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-(1H-pyrazol-1-yl)-κN2)benzoic acid-κC3)(H2O)2SO4, 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 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. HCOOH can be formed by reduction of CO2 with H2 and the catalytic interconversion between HCOOH and H2 (eqn (1)) has been reported to be ideal for carbon-neutral storage and transportation of H2.

\[ H_2 + CO_2 \rightleftharpoons HCOOH \]  

(1)

In a natural enzymatic system, formate oxidase and formate:oxygen oxidoreductase reduce dioxygen (O2) 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 O2 to conduct enzymatic oxygenation and for reduction of NAD+ and FAD to regenerate NADH and FADH2, respectively. Subsequently, NADH or FADH2 is supplied as an electron donor to either reductase or oxidase, enabling regioselective oxidation such as epoxidation.

In addition to its importance as a renewable hydrogen source for both enzymatic and non-enzymatic useful synthetic reactions, formic acid is also utilised as a fuel for direct formic acid fuel cells. The theoretical output potential is 1.45 V, which is higher than those of H2 (1.23 V) and methanol (1.21 V) fuel cells. 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 (ΔH0 = −255 kJ mol−1).

\[ 2HCOOH + O_2 \rightleftharpoons 2H_2O + 2CO_2 \]  

(2)

Formic acid is the most aggressive contributor of atmospheric corrosion for indoor environments, being also contained as a hazardous compound in wastewaters. The best way of removing formic acid is through oxidation by O2 into H2O and CO2 (eqn (2)). Heterogeneous catalysts have been reported to act as catalysts for oxidation of HCOOH by O2. From an economical point of view, there is still a need to improve the catalytic activity of oxidation of HCOOH by O2 at temperatures and pressures as low as possible. There has been no report so far on the use of a homogeneous catalyst for efficient oxidation of HCOOH by O2 at ambient pressure and temperature or its catalytic mechanism.

We report herein the catalytic oxidation of HCOOH by O2 in water and a water-containing protic solvent, ethylene glycol, in the presence of a water-soluble iridium aqua complex ([Ir(III)(Cp*)(4-(1H-pyrazol-1-yl)-κN2)benzoic acid-κC3]((H2O)2)SO4; see the ESI†) acting as an efficient catalyst for the removal of HCOOH by O2. 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. 1 reacts with HCOOH to produce the corresponding Ir--hydride complex (3), which can reduce O2 to H2O.

Synthesis and characterization of 1 were carried out according to the previous reports and are briefly described in the Experimental section in the ESI. 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 the pK_a of 1 was
determined to be 4.0.\textsuperscript{5,19}

\[
\begin{array}{c}
\text{HCOO}^- + \text{H}^+ \\
\rightarrow
\end{array}
\]

(3)

Under an N\textsubscript{2} atmosphere at pH 2.8 in the presence of 1,
formic acid decomposed efficiently to produce CO\textsubscript{2} (Fig. 1a)
and H\textsubscript{2} (Fig. 1b) according to eqn (4).\textsuperscript{4} When the reaction
was conducted under an O\textsubscript{2} atmosphere,

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2
\]  (4)

the stoichiometric CO\textsubscript{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

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2
\]

(4)

Since the pK\textsubscript{a} of bicarbonate (HCO\textsubscript{3}\textsuperscript{-}) to form carbon
dioxide (CO\textsubscript{2}) is 6.35, which is significantly higher than the
pH of the reaction solution (2.8),\textsuperscript{4} carbon dioxide may

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2
\]

(4)

evolve as a form of gas when dissolved CO\textsubscript{2} gas is saturated
in the solution. However, the amount of H\textsubscript{2} was largely

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2
\]

(4)

suppressed under an O\textsubscript{2} atmosphere, as shown in Fig. 1b.
No H\textsubscript{2}O\textsubscript{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,\textsuperscript{20} indicating that the four-electron reduc-
tion of O\textsubscript{2} occurred to produce H\textsubscript{2}O, as expressed by eqn (2).

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2
\]

(2)

The conversion of formic acid was determined to be higher
than 99%.

