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Catalytic oxidation of formic acid by dioxygen with an organoiridium complex†

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Catalytic oxidation of formic acid by dioxygen occurred efficiently using an organoiridium complex ([Ir^{III}(Cp*)(4-(1*H*-pyrazol-1-yl-κN^2)benzoic acid-κC^3)(H_2O)]$_2$$SO_4$, **1**) as a catalyst in a water-containing organic solvent as well as in water at ambient temperature. The catalytic cycle is composed of the reduction of **1** by formate to produce the hydride complex, which reduces dioxygen to water to regenerate **1**.

Formic acid (HCOOH) is liquid at room temperature[1] with a relatively high volumetric density (d = 1.22 g cm^{-3}) and is widely utilised as a preservative and an antibacterial additive for livestock feed.[2] HCOOH can be formed by reduction of CO_2 with H_2 and the catalytic interconversion between HCOOH and H_2 (eqn (1)) has been reported to be ideal for carbon-neutral storage and transportation of H_2.[3–6]

$$H_2 + CO_2 \rightleftarrows HCOOH \qquad (1)$$

In a natural enzymatic system, formate oxidase[7] and formate:oxygen oxidoreductase[8] reduce dioxygen (O_2) to reactive oxygen species, *e.g.*, superoxide and hydrogen peroxide that would be further reduced to water. Formate is often used as an electron donor for reductive activation of O_2 to conduct enzymatic oxygenation[9] and for reduction of NAD$^+$ and FAD to regenerate NADH and FADH$_2$,[10] respectively. Subsequently, NADH or FADH$_2$ is supplied as an electron donor to either reductase or oxidase, enabling regioselective oxidation such as epoxidation.[11]

In addition to its importance as a renewable hydrogen source for both enzymatic and non-enzymatic useful synthetic reactions,[12] formic acid is also utilised as a fuel for direct formic acid fuel cells.[13,14] The theoretical output potential is 1.45 V, which is higher than those of H_2 (1.23 V) and methanol (1.21 V) fuel cells.[13,14] Hence, the overall reaction for the cathodic oxidation of formic acid and the anodic reduction of oxygen is expressed in eqn (2), which is largely exergonic ($\Delta_c H^0$ = −255 kJ mol^{-1}).

$$2HCOOH + O_2 \rightarrow 2H_2O + 2CO_2 \qquad (2)$$

Formic acid is the most aggressive contributor of atmospheric corrosion for indoor environments,[15] being also contained as a hazardous compound in wastewaters.[16,17] The best way of removing formic acid is through oxidation by O_2 into H_2O and CO_2 (eqn (2)). Heterogeneous catalysts have been reported to act as catalysts for oxidation of HCOOH by O_2.[17] From an economical point of view, there is still a need to improve the catalytic activity of oxidation of HCOOH by O_2 at temperatures and pressures as low as possible.[17] There has been no report so far on the use of a homogeneous catalyst for efficient oxidation of HCOOH by O_2 at ambient pressure and temperature or its catalytic mechanism.

We report herein the catalytic oxidation of HCOOH by O_2 in water and a water-containing protic solvent, ethylene glycol, in the presence of a water-soluble iridium aqua complex ([Ir^{III}(Cp*)(4-(1*H*-pyrazol-1-yl-κN^2)benzoic acid-κC^3)(H_2O)]$_2$$SO_4$, [**1**]$_2$·$SO_4$; see the ESI†) acting as an efficient catalyst for the removal of HCOOH by O_2. A mixture solvent of water and ethylene glycol was examined because ethylene glycol has been used to improve the energy density of electric capacitors, in which a trace of HCOOH has to be removed.[18] **1** reacts with HCOOH to produce the corresponding Ir–hydride complex (**3**),[4,19] which can reduce O_2 to H_2O.

Synthesis and characterization of **1** were carried out according to the previous reports and are briefly described in the Experimental section in the ESI.†[5,19] The carboxylate form **1-H**$^+$ is protonated to give the carboxylic acid group

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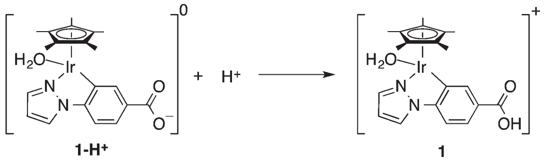
in **1**, as shown in eqn (3), at pH 2.8 since the pK_a of **1** was determined to be 4.0.[5,19]



(3)

