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Photocatalytic Hydrogen Evolution from Aqueous Hydrazine Solution over Precious-metal/Anatase Catalysts

By YOSHINAO OOSAWA

National Chemical Laboratory for Industry, Higashi, Yatabe, Tsukuba, Ibaraki 305, Japan

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Aqueous hydrazine solution has been photocatalytically decomposed over preciousmetal/anatase catalysts yielding only H_2 , N_2 and NH_3 . H_2/N_2 (molar ratio of H_2 evolved to N_2 evolved) is usually *ca.* 1 and does not depend on the reaction conditions (pH, metal, reactant concentration). However, the value is > 1 when another hole scavenger (CH₃OH) is present. N_2/NH_3 is *ca.* 0.5 and does not change in the presence of CH₃OH. On the basis of these results, the reaction scheme is considered to be as follows: the electrons photoexcited into the conduction band of anatase are consumed through H_2 formation and the positive holes generated in the valence band are consumed through the simultaneous formation of N_2 and NH_3 . The dependence of the reaction rate on the concentration of N_2H_4 and on the metal suggests that the rate-determining step is the formation of H_2 over the metal.

In recent years, photocatalytic H_2 evolution from water¹⁻⁵ or organiccompound + water systems^{6, 7} using precious-metal/semiconductor powders has been widely investigated from the standpoints of photo-to-chemical energy conversion assisted by light energy, reaction mechanism and so on. On the other hand, few reports^{8, 9} have been published on photocatalytic H_2 evolution from systems with an inorganic electron donor other than water, although in some systems high photocatalytic reaction rates and some simple products are expected, making it easier to determine the products and follow the reaction.

Hydrazine, which is an inorganic electron donor, can reduce protons and produce H_2 thermodynamically. However, it has been reported that the thermal-catalytic decomposition of an acidic aqueous solution over platinum black proceeds according to the following reaction with no evolution of H_2 :¹⁰

 $3N_2H_4 \rightarrow N_2 + 4NH_3$.

In a previous communication⁸ photocatalytic evolution of H_2 from an aqueous solution of $N_2H_4 \cdot 2HCl$ in the presence of Pt/TiO_2 has been reported:

$$2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3$$

On the basis of preliminary experiments it has been proved that this reaction has the following features: (i) the rate of reaction is fast, (ii) the reaction produces only a few products $(H_2, N_2 \text{ and } NH_3)$ and so it is easy to obtain good mass balance and charge balance, which, despite their importance, have been reported for only a few cases of photocatalytic reactions in aqueous solution, and (iii) the successive reaction of primary products is minimal, which is rather different from organic electron donors. Therefore, this reaction system is considered to be suitable for an investigation of the features of photocatalytic reactions.

This paper presents the results of a study of the photocatalytic decomposition of N_2H_4 in aqueous solution over precious-metal/anatase catalysts.

PHOTOCATALYTIC HYDROGEN EVOLUTION

EXPERIMENTAL

MATERIALS

 $N_2H_4 \cdot H_2O$, $N_2H_4 \cdot 2HCl$, NH_4Cl and CH_3OH were all reagent grade. Deionized water was used without further purification. Purest-grade anatase (TP-2) was purchased from Fuji Titan. Each precious-metal/anatase was prepared by an impregnation H_2 reduction method (H_2 , 101 kPa, 200 °C, 4 h) from anatase and an aqueous solution of the precious-metal chloride (except for OsO₄). X-ray powder diffraction measurements (Rigaku, Geigerflux, Cu K α) confirmed that the crystal structure was not changed by loading of the precious metals. Average particle diameters of the anatase and the Pt/anatase (10^{-2} wt/wt) were measured using a centrifugal automatic particle analyser (Horiba, CAPA-500) and were both 0.26 μ m. Their specific surface areas were measured by the B.E.T. method (Shimadzu surface-area analyser 2205) with Ar as an adsorbate and were 18.3 m² g⁻¹ and 17.8 m² g⁻¹, respectively.

APPARATUS AND PROCEDURE

The reaction was performed in a photocell (108 cm³) with a rectangular-parallelepiped lower part ($35 \times 35 \times 60$ mm) and a septum. Usually, the reaction mixture, consisting of precious-metal/anatase (10 mg) and an aqueous solution of reactant (30 cm³ of 0.1 mmol dm⁻³) in an argon atmosphere, was stirred and irradiated using a 500 W ultra-high-pressure mercury lamp (Ushio) at *ca*. 40 °C in the stationary state. The dark reaction was performed at 50 °C.

