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with an organoiridium complex†

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Catalytic oxidation of formic acid by dioxygen occurred efficiently using an organoiridium complex ( $[\text{Ir}^{\text{III}}(\text{Cp}^*)(4\text{-(1H-pyrazol-1-yl-}\kappa\text{N}^2)\text{benzoic acid-}\kappa\text{C}^3](\text{H}_2\text{O})_2\text{SO}_4$ , **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**.

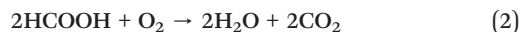
Formic acid ( $\text{HCOOH}$ ) is liquid at room temperature<sup>1</sup> with a relatively high volumetric density ( $d = 1.22 \text{ g cm}^{-3}$ ) and is widely utilised as a preservative and an antibacterial additive for livestock feed.<sup>2</sup>  $\text{HCOOH}$  can be formed by reduction of  $\text{CO}_2$  with  $\text{H}_2$  and the catalytic interconversion between  $\text{HCOOH}$  and  $\text{H}_2$  (eqn (1)) has been reported to be ideal for carbon-neutral storage and transportation of  $\text{H}_2$ .<sup>3–6</sup>



In a natural enzymatic system, formate oxidase<sup>7</sup> and formate: oxygen oxidoreductase<sup>8</sup> reduce dioxygen ( $\text{O}_2$ ) 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  $\text{O}_2$  to conduct enzymatic oxygenation<sup>9</sup> and for reduction of  $\text{NAD}^+$  and  $\text{FAD}$  to regenerate  $\text{NADH}$  and  $\text{FADH}_2$ ,<sup>10</sup> respectively. Subsequently,  $\text{NADH}$  or  $\text{FADH}_2$  is supplied as an electron donor to either reductase or oxidase, enabling regioselective oxidation such as epoxidation.<sup>11</sup>

In addition to its importance as a renewable hydrogen source for both enzymatic and non-enzymatic useful synthetic reactions,<sup>12</sup> formic acid is also utilised as a fuel for direct

formic acid fuel cells.<sup>13,14</sup> The theoretical output potential is 1.45 V, which is higher than those of  $\text{H}_2$  (1.23 V) and methanol (1.21 V) fuel cells.<sup>13,14</sup> 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 ( $\Delta_c H^\circ = -255 \text{ kJ mol}^{-1}$ ).



Formic acid is the most aggressive contributor of atmospheric corrosion for indoor environments,<sup>15</sup> being also contained as a hazardous compound in wastewaters.<sup>16,17</sup> The best way of removing formic acid is through oxidation by  $\text{O}_2$  into  $\text{H}_2\text{O}$  and  $\text{CO}_2$  (eqn (2)). Heterogeneous catalysts have been reported to act as catalysts for oxidation of  $\text{HCOOH}$  by  $\text{O}_2$ .<sup>17</sup> From an economical point of view, there is still a need to improve the catalytic activity of oxidation of  $\text{HCOOH}$  by  $\text{O}_2$  at temperatures and pressures as low as possible.<sup>17</sup> There has been no report so far on the use of a homogeneous catalyst for efficient oxidation of  $\text{HCOOH}$  by  $\text{O}_2$  at ambient pressure and temperature or its catalytic mechanism.

We report herein the catalytic oxidation of  $\text{HCOOH}$  by  $\text{O}_2$  in water and a water-containing protic solvent, ethylene glycol, in the presence of a water-soluble iridium aqua complex ( $[\text{Ir}^{\text{III}}(\text{Cp}^*)(4\text{-(1H-pyrazol-1-yl-}\kappa\text{N}^2)\text{benzoic acid-}\kappa\text{C}^3](\text{H}_2\text{O})_2\text{SO}_4$ , [**1**] $\cdot\text{SO}_4$ ; see the ESI†) acting as an efficient catalyst for the removal of  $\text{HCOOH}$  by  $\text{O}_2$ . 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  $\text{HCOOH}$  has to be removed.<sup>18</sup> **1** reacts with  $\text{HCOOH}$  to produce the corresponding Ir-hydride complex (**3**),<sup>4,19</sup> which can reduce  $\text{O}_2$  to  $\text{H}_2\text{O}$ .

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

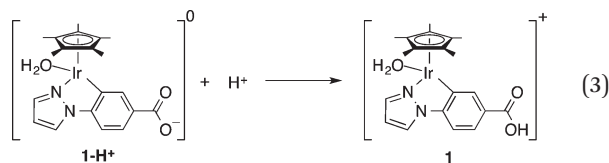
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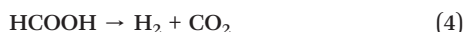
† Electronic supplementary information (ESI) available: Experimental and kinetic details. See DOI: 10.1039/c4cy00957f



