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Mechanism of a one-photon two-electron process in photocatalytic hydrogen evolution from ascorbic acid with a cobalt chlorin complex†

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A one-photon two-electron process was made possible in photocatalytic H₂ evolution from ascorbic acid with a cobalt(II) chlorin complex [Co^{II}(Ch)] via electron transfer from ascorbate to the excited state of [Ru(bpy)₃]²⁺ followed by electron transfer from [Ru(bpy)₃]⁺ to Co^{II}(Ch) with proton to give the hydride complex, which reacts with proton to produce H₂. [Co^{III}(Ch)]⁺ was reduced by ascorbate to reproduce Co^{II}(Ch).

Photocatalytic production of hydrogen (H₂) has attracted increasing attention as a clean energy source because of the ever-increasing demand for energy and climate change on our planet.¹ A number of highly efficient hydrogen evolving systems have been developed including homogeneous and heterogeneous photocatalytic systems.^{2–13} Two electrons are required to produce H₂ from protons, although one photon generates normally only one electron. A mechanism of photocatalytic production of H₂ was reported to clarify how photoinduced electron transfer of a photosensitizer (a one-electron process) leads to H₂ production (a two-electron process).^{14–16} Disproportionation of one-electron reduced species of metal complexes resulted in formation of the two-electron reduced species from which H₂ is formed.¹⁷ Bimolecular reactions of metal(III)–hydride complexes also generate H₂ accompanied by regeneration of metal(II) complexes.¹⁸ In each case, the maximum quantum yield of H₂ production per photon is 50%, because two photons are required to produce two electrons. Thus there has so far been no example for one photon to generate one H₂ molecule.

We report herein photocatalytic H₂ evolution from ascorbic acid (AsCH₂) with a cobalt(II) chlorin complex [Co^{II}(Ch)] (a chemical structure shown in Scheme 1)¹⁹ in an aqueous acetonitrile solution (H₂O/MeCN), which proceeds *via* a one-photon two-electron process. The photocatalytic mechanism is clarified by nano-second laser transient absorption spectra and by examining each step in the catalytic cycle independently.

Visible light irradiation of a deaerated (Ar-saturated) H₂O/MeCN solution (1 : 1 v/v) of [Ru(bpy)₃]²⁺ (bpy = 2,2′-bipyridine) containing ascorbic acid (AsCH₂) and ascorbate (AsCH₂[−]) (*E*_{ox} = 0.43 V vs. SCE) as an electron donor and Co^{II}(Ch) (*E*_{red} = −0.96 V vs. SCE) (Fig. S1 in the ESI†) as a catalyst resulted in H₂ evolution (Fig. 1, black line). When the ratio of AsCH₂[−] to AsCH₂ was changed as fixed total concentrations of AsCH₂ and AsCH₂[−] ([AsCH₂] + [AsCH₂[−]] = 1.1 M), the largest H₂ evolution activity was attained with AsCH₂[−] (0.30 M) and AsCH₂ (0.80 M) (Fig. S2 in ESI†). The smaller concentration of AsCH₂[−] results in less efficient reductive quenching of the [Ru(bpy)₃]²⁺* emission (* denotes the excited state).

Fig. 1 Time courses of H₂ evolution in the photocatalytic reduction of proton in an Ar-saturated H₂O/MeCN (black) and D₂O/MeCN (red) mixed solution (1 : 1 v/v) containing [Ru^{II}(bpy)₃]²⁺ (2.0 mM), AsCH₂ (0.80 M), AsCH₂Na (0.30 M) and Co^{II}(Ch) (25 μM) under irradiation of visible light (λ > 420 nm) at 298 K.

