Extraction of Electrons from H_2 with a Ni^IRu^I Catalyst

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The mechanism of extraction of electrons from H_2 catalyzed by hydrogenases has proven challenging to elucidate. Catalytic extraction of electrons from H_2 has been achieved by use of a low-valent Ni^IRu^I complex $[Ni^I(\mu\text{-SR})_2Ru^I(\eta^6\text{-}C_6Me_6)]$ {$(\mu\text{-SR})_2$ = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine} as the active catalyst with evolution of H_2 under ambient conditions. The electrons extracted from H_2 have been used for a catalytic reduction of Cu^{2+} to Cu^0 with the NiRu complexes.

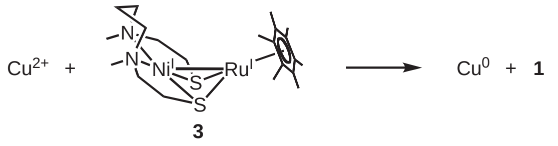
Hydrogenases (H_2ases) are enzymes that catalyze the activation of H_2 into two protons and two electrons under ambient conditions (eq 1).[1–4] Hydrogen isotope exchange experiments implicate as a first step the heterolytic cleavage of H_2 into a proton and a hydride ion (eq 1).[1] Extraction of electrons from H_2 with metal hydride species (MH) has been investigated by Halpern and James,[5] Hembre and co-workers,[6] Collman and co-workers,[7] and other groups.[8]

$$H_2 \rightarrow H^+ + H^- \rightarrow 2H^+ + 2e^- \qquad (1)$$

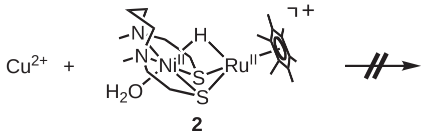
Recently, we showed a heterolytic activation of H_2 and a subsequent hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes with a $Ni^{II}Ru^{II}$ aqua complex $[Ni^{II}(\mu\text{-SR})_2Ru^{II}(H_2O)(\eta^6\text{-}C_6Me_6)](NO_3)_2$ {**1**, $(\mu\text{-SR})_2$ = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine}, a $Ni^{II}Ru^{II}$ hydride complex $[Ni^{II}(OH_2)(\mu\text{-SR})_2(\mu\text{-H})Ru^{II}(\eta^6\text{-}C_6Me_6)](NO_3)$ (**2**), and a low-valent Ni^IRu^I complex $[Ni^I(\mu\text{-SR})_2Ru^I(\eta^6\text{-}C_6Me_6)]$ (**3**) in water at pH 4–6 under ambient conditions (23 °C, 0.1 MPa).[9,10] However, the extraction of electrons from H_2 was not achieved.

Here, we report the successful catalytic extraction of electrons from H_2 by use of the low-valent Ni^IRu^I complex **3** as the active catalyst with evolution of H_2 under ambient conditions. The extracted electrons are used for the reduction of Cu^{2+} to Cu^0 {$E^\circ(Cu^{2+}/Cu^0) = 0.340$ V vs. NHE}.

In the absence of H_2, under stoichiometric conditions, the low-valent complex **3** (20 μmol) reacted with $Cu(CF_3SO_3)_2$ (20 μmol) at 23 °C to give Cu^0 in acetonitrile under conditions without the formation of **2** (eq 2), whereas the hydride complex **2** did not react with Cu^{2+} in acetonitrile or water (eq 3). Figure 1a shows the result of a reaction of **3** with Cu^{2+} to give **1** (or the corresponding acetonitrile complex) and Cu^0. It was confirmed by X-ray photoelectron spectrum (XPS) that the binding energy (Cu $2p_{3/2}$) of the obtained Cu^0 is 932.0 eV, which corresponds to Cu^0 (Figure S1 in Supporting Information).[11]



(2)



(3)

In the presence of H_2 (0.1 MPa, 47.5 μmol), under stoichiometric conditions, the aqua complex **1** (5 μmol) reacted with $CuSO_4 \cdot 5H_2O$ (5 μmol) in D_2O (100 mmol) at pD 4 at 23 °C ($\mathbf{1}/Cu^{2+}/H_2/D_2O = 1/1/9.5/20000$) to give Cu^0 together with the consumption of H_2 and the generation of D_2 and HD, which were determined by GC analysis. Figure 1b shows the time-dependent changes of the moles (|Δμmol|) of the consumption of H_2 and the generation of D_2 and Cu^0 in the reaction of **1** with Cu^{2+} in D_2O at pD 4 at 23 °C in the presence of H_2.[12] It is important to note that the ratio of the changes of the moles (|Δμmol|) of H_2, D_2, and Cu^0 are ca. 2:1:1 as shown in Figure 1b.

