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Aqueous hydrogenation of carbon dioxide catalysed by water-soluble ruthenium aqua complexes under acidic conditions

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Hydrogenation of carbon dioxide ($P(H_2/CO_2)$ = 5.5/2.5 MPa) into formic acid (HCOOH) under acidic conditions (pH 2.5–5.0) in water has been achieved by using water-soluble ruthenium aqua catalysts $[(\eta^6\text{-}C_6Me_6)Ru^{II}(L)(OH_2)]SO_4$ (L = 2,2′-bipyridine or 4,4′-dimethoxy-2,2′-bipyridine).

Catalytic reduction of CO_2 with H_2 in water (*i.e.*, aqueous hydrogenation of CO_2) is one of the attractive approaches to utilizing CO_2 as an economical and ecological C_1 source.[1] Extensive efforts have so far been devoted to the study of aqueous hydrogenations of HCO_3^- {as a deprotonated form of CO_2 dissolved in H_2O, eqn. (1)}[2] catalysed by transition metal complexes under basic conditions.[3] Such hydrogenations of HCO_3^- under basic conditions have required a stoichiometric amount of base (*e.g.*, triethylamine or KOH) to thermodynamically facilitate the formation of $HCOO^-$.[4] But, after the reaction, the used base has to be removed from the reaction solution by neutralisation to yield HCOOH (pK_a = 3.6).

$$CO_2 + H_2O \xrightleftharpoons{pK_a = 6.35} HCO_3^- + H^+ \qquad (1)$$

We recently reported a non-catalytic CO_2 reduction to $HCOO^-$ by an acid-stable ruthenium hydride complex $[(\eta^6\text{-}C_6Me_6)Ru^{II}(bpy)H]^+$ (bpy = 2,2′-bipyridine) in acidic media (pH 4.0).[5a] The hydride complex was prepared by a reaction of an aqua complex $[(\eta^6\text{-}C_6Me_6)Ru^{II}(bpy)(OH_2)]^{2+}$ ($\mathbf{1_a}$) with $NaBH_4$ in water.[5a,b] However, aqueous hydrogenation of CO_2 catalysed by transition metal aqua complexes under acidic conditions has yet to be achieved.

We report herein the hydrogenation of CO_2 into HCOOH under acidic conditions (pH 2.5–5.0) without any base, catalysed by a new water-soluble aqua complex $[(\eta^6\text{-}C_6Me_6)Ru^{II}(4,4'\text{-OMe-bpy})(OH_2)]SO_4$ {$\mathbf{1_b}(SO_4)$, 4,4′-OMe-bpy = 4,4′-dimethoxy-2,2′-bipyridine} as well as by $\mathbf{1_a}(SO_4)$. The structure of $\mathbf{1_b}(PF_6)_2$ was unequivocally determined by X-ray analysis.

The new water-soluble aqua complex $\mathbf{1_b}(SO_4)$ with the 4,4′-OMe-bpy ligand was synthesized by the same method as $\mathbf{1_a}(SO_4)$ with the bpy ligand.†[5c] Orange crystals of $\mathbf{1_b}(PF_6)_2$ used in the X-ray analysis were obtained from a water/methanol solution of $\mathbf{1_b}(PF_6)_2$, which was prepared by an anion exchange of $\mathbf{1_b}(SO_4)$ with NH_4PF_6 in water. An ORTEP drawing of $\mathbf{1_b}(PF_6)_2$ is shown in Fig. 1.‡

Complex $\mathbf{1_b}$ adopts a distorted octahedral coordination that is surrounded by one $\eta^6\text{-}C_6Me_6$, one 4,4′-OMe-bpy, and one H_2O ligand. The Ru1–O1 bond length of the aqua ligand in $\mathbf{1_b}$ is 2.139(4) Å which is close to the Ru–O bond length observed in $\mathbf{1_a}$ (2.153(2) Å). The distances between Ru atom and carbons of the $\eta^6\text{-}C_6Me_6$ ring of complex $\mathbf{1_b}$ in the solid state are not equivalent: the distances of Ru1–C1 and Ru1–C2 (2.182(4) and 2.194(4) Å, respectively) trans to the aqua ligand are shorter than those of Ru1–C3, Ru1–C4, Ru1–C5, and Ru1–C6 (2.203–2.233 Å) trans to the 4,4′-OMe-bpy ligand. This indicates that the 4,4′-OMe-bpy ligand has a greater trans influence than the aqua ligand.

The aqua complex **1** reacts with H_2 (5.5 MPa) and CO_2 (2.5 MPa) under acidic conditions (pH 2.5–5.0) in H_2O without base to catalytically provide HCOOH. The formation of HCOOH was determined by ^{1}H NMR.§ Turnover numbers (TONs) of the aqueous hydrogenation catalysed by $\mathbf{1_a}(SO_4)$ or $\mathbf{1_b}(SO_4)$ at 40 °C after 70 h are 35 or 55, respectively.

