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Hydrogen Production by Ultraviolet Irradiation of Alkylammonium Polytungstate in Neutral Aqueous Solutions

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Introduction

In studies of the photogalvanic electrolysis of water using the alkylammonium polytungstate, it has been described that hydrogenhexatungstate (5–) $[W_6O_{20}(OH)]^{5-}$, showing intense ligand to metal charge transfer absorption bands at $\lambda < 300$ nm, exhibits a photogalvanic effect based on the photoreduction of W^{VI} to W^{V} [1]. The photoelectrolysis of water was observed for the photogalvanic cell consisting of two separate compartments (the anodic solution of the pentakis(isopropylammonium) hydrogenhexatungstate and 5*N* H_2SO_4 cathode solution) connected by a KCl–agar salt bridge, Pt|5*N*H_2SO_4||$[NH_3Pr^i]_5[W_6O_{20}(OH)]$ solution|Pt. In the photogalvanic cell of the anode solution at pH 7, the pH gradient across the KCl–agar salt bridge supplies a voltage of about 0.47 V for the water-splitting reaction of $H_2O \rightarrow 1/2H_2 + {\cdot}OH$ [1–2] and the prolonged irradiation would cause the pH gradient to be lowered, which would result in a decrease of the H_2-production efficiency [3]. In an approach to develop the water-splitting method, we found that hydrogen was also obtained using a heterogeneous Pt catalyst associated to the alkylammonium polytungstate electron transfer mediator. The present paper describes the coupling of the photoreduction of pentakis(isopropylammonium) hydrogenhexatungstate $[NH_3Pr^i]_5[W_6O_{20}(OH)]$ with the reduction of water leading to hydrogen evolution by the use of a heterogeneous Pt catalyst. This involves a very simple method of water splitting compared with the photogalvanic cell, having a moderate pH-gradient between the two half-cells.

Experimental

All chemicals were from Tokyo Kasei G. R. or analytical grade and were used without further purification. Sample solutions of pentakis(isopropylammonium) hydrogenhexatungstate $[NH_3Pr^i]_5[W_6O_{20}(OH)]$ were prepared by mixing 0.16 *M* Na_2WO_4 and 0.64 *M* $[NH_3Pr^i][ClO_4]$ in the colloidal platinum solution and subsequent adjusting to a pH of 7 by $HClO_4$ [1]. Colloidal Pt was prepared by reduction of H_2PtCl_6 with sodium citrate, followed by stirring with Amberlite-MB-3 exchange resin to remove the citrate [4]. A brown solution results which contains 4.4×10^{-4} *M* of the total concentration of Pt. A sample solution of 60 ml was magnetically stirred and exposed to UV light ($\lambda > 200$ nm) from an USHIO UM-102 100 W Hg lamp fitted with a water jacket to remove IR irradiation. The gas evolved was conducted to a gas volumeter. The gas was analyzed by both G. C. (Carbosieve S column at 50 °C, argon carrier) and mass spectrometry.

Hydrogen quantum yield was measured as follows: A sample solution of 4 ml was evacuated by several freeze–pump–thaw cycles to 10^{-4} Torr and then exposed to 254 nm light from an USHIO SUV-110-OL 110 W Hg lamp with filters. Irradiations were carried out in the 1-cm quartz cell connected to a gas sampling valve, allowing for both gas analysis and absorbance readings during short interruptions in the photolyses. Light intensities were measured with the use of a potassium ferrioxalate actinometer.

