Carbon Dioxide Reduction

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An Organic Hydride Transfer Reaction of a Ruthenium NAD Model Complex Leading to Carbon Dioxide Reduction**

*Hideki Ohtsu and Koji Tanaka**

The growing atmospheric concentration of carbon dioxide (CO_2), caused in part by the excessive use of fossil fuels, has resulted in global warming. To prevent a global crisis and to cope with the growing demand for energy worldwide, it is crucial to clarify how the chemical conversion of CO_2 into value-added chemical compounds,[1,2] such as methanol (CH_3OH)[3,4] and formic acid (HCO_2H),[5,6] can be accomplished. The single-electron reduction of CO_2 to form $CO_2^{\bullet -}$ is highly unfavorable, and therefore, the reduction of CO_2 through proton-assisted multiple-electron transfer has been investigated.[7,8] In biological systems, the NAD^+/NADH redox couple in NAD (NAD = nicotinamide adenine dinucleotide) plays a pivotal role as a generator and/or a reservoir of hydride ion (H^-), which is equivalent to two electrons and one proton.[9]

Much information about organic NAD model compounds has so far been accumulated to understand their unique redox and photophysical properties as well as their photochemical and thermal reactivity.[10] However, facile C−C coupling reactions of NAD radical intermediates, which can form either by the reduction of NAD^+ or by the oxidation of NADH followed by deprotonation, has precluded reversible interconversion of NAD^+ and NADH analogues.[11] In contrast to organic NAD model compounds, few transition-metal complexes containing NAD analogues have been reported.[12] We have recently demonstrated that a ruthenium complex containing a new type of NAD^+ model ligand $[Ru(bpy)_2(pbn)](PF_6)_2$ (**1**; bpy = 2,2′-bipyridine, pbn = 2-(pyridin-2-yl)benzo[*b*][1,5]naphthyridine)[13] is efficiently reduced, in a two-electron process, to the corresponding NADH-type complex $[Ru(bpy)_2(pbnHH)](PF_6)_2$ (**1·HH**; pbnHH = 2-(pyridin-2-yl)-5,10-dihydrobenzo[*b*][1,5]naphthyridine) through irradiation with visible light in the presence of a sacrificial reagent.[14] Despite the potential use of an NADH model compound as a photorenewable hydride reagent, neither NAD model complexes exhibiting an ability to donate hydride to CO_2 nor renewable organic hydrides that can reduce CO_2 in a photocatalytic manner have been reported.

Herein, we report on the successful transfer of organic hydride to CO_2 by using a ruthenium-based NADH model complex **1·HH**, a process that is triggered by the association of the base, benzoate anion ($PhCOO^-$), to **1·HH**. The association of $PhCOO^-$ to the NH moiety of the pbnHH ligand in **1·HH** has been found to be crucial for the organic hydride transfer reaction that converts CO_2 into formate (HCO_2^-). Additionally, a photocatalytic CO_2-reduction process using ruthenium-based NAD^+ model complex **1** has also been successfully developed.