ANALYSIS

Gaseous products (H₂ and N₂) were analysed quantitatively by gas chromatography (Yanaco G 180; MS-13X column). The liquid reaction mixture was filtered to remove solid photocatalyst, which was washed with HCl (10 cm³ of 1 mol dm⁻³) in order to desorb reactant and products adsorbed on it. The filtrates and the washings were combined together and analysed.¹¹ N₂H₄ was analysed quantitatively by titration with KIO₃ solution.¹² Concentrated NaOH was then added to the mixture and the resulting solution was distilled. NH₃ was analysed qualitatively by the indophenol method¹³ and quantitatively by acid–base titration¹⁴ of the distillate. U.v.–visible spectrophotometric analysis (Shimadzu u.v. 240) ascertained that no reaction mixture except for anatase had absorption in the wavelength region transmitted through the Pyrex glass ($\lambda > ca$. 300 nm).

RESULTS

REACTION OVER Pt/ANATASE

Fig. 1 shows the time dependence of the volume of gases evolved when the aqueous solution of N_2H_4 or $N_2H_4 \cdot 2HCl$ was irradiated in the presence of Pt/anatase (10^{-2} wt/wt) . The gas evolution rate was higher when N_2H_4 was used as a reactant than when $N_2H_4 \cdot 2HCl$ was used. The volume of the gases is expressed in cm³ at s.t.p. (0 °C, 101 kPa) unless otherwise stated. No reaction occurred when a 420 nm cut-off filter was used or in the dark. When water (30 cm³) was irradiated in the presence of the Pt/anatase (10^{-2} wt/wt), a small amount of H_2 was evolved: 0.17 cm³ after a 19 h reaction. So H_2 evolution in the absence of N_2H_4 (or $N_2H_4 \cdot 2HCl$) may be due to photocatalytic decomposition of water¹⁵

Products were analysed in a few reactions. Table 1 shows the results of the analysis. No compounds other than H_2 , N_2 , NH_3 and N_2H_4 were found by gas-chromatographic analysis with MS-13X (1 m, 50 °C) and chromosorb 103 (2.25 m, 170 °C). It is clear that the reactions presented in table 1 proceed photocatalytically, because they fulfil all of the following requisites: (i) dark reaction does not occur, (ii) the reaction stops when irradiated through a 420 nm cut-off filter (the band gap of anatase is 3.2 eV, therefore light of energy greater than that of the band gap is cut off), (iii) mass balance

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Fig. 1. Photocatalytic H₂ and N₂ evolution over Pt/anatase (10^{-2} wt/wt). Reaction conditions: Pt/anatase, 10 mg; reactant, 30 cm³ of 0.1 mol dm⁻³ N₂H₄, \triangle , H₂ and \blacktriangle , N₂; reactant, 30 cm³ of 0.1 mol dm⁻³ N₂H₄·2HCl, \bigcirc , H₂ and \bigoplus , N₂; (---) when the 420 nm cut-off filter was used.

(N and H) and charge balance hold well and (iv) the turnover number (moles of N_2H_4 consumed/moles of photocatalyst)* is > 1.

Table 2 shows the average evolution rate of H_2 and N_2 for the initial few hours over various precious-metal/anatase catalysts (10^{-2} wt/wt). Neither the reaction with the cut-off filter nor the dark reaction at 50 °C proceeded. Therefore, the gas evolutions presented in table 2 are also assumed to proceed photocatalytically. In almost all cases, H_2/N_2 was *ca.* 1. The gas-evolution rate decreased in the following order: Pt > Pd > Ir > Rh > Os > Ru. This order seems to reflect the magnitude of hydrogen overvoltage required to obtain a current density of 2 mA cm⁻² in 0.05 mol dm⁻³ H_2SO_4 (Pt < Ir < Os and Pd < Rh < Ru).¹⁶

REACTION IN THE PRESENCE OF CH₃OH

In order to obtain information on the photocatalytic decomposition of N_2H_4 in aqueous solution, the reaction was performed in the presence of another electron donor, *i.e.* CH₃OH. Neither photocatalytic H₂ evolution from CH₃OH+H₂O(v/v = 1/1) in the presence of anatase nor the dark reaction in the presence of Pt/anatase (10⁻² wt/wt) proceeded. The results of the analysis are shown in table 1. The mass balance of nitrogen held fairly well in both cases. Note that N₂/NH₃ is close to 0.5

^{*} Turnover number (moles of reactant consumed/moles of photocatalyst used) is used as a guide as to whether the reaction is stoichiometric or catalytic.

