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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 (1, $[Ir^{III}(Cp^*)(4\text{-}(1H\text{-pyrazol-1-yl-}\kappa N^2)\text{benzoic acid-}\kappa C^3)(H_2O)]_2SO_4$) 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 2, which reduces dioxygen to water to regenerate 1.

Formic acid (HCOOH) is liquid at room temperature[1] with relatively high volumetric density (d = 1.22 g cm^{-3}) and widely utilised as a preservative and an antibacterial agent in 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 as an ideal carbon-neutral storage and transportation of H_2.[3-6]

$$H_2 + CO_2 \rightleftharpoons HCOOH \quad (1)$$

In 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 the enzymatic oxygenation,[9] and 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]

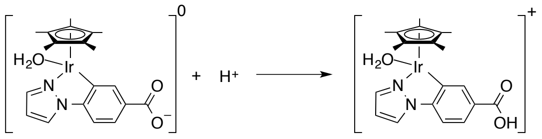
In addition to the importance as a renewable hydrogen source for both enzymatic and non-enzymatic useful synthetic reactions,[12] formic acid is utilised as a fuel for the direct formic acid fuel cell.[13,14] The theoretical output potential is 1.45 V, which is higher than those of H_2 (1.23 V) and methanol (1.21 V) fuel cells.[13,14] Hence, the overall reaction of the cathodic oxidation of formic acid and the anodic reduction of oxygen is expressed by eqn (2), which is largely exergonic ($\Delta H^0{}_{298\,K} = -298$ kJ mol^{-1}).

$$2HCOOH + O_2 \longrightarrow 2H_2O + 2CO_2 \quad (2)$$

Formic acid is the most aggressive contributors of atmospheric corrosion for indoor environments,[15] being also contained as a hazardous compound in wastewaters.[16,17] The best way is to remove formic acid by the 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 the economical point of view, there is still a need to improve catalytic activity of oxidation of HCOOH by O_2 at temperatures and pressures as low as possible.[17] There has so far been no report on a homogeneous catalyst for efficient oxidation of HCOOH by O_2 at ambient pressure and temperature or the catalytic mechanism.

We report herein the catalytic HCOOH oxidation by O_2 in water and water-containing protic solvent, ethylene glycol, in the presence of a water-soluble iridium aqua complex $[Ir^{III}(Cp^*)(4\text{-}(1H\text{-pyrazol-1-yl-}\kappa N^2)\text{benzoic acid-}\kappa C^3)(H_2O)]_2SO_4$ $[\mathbf{1}]_2$•SO_4 (see ESI) acting as an efficient catalyst for 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 ESI.[5,19] The carboxylate form **1-H$^+$** is protonated to give the carboxylic acid group in **1** as shown in eqn (3) at pH 2.8, since pK_a of **1** was determined to be 4.0.[5,19]



1-H+ **1** (3)

Under N_2 atmosphere at pH 2.8 in the presence of **1**, formic acid decomposed efficiently to produce CO_2 as shown in Figure 1a and H_2 as shown in Figure 1b according to eqn (4).[4] When this

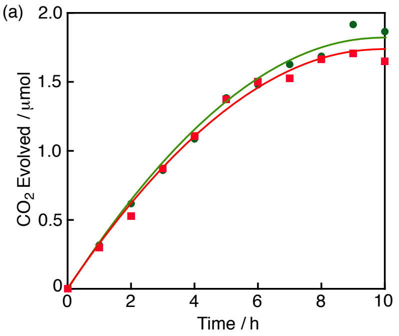
$$HCOOH \longrightarrow H_2 + CO_2 \quad (4)$$

reaction was conducted under O_2 atmosphere, the stoichiometric CO_2 was evolved with TON of 170 at 9 h exhibiting the same time course as shown in Figure 1a, indicating that formic acid was decomposed according to eqn (4). Since pK_a of bicarbonate (HCO_3^-) to form carbon dioxide (CO_2) is 6.35 that is significantly higher than 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 O_2 atmosphere as shown in Figure 1b. No H_2O_2 was detected by spectral titration with 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%.