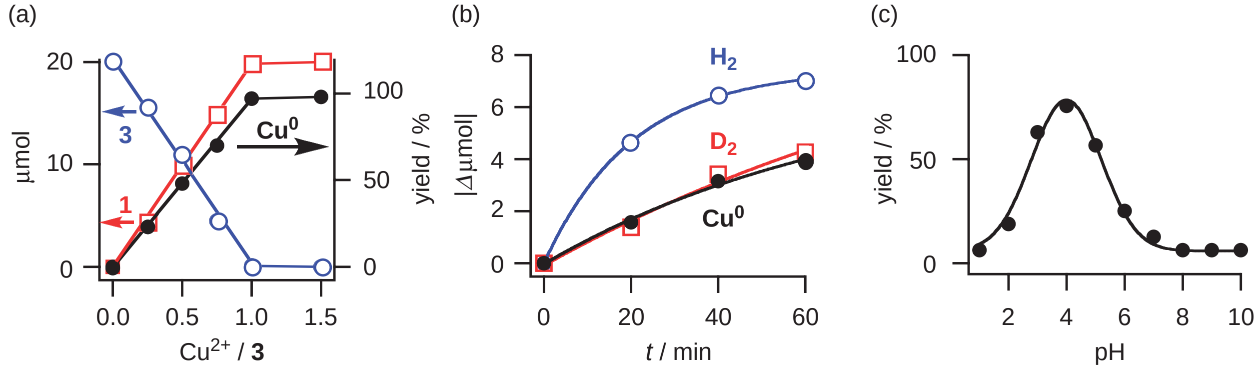
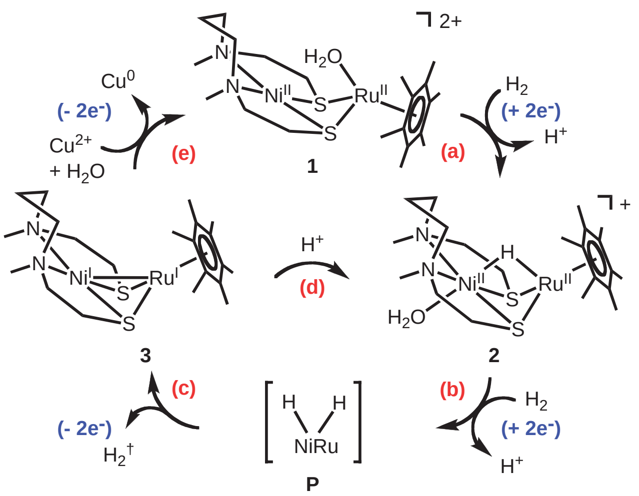


Figure 1. (a) Reaction of **3** (20 μmol) with $Cu(CF_3SO_3)_2$ (0, 5, 10, 15, 20, and 30 μmol) in acetonitrile at 23 °C in the absence of H_2 to give **1** (or the corresponding acetonitrile complex) and Cu^0. (b) Time-dependent changes of the moles (|Δμmol|) of the consumption of H_2 and the generation of D_2 and Cu^0 in the reaction of **1** (5 μmol) with $CuSO_4 \cdot 5H_2O$ (5 μmol) in D_2O (100 mmol) at pD 4 at 23 °C in the presence of H_2 (0.1 MPa, 47.5 μmol).[12] (c) pH-dependent yields of Cu^0 in the reaction of **1** (5 μmol) with $CuSO_4 \cdot 5H_2O$ (5 μmol) in H_2O (100 mmol) at pH 1–10 at 23 °C for 1 h in the presence of H_2 (0.1 MPa, 47.5 μmol).