The catalytic cycle of the aqueous hydrogenation of CO_2 with the ruthenium complexes under acidic conditions (pH 2.5–5.0) is shown in Scheme 1, in which the hydride species **2** is generated by

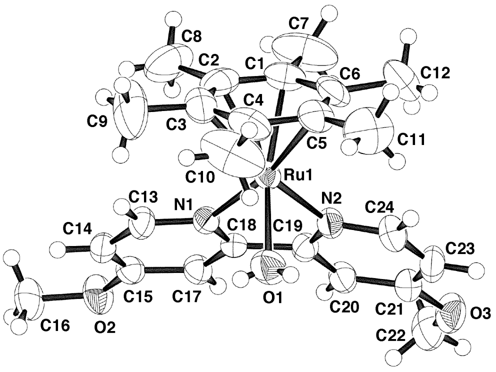
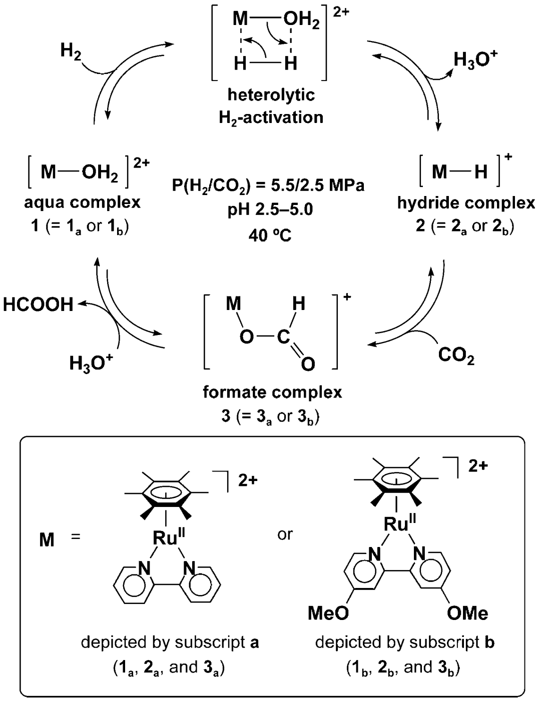


Fig. 1 ORTEP drawing of $\mathbf{1_b}$. The counter anions (PF_6) are omitted for clarity. Selected bond lengths (l/Å) and angles (ϕ/deg): Ru1–O1 = 2.139(4), Ru1–N1 = 2.089(3), Ru1–N2 = 2.090(3), Ru1–C1 = 2.182(4), Ru1–C2 = 2.194(4), Ru1–C3 = 2.221(4), Ru1–C4 = 2.203(4), Ru1–C5 = 2.231(4), Ru1–C6 = 2.233(4), N1–Ru1–N2 = 76.2(1).



Scheme 1 Aqueous hydrogenation of CO_2 under acidic conditions.

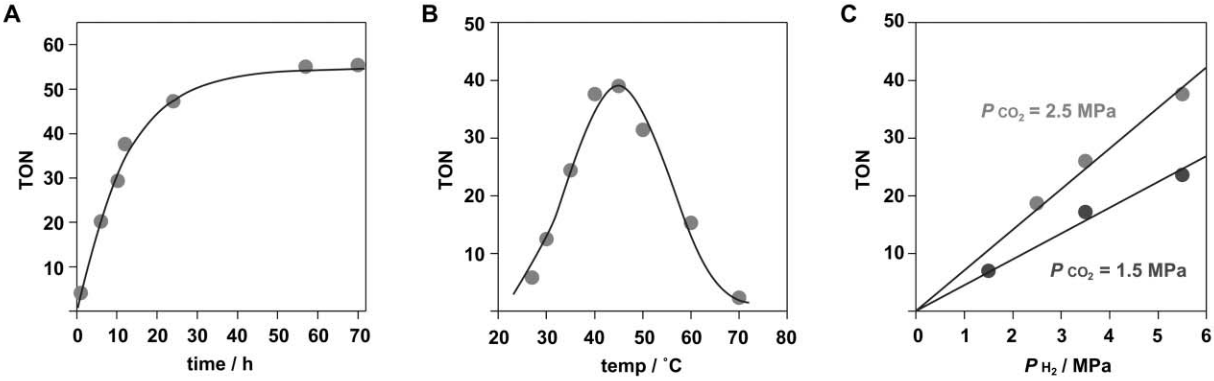


Fig. 2 (A) Time-dependent TONs to provide HCOOH in H_2O for the aqueous hydrogenation of CO_2 catalysed by $\mathbf{1_b}$(SO_4) at H_2 (5.5 MPa) and CO_2 (2.5 MPa) at 40 °C. (B) Temperature-dependence of TONs for the aqueous hydrogenation of CO_2 catalysed by $\mathbf{1_b}$(SO_4) at H_2 (5.5 MPa) and CO_2 (2.5 MPa) after 12 h. (C) Dependence of the TONs for the aqueous hydrogenation of CO_2 on the pressure of H_2 at 1.5 (dark grey circles) and 2.5 (light grey circles) MPa CO_2 catalysed by $\mathbf{1_b}$(SO_4) at 40 °C after 12 h.