In the catalytic reaction at pH 2.8 under 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 regeneration of **1** as shown in Scheme 1.[5] The formation of the hydride complex **3** was confirmed by comparison with the ^{1}H 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 was too low to be detected by ^{1}H 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 of 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. From the time course of oxidation of HCOOH by O_2 as compared with that of DCOOH in Figure 2 (also see Figure S1 in ESI), KIE was determined to be 4.1 ± 0.2 at pH 2.8 and 298 K. This value is nearly equal to the value (4.0) reported for hydrogen evolution reaction under 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 an ethylene glycol and water [4:1 (v/v)] and the yield of H_2 was decreased as compared with that under N_2 atmosphere (Fig. 3). By the same manner, various concentrations of HCOOH were oxidised by O_2 under O_2 atmosphere by using **1** in



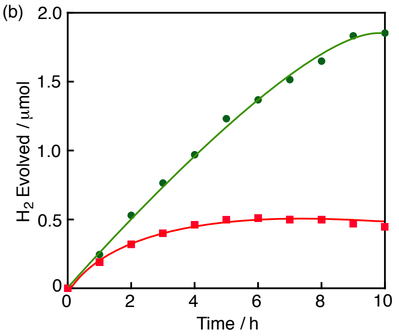
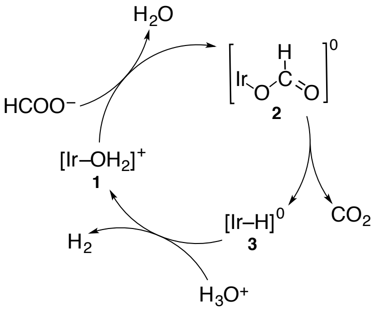
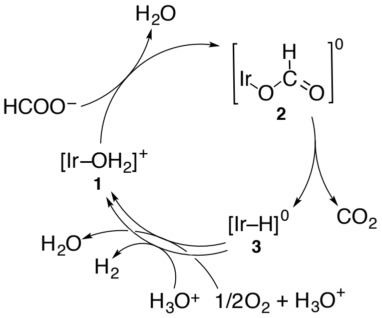


Fig. 1 (a) Time courses of CO_2 evolution from an aqueous formic acid (2.0 mM) solution (1.0 mL) in the presence of **1** (10 µM) under N_2 and O_2 atmosphere (green circle and red square, respectively) at pH 2.8 at 298 K. (b) Time courses of H_2 evolution from formic acid (2.0 mM) solution in the presence 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 ESI).



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



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

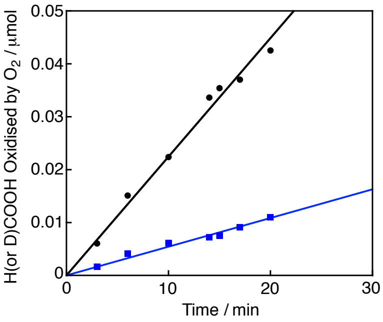


Fig. 2 Time courses of oxidation of HCOOH (2.0 mM; black circle) and DCOOH (2.0 mM; blue square) by O_2 in the presence of **1** (10 µM) under O_2 atmosphere in water (1.0 mL) at pH 2.8 at 298 K. R^2 = 0.99 and 0.98 for the linear correlations (black and blue, respectively).

water-containing ethylene glycol at various pH (Figs. S2 and S3 in ESI). The amount of remaining HCOOH was quantified by ^{1}H NMR in which no oxidized product of ethyele glycol was detected. The mount of H_2O_2 produced was analysed by spectral titration with use of 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 of HCOOH was 13 μM at 5 h, which is also negligible as the case of the reaction in water. The TON reached 1300 at 22 h in Figure 3. The amount of H_2O_2 was significantly increased by adding flavin mononucleotide (FMN) as shown in Fig. S4 in 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.[18c]

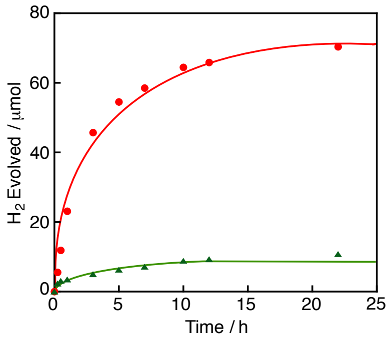


Fig. 3 Time courses of H_2 evolution from an ethylene glycol and water [4:1 (v/v)] mixed solution (3.0 mL) of formic acid (0.50 M) in the presence of **1** (18 μM) under N_2 and O_2 atmosphere (red circle and green triangle, respectively) at pH 5.9 at 298 K.

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 underwent in both water and water-containing ethylene glycol. The rate-determining step of the catalytic cycle is β-hydrogen elimination of the formate complex (**2**) to form the hydride complex (**3**) by the same manner as hydrogen evolution from HCOOH catalysed by **1**. This study provides an efficient way to remove undesired formic acid in water as well as in a water-containing ethylene glycol.

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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

Catalytic oxidation of formic acid by dioxygen occurred efficiently using an organoiridium complex as a catalyst in a water-containing organic solvent as well as in water at ambient temperature.