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The quenching efficiency of $[\text{Ru}(\text{bpy})_3]^{2+*}$ ($E_{\text{red}} = 0.77$ V vs. SCE in MeCN)²⁰ by AsCH^- (0.30 M) with AsCH_2 (0.80 M) was determined to be 95% (Fig. S3 in ESI†). On the other hand, the smaller concentration of AsCH_2 may retard H_2 production due to decreasing the acidity. When H_2O was replaced by D_2O , D_2 and HD were produced without formation of H_2 . Thus, hydrogen was produced from water and ascorbic acid as electron and proton sources. The observed deuterium kinetic isotope effect (KIE) in Fig. 1 ($k_{\text{H}}/k_{\text{D}} = 1.8$ in the initial stage) suggests that the Co–H bond cleavage of a cobalt hydride intermediate ($[\text{Co}^{\text{III}}(\text{H})(\text{Ch})]$) by proton may be the rate-determining step for the photocatalytic H_2 evolution (*vide infra*).

The concentration of $\text{Co}^{\text{II}}(\text{Ch})$ was optimised to be 50 μM for the efficient photocatalytic H_2 evolution. The absorption of $[\text{Ru}(\text{bpy})_3]^{2+}$ is blocked by the larger concentration of $\text{Co}^{\text{II}}(\text{Ch})$ (Fig. S4 in ESI†).²¹ The quantum yield of the photocatalytic H_2 evolution was determined to be 12% using a ferric oxalate actinometer (see the Experimental section in ESI†). This value is similar to the highest value reported for photocatalytic H_2 evolution using a cobalt terpyridine complex ($\Phi = 0.13$).²²

Nanosecond transient absorption spectra of an $\text{H}_2\text{O}/\text{MeCN}$ solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ with AsCH_2 and AsCH^- are shown in Fig. 2, where appearance of the absorption band at 500 nm due to $[\text{Ru}(\text{bpy})_3]^+$ is observed upon the nanosecond laser excitation. Thus, electron transfer from AsCH^- to $[\text{Ru}(\text{bpy})_3]^{2+*}$ occurred to produce $\text{AsCH}^\bullet$ and $[\text{Ru}(\text{bpy})_3]^+$. The rate constant of electron transfer from AsCH^- to $[\text{Ru}(\text{bpy})_3]^{2+*}$ (k_{et}) was determined to be $8.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ from a slope of Stern–Volmer plot ($K_{\text{SV}} = 3.5 \times 10^2 \text{ M}^{-1}$) and the lifetime of $[\text{Ru}(\text{bpy})_3]^{2+*}$ (0.44 μs in water/MeCN 1:1 v/v) (Fig. S5 in ESI†).²³ The decay rate of absorbance at 500 nm due to $[\text{Ru}(\text{bpy})_3]^+$ obeyed the second-order kinetics of bimolecular back electron transfer from $[\text{Ru}(\text{bpy})_3]^+$ to $\text{AsCH}^\bullet$. In the presence of $\text{Co}^{\text{II}}(\text{Ch})$, the decay of absorbance became much faster because of electron transfer from $[\text{Ru}(\text{bpy})_3]^+$ to $\text{Co}^{\text{II}}(\text{Ch})$ as shown in Fig. 2b. The decay rate constant linearly increased with increasing the concentration of $[\text{Co}^{\text{II}}(\text{Ch})]$ (Fig. S6 in ESI†). The rate constant of electron transfer from $[\text{Ru}(\text{bpy})_3]^+$ to $\text{Co}^{\text{II}}(\text{Ch})$ was determined to be $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ from the slope of dependence of the first-order decay rate constant on concentration of $\text{Co}^{\text{II}}(\text{Ch})$ (Fig. S6b in ESI†).

Fig. 2 (a) Transient absorption spectra after laser excitation ($\lambda = 450$ nm) of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ (80 μM) in the presence of AsCH_2 (0.80 M) and AsCHNa (0.30 M) in a deaerated $\text{H}_2\text{O}/\text{MeCN}$ mixed solution (1:1 v/v) at 298 K. (b) Time profiles of absorbance at 500 nm due to decay of $[\text{Ru}(\text{bpy})_3]^+$ in the presence of various concentrations of $\text{Co}^{\text{II}}(\text{Ch})$ (0–20 μM) in deaerated $\text{H}_2\text{O}/\text{MeCN}$ mixed solutions (1:1 v/v) containing $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ (80 μM), AsCH_2 (0.80 M), AsCHNa (0.30 M).

