Hydrogen generation from organic hydrides induced by the photoactivation of aromatic amines

(Hokkaido Univ. Shinshu Univ.) USUI, Akane; OKANO, Yuka; YOSHIDA, Masaki; KOBAYASHI, Atsushi; DOI, Takumi; USAMI, Hisanao; KATO, Masako

[Introduction] Among the several types of energy carriers instead of fossil fuel supply, molecular hydrogen is the one of the most promising and cleanest energy carriers with the least effect on the environment. However, storage and transportation of hydrogen are extremely difficult because hydrogen exists as a gas at room temperature. Therefore, the creation of hydrogen storage systems is currently the subject of intensive investigation.

In recent years, organic hydrides attract much attention as fascinating hydrogen production/storage materials because they are inexpensive and easy to transport, and have excellent values for gravimetric capacities. Many approaches have been actively done for the hydrogen production from organic hydrides. However, the development of effective hydrogen-evolution reactions from organic hydrides that can be driven at moderate temperature without the use of precious-metal catalysts is still an important issue to be investigated.

We recently found the hydrogen evolution from nonprecious-metal complexes with a redox-active ligand, o-phenylenediamine (Figure 1) by the irradiation of UV light. The photochemical reactions suggested that hydrogen evolution would proceed by the N-H activation of the amino group. The ultrafast dynamics of the photoactivation pathways of the N-H \( \sigma \)-bond of aniline was previously investigated using several spectroscopic and theoretical techniques. In these reaction, it was elucidated that the generation of transient aniline radical species via hydrogen atom elimination was initiated by photoexcitation of the \( \pi-\pi^* \) transition through 3s Rydberg state of the nitrogen atom. On the basis of these findings, we have developed more convenient hydrogen evolution from various organic hydrides induced by the N-H bond photolysis of aromatic amines.

[Experimental] All measurements were performed under a N\(_2\) atmosphere. A solution of

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\text{aniline} \quad \begin{array}{c}
\text{o-phenylenediamine (opda)} \\
\text{m-phenylenediamine (mpda)} \\
\text{p-phenylenediamine (ppda)}
\end{array}
\]

Figure 1. aromatic amines studied in this work
each aromatic amine (Figure 1, 0.03 mmol) in various organic solvents (20 ml) was irradiated by a conventional mercury lamp (λ = 254 nm) in a flow reactor made of quartz glass. The amount of photochemically evolved hydrogen gas was determined by using a gas chromatography instrument (Shimadzu GC-14B, Ar carrier).

[Results and Discussion] Figure 2 shows UV-Vis spectra of aniline, opda, mpda and ppda in THF. All of aromatic amines have enough absorption at 254 nm. On irradiating the solutions with the light of 254 nm, gas evolution occurred, and GC analysis proved the formation of hydrogen. In contrast, the hydrogen evolution reaction was not observed under a dark condition at all, suggesting hydrogen evolution reaction was driven photochemically. Figure 3 shows the photochemical hydrogen production from various organic hydrides in the presence of opda. The amounts of hydrogen evolved suggest that the hydrogen evolution occurred from organic hydrates. In the absence of opda, however, hydrogen evolution was not observed. These results clearly demonstrate that coexistence of opda is necessary for efficient hydrogen evolution reaction and stimulated us to characterize the active species of the hydrogen evolution.

Figure 4 shows photochemical hydrogen production from THF in the presence of various aromatic amines. The amount of photochemical hydrogen evolution with opda was larger than that the case with aniline, but similar to that the case with ppda. The detailed hydrogen evolving mechanisms will also be discussed.