The ruthenium complex **1·HH**, bearing the NADH model ligand pbnHH, was prepared by chemical reduction of the ruthenium-based NAD^+ model complex **1** by using $Na_2S_2O_4$, as reported previously.[14a] The ruthenium-based NADH model complex **1·HH** exhibits organic hydride transfer activity toward CO_2; the reaction is triggered by the association of base and is accompanied by the C−H bond dissociation of the NADH model ligand. The addition of excess amounts (10 equivalents) of tetra-*n*-butylammonium benzoate to an acetonitrile (CH_3CN) solution of **1·HH** at 293 K under a saturated CO_2 atmosphere results in a color change of the solution from yellow to red. The reaction consists of two distinct steps, each of which corresponds to a distinct spectral change (Figure 1). Firstly, the characteristic absorption band associated with **1·HH** that is located at 420 nm (Figure 1, blue line) rapidly shifts to slightly higher wavelengths upon addition of tetra-*n*-butylammonium benzoate (Figure 1, purple line). Subsequently, the intensity of the resulting spectrum, at approximately 460 nm, decreases together with the appearance of an absorption band at 530 nm. The final spectrum corresponds to the NAD^+ model complex **1** (Figure 1, red line), and by viewing the spectral changes, an isosbestic point at 499 nm can be identified. In the resulting reaction mixture, the reduction product of CO_2 (HCO_2^-) has been detected in 38.0 % yield based on **1·HH**, as determined by capillary electrophoresis analyses; the corresponding NAD^+ model complex **1** has also been detected by ESI mass spectrometry ($m/z = 335.5$; see the Supporting Information, Figure S1). An isotope-labeling experiment involving a reaction employing $^{13}CO_2$ instead of $^{12}CO_2$ and analysis by ESI mass spectrometry have confirmed that the carbon-atom source of the product, formate, is indeed carbon dioxide (see the Supporting Information, Figure S2). Furthermore, when $[Ru(bpy)_2(pbnDD)](PF_6)_2$ (**1·DD**; pbnDD is the 5,10,10-trideuterated analogue of pbnHH)

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[*] Dr. H. Ohtsu,[$],[+] Prof. K. Tanaka[+]
Institute for Molecular Science
5-1 Higashiyama, Myodaiji, Okazaki, Aichi 444-8787 (Japan)

[+] Current address: Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Funai Center, Kyoto University Katsura, Nishikyo-ku, Kyoto 615-8530 (Japan)
E-mail: koji.tanaka@icems.kyoto-u.ac.jp

[$] ALCA, Japan Science and Technology Agency (Japan)

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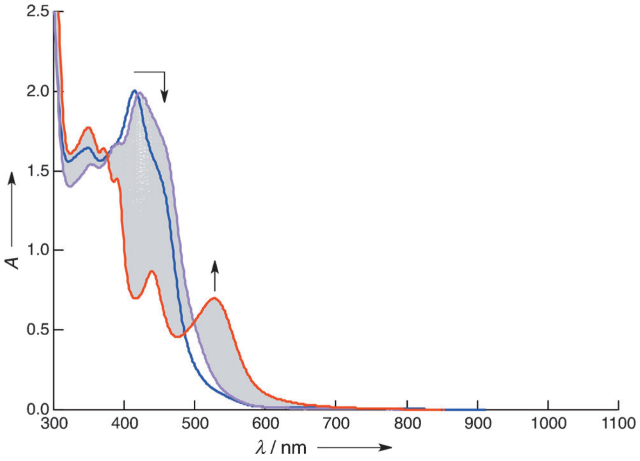
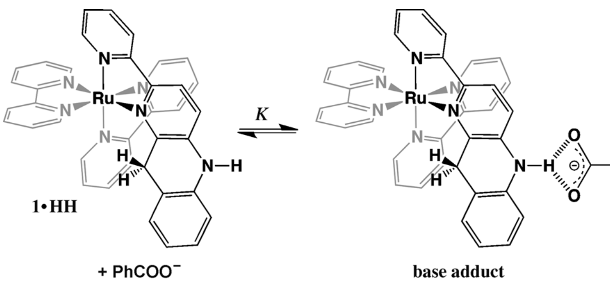


Figure 1. Absorption spectrum of an acetonitrile solution of **1·HH** (1.0×10^{-4} M) under a saturated CO_2 atmosphere at 293 K (blue line). Absorption spectrum recorded immediately after the addition of $PhCOO^-$ (10 equiv; purple line). An overlapping series of absorption spectra recorded every 5 sec after addition of $PhCOO^-$ for a period of 1800 sec (grey area). Absorption spectrum of an acetonitrile solution of **1** (red line).

was used instead of **1·HH**, the ESI mass spectrum has exhibited a signal at $m/z = 46$, which corresponds to the ion, DCO_2^- (Figure S2). These results clearly demonstrate that the hydride is transferred from pbnHH in the ruthenium complex to CO_2, thus producing HCO_2^-; similarly, deuteride transfer from pbnDD produces DCO_2^-. The findings are consistent with the large kinetic isotope effect, which is described below.

