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Evidence for Pt(II)-Based Molecular Catalysis in the Thermal Reduction of Water into Molecular Hydrogen

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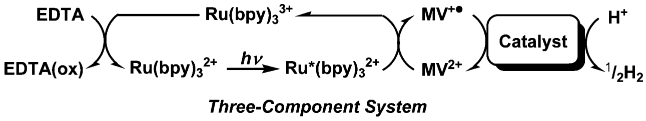
Visible-light-induced water splitting has received considerable attention from the viewpoint of solar energy conversion and hydrogen energy storage. Photocatalysis based on dispersion of heterogeneous semiconductor particles has been considered as one of the promising candidates for practical use in the future because of the high robustness of these particles under strong light illumination.[1] Nevertheless, it is important to control the chemical conversion processes at the molecular level in order to achieve highly efficient catalytic cycles like those established in nature. In this context, we have made continuous efforts to better understand Pt(II)-based molecular catalysis of the H_2-evolving cycle, since particular Pt(II) complexes have been rare examples of molecular catalysts sufficiently active toward H_2 formation in aqueous media.[2] Several Co, Ni, Rh, and Ir complexes,[3a−d] and hydrogenase[3e] have also been investigated as molecular catalysts for H_2 formation.

Scheme 1. Photochemical H_2 Production from Water



The well-known three-component system (Scheme 1) made up of $Ru(bpy)_3^{2+}$ (photosensitizer), methylviologen (MV^{2+}; electron relay), and an H_2-evolving catalyst (e.g., colloidal platinum) was originally examined by Kirch, Lehn, and Sauvage[4a] and also by Grätzel and co-workers.[4b] We originally discovered that amidate-bridged *cis*-diammineplatinum(II) dimers $[Pt^{II}_2(NH_3)_4(\mu\text{-amidato})_2]^{2+}$ (amidate = α-pyridonate, acetamidate, etc.) serve as H_2-evolving catalysts in the three-component system in the presence of a sacrificial electron donor (EDTA) at pH 5.0.[2a−c] We also confirmed that mere dissolution of these $Pt(II)_2$ dimers into aqueous media in the dark results in evolution of H_2, although the amount of H_2 evolved was less than that expected from a stoichiometric reaction (∼4−11% yield).[2b] With the same photosystem (Scheme 1), the H_2-evolving activities of a large variety of mononuclear and dinuclear Pt(II) complexes have also been examined to date in our group.[2h] In this photosystem, H_2-evolving catalysts must be capable of promoting the reduction of water by $MV^{+\bullet}$ into H_2 at pH 5.0 with a driving force of ∼150 mV, which corresponds to the difference between the redox potentials of $MV^{2+}/MV^{+\bullet}$ (−690 mV vs SCE)[5] and $2H^+/H_2$ (−540 mV vs SCE at pH 5.0). We also demonstrated that an organized system obtained from a covalent linkage of a $Ru(bpy)_3^{2+}$ derivative and an H_2-evolving $PtCl_2(bpy)$ derivative exhibits "photo-hydrogen-evolving" activity in the presence of EDTA at pH 5.0.[2e,g] Through studies of such Ru(II)Pt(II)-based molecular devices, we also became convinced that some Pt(II) complexes are indeed active as H_2-evolving catalysts, since a mere mixture of EDTA, $Ru(bpy)_3^{2+}$, and colloidal platinum never leads to photoinduced hydrogen production from water (data not shown).