Fig. 3 (a) UV-vis absorption spectral changes of $[\text{Co}^{\text{I}}(\text{Ch})]^-$ (30 μM) upon addition of CH_3COOH (0.30 M) in deaerated MeCN at 298 K. The black and blue lines show the spectra taken at 66 ms and 1 s after mixing, respectively. The red line shows UV-vis absorption spectrum of $[\text{Co}^{\text{I}}(\text{Ch})]^-$ (15 μM) formed by the electron-transfer reduction of $\text{Co}^{\text{II}}(\text{Ch})$ (15 μM) with CoCp_2^* (300 μM) in deaerated MeCN at 298 K. (b) Plot of k_{obs} for the rate of formation of $[\text{Co}^{\text{III}}(\text{Ch})]^+$ vs. $[\text{CH}_3\text{COOH}]$.

To examine the reaction of $[\text{Co}^{\text{I}}(\text{Ch})]^-$ that is produced by electron transfer from $[\text{Ru}(\text{bpy})_3]^{2+}$ to $\text{Co}^{\text{II}}(\text{Ch})$, $[\text{Co}^{\text{I}}(\text{Ch})]^-$ was prepared by the one-electron reduction of $\text{Co}^{\text{II}}(\text{Ch})$ by decamethylcobaltocene $[\text{Co}(\text{Cp}^*)_2]$ in MeCN (Fig. S7 in ESI†). The UV-vis absorption band of $[\text{Co}^{\text{I}}(\text{Ch})]^-$ (red line in Fig. 3a; $\lambda_{\text{max}} = 510$ nm) decreased with increasing absorption band at 660 nm (black line) at 66 ms after addition of acetic acid (CH_3COOH) (0.30 M). Then, this absorption band was finally blue shifted to $\lambda_{\text{max}} = 652$ nm, which is due to $[\text{Co}^{\text{III}}(\text{Ch})]^+$.^{24,25} Thus, $[\text{Co}^{\text{I}}(\text{Ch})]^-$ may react with CH_3COOH to form the hydride complex ($[\text{Co}^{\text{III}}(\text{H})(\text{Ch})(\text{CH}_3\text{COO})]^-$; $\lambda_{\text{max}} = 660$ nm), from which H_2 was evolved by the reaction with CH_3COOH to produce $[\text{Co}^{\text{III}}(\text{Ch})]^+$. The reaction of $[\text{Co}^{\text{I}}(\text{Ch})]^-$ with CH_3COOH was monitored by the absorption change at 652 nm due to $[\text{Co}^{\text{III}}(\text{Ch})]^+$ as shown in Fig. 3, where the rate of the formation of $[\text{Co}^{\text{III}}(\text{Ch})]^+$ obeyed first-order kinetics (Fig. S8 in ESI†). The first-order rate constant increased with increasing concentration of CH_3COOH to approach a constant value (Fig. 3b). Such a saturation behaviour indicates that CH_3COOH is not involved in the rate-determining step and that the reaction of $[\text{Co}^{\text{I}}(\text{Ch})]^-$ with CH_3COOH proceeds *via* formation of the hydride complex ($[\text{Co}^{\text{III}}(\text{H})(\text{Ch})(\text{CH}_3\text{COO})]^-$), followed by the rate-determining heterolytic cleavage of the $\text{Co}^{\text{III}}\text{–H}$ bond. The subsequent reaction of the released hydride ion with CH_3COOH to produce H_2 and $[\text{Co}^{\text{III}}(\text{Ch})]^+$ may be fast as compared with the back reaction of the $\text{Co}^{\text{III}}\text{–H}$ bond cleavage (Scheme 1). The kinetic equation for the formation of $[\text{Co}^{\text{III}}(\text{Ch})]^+$ is given by eqn (1),

Scheme 1 Mechanism of hydrogen formation by the reaction of $[\text{Co}^{\text{I}}(\text{Ch})]^-$ with CH_3COOH .