the reaction of the aqua complex **1** with H_2 at pH 2.5–5.0.[6] It is known that the H_2O ligand accelerates the heterolytic H_2-activation in polar solvents to release H_3O^+.[7,8] The hydride species **2** reacts with CO_2 to afford the formate complex $\mathbf{3_b}$ (Scheme 1). The formation of $\mathbf{3_b}$ was confirmed by ^{1}H NMR and electrospray ionization mass spectrometry.†

The catalytic conditions were optimised for the reaction time (Fig. 2A), reaction temperature (Fig. 2B), and pressures of H_2 and CO_2 (Fig. 2C). The time dependence of TON to give HCOOH for the $\mathbf{1_b}$(SO_4)-catalysed aqueous hydrogenation with H_2 (5.5 MPa) and CO_2 (2.5 MPa) at 40 °C is depicted in Fig. 2A. The TON increases with reaction time to reach an equilibrium value in 55 h. The TON in 12 h increases with increasing temperature to reach a maximum value at 40 °C and then decreases with further increase in temperature (Fig. 2B). The backward reaction in Scheme 1 at a higher temperature, which results in a decrease in TON, was examined by the reaction of $\mathbf{1_b}$ with 10 equivalent of HCOOH in H_2O at pH 2.4 at 60 °C. After 1 h, disappearance of HCOOH ($>$ 90%) and evolutions of H_2 and CO_2 were confirmed by ^{1}H NMR and GC. On the other hand, the TON in 12 h at 40 °C increases linearly with increasing H_2 pressure and the slope becomes larger at a higher CO_2 pressure (Fig. 2C).

In conclusion, the aqueous hydrogenation of CO_2 into HCOOH under acidic conditions has been made possible by using the water-soluble aqua complexes under the optimised catalytic conditions.

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Notes and references

† Selected data for $\mathbf{1_b}$(SO_4): Yield 98%. ^{1}H NMR (300 MHz, in D_2O): δ = 2.12 (s, 18H, η^6-C_6Me_6), 4.08 (s, 6H, OMe), 7.42 (dd, J = 6.61, 2.57 Hz, 2H, bpy), 7.86 (d, J = 2.57 Hz, 2H, bpy), 8.91 (d, J = 6.61 Hz, 2H, bpy). Selected data for $\mathbf{3_b}$(PF_6): ^{1}H NMR (300 MHz, in DMSO-d$_6$): δ = 2.04 (s, 18H, η^6-C_6Me_6), 4.04 (s, 6H, OMe), 7.36 (dd, J = 6.42, 2.75 Hz, 2H, bpy), 7.65 (s, 1H, OCHO), 8.17 (d, J = 2.75 Hz, 2H, bpy), 8.92 (d, J = 6.41 Hz, 2H, bpy). ESI-MS (in MeOH): m/z 525.2 {[$\mathbf{3_b}$]$^+$, relative intensity (I) = 66% in the m/z range 200–1000}.

‡ Crystal data for $\mathbf{1_b}(PF_6)_2\cdot 2H_2O$: $C_{24}H_{36}N_2O_5P_2F_{12}Ru$, M = 823.56, monoclinic, a = 15.511(5), b = 12.878(4), c = 16.840(5) Å, β = 106.376(3)°, V = 3227(1) Å^3, T = 173 K, space group $P2_1/a$ (No. 14), Z = 4, μ (MoKα) = 6.91 cm^{-1}, 25926 reflections measured, 7212 unique (R_{int} = 0.035), final $R1$ [$I > 2\sigma(I)$] (wR_2) = 0.050 (0.147) parameters. CCDC 245736. See http://www.rsc.org/suppdata/cc/b4/b411633j/ for crystallographic data in .cif or other electronic format.

§ General procedure: 20.0 mmol of **1** was dissolved in 20 mL of water (pH 5.0) in a pressure vessel (25 mL). The temperature was raised to 40 °C, and then the solution was pressurized with CO_2 (2.5 MPa) and H_2 (5.5 MPa) for 70 h. After it was returned to atmospheric pressure, the solution was quickly cooled down to ambient temperature (pH 2.5). The yield of formic acid was determined by ^{1}H NMR measurement of the resulting solution with TSP in D_2O as the reference and the internal standard {TSP = 3-(trimethylsilyl)propionic-2,2,3,3-d$_4$ acid sodium salt}.

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6 The hydride species **2a** has been spectroscopically detected under the stoichiometric conditions (see ref. 5*a*). The hydride species **2a** and **2b**, however, were not detected in the reaction of the aqua complexes with H_2 in H_2O, probably because of the instability under the acidic conditions.

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