

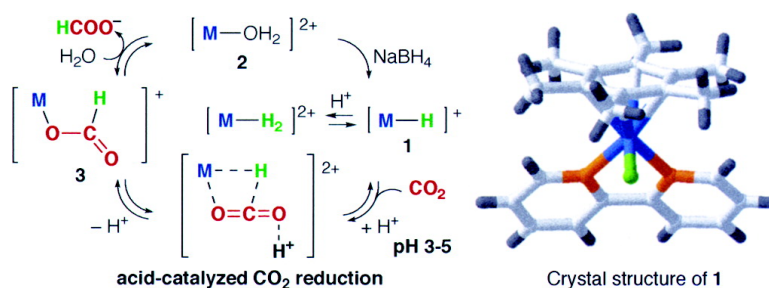
Communication

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## Accelerating Effect of a Proton on the Reduction of CO<sub>2</sub> Dissolved in Water under Acidic Conditions. Isolation, Crystal Structure, and Reducing Ability of a Water-Soluble Ruthenium Hydride Complex

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Reduction of carbon dioxide (CO<sub>2</sub>) dissolved in water to formate ion (HCOO<sup>-</sup>) by transition metal hydride complexes is one of the attractive reactions that utilizes CO<sub>2</sub> as an economical and ecological C<sub>1</sub> building block for chemical synthesis.<sup>1</sup> The dissolved CO<sub>2</sub> shows the following equilibrium (eq 1, pK<sub>1</sub> = 6.35 and pK<sub>2</sub> = 10.33).<sup>2</sup>



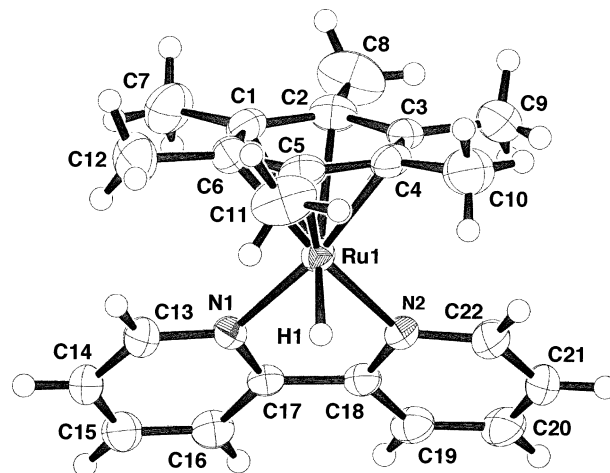
Although reduction of HCO<sub>3</sub><sup>-</sup> by in-situ formed transition metal hydride complexes in water has been reported,<sup>3</sup> reduction of CO<sub>2</sub> as the actual substrate by transition metal hydride complexes in water under acidic conditions has not been achieved. The thermodynamic effect of HCO<sub>3</sub><sup>-</sup> as a base on the reduction of HCO<sub>3</sub><sup>-</sup> dissolved in water has been investigated,<sup>3</sup> although the kinetic effect of a proton on the reduction of CO<sub>2</sub> dissolved in water under acidic conditions has yet to be reported.

The effect of a trace amount of water (or alcohol) on the reduction of CO<sub>2</sub> dissolved in organic solvents or supercritical CO<sub>2</sub> by transition metal hydride complexes has been attracting great interest.<sup>4</sup> The water is suggested to be a protonic cocatalyst that accelerates the reduction of CO<sub>2</sub>, although the acceleration mechanism has yet to be clarified because most of such transition metal hydride complexes are unstable in water under acidic conditions.

We have previously reported transfer hydrogenations of a variety of carbonyl compounds catalyzed by an in-situ formed hydride species [(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)Ru<sup>II</sup>(bpy)H]<sub>2</sub>(SO<sub>4</sub>) {[1]<sub>2</sub>(SO<sub>4</sub>), bpy = 2,2'-bipyridine} that is stable enough to reduce the carbonyl compounds even at pH 3 in water.<sup>5</sup> However, the definitive structure of **1** has yet to be disclosed.

We report herein the isolation of **1** whose structure was unequivocally determined by X-ray analysis. Complex **1** acts as a robust reducing agent for the reduction of CO<sub>2</sub> in water in a pH range of about 3–5 at ambient temperature under stoichiometric conditions.<sup>6</sup> The isolation and structural determination of **1** provide one with an excellent opportunity to elucidate the role of a proton in the reduction of CO<sub>2</sub> dissolved in water under acidic conditions.

