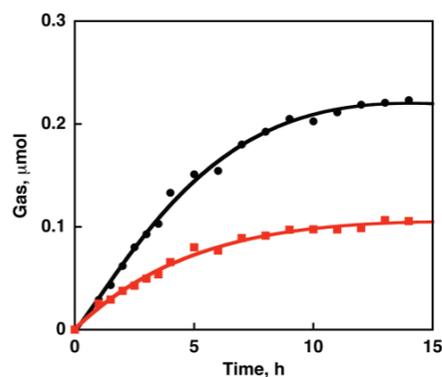


Fig. 1 Time course of catalytic production of H_2 (black line) and CO_2 (red line) from paraformaldehyde (2.0 mg, $66.7 \mu\text{mol}$) with **3** ($5.0 \mu\text{M}$) in an aqueous solution (1.0 mL at pH 11) at 298 K.

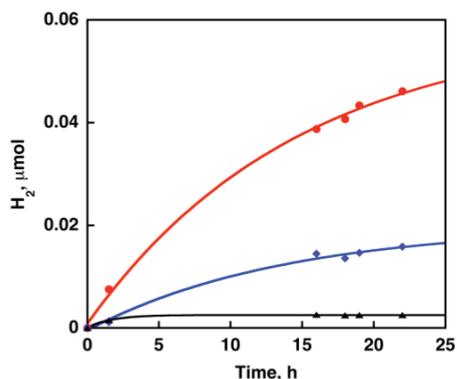


Fig. 2 pH Dependence of catalytic production of H_2 from paraformaldehyde (2.0 mg, 66.7 μmol) with **2** or **3** (5.0 μM) in an aqueous solution (1.0 mL) at pH 6.0 (black line) and 8.0 (blue line) and 10 (red line) at 298 K.

with **3** was observed at pH 3. Thus, the hydroxo form **3** rather than **1** or **2** is the actual catalyst for the production of H_2 and CO_2 . This is confirmed by no spectral change of **2** with paraformaldehyde at pH 7 (Fig. 3a).¹⁷

At pH 11, however, **3** reacted with paraformaldehyde to produce the hydride complex ($\lambda_{\text{max}} = 340 \text{ nm}$)¹⁶ as shown in Fig. 3b.

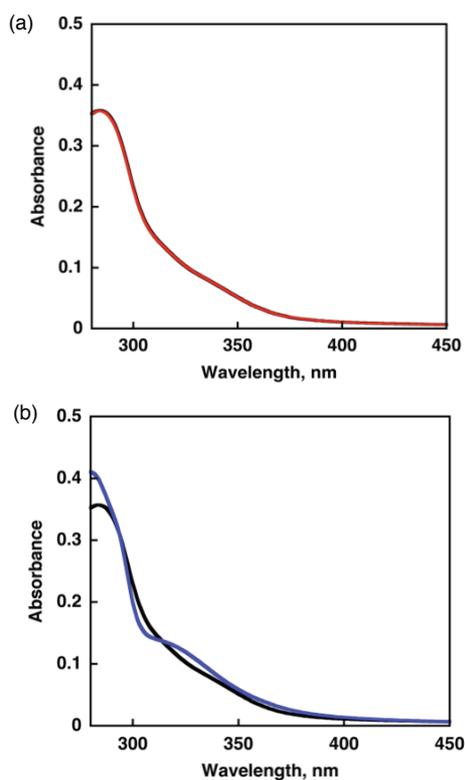
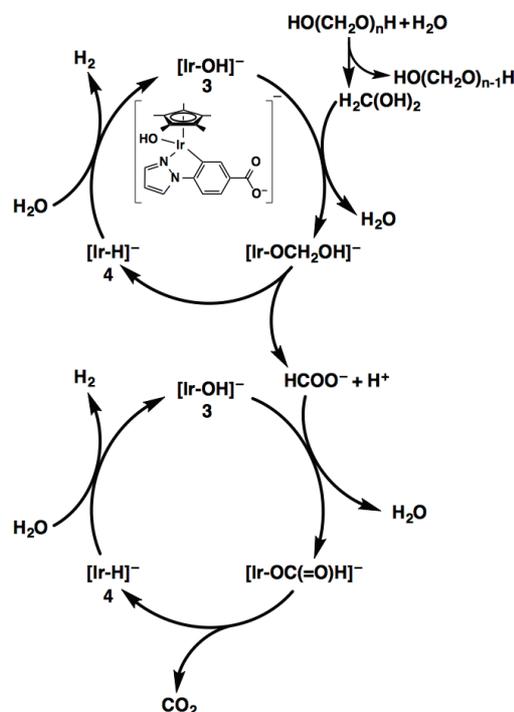


Fig. 3 UV-visible absorption spectra of (a) an aqueous solution of **2** (25 μM , 2.0 mL, pH 7) before (black line) and after (red line) addition of paraformaldehyde (31 μM) and (b) the resulting solution before (black line) and after (blue line) addition of an aliquot of conc. NaOH solution (1 M) for the adjustment of pH at 11.