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reactant	$N_2H_4 \cdot 2HCl^d$	$N_2 H_4^{\ d}$	$N_2H_4 \cdot 2HCl + CH_3OH^{e, f}$	$N_2H_4 \cdot 2HCl + CH_3OH^{e,g}$
reaction time/h	8	6.5	15	15
N_2H_4 consumed/mmol	0.84	0.95	0.66	0.23
product/mmol				
H ₂	0.42	0.56	0.47	0.68
N_2	0.46	0.50	0.31	0.14
NH ₃	0.79	0.83	0.58	0.24
mass balance/mequiv.				
N reactant	1.68	1.90	1.32	0.46
N product	1.71	1.83	1.20	0.52
H reactant	3.36	3.80		
H product	3.21	3.64		
charge balance/mequiv.				
e^{-} consumed ^{<i>a</i>}	1.63	1.95		
p^+ consumed ^b	1.84	2.00	_	
turnover number ^c	6.7	7.6	5.3	1.8

Table 1. Analysis data

Reaction conditions: 0.1 mol dm⁻³ N₂H₄ or N₂H₄·2HCl; amount of reactant, 30 cm³; photocatalyst, Pt/anatase (10^{-2} wt/wt), 10 mg.

^{*a*} Calculated as $2H_2 + NH_3$. ^{*b*} Calculated as $4N_2$. ^{*c*} Calculated as [moles of N_2H_4 consumed per mol of Pt/anatase (10⁻² wt/wt) used]. ^{*d*} 500 W ultra-high-pressure Hg lamp (Ushio) was used. ^{*e*} 450 W Xe lamp (Oriel) was used. ^{*f*} 0.1 mol dm⁻³ CH₃OH. ^{*g*} 1 mol dm⁻³ CH₃OH.

Table 2. H_2 and N_2 evolution rates (cm³ h⁻¹) over precious-metal/anatase catalysts

photocatalyst	H_2	N_2	
Pt/anatase	2.06	2.07	
Pd/anatase	1.58	1.55	
Ir/anatase	0.80	0.81	
Rh/anatase	0.70	0.74	
Os/anatase	0.061	0.068	
Ru/anatase	0	0	
anatase	0	0	

Reaction conditions: reactant, 0.1 mol dm⁻³ N₂H₄·2HCl; photocatalyst, 10 mg.

even in the presence of a large excess of CH_3OH . On the other hand, $H_2/N_2 > 1$ in the absence of CH_3OH .

DEPENDENCE OF THE REACTION ON N_2H_4 concentration

The dependence of the H₂ evolution rate on the concentration of N₂H₄ is shown in fig. 2. In these experiments, a small amount of the Pt/anatase (10⁻² wt/wt, 2 mg) was used in order to keep the conversion and the decrease in the concentration of reactant small even in the most dilute solution. In this concentration region, the rate was higher at lower concentrations and became constant at concentrations > 0.1 mol dm⁻³. H₂/N₂ was 1 even at a concentration of 10 mol dm⁻³: reaction time, 14 h; H₂ evolved, 21.9 cm³; N₂ evolved, 20.8 cm³; H₂/N₂ = 1.05.



Fig. 2. Dependence of H_2 evolution rate on N_2H_4 concentration. Reaction conditions: Pt/anatase (10⁻² wt/wt), 2 mg.

photocatalyst	Pt	Pd	Rh	Ir, Ru, Os
	/anatase	/anatase	/anatase	/anatase
reaction time/h volume of gas/cm ³	5	6	23	4-15
H_2 N ₂	0.52	0.29	0.46	< 0.01
	0.28	< 0.01	0.21	< 0.01

Table 3. Photocatalytic decomposition of NH₃

Reaction conditions: reactant 0.1 mol dm⁻³ NH₄Cl; photocatalyst, 10 mg.

DECOMPOSITION OF NH₃

 NH_3 was formed in the photocatalytic reaction of aqueous N_2H_4 solution over Pt/anatase as shown in table 2. NH_3 formed photocatalytically is also able to decompose photocatalytically.¹⁷ A few experiments were performed to confirm this point. NH_4Cl and precious-metal/anatase (10^{-2} wt/wt) were used as reactant and photocatalyst. The results are shown in the table 3. Neither the reaction with the cut-off filter nor the dark reaction proceeded. Therefore the gas evolution in table 3 is considered to proceed photocatalytically. The gas evolution rates with NH_4Cl were much lower than those with N_2H_4 . Therefore the contribution from the photocatalytic decomposition of NH_3 is negligibly small compared with that of N_2H_4 under the present reaction conditions.