$$d[\text{Co}^{\text{III}}(\text{Ch})^+]/dt = k[\text{Co}^{\text{III}}(\text{H})(\text{Ch})(\text{CH}_3\text{COO})^-] \quad (1)$$

where k is the rate constant of the hydrogen evolution. From the equilibrium constant (K), the concentration of a complex between $[\text{Co}^{\text{I}}(\text{Ch})]^-$ and CH_3COOH is given by eqn (2), where

$$[\text{Co}^{\text{III}}(\text{H})(\text{Ch})(\text{CH}_3\text{COO})^-] = K[\text{CH}_3\text{COOH}][[\text{Co}^{\text{I}}(\text{Ch})]^-]_0 - [\text{Co}^{\text{III}}(\text{Ch})^+]/(1 + K[\text{CH}_3\text{COOH}]) \quad (2)$$

$[\text{Co}^{\text{I}}(\text{Ch})]^-$ is the initial concentration. Eqn (1) is rewritten by eqn (3).

$$d[\text{Co}^{\text{III}}(\text{Ch})^+]/dt = kK[\text{CH}_3\text{COOH}][[\text{Co}^{\text{I}}(\text{Ch})]^-]_0 - [\text{Co}^{\text{III}}(\text{Ch})^+]/(1 + K[\text{CH}_3\text{COOH}]) \quad (3)$$

Under the conditions, the concentration of CH_3COOH is much higher than that of $[\text{Co}^{\text{I}}(\text{Ch})]^-$, the k_{obs} value is given by eqn (4). To determine the k value, eqn (4) is rewritten by eqn (5), which predicts

$$k_{\text{obs}} = kK[\text{CH}_3\text{COOH}]/(1 + K[\text{CH}_3\text{COOH}]) \quad (4)$$

$$k_{\text{obs}}^{-1} = 1/kK \cdot [\text{CH}_3\text{COOH}]^{-1} + 1/k \quad (5)$$

a linear correlation between k_{obs}^{-1} and $[\text{CH}_3\text{COOH}]^{-1}$ (Fig. S9 in ESI†). The k and K values were determined from the intercept and slope of the linear plot of k_{obs}^{-1} vs. $[\text{CH}_3\text{COOH}]^{-1}$ to be 5.9 s^{-1} and 7.1 M^{-1} .

When CH_3COOH was replaced by CH_3COOD , the deuterium kinetic isotope effect (KIE) was observed (Fig. S10 in ESI†),²⁶ indicating that the cleavage of the Co–H bond of $[\text{Co}^{\text{III}}(\text{H})(\text{Ch})(\text{CH}_3\text{COO})^-]$ or O–H bond of CH_3COOH is involved in the rate-determining step of the reaction of $[\text{Co}^{\text{I}}(\text{Ch})]^-$ with CH_3COOH . Because CH_3COOH is not involved in the rate-determining step (*vide infra*), the cleavage of the Co–H bond of $[\text{Co}^{\text{III}}(\text{H})(\text{Ch})(\text{CH}_3\text{COO})^-]$ is the rate-determining step of the reaction of $[\text{Co}^{\text{I}}(\text{Ch})]^-$ with CH_3COOH . The KIE value was 1.7 which is virtually the same as observed for the photocatalytic H_2 evolution (KIE = 1.8, Fig. 1), indicating that the heterolytic Co–H bond cleavage of $[\text{Co}^{\text{III}}(\text{H})(\text{Ch})(\text{CH}_3\text{COO})^-]$ is also the rate-determining step in the photocatalytic H_2 evolution.

Scheme 2 Mechanism of photocatalytic hydrogen evolution from AscH^- and AscH_2 with $[\text{Ru}(\text{bpy})_3]^{2+}$ and $\text{Co}^{\text{II}}(\text{Ch})$.