Under an N_2 atmosphere at pH 2.8 in the presence of **1**, formic acid decomposed efficiently to produce CO_2 (Fig. 1a) and H_2 (Fig. 1b) according to eqn (4).[4] When the reaction was conducted under an O_2 atmosphere,

$$HCOOH \rightarrow H_2 + CO_2 \tag{4}$$

the stoichiometric CO_2 was evolved with a TON of 170 at 9 h, exhibiting the same time course shown in Fig. 1a, indicating that formic acid was decomposed according to eqn (4). Since the pK_a of bicarbonate (HCO_3^-) to form carbon dioxide (CO_2) is 6.35, which is significantly higher than the pH of the reaction solution (2.8),[4] carbon dioxide may evolve as a form of gas when dissolved CO_2 gas is saturated in the solution. However, the amount of H_2 was largely suppressed under an O_2 atmosphere, as shown in Fig. 1b. No H_2O_2 was detected by spectral titration with the use of the oxo[5,10,15,20-tetra(4-pyridyl)porphyrinato]titanium(IV) complex in water,[20] indicating that the four-electron reduction of O_2 occurred to produce H_2O, as expressed by eqn (2). The conversion of formic acid was determined to be higher than 99%.

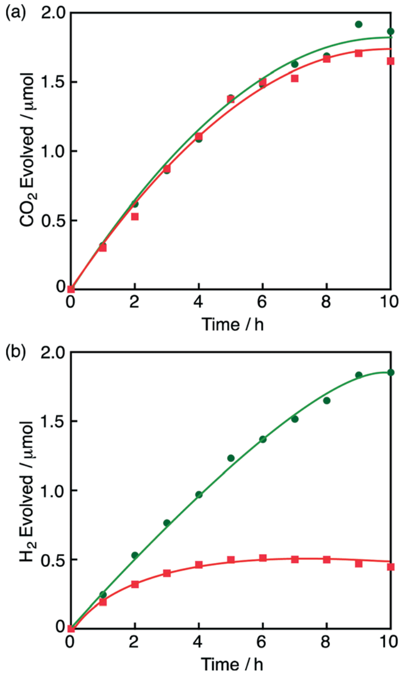
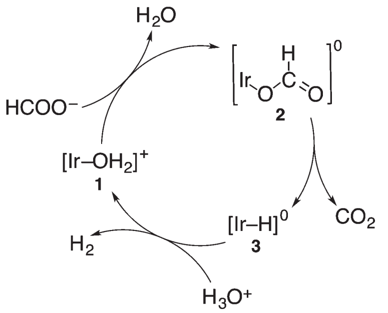


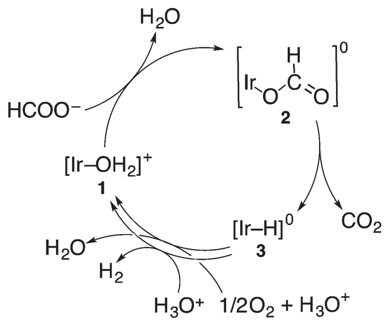
Fig. 1 (a) Time courses of CO_2 evolution from an aqueous formic acid (2.0 mM) solution (1.0 mL) in the presence of **1** (10 µM) under N_2 and O_2 atmosphere (green circle and red square, respectively) at pH 2.8 at 298 K. (b) Time courses of H_2 evolution from a formic acid (2.0 mM) solution in the presence of **1** (10 µM) under N_2 and O_2 atmosphere (green circle and red square, respectively) at pH 2.8 at 298 K. The red and green lines correspond to the reactions [(eqn (2) + eqn (4)) and eqn (4), respectively]. The amounts of H_2 and CO_2 were analysed by GC (see the ESI†).



Scheme 1 Catalytic cycle for decomposition of formic acid to form H_2 and CO_2 by using **1** under an N_2 atmosphere.[4]

In the catalytic reaction at pH 2.8 under an N_2 atmosphere, **1** reacted with $HCOO^-$ to afford the formate complex **2**, which is converted to the hydride complex **3** *via* β-hydrogen elimination from **2**. Then, **3** reacts with H_3O^+ to produce H_2, accompanied by the regeneration of **1**, as shown in Scheme 1.[5] The formation of the hydride complex (**3**) was confirmed by comparison with the ^1H NMR spectrum of the isolated hydride complex in DMSO-d_6 obtained by the reaction of **1** with H_2, which showed a typical hydride peak at δ = −14.74 ppm.[5] Because the iridium hydride complex (**3**) is a neutrally charged complex, the solubility of **3** in water is too low to be detected by ^1H NMR in D_2O.