The hydride complex **1** was synthesized from the reaction of an aqua complex [(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)Ru<sup>II</sup>(bpy)(OH<sub>2</sub>)](SO<sub>4</sub>) {2(SO<sub>4</sub>)} with NaBH<sub>4</sub> as a hydrogen donor in H<sub>2</sub>O at about pH 7 at 25 °C. Addition of CF<sub>3</sub>SO<sub>3</sub>Na into the aqueous solution of **1** gave an orange powder of **1**(CF<sub>3</sub>SO<sub>3</sub>). Orange crystals of **1**(CF<sub>3</sub>SO<sub>3</sub>) used in X-ray analysis (Figure 1)<sup>7</sup> were obtained by diffusion of diethyl ether into a methanol solution of **1**(CF<sub>3</sub>SO<sub>3</sub>) at 25 °C. Complex **1** adopts a distorted octahedral coordination which is surrounded by one η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub> ligand, one bpy ligand, and one terminal hydrido ligand (H1) that occupies a bond position. In the IR spectra as KBr disks of **1**, the peak at 1908 cm<sup>-1</sup> was assigned to ν(Ru–H) that shifts to 1370 cm<sup>-1</sup> by isotopic substitution of D for H (see Supporting Information, Figure S1). The shift value (538 cm<sup>-1</sup>)



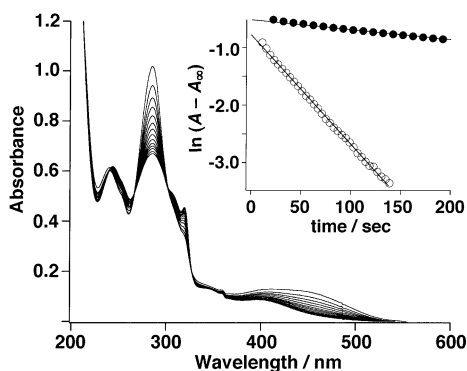
**Figure 1.** ORTEP drawing of **1**. The counteranion (CF<sub>3</sub>SO<sub>3</sub>) is omitted for clarity. Selected bond lengths (l/Å) and angles (φ/deg): Ru1–H1 = 1.51(4), Ru1–N1 = 2.077(3), Ru1–N2 = 2.071(3), Ru1–C1 = 2.257(4), Ru1–C2 = 2.312(4), Ru1–C3 = 2.233(3), Ru1–C4 = 2.219(4), Ru1–C5 = 2.197(3), Ru1–C6 = 2.218(4); N1–Ru1–N2 = 77.1(1).

agrees well with that expected by Hooke's law calculation for a pure Ru–hydrido stretching mode.<sup>8</sup>

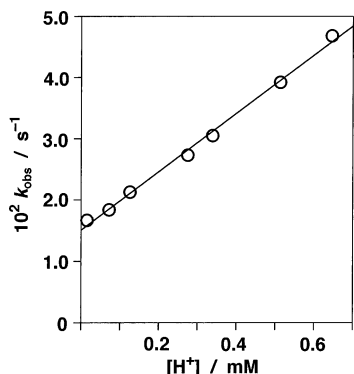
Complex [1]<sub>2</sub>(SO<sub>4</sub>) has high solubility in water (20 mg/mL at pH 7.0 at 25 °C). It has been confirmed by <sup>1</sup>H NMR,<sup>5</sup> IR, and electrospray ionization mass spectrometry (ESI-MS) that the structure of **1** is preserved in aqueous solution. In the IR spectrum of **1** in H<sub>2</sub>O, the ν(Ru–H) band is observed at 1889 cm<sup>-1</sup> which is similar to that observed in the solid sample. The positive-ion ESI mass spectrum of **1** in H<sub>2</sub>O/acetone shows a prominent signal at *m/z* 421.2 {relative intensity (*I*) = 100% in the range of *m/z* 100–1000} which corresponds to **1** (Supporting Information, Figure S2).