Scheme 1. A proposed mechanism for the catalytic reduction of Cu^{2+} to Cu^0 with NiRu complexes in water at pH 4–6 at 0.1 MPa of H_2. (**a**): Heterolytic activation of H_2 (see ref 9). (**b**): Heterolytic activation of H_2. (**c**): Reductive elimination of H_2. (**b**, **c**, and **d**): H_2/D_2O isotope exchange (see ref 10).[13] (**e**): Reduction of Cu^{2+} to Cu^0 (this work). $H_2^\dagger$: Isotope labeled hydrogen gas (see Scheme S1 in Supporting Information).[11]

In the presence of H_2 (0.1–0.8 MPa), under catalytic conditions (**1**/Cu^{2+}/H_2O = 1/200/20000), electrons were extracted from H_2 to reduce $CuSO_4 \cdot 5H_2O$ to Cu^0. The catalytic conditions for the reduction of Cu^{2+} to Cu^0 were optimized for reaction time (Figure S2),[11] reaction temperature (Figure S3),[11] and pressure of H_2 (Figure S4).[11] Turn over numbers (TONs: mol of Cu^0/mol of **1**) of the reduction of Cu^{2+} increased with increased reaction time, reaction temperature, and pressure of H_2.

Figure 1c shows the pH-dependent yields of Cu^0 in the reaction of **1** (5 µmol) and $CuSO_4 \cdot 5H_2O$ (5 µmol) with H_2 (0.1 MPa, 47.5 µmol) in H_2O (100 mmol) at pH 1–10 at 23 °C for 1 h (**1**/Cu^{2+}/H_2/H_2O = 1/1/9.5/20000), which indicates a maximum around pH 4. It was confirmed that no reduction of Cu^{2+} occurred at pH 4 in the absence of **1** or H_2 (as blank experiments shown in Figure S5).[11] The pH-dependence of the catalytic reduction of Cu^{2+} is similar to the pD-dependence of the hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes.[10]

A proposed mechanism for the catalytic cycle of the reduction of Cu^{2+} to Cu^0 with the NiRu complexes in the presence of H_2 in water at pH 4–6 is shown in Scheme 1. H_2 is heterolytically activated twice. The first heterolytic activation of H_2 with **1** (**a** in Scheme 1) gave the hydride complex **2**.[9] The second heterolytic activation of H_2 with **2** (**b** in Scheme 1) resulted in formation of **3** via a reductive elimination of hydrido ligands of a dihydride species **P** (**c** in Scheme 1).[10] The formation of H_2 (**c** in Scheme 1) was confirmed by isotope-labeling experiments (Scheme S1 in Supporting Information).[11] Complex **1** is regenerated by a reduction of Cu^{2+} to Cu^0 with **3** (**e** in Scheme 1) to complete the catalytic cycle. Thus, four electrons derived from H_2 are introduced into the $Ni^{II}Ru^{II}$ complexes **1** and **2** (**a** and **b** in Scheme 1). The evolving H_2 removes two electrons from the dihydride species **P** (**c** in Scheme 1). The remaining two electrons of the Ni^IRu^I complex **3** are released to reduce Cu^{2+} to Cu^0 (**e** in Scheme 1).

In conclusion, we have succeeded in the catalytic extraction of electrons from H_2 by use of the low-valent Ni^IRu^I complex **3** as the active catalyst with evolution of H_2 for the first time. The extracted electrons were used for the reduction of Cu^{2+} to Cu^0. In place of the two electron system of eq 1, the four electron system of this study is described as eq 4 with omission of the NiRu catalysts. The present study should provide a valuable insight into the elucidation of the mechanism of the action of H_2ases.

$$2H_2 \rightarrow 2H^+ + 2H^- \rightarrow 2H^+ + 2e^- + H_2 \qquad (4)$$

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12 Although both D_2 and HD were generated (the ratio of D_2/HD is ca. 10:1), only the dominant product, D_2, was plotted in Figure 1b.
13 The mechanism for the hydrogen isotope exchange reaction is shown in Scheme S1 in Supporting Information.[11] The detailed mechanism of the hydrogen isotope exchange reaction has been described in Ref. 10.