$[\text{Co}^{\text{III}}(\text{Ch})]^+$ produced by the reaction of $[\text{Co}^{\text{III}}(\text{H})(\text{Ch})(\text{CH}_3\text{COO})^-]$ with CH_3COOH is reduced by AscH^- to form $\text{Co}^{\text{II}}(\text{Ch})$ as shown by stopped-flow measurements in Fig. 4.²⁷ The rate constant of electron transfer from AscH^- to $[\text{Co}^{\text{III}}(\text{Ch})]^+$ that was prepared by the one-electron oxidation of $\text{Co}^{\text{II}}(\text{Ch})$ with $(p\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6^-$ in $\text{H}_2\text{O}/\text{MeCN}$ was determined to be $1.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ from the linear dependence of the first-order rate constant on concentration of AscH^- (Fig. S11 in ESI†).

The photocatalytic cycle is summarized in Scheme 2. Photoexcitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ resulted in electron transfer from AscH^- to $[\text{Ru}(\text{bpy})_3]^{2+*}$ to produce $[\text{Ru}(\text{bpy})_3]^+$, followed by electron transfer from $[\text{Ru}(\text{bpy})_3]^+$ to $\text{Co}^{\text{I}}(\text{Ch})$ to produce $[\text{Co}^{\text{I}}(\text{Ch})]^-$, which reacts with AscH_2 to produce $[\text{Co}^{\text{III}}(\text{H})(\text{Ch})(\text{AscH})^-]$. Hydrogen is generated by the reaction of $[\text{Co}^{\text{III}}(\text{H})(\text{Ch})(\text{AscH})^-]$ with AscH_2 via the Co–H bond heterolysis to produce $[\text{Co}^{\text{III}}(\text{Ch})]^+$,^{28,29} which is reduced by AscH^- to regenerate $\text{Co}^{\text{II}}(\text{Ch})$. In such a case, a one-photon two-electron process is made possible, because one photon is required to produce $[\text{Co}^{\text{I}}(\text{Ch})]^-$ for H_2 evolution and another electron is provided thermally by AscH^- .

In conclusion, $\text{Co}^{\text{II}}(\text{Ch})$ acts as an efficient catalyst for photocatalytic H_2 evolution from ascorbic acid with $[\text{Ru}(\text{bpy})_3]^{2+}$ as a photocatalyst to attain the high quantum yield via a one-photon two-electron process in which the second electron is provided thermally from ascorbic acid.

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Fig. 4 (a) UV-vis absorption spectral changes in the electron-transfer reduction of $[\text{Co}^{\text{III}}(\text{Ch})]^+$ ($15 \mu\text{M}$) with AscHNa (50 mM) in air-saturated $\text{H}_2\text{O}/\text{MeCN}$ mixed solutions ($1:1 \text{ v/v}$) at 298 K taken at 70 ms and 118 ms after mixing. (b) Decay time profiles of absorbance at 652 nm due to $[\text{Co}^{\text{III}}(\text{Ch})]^+$ in the presence of various concentrations of AscHNa in air-saturated $\text{H}_2\text{O}/\text{MeCN}$ mixed solutions ($1:1 \text{ v/v}$) at 298 K .

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- 24 The spectrum of [Co^{III}(Ch)]⁺ obtained by the reaction [Co^I(Ch)]⁻ with CH₃COOH was identical to that of [Co^{III}(Ch)]⁺ prepared by the electron-transfer oxidation of Co^{II}(Ch) by a one-electron oxidizing reagent of (*p*-BrC₆H₄)₃N⁺SbCl₆⁻ ($E_{\text{red}} = 1.05 \text{ V vs. SCE}$).¹⁹
- 25 [Co^{III}(Ch)]⁺ or Co^{III}(H)(Ch) species is not re-reduced by large excess of Co(Cp^{*})₂, under the present reaction conditions because Co^{II}(Ch) with 20 molar equiv. of Co(Cp^{*})₂ is necessary to quantitatively produce [Co^I(Ch)]⁻ as shown in ESI,† Fig. S7. Co(Cp^{*})₂ ($E_{1/2}^{+/0} = -1.47 \text{ V vs. SCE}$) is unstable even in carefully degassed and dehydrated MeCN.
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