On the other hand, the hydride complex (**3**) reacts with O_2 to produce H_2O and reproduce **1**. The overall catalytic cycle for the four-electron reduction of O_2 by $HCOO^-$ with **1** in competition with H_2 evolution is shown in Scheme 2. The rate-determining step of this catalytic oxidation cycle was independently examined by the deuterium kinetic isotope effect (KIE) on the catalytic oxidation of formic acid-*d* (DCOOH) *vs.* HCOOH. By comparing the time course of oxidation of HCOOH by O_2 with that of DCOOH in Fig. 2 (also see Fig. S1 in the ESI†), the KIE was determined to be 4.1 ± 0.2 at pH 2.8 at 298 K. This value is nearly equal to the



Scheme 2 Catalytic cycle for the formation of H_2, CO_2 and H_2O from formic acid in the presence of **1** under an O_2 atmosphere.

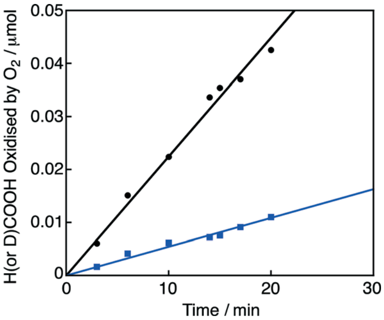


Fig. 2 Time courses of oxidation of HCOOH (2.0 mM; black circle) and DCOOH (2.0 mM; blue square) by O_2 in the presence of **1** (10 μM) under an O_2 atmosphere in water (1.0 mL) at pH 2.8 at 298 K. R^2 = 0.99 and 0.98 for the linear correlations (black and blue, respectively).

value (4.0) reported for the hydrogen evolution reaction under an N_2 atmosphere under otherwise the same experimental conditions.[19] This indicates that the rate-determining step in the overall catalytic cycle for oxidation of HCOOH by O_2 is the β-hydrogen elimination of the formate complex (2) to form the hydride complex (3).

The catalytic oxidation of HCOOH by O_2 also occurred in a mixed solution (3.0 mL) of ethylene glycol and water [4 : 1 (v/v)] and the yield of H_2 was decreased as compared with that under an N_2 atmosphere (Fig. 3). In the same manner, various concentrations of HCOOH were oxidised by O_2 under an O_2 atmosphere by using **1** in water-containing ethylene glycol at various pH values (Fig. S2 and S3 in the ESI†). The amount of the remaining HCOOH was quantified by ^{1}H NMR, in which no oxidized product of ethylene glycol was detected. The amount of H_2O_2 produced was analysed by spectral titration using the oxo[5,10,15,20-tetra(4-pyridyl) porphyrinato]titanium(IV) complex in water.[20] Neither H_2O_2 nor H_2 was formed in the absence of HCOOH. The amount of H_2O_2 generated in the reaction of 2.0 mM HCOOH was 13 μM at 5 h, which is also negligible as in the case of the reaction in water. The TON reached 1300 at 22 h (Fig. 3). The amount of H_2O_2 was significantly increased by adding flavin mononucleotide (FMN), as shown in Fig. S4 in the ESI.† In the presence of FMN, the hydride complex (3) reacts with FMN in competition with the four-electron reduction of O_2 and the reduced FMN reacts with O_2 to produce H_2O_2.[19c]

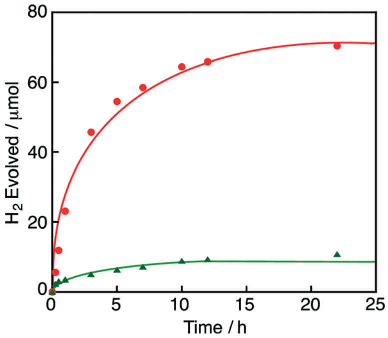


Fig. 3 Time courses of H_2 evolution from formic acid (0.50 M) in an ethylene glycol and water [4 : 1 (v/v)] mixed solution (3.0 mL) in the presence of **1** (18 μM) under N_2 and O_2 atmosphere (red circle and green triangle, respectively) at pH 5.9 at 298 K.

In conclusion, a water-soluble iridium(III) complex (**1**) can efficiently catalyse the oxidation of HCOOH by O_2 to mainly generate water with evolution of a little amount of H_2 under acidic conditions at 298 K. This reaction occurred in both water and water-containing ethylene glycol. The rate-determining step of the catalytic cycle is the β-hydrogen elimination of the formate complex (2) to form the hydride complex (3) in the same manner as the hydrogen evolution from HCOOH catalysed by **1**. This study provides an efficient way to remove undesired formic acid in water as well as in water-containing ethylene glycol.

Acknowledgements

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