The spectral data (Figure 1) show that there are two distinct steps in the reaction. The initial step is rapid (characterized by the shift from the blue line to the purple line, Figure 1) and could be followed when the reaction of **1·HH** and $PhCOO^-$ was conducted at 233 K. Absorption spectra resulting from the addition of varying quantities of $PhCOO^-$ to a solution of **1·HH** in CH_3CN at 233 K have been obtained (see the Supporting Information, Figure S3). Based on the resulting spectral changes at 460 nm, an absorption-spectrum-based titration graph for the reaction of **1·HH** with $PhCOO^-$ has been plotted (inset of Figure S3). The graph indicates that a 1:1 base adduct of **1·HH** is formed [Eq. (1)]. The formation constant (K) of the base adduct is estimated to be $7.8\times10^4\,M^{-1}$ [Eq. (2);[15] $[PhCOO^-]_0$ and $[\mathbf{1\cdot HH}]_0$ are the initial concentrations of $PhCOO^-$ and **1·HH**, respectively, and A is the absorbance associated with the base adduct at 460 nm]. The formation of the 1:1 base adduct has been confirmed using ESI mass spectrometry and ^1H NMR spectroscopy. Signals in the mass spectrum corresponding to the monocationic species derived from the base adduct, that is, $[Ru(bpy)_2(pbnHH)(PhCOO^-)]^+$ ($m/z = 794.2$), have been observed upon addition of 10 equivalents of $PhCOO^-$ to a CH_3CN solution of **1·HH** at 233 K; the observed natural-abundance isotope pattern agrees well with the simulated pattern (see the Supporting Information, Figure S4). The ^1H NMR spectrum of the mixture, which was prepared using the above-mentioned conditions and using CD_3CN as the solvent, has exhibited a singlet at 12.81 ppm, which is assigned to the benzoate-bound NH moiety of the 1:1 base adduct (see the Supporting Information, Figure S5). To estimate the oxidation potential of the base adduct $[Ru(bpy)_2(pbnHH)(PhCOO^-)]^+$, a cyclic voltammogram has been obtained and compared with that of **1·HH** at 233 K. The addition of 10 equivalents of $PhCOO^-$ to a CH_3CN solution of **1·HH** has resulted in a large negative shift of the oxidation peak potential associated with the pbnHH moiety (shift from 0.77 V versus Ag/Ag^+ to 0.15 V versus Ag/Ag^+; see the Supporting Information, Figure S6). This electrochemical behavior suggests that the benzoate anion adduct $[Ru(bpy)_2(pbnHH)(PhCOO^-)]^+$ is a much stronger reductant than the parent **1·HH**, thus explaining why the former is able to reduce CO_2 to HCO_2^-.



(1)

$$(\alpha^{-1}-1)^{-1} = K([PhCOO^-]_0-\alpha[\mathbf{1\cdot HH}]_0),\ \alpha = A-A_0/A_\infty-A_0 \qquad (2)$$

To investigate the organic hydride transfer mechanism, the kinetics of the second step, which is characterized by the spectral change from the purple to the red line in Figure 1 and involves a reaction between the base adduct $[Ru(bpy)_2(pbnHH)(PhCOO^-)]^+$ and CO_2, has been analyzed. Figure 2 shows a plot of absorption at 530 nm versus time for the reaction between **1·HH** and $PhCOO^-$ (10 equivalents) under a saturated CO_2 atmosphere at 293 K. The reaction has first-order kinetics, as shown by the graph in the inset of Figure 2. The pseudo-first-order rate constant ($k_{obs(530)}$) is almost