DEPENDENCE OF H_2 EVOLUTION RATE ON THE Pt loading ratio

Eight kinds of Pt/anatase with different Pt loading ratios were prepared and H_2 evolution over them was investigated. The results are presented in fig. 3. H_2 evolution was detected even when Pt/anatase (10^{-6} wt/wt) was used. The H_2 evolution rate increased with increasing Pt loading ratio and reached saturation above a loading ratio of 10^{-4} wt/wt. It was observed that the H_2 evolution rate is almost constant over a wide range of Pt loading ratios. The Pt coverage in Pt/anatase (5×10^{-2} wt/wt) was estimated to be *ca*. 4%: the Pt surface area estimated from the half-width of the X-ray diffraction peak was $0.71 \text{ m}^2 \text{ g}^{-1}$ and the B.E.T. surface area was $17.5 \text{ m}^2 \text{ g}^{-1}$. Therefore the cause of the saturation in the H_2 evolution rate at low Pt loading ratios



Fig. 3. Dependence of H_2 evolution rate on Pt loading ratio. Reaction conditions: Pt/anatase, 10 mg; 30 cm³ of 0.1 mol dm⁻³ N₂H₄.

is not caused by a decrease in the number of photons striking the anatase surface. Note that even Pt/anatase with a very low Pt loading ratio showed high activity: *e.g.* Pt/anatase (10^{-5} wt/wt) showed an activity of approximately one-fourth that of the Pt/anatase (10^{-2} wt/wt) . Further study is required to understand these points.

DISCUSSION

REACTION SCHEME

A few standard redox potentials¹⁸ for the present reaction system are presented in fig. 4, together with the bottom of the conduction band $(V_{cb})^{19}$ and the top of the valance band $(V_{vb})^{19}$ of anatase at pH 7. Their relative location changes little with a change of pH. Reactions (1)–(3) correspond to the three redox pairs in fig. 4. Aqueous hydrazine solution is thermodynamically unstable and can be decomposed thermodynamically according to reaction (4) or (5) by combination of reactions (1) and (2) or reactions (1) and (3), respectively. As has been stated already, however, these reactions did not take place thermocatalytically under the reaction conditions used in the present study.

$$N_{2} + 5H^{+} + 4e^{-} \rightarrow N_{2}H_{5}^{+}$$
 (1)

$$2H^+ + 2e^- \rightarrow H_2 \tag{2}$$

$$N_{2}H_{5}^{+} + 3H^{+} + 2e^{-} \rightarrow 2NH_{4}^{+}$$
(3)

$$N_2H_4 \rightarrow N_2 + 2H_2 \quad \Delta G^\circ = -22 \text{ kcal mol}^{-1} \tag{4}$$

$$N_2H_4 \rightarrow \frac{1}{3}N_2 + \frac{4}{3}NH_3 \quad \Delta G^\circ = -46 \text{ kcal mol}^{-1}.$$
 (5)

When the anatase is irradiated by light of energy greater than that of the band gap, the electrons photoexcited into the conduction band can reduce protons producing H₂ [reaction (2)] or reduce N₂H₄ producing NH₃ [reaction (3)] thermodynamically. On the other hand, the positive holes generated in the valence band can oxidize N₂H₄ producing N₂ [reaction (1)] thermodynamically.

Following three features of the reaction can be used to elucidate the photocatalytic reaction scheme:

(i) H_2/N_2 is ca. 1 over a wide range of reaction conditions (pH, loaded metal, N_2H_4



Fig. 4. Energetic correlation between a few standard redox potentials,¹⁸ the bottom of the conduction band $(V_{\rm cb})^{19}$ and the top of the valence band $(V_{\rm vb})^{19}$ of anatase at pH 7.

concentration), (ii) N_2/NH_3 is *ca.* 0.5 and the value does not change even in the presence of another electron donor (CH₃OH) and (iii) the photocatalytic decomposition does not proceed over anatase without loaded metal, which is different from the case of NH_2OH .²⁰

At first sight, feature (i) can be explained by the combination of reactions (1), (2) and (3); that is (2)+(3)-(1). However, it is difficult to explain features (ii) and (iii) using this reaction scheme.

At first, it is reasonable to assume that N_2 is formed through the hole-consumption pathway, because N_2 is the only oxidation product in the present reaction system. Seemingly, there are two kinds of reduction product: H_2 and NH_3 . It may also be assumed that H_2 is formed through the electron-consumption pathway, because H_2 evolution was only possible by loading precious metals which have a low H_2 overpotential, as shown in table 2.