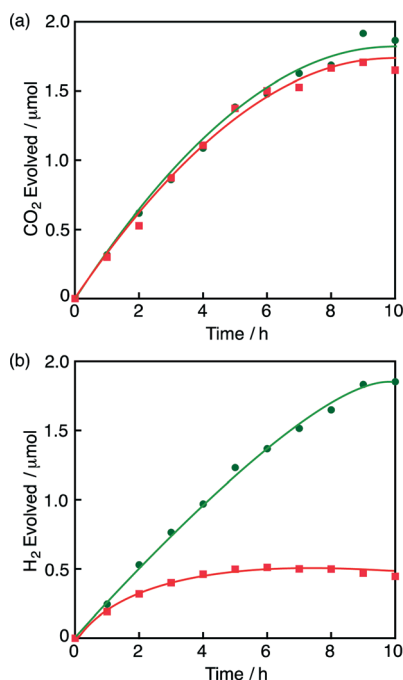
in **1**, as shown in eqn (3), at pH 2.8 since the  $pK_a$  of **1** was determined to be 4.0.<sup>5,19</sup>



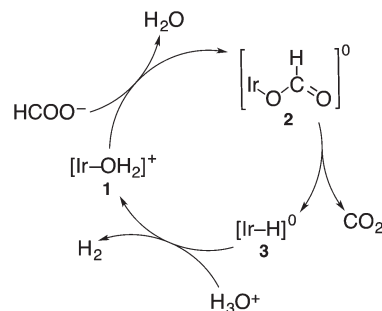
Under an  $N_2$  atmosphere at pH 2.8 in the presence of **1**, formic acid decomposed efficiently to produce  $CO_2$  (Fig. 1a) and  $H_2$  (Fig. 1b) according to eqn (4).<sup>4</sup> When the reaction was conducted under an  $O_2$  atmosphere,



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),<sup>4</sup> 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



**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  $\mu M$ ) 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  $\mu M$ ) 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†).

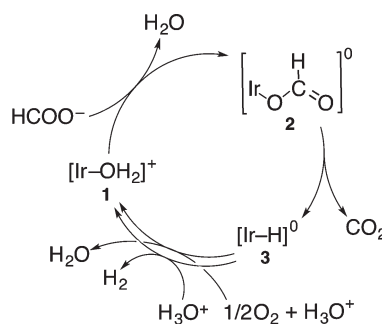


**Scheme 1** Catalytic cycle for decomposition of formic acid to form  $H_2$  and  $CO_2$  by using **1** under an  $N_2$  atmosphere.<sup>4</sup>

the oxo[5,10,15,20-tetra(4-pyridyl)porphyrinato]titanium(IV) complex in water,<sup>20</sup> 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 an  $N_2$  atmosphere, **1** reacted with  $HCOO^-$  to afford the formate complex **2**, which is converted to the hydride complex **3** via  $\beta$ -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.<sup>5</sup> 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  $\delta = -14.74$  ppm.<sup>5</sup> 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  $4.1 \pm 0.2$  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.



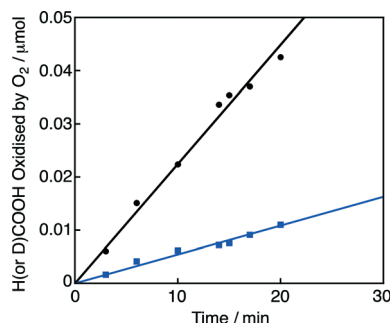


Fig. 2 Time courses of oxidation of HCOOH (2.0 mM; black circle) and DCOOH (2.0 mM; blue square) by  $O_2$  in the presence of **1** (10  $\mu$ M) under an  $O_2$  atmosphere in water (1.0 mL) at pH 2.8 at 298 K.  $R^2 = 0.99$  and  $0.98$  for the linear correlations (black and blue, respectively).

value (4.0) reported for the hydrogen evolution reaction under an  $N_2$  atmosphere under otherwise the same experimental conditions.<sup>19</sup> This indicates that the rate-determining step in the overall catalytic cycle for oxidation of HCOOH by  $O_2$  is the  $\beta$ -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  $^1H$  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.<sup>20</sup> 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  $\mu$ M 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

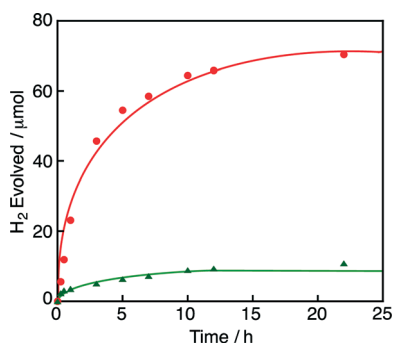


Fig. 3 Time courses of  $H_2$  evolution from formic acid (0.50 M) in an ethylene glycol and water [4 : 1 (v/v)] mixed solution (3.0 mL) in the presence of **1** (18  $\mu$ M) under  $N_2$  and  $O_2$  atmosphere (red circle and green triangle, respectively) at pH 5.9 at 298 K.

FMN in competition with the four-electron reduction of  $O_2$  and the reduced FMN reacts with  $O_2$  to produce  $H_2O_2$ .<sup>19c</sup>

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  $\beta$ -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.

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