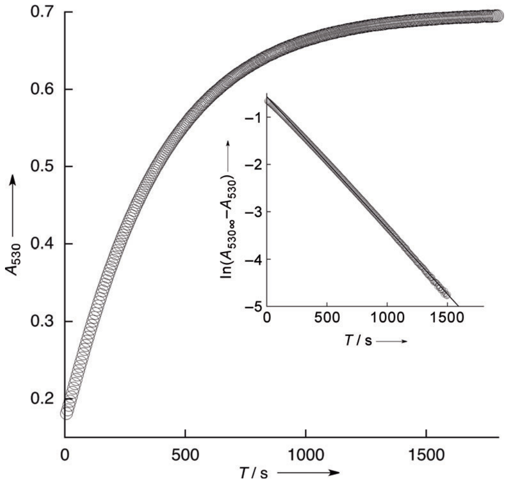


Figure 2. Absorbance (530 nm) versus time in the reaction of **1·HH** (1.0×10^{-4} M) and $PhCOO^-$ (10 equiv) under a saturated CO_2 atmosphere in CH_3CN at 293 K. Inset: first-order plot based on the absorbance values at 530 nm.

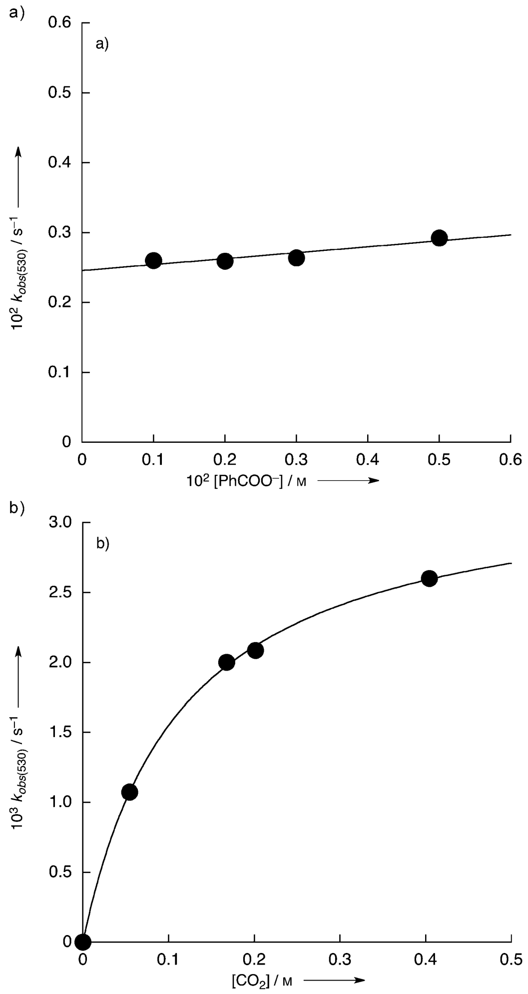
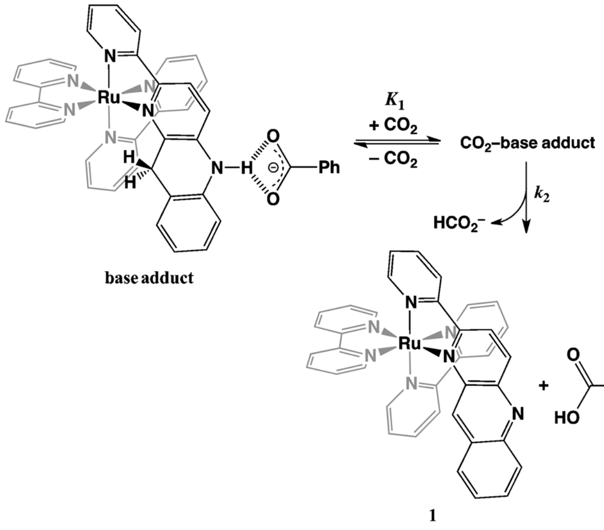


Figure 3. Plots of $k_{obs(530)}$ versus a) [PhCOO$^-$] and b) [CO$_2$] for the reaction of **1·HH**, PhCOO$^-$, and CO$_2$ in CH$_3$CN at 293 K.