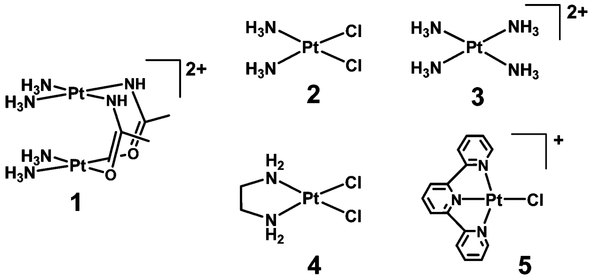
On the other hand, some reports have recently pointed out that the photodecomposition products, such as colloidal metal particles obtained from Pt(II)- or Pd(II)-based molecular systems, might play a major role in the catalysis of H_2 formation.[6] However, we think it is still important to further investigate the catalytic activity of the molecular species itself *in solution*. In order to obtain more direct evidence for the H_2-evolving activity of the Pt(II)-based molecular catalysts, it is highly important to investigate the thermal reduction of water into molecular hydrogen catalyzed by such molecular systems in the dark.

In this communication, it is unambiguously demonstrated that Pt(II)-based hydrogenic activation indeed proceeds as a thermal process. This has been done through studies of the reduction of water into molecular hydrogen by electrochemically generated $MV^{+\bullet}$ (eq 1) in the presence of mononuclear and dinuclear platinum(II) complexes **1**−**5** (see Scheme 2), as shown in eq 2:

$$MV^{2+} + e^- \xrightarrow{\text{Electrolysis}} MV^{+\bullet} \qquad (1)$$

$$2MV^{+\bullet} + 2H^+ \xrightarrow[\text{Molecular Catalyst}]{\text{Pt(II)-based}} 2MV^{2+} + H_2 \qquad (2)$$

Scheme 2. Mononuclear and Dinuclear Platinum(II) Complexes Employed in This Study



$MV^{+\bullet}$ generated in situ by a controlled-potential electrolysis was reacted with each Pt(II)-based molecular catalyst. Each reaction was conducted under an Ar atmosphere, since $MV^{+\bullet}$ is readily quenched by O_2 via the formation of superoxide anion: $MV^{+\bullet} + O_2 \rightarrow MV^{2+} + O_2^{-\bullet}$.[7] The reaction was initiated by the stopped-flow technique and monitored by the decay at 602 nm, which corresponds to the maximum absorption wavelength of $MV^{+\bullet}$.[5] Although similar rapid-mixing experiments were carried out for H_2 production catalyzed by colloidal platinum,[8] this is the first such study for the molecular catalysts. Since Lee et al.[9] reported that $MV^{+\bullet}$ gives a dimer in aqueous media with a dimerization constant (K_d) of 660 M^{-1} at 21 °C, the relative abundance of the dimer $(MV^{+\bullet})_2$ at the total $MV^{+\bullet}$ concentration of 0.05 mM was estimated as ∼6%. Therefore, the monomeric species (i.e., $MV^{+\bullet}$) is the major species in the stopped-flow experiments. Unexpectedly, the decay of $MV^{+\bullet}$ was promoted even in the absence of an H_2-evolving

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catalyst with the use of the stopped-flow apparatus [see Figure 1a and Figure S1a in the Supporting Information (SI)]. This component (i.e., blank decay) was found to obey the autocatalysis mechanism and could not be eliminated, presumably because of the presence of unavoidable contamination within the stopped-flow apparatus (non-stopped-flow measurements showed a much lower rate of blank decay than in those catalyzed by **2** and **4**; see the SI and Figure S2.). Since the rate of blank decay in Figure 1a was quite well reproduced under the same experimental conditions, these conditions were finally adopted for the examination of the enhancement of the MV$^{+\bullet}$ decay in the presence of Pt(II)-based molecular catalysts. In these experiments, the total Pt concentration after mixing was always adjusted to be 0.1 mM.