It was confirmed that no hydrogen evolution was observed from methanol with **1** at pH 3-11 in water.^{16b} Thus, hydrogen evolution occurs from either paraformaldehyde or its monomerised as well as hydrated equivalent, methanediol rather than via disproportionation of formaldehyde to methanol and formic acid.

The catalytic cycle is shown in Scheme 2. At pH 11, **1** is converted to the hydroxo complex **3**, which reacts with paraformaldehyde $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ to produce the methanediol adduct $[\text{Ir}-\text{OCH}_2\text{OH}]^-$ and $\text{HO}(\text{CH}_2\text{O})_{n-1}\text{H}$. The β -hydrogen elimination from $[\text{Ir}-\text{OCH}_2\text{OH}]^-$ occurs to produce the hydride complex (**4**) and formic acid. The hydride complex (**4**) reacts with H_2O to produce H_2 , accompanied by regeneration of **3** (upper-side catalytic cycle in Scheme 2). The hydroxo complex **3** also reacts with formate to produce the hydride complex (**4**) and CO_2 by β -hydrogen elimination. The characteristic visible absorption bands at $\lambda_{\text{max}} = 420 \text{ nm}$ appeared due to formation of a formate complex^{16b} in the reaction between **3** and paraformaldehyde at pH 7 as shown in Fig. S3 in ESI. The hydride complex also reacts with H_2O to produce H_2 , accompanied by regeneration of **3** (lower-side catalytic cycle in Scheme 2).¹⁴ The formation of the methanediol adduct, the formate complex as well as hydride species in Scheme 2 has been supported by $^1\text{H-NMR}$ and ESI-MS analyses as shown in Fig. S4 and S5, respectively. The IR bands as well as NMR peaks of the hydride species in the steady state of the catalytic reaction would be too weak to be assigned well. Thus, the overall stoichiometry is given by eqn (4), where H_2 and CO_2 are produced with 2:1 molar ratio as observed in Fig. 1.¹⁸

When formalin without a stabilizer, i.e., methanol was used instead of paraformaldehyde, HCHO that exists as a form of



Scheme 2 Catalytic cycles for decomposition of paraformaldehyde to H_2 and formate that is further decomposed to H_2 and CO_2 with **3**.

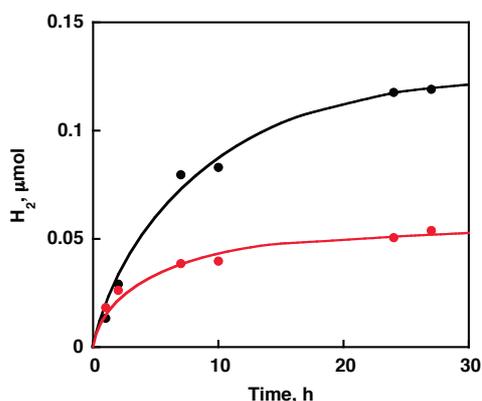
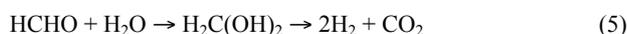


Fig. 4 Time courses of catalytic production of H₂ (black line) and CO₂ (red line) from formalin (66.7 μmol) with **3** (5.0 μM) in an aqueous solution (1.0 mL at pH 11) at 298 K.

methanediol [eqn (2)] in water under basic conditions, also decomposed to produce H₂ and CO₂ with 2:1 molar ratio [eqn (5)]



as shown in Fig. 4. However, the rate of formation of H₂ and CO₂ from formalin (Fig. 4) is much slower as compared with that from paraformaldehyde (Fig. 1). The formation of the methanediol adduct from paraformaldehyde may be faster than that from formalin because of partial polymerization of HCHO in formalin without stabilizer. When formaldehyde was replaced by propanal, butanal or 2-methylpropanal (4.2 M) at pH 11.8, no reaction occurred with **3**. Because only formaldehyde can be converted in water to the hydrated form as methanediol,⁷ methanediol may act as a hydride source as well as a proton source for the hydrogen production as suggested by Prechtel and coworkers.¹⁵ On the other hand, the catalytic transformation of primary alcohols to the corresponding carboxylic acid salts and H₂ has recently been reported by using a ruthenium complex at high temperature under reflux conditions.¹⁹ In the same manner, methanol can directly be converted to carbon dioxide with evolution of H₂ in the presence of a transition metal complex as a catalyst in aqueous solution at temperatures higher than 65 °C.^{20,21}

In conclusion, a water-soluble iridium(III)-hydroxo complex **3** catalyses production of H₂ from paraformaldehyde in water under basic conditions at 298 K. Although the catalytic activity and stability of **3** should be further improved, this study provides a convenient way to produce hydrogen from paraformaldehyde as a solid hydrogen carrier at ambient temperature.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental and kinetic details. See DOI: 10.1039/c4cc00000x/

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TOC Graphics

A water-soluble iridium(III)-hydroxo complex catalyses
production of H₂ from paraformaldehyde in water under basic
conditions at 298 K.