The hydride complex **1**(CF<sub>3</sub>SO<sub>3</sub>) (18 μmol) reacts with CO<sub>2</sub>-saturated H<sub>2</sub>O (3 mL) at pH 4.0 at 25 °C under CO<sub>2</sub> atmosphere (0.1 MPa) to give a formate complex [(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)Ru<sup>II</sup>(bpy)-(OCHO)](CF<sub>3</sub>SO<sub>3</sub>) **3**(CF<sub>3</sub>SO<sub>3</sub>) that is in equilibrium with the aqua complex **2**(CF<sub>3</sub>SO<sub>3</sub>) and HCOO<sup>-</sup>. The structures of **2** and **3** were determined by <sup>1</sup>H NMR, ESI-MS, and X-ray analysis.<sup>5</sup> The release of HCOO<sup>-</sup> was observed by <sup>1</sup>H NMR analysis (Supporting Information, Figure S3). The yields of **3** and HCOO<sup>-</sup> are 16% and 48%, respectively, based on **1**. To establish the origin of the formate ligand in **3**, the reaction of **1** with <sup>13</sup>CO<sub>2</sub> in H<sub>2</sub>O has also been carried out. ESI-MS results show that the signal at *m/z* 465.2 shifts to *m/z* 466.2 (Supporting Information, Figure S4). This indicates that the labeled carbon atom is incorporated into the formate ligand.

Analysis of kinetic data obtained by monitoring a decrease of the absorption band at 285 nm of **1** revealed that the reaction of **1** with CO<sub>2</sub>-saturated H<sub>2</sub>O at pH 4.2 at 25 °C was pseudo first-order with respect to **1** as shown in Figure 2. The rate of the reaction

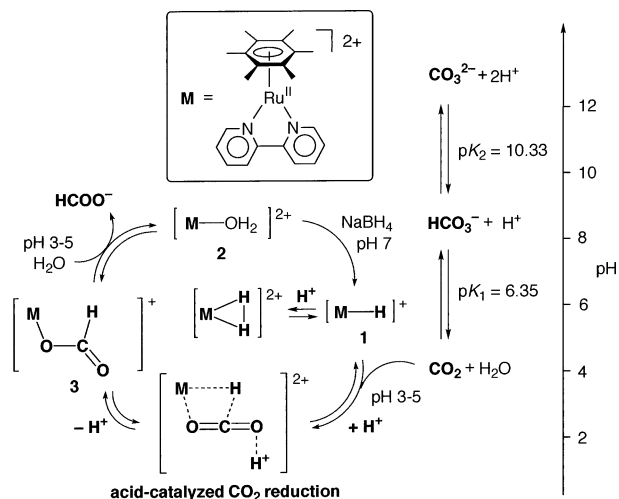


**Figure 2.** Spectral change for the reaction of **1** with CO<sub>2</sub> in H<sub>2</sub>O at pH 4.2 at 25 °C at 8 s intervals. Inset: Plots of ln(A - A<sub>∞</sub>) versus *t* based on the absorption changes at 285 nm for the reaction of **1** with CO<sub>2</sub> (O) and without CO<sub>2</sub> (●).



**Figure 3.** The plots of  $k_{\text{obs}}$  as a function of concentration of H<sup>+</sup>.

#### Scheme 1



$\{k_{\text{obs}} = (1.87 \pm 0.03) \times 10^{-2} \text{ s}^{-1}, \text{ O in inset of Figure 2}\}$  is significantly faster than the rate without CO<sub>2</sub> under otherwise the same experimental conditions ( $k_{\text{obs}} = 1.52 \times 10^{-3} \text{ s}^{-1}, \text{ ● in inset of Figure 2}$ ). It is important to note that the  $k_{\text{obs}}$  value at pH 8.5, where HCO<sub>3</sub><sup>−</sup> is the major species, is 46 times smaller than the value at pH 4.2, where CO<sub>2</sub> is the major species.<sup>9</sup> The plot of  $k_{\text{obs}}$  as a function of the concentration of proton in the CO<sub>2</sub>-saturated solution at 25 °C shows that the  $k_{\text{obs}}$  linearly increases with an increasing concentration of proton (Figure 3).

The mechanism of acid-catalyzed reduction of CO<sub>2</sub> dissolved in water under acidic conditions may be summarized in Scheme 1.<sup>10</sup> We have found an inverse kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}} = 0.59$ ) in the CO<sub>2</sub> reduction by the hydride complex **1** (Supporting Information, Figure S5). Such an inverse isotope effect indicates a product-like transition state.<sup>6b,11</sup> This study indicates that the development of robust hydride catalysts for acid-catalyzed hydrogenation of CO<sub>2</sub> in water under acidic conditions is a worthy endeavor in the construction of new CO<sub>2</sub> reduction systems in water.

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**Supporting Information Available:** Experimental procedures, figures (S1–S5), and crystallographic information (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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