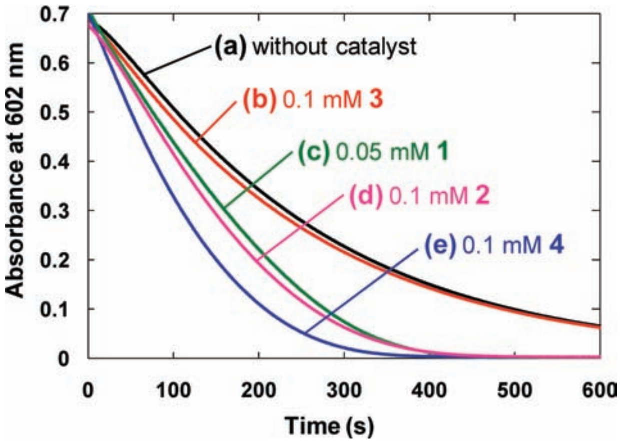

Figure 1. Time courses of absorbance changes at 602 nm after mixing an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa, 0.1 M NaCl, pH 5.0) containing MV$^{+\bullet}$ (0.1 mM) and MV^{2+} (0.4 mM) with solutions of catalysts **1**−**4** in the same buffer solution at 20 °C under an Ar atmosphere. The latter solutions contained (a) no catalyst, (b) 0.2 mM [**3**]Cl_2, (c) 0.1 mM [**1**]$(ClO_4)_2$, (d) 0.2 mM **2**, and (e) 0.2 mM **4**. The MV$^{+\bullet}$/MV^{2+} solution was prepared in situ by bulk electrolysis of a solution of 0.5 mM [MV]$Cl_2 \cdot 3H_2O$ in the same buffer solution at −0.7 V vs SCE. In the case of **1**, nitrate salts (KNO_3 and [MV]$(NO_3)_2$) were used instead of the chloride salts to avoid ligand substitution of **1** by chloride.

As shown in Figure 1, the bleaching rate depended on the Pt(II)-based molecular catalyst employed. The rate increased as the catalyst concentration increased (Figure S1). More interestingly, the order of the bleaching rates (**4** > **2** > **1** > **3**) was roughly correlated with the order of catalytic activity previously determined using the three-component system in Scheme 1; the initial rates of H_2 production were reported to be ordered as **1** (17.5 mL/min for a 10 mL solution; [**1**] = 0.05 mM) > **4** (16.9 mL/min; [**4**] = 0.1 mM) > **2** (14.1 mL/min; [**2**] = 0.1 mM) > **5** (1.8 mL/min; [**5**] = 0.1 mM) > **3** (too low to be analyzed; [**3**] = 0.1 mM).[2f] Importantly, $[Pt(NH_3)_4]^{2+}$ (**3**) did not enhance the bleaching of MV$^{+\bullet}$ at all, which is consistent with the fact that **3** exhibited no activity toward H_2 formation in the three-component system (see above).[2f] Moreover, the bleaching enhancement was much greater for $PtCl_2$(en) (en = ethylenediamine) (**4**) than for *cis*-$PtCl_2(NH_3)_2$ (**2**), consistent with the results obtained from the photochemical studies (see above). An exception is that the acetamidate-bridged Pt(II)$_2$ dimer (**1**) was not the catalyst showing the highest activity of all, which disagrees with the results given by the photochemical method (see above) and will be further discussed below. It should also be noted that attempts to clarify the reaction mechanisms have been unsuccessful to date, primarily because of the concomitant occurrence of the unidentified autocatalytic process discussed above (see Figure 1a and Figure S1a).

On the other hand, unusual behavior was observed for [PtCl(terpy)]$^+$ (**5**). After **5** and MV$^{+\bullet}$ were mixed, the 602-nm band decayed similarly, and a broad absorption band corresponding to the one-electron-reduced form of [PtCl(terpy)]$^+$ [i.e., PtCl(terpy)•], as reported by Gray and co-workers,[10] simultaneously appeared (Figure S3). The broad band decayed very slowly over several hours, revealing that only **5** affords a one-electron-reduced intermediate prior to H_2 formation.