On the other hand, problems arise if it is assumed that NH_3 is formed in the electron-consumption pathway. Feature (ii) is very significant. When CH_3OH is added to the N_2H_4 system, some of the positive holes generated by irradiation will react with CH_3OH . Then some electrons generated by irradiation will not recombine with positive holes. If NH_3 were formed in the electron-consumption pathway, some of the electrons not recombining with positive holes would be used in the formation of both H_2 and NH_3 . As a result, N_2/NH_3 would be < 0.5, the value obtained in the absence of CH_3OH . On the other hand, H_2/NH_3 would be 2, the value obtained in the expectations. Therefore feature (ii) shows that NH_3 is not formed in the electron-consumption pathway.

Concerning feature (iii), it is useful to compare it to the case where NH_2OH is a reactant.²⁰ When NH_2OH was used as the reactant, the photocatalytic reaction proceeded even over anatase without any loaded metal, yielding N_2 , N_2O and NH_3 . In that case, NH_3 was formed in the electron-consumption pathway, because NH_3 is the only reduction product. If NH_3 could have been formed in the electron-consumption pathway for N_2H_4 system also, the photocatalytic reaction [reactions (1) and (3)] over the anatase should have occurred. In practice, however, the photocatalytic reaction over anatase does not proceed. Therefore, feature (iii) also supports the idea that NH_3 formation over anatase cannot be an electron-consumption pathway in the N_2H_4 system.

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As NH_3 formation cannot be an electron-consumption pathway, H_2 formation should be the only electron-consumption pathway. Therefore, on the basis of the above discussion, it is reasonable to assume that N_2 and NH_3 are formed together in the hole-consumption pathway. It is tentatively postulated that tetrazane (N_4H_6) is formed as a reaction intermediate. In several reaction systems it has been assumed that positive holes are consumed through the formation of hydroxy radical and through direct reaction with reactant.²¹ This may also be the case in the present reaction system. Therefore the main reaction will be represented by the reaction scheme shown below.

anatase
$$\rightleftharpoons e^{-}$$
(electron) + p⁺(hole)

(electron-consumption pathway)

 $H^+ + e^- \rightarrow H^-$ 2H[•] → H₂ (over precious metal)

(hole-consumption pathway)

$$\begin{split} H_{2}O + p^{+} &\rightarrow H^{+} + OH^{*} \\ N_{2}H_{4} + p^{+} &\rightarrow N_{2}H_{3}^{*} + H^{+} \\ N_{2}H_{4} + OH^{*} &\rightarrow N_{2}H_{3}^{*} + H_{2}O \\ & 2N_{2}H_{3}^{*} &\rightarrow N_{4}H_{6}[= NH_{2}(NH)_{2}NH_{2}] \\ & N_{4}H_{6} &\rightarrow N_{2} + 2NH_{3}. \end{split}$$

This reaction scheme can explain the three features of the reaction described above.

In some cases: $H_2/N_2 < 1$. It can be explained by assuming that the following reaction scheme is a side reaction.

$$\begin{array}{c} H' + N_2 H_4 \rightarrow N_2 H_5' \\ N_2 H_5' + H' \rightarrow 2 N H_3 \end{array} \right\} \text{ over precious metal.}$$

In some cases, on the other hand, $H_2/N_2 > 1$. It can be explained by assuming that the following reaction scheme is a side reaction or by assuming the decomposition of the NH₃ formed photocatalytically:

$$\begin{split} N_2 H_4 + 2 p^+ &\to N_2 H_3^+ + H^+ \\ N_2 H_3^+ &\to N_2 H_2 + H^+ \\ N_2 H_2 + 2 p^+ &\to N_2 + 2 H^+. \end{split}$$

RATE-DETERMINING STEP

The dependence of the reaction rate on reactant concentration often provides useful information about the rate-determining step of the reaction. Nevertheless, the dependence of the rate of photocatalytic H_2 evolution on the reactant concentration is reported only for a few cases. In the case of N_2H_4 solution, the rate decreased with increasing concentration above 0.1 mol dm⁻³. It is clear that N_2H_4 depresses H_2 evolution in this concentration region in the present reaction system. This means that the N_2H_4 -consumption step is not rate-determining. Moreover, as described already, the order of the H_2 evolution rate over precious-metal/anatase corresponded well to the order of magnitude of the hydrogen overvoltage of these precious metals. This

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suggests that the rate-determining step is H_2 formation on the surface of the precious metal. Electrolytic H_2 formation over precious metals is considered to be a combination of hydrogen atoms adsorbed on the surface of the precious metal. On the surface of these metals loaded on anatase, N_2H_4 may also be adsorbed. The dependence of the H_2 evolution rate on the N_2H_4 concentration depicted in fig. 2 may be understood through the inhibition effect of N_2H_4 on the combination of hydrogen atoms on the Pt surface.

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