(3)

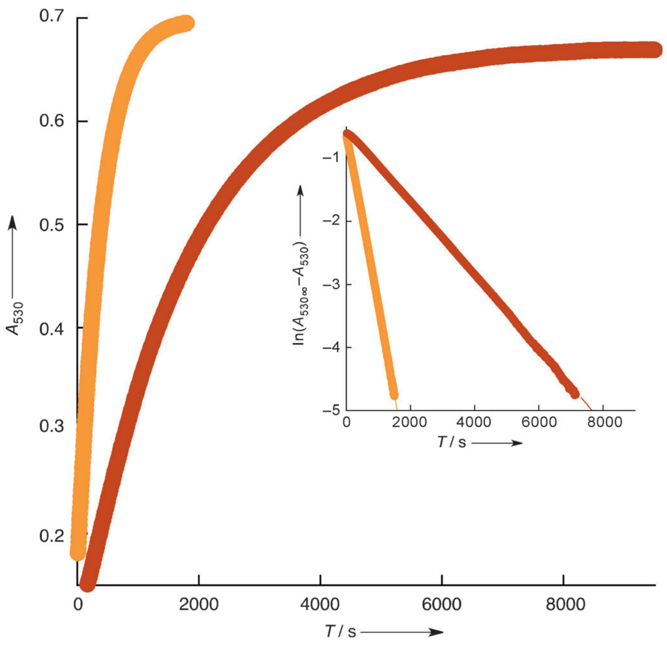


Figure 4. Absorbance (530 nm) versus time in the reactions of either **1·HH** (1.0×10^{-4} M; light-brown curve) or **1·DD** (1.0×10^{-4} M, deep-brown curve) and PhCOO$^-$ (10 equiv) under a saturated CO$_2$ atmosphere in CH$_3$CN at 293 K. Inset: first-order plots based on the absorbance values (530 nm) obtained for the reaction of **1·HH** (light-brown line) and **1·DD** (deep-brown line).

independent of the PhCOO$^-$ concentration,[16] and the plot of this pseudo-first-order rate constant versus CO$_2$ concentration exhibits a Michaelis—Menten-type saturation curve (Figure 3). The results clearly indicate that CO$_2$ and the base adduct form a complex in the course of the reaction [Eq. (3)]. After fitting the data to the equation $1/k_{obs(530)} = 1/k_2 + 1/(K_1 k_2)[CO_2]^{-1}$, the K_1 and k_2 values are determined ($K_1 = 8.7\,\text{M}^{-1}$ and $k_2 = 3.3\times10^{-3}\ \text{s}^{-1}$).[17] In addition, a large kinetic isotope effect (KIE) is found (Figure 4) by comparing the rate of reaction of **1·HH** ($k_{obs(530,\mathbf{1\cdot HH})} = 2.6\times10^{-3}\ \text{s}^{-1}$) and **1·DD** ($k_{obs(530,\mathbf{1\cdot DD})} = 5.6\times10^{-4}\ \text{s}^{-1}$).[17] The KIE ($k_{obs(530,\mathbf{1\cdot HH})}/k_{obs(530,\mathbf{1\cdot DD})}$) is calculated to be 4.6, and the large KIE value strongly indicates that the reduction of CO$_2$ to HCO$_2^-$ is a hydride-transfer reaction.[18]