In the catalytic reaction at pH 2.8 under an N\textsubscript{2} atmosphere,
1 reacted with HCOO\textsuperscript{-} to afford the formate complex 2, which
is converted to the hydride complex 3 via β-hydrogen elimina-
tion from 2. Then, 3 reacts with H\textsubscript{3}O\textsuperscript{+} to produce H\textsubscript{2}O, accom-
panied by the regeneration of 1, as shown in Scheme 1.\textsuperscript{5}

The formation of the hydride complex (3) was confirmed by

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2
\]

(4)

comparison with the \textsuperscript{1}H NMR spectrum of the isolated
hydride complex in DMSO-d\textsubscript{6} obtained by the reaction of
1 with H\textsubscript{2}, which showed a typical hydride peak at δ = −14.74 ppm.\textsuperscript{5} Because the iridium hydride complex (3) is a

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2
\]

(4)

neutrally charged complex, the solubility of 3 in water is too

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2
\]

(4)

low to be detected by \textsuperscript{1}H NMR in D\textsubscript{2}O.
On the other hand, the hydride complex (3) reacts with O\textsubscript{2} to produce H\textsubscript{2}O and reproduce 1. The overall catalytic
cycle for the four-electron reduction of O\textsubscript{2} by HCOO\textsuperscript{-} with
1 in competition with H\textsubscript{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\textsubscript{2} with that of DCOOH in Fig. 2
(see also Fig. S1 in the ESI\textsuperscript{†}), the KIE was determined to be

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2
\]

(4)

4.1 ± 0.2 at pH 2.8 at 298 K. This value is nearly equal to the

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2
\]

(4)

Fig. 1  (a) Time courses of CO\textsubscript{2} evolution from an aqueous formic acid
(2.0 mM) solution (1.0 mL) in the presence of 1 (10 μM) under N\textsubscript{2} and
O\textsubscript{2} atmosphere (green circle and red square, respectively) at pH 2.8 at
298 K. (b) Time courses of H\textsubscript{2} evolution from a formic acid (2.0 mM)
solution in the presence of 1 (10 μM) under N\textsubscript{2} and O\textsubscript{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\textsubscript{2} and CO\textsubscript{2} were analysed by
GC (see the ESI\textsuperscript{†}).

Scheme 1  Catalytic cycle for decomposition of formic acid to form
H\textsubscript{2} and CO\textsubscript{2} by using 1 under an N\textsubscript{2} atmosphere.\textsuperscript{4}

Scheme 2  Catalytic cycle for the formation of H\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2}O from
formic acid in the presence of 1 under an O\textsubscript{2} atmosphere.
value (4.0) reported for the hydrogen evolution reaction under an N₂ atmosphere under otherwise the same experimental conditions. This indicates that the rate-determining step in the overall catalytic cycle for oxidation of HCOOH by O₂ is the β-hydrogen elimination of the formate complex (2) to form the hydride complex (3).

The catalytic oxidation of HCOOH by O₂ also occurred in a mixed solution (3.0 mL) of ethylene glycol and water (4:1 (v/v)) and the yield of H₂ was decreased as compared with that under an N₂ atmosphere (Fig. 3). In the same manner, various concentrations of HCOOH were oxidised by O₂ under an O₂ 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 1H NMR, in which no oxidized product of ethylene glycol (ESIethylene glycol at various pH values (Fig. S2 and S3 in the ESI†). The amount of the remaining HCOOH was quantified by 1H NMR, in which no oxidized product of ethylene glycol was detected. The amount of H₂O₂ produced was analysed by spectral titration using the oxo[5,10,15,20-tetra(4-pyridyl)porphyrinato]titanium(IV) complex in water. Neither H₂O₂ nor H₂ was formed in the absence of HCOOH. The amount of H₂O₂ 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 H₂O₂ 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 O₂ and the reduced FMN reacts with O₂ to produce H₂O₂.¹⁹c

In conclusion, a water-soluble iridium(III) complex (1) can efficiently catalyse the oxidation of HCOOH by O₂ to mainly generate water with evolution of a little amount of H₂ 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 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.

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