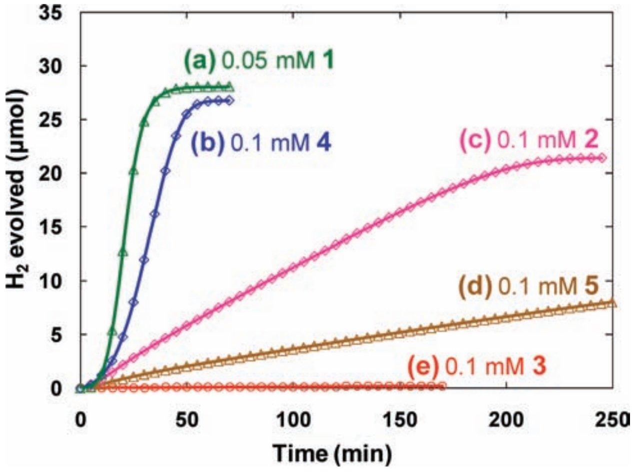

Figure 2. Hydrogen production after mixing MV$^{+\bullet}$ (68 μmol) and (a) 2.25 μmol [**1**]$(ClO_4)_2$, (b) 4.5 μmol **4**, (c) 4.5 μmol **2**, (d) 4.5 μmol [**5**]$Cl \cdot 2H_2O$, and (e) 4.5 μmol [**3**]Cl_2 in an aqueous acetate buffer solution containing 0.03 M CH_3COOH, 0.07 M CH_3COONa, and 0.1 M NaCl (pH 5.0, 45 mL) at 20 °C under an Ar atmosphere. The solution of MV$^{+\bullet}$ was prepared by bulk electrolysis of a solution of 5.0 mM [MV]$Cl_2 \cdot 3H_2O$ in the same buffer solution at −0.9 V vs SCE. The electrolysis was continued until the reduction yield reached 60%, as judged from the absorbance of the solution at 550 nm, where the molar absorptivity of monomer is exactly half that of dimer ($\varepsilon_{monomer} = {}^1/_2\varepsilon_{dimer} = 8800$ M^{-1} cm^{-1}).[9] The MV$^{+\bullet}$ and MV^{2+} concentrations in the resulting solution were 3.0 and 2.0 mM, respectively. Finally, 22.5 mL of this solution was mixed with a solution of each catalyst (22.5 mL solution) in the same buffer solution. In the case of **1**, nitrate salts (KNO_3 and [MV]$(NO_3)_2$) were used instead of the chloride salts. No H_2 was evolved in the absence of catalyst.

Next, the above dark reactions were examined by monitoring the amount of H_2 evolved after mixing MV$^{+\bullet}$ and each Pt(II) catalyst within an argon-purged glass vial equipped with a septum. In this case, the bleaching in the absence of catalyst was very slow. During the reaction, the solution was continuously bubbled with Ar (10 mL/min), and the vent gas from the vial was analyzed every 5 min to determine the H_2 evolution rate (mL of H_2/min) at each sampling point. In order to gain accuracy in the chromatographic analysis of H_2, the initial MV$^{+\bullet}$ concentration ([MV$^{+\bullet}$]$_{total}$ = 1.5 mM) was adjusted to be 30 times higher than that used in the stopped-flow experiments (0.05 mM). The total volume of the reaction mixture was also raised to 45 mL. For each of the Pt(II)-based molecular catalysts, an aqueous solution of MV$^{+\bullet}$ prepared in situ by bulk electrolysis was transferred into the vial containing an argon-purged solution of catalyst using a Nalgene tube, which is known to have improved resistance to oxygen permeation. The total Pt concentration after mixing of the two solutions was adjusted to be 0.1 mM. As shown in Figure 2, thermal reduction of water by MV$^{+\bullet}$ according to eq 2 was indeed promoted in the presence of either **1**, **2**, **4**, or **5**. Very interestingly, the order of the H_2 evolution rate was fully consistent with the activity order previously observed by the photochemical method (see above). Importantly, the H_2 generation catalyzed by the Pt(II)$_2$ dimer was the fastest of all in this experiment. Under the present experimental conditions, the relative abundance of (MV$^{+\bullet}$)$_2$ (∼50% at [MV$^{+\bullet}$]$_{total}$ = 1.5 mM) is much higher than that in the stopped-flow experiments (~6% at $[MV^{+\bullet}]_{total} = 0.05$ mM). Our previous photochemical studies employed MV^{2+} at a concentration of 2.0 mM.[2a−c,f] A possible interpretation is that the H_2-evolving path shown in eq 3 plays a significant role in the outstanding catalytic performance of **1** at higher $MV^{+\bullet}$ concentrations:

$$2H^+ + (MV^{+\bullet})_2 \xrightarrow{Pt(II)_2} 2MV^{2+} + H_2 \tag{3}$$

On the other hand, it is also important to realize that almost no H_2 was evolved when $[Pt(NH_3)_4]^{2+}$ (**3**) was employed as the catalyst. These observations are in good agreement with our previous suggestions that destabilization of the HOMO resulting from either the strong intradimer Pt(II)−Pt(II) interaction in **1** or the ligation of negatively charged chloride ions in **2**, **4**, and **5** results in improved catalytic activity toward the H_2 evolution from water.[2f,h]

In addition, it was also found that the H_2 formation catalyzed by **2** proceeded even at pH 6.0 and 7.0, where the driving forces for H_2 formation are 91 and 32 mV, respectively (see Figure S4). The rate of H_2 formation at pH 6.0 was only slightly smaller than that at pH 5.0. The reaction rate dropped off dramatically at pH 7.0, revealing that the driving force of 32 mV is too small for efficient H_2 evolution.

Furthermore, there was no deposition of solids attributable to the formation of colloidal platinum at the final stage of each reaction, which was strongly supported by the fact that the absorbance at 602 nm returned to zero at the end of each reaction (Figure 1 and Figure S2). In other words, there was no increase in baseline derived from scattering of light by solid dispersion in the stopped-flow experiments. Importantly, the stability of **2** was further confirmed by X-ray photoelectron spectroscopy (XPS) (see Figure 3). In this test case, a solution of **2** was reacted with $MV^{+\bullet}$ under conditions similar to those for Figure 2c, and the resulting solution was freeze-dried to afford a sample to be analyzed by XPS.

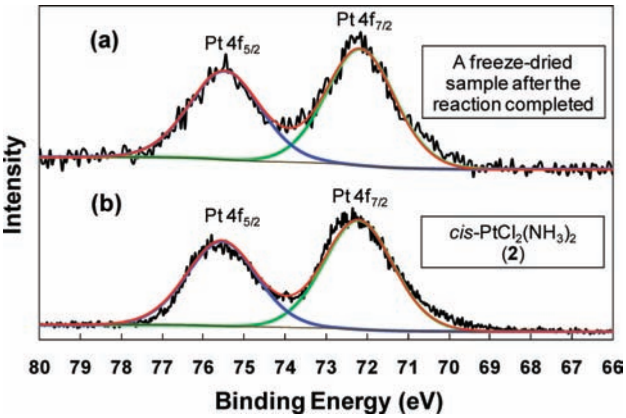

Figure 3. (a) XPS spectrum for the Pt species in a freeze-dried sample obtained from the reaction mixture prepared in the same manner as for Figure 2c. (b) XPS spectrum for **2**. The Pt $4f_{7/2}$ and $4f_{5/2}$ binding energies were respectively determined as 72.2 and 75.5 eV for the freeze-dried sample and 72.2 and 75.6 eV for **2**.

Consequently, the major Pt species after the reaction was judged to be the Pt(II) species attributable to **2**, while signals assignable to Pt(0) species were not observable. It should be noted that the Pt $4f_{7/2}$ and $4f_{5/2}$ binding energies were respectively reported as 72.8 and 76.1 eV for **2**[11a] and 71.2 and 74.5 eV for Pt metal.[11b]

In summary, we have demonstrated that some Pt(II) complexes indeed serve as H_2-evolving molecular catalysts even without light irradiation. Another important observation is that the activity order established by observing the dark reactions in this study correlates well with that previously observed using the photochemical method. Extended studies are actively in progress in our laboratory.

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Supporting Information Available: Experimental details and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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