The reduction of CO$_2$ by hydride transfer can be carried out using catalytic amounts of **1** when using photoirradiation. Irradiation (visible light, $\lambda > 450$ nm) of a solution of NAD$^+$ model complex **1** in CH$_3$CN, in the presence of PhCOO$^-$ (100 equivalents) and triethanolamine (TEOA, 5000 equivalents), the latter being a sacrificial reagent, under a saturated CO$_2$ atmosphere led to the generation of relatively large amounts of HCO$_2^-$ (1.25 times the amount of **1**) in comparison to that obtained using noncatalytic conditions (38.0 % yield based on **1·HH**). The large increase in HCO$_2^-$ yield can be due to a photodriven catalytic cycle that involves conversion of NAD$^+$ model complex **1** into NADH model complex **1·HH** through a photochemical two-electron reduction process.[14a]

In conclusion, we have demonstrated that CO$_2$ can be reduced to HCO$_2^-$ through hydride transfer involving C–H bond dissociation of the NADH model ligand in **1·HH** driven by the association of the base PhCOO$^-$ (Scheme 1). Moreover, we have also successfully developed a photocatalytic variant of the CO$_2$-reduction process, which involves photoinduced reduction of **1** to **1·HH**, a process that is similar to NAD$^+$/NADH interconversion. To the best of our knowledge, this is the first example of CO_2 reduction involving a renewable organic hydride.

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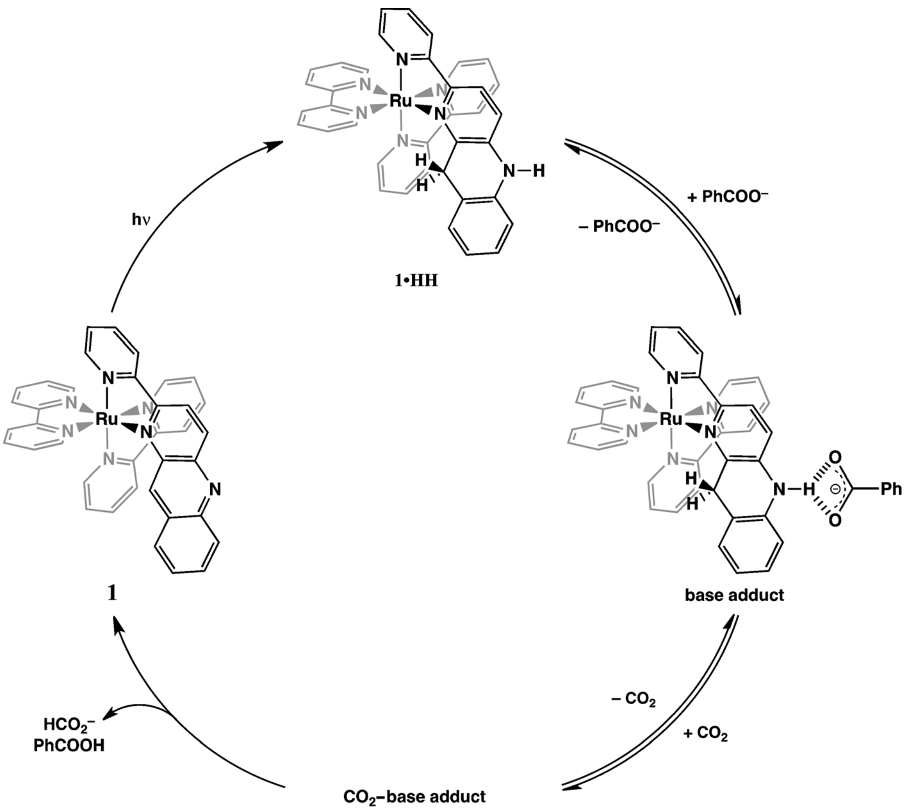

Scheme 1. Proposed mechanism for the photocatalytic reduction of CO_2 in the presence of the NADH model complex.

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[16] This result indicates that the initial rapid spectral change in this reaction is due to an equilibrium involving **1·HH** and the base adduct $[Ru(bpy)_2(pbnHH)(PhCOO^-)]^+$; this is consistent with the considerably large formation constant ($K = 7.8 \times 10^4\,M^{-1}$), as described herein.

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