Results and Discussion

Sample solutions, usually deaerated by argon bubbling, containing $[NH_3Pr^i]_5[W_6O_{20}(OH)]$ and colloidal Pt were irradiated with UV light ($\lambda > 200$ nm). Hydrogen bubble formation was confirmed by mass spectral analysis and was rapidly noticeable at atmospheric pressure as a function of irradiation time. The result is shown in Fig. 1. There was no

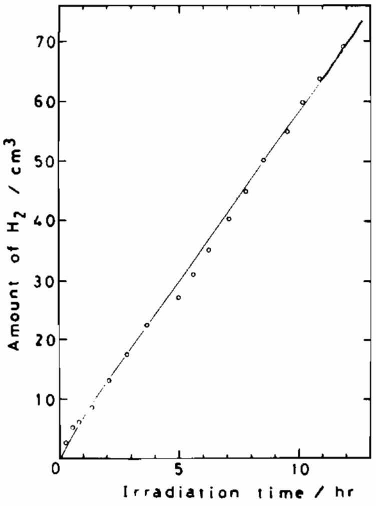

Fig. 1. H_2 evolution from 60 ml samples containing $[NH_3Pr^i]_5[W_6O_{20}(OH)]$ and colloidal Pt (pH 7) when irradiated with $\lambda > 200$ nm light.

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change in solution pH at least within 30 hr of the irradiation time. The 313 or 365 nm irradiation resulted in no observable H_2 evolution, since $[W_6O_{20}(OH)]^{5-}$ exhibited little photoabsorption at the region of $\lambda > 300$ nm [1]. No H_2 evolution was observed in the absence of colloidal Pt. An optimum pH of approximately 7 was observed, which had been also obtained for the anodic photocurrent (through Pt electrode) by 260 nm light excitation in the absence of colloidal Pt [1]. This implies that the colloidal Pt catalyst functions as a microelectrode [5–7] providing a surface at which the donor potential of the electrochemically active species W^V can be matched to the water reduction potential, analogous to the potential matching at a bulk electrode. As the irradiation at pH 7 proceeds, the aggregation of colloidal Pt occurs and the solution changes to the blue color (probably due to W^V) exhibiting its absorption bands at $\lambda_{max} = 650$ nm and $\lambda_{sh} \approx 490$ nm. Figure 2 shows absorption changes for the 254 nm photoexcitation of the sample solution at pH 7. The quantum yield of H_2 evolution by 254 nm irradiation was 0.017 which was obtained for less than 1.0 of the absorbance appearing at $\lambda_{max} = 650$ nm.

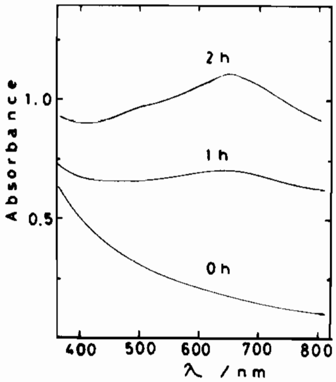

Fig. 2. Electronic absorption spectral changes during 254 nm irradiation (4.37×10^{-3} Einstein absorbed dm^{-3} hr^{-1}).

We have reported that an optimum pH of the polymolybdate solution is approximately 7 for the water photolysis by the photogalvanic cell $Pt|5N\ H_2SO_4||[NH_3Pr^i]_6[Mo_7O_{24}]$ solution|Pt [2]. In contrast to the case of polytungstate system, however, no H_2 evolution was observed for $\lambda > 200$ nm irradiation of the solution containing 54.4 mM $[NH_3Pr^i]_6[Mo_7O_{24}]$ and 4.4×10^{-4} M colloidal Pt at pH 7 under similar conditions. Photocurrent–applied potential curves indicated that the photocurrent onset (about −0.5 V *vs.* SCE) for the polymolybdate at pH 7 was more positive (about −0.7 V *vs.* SCE) than that for the polytungstate at the same pH [1, 2]. Based on the fact that the photocurrent onset corresponds to the redox potential of the electrochemically active species produced by UV irradiation, the lack of observable H_2 evolution ofr the $[NH_3Pr^i]_6[Mo_7O_{24}]$–colloidal Pt system (pH 7) can be explained by the deficient potential of the electrochemically active species, whereas the electrochemically active one for the polytungstate system exhibits the potential matching to the water reduction potential (−0.65 V *vs.* SCE at pH 7). As for the polymolybdate system, a voltage from the pH gradient as the potential source associated to the potential deficiency must be supplied for the water reduction, as seen for the photogalvanic cell $Pt|5N\,H_2SO_4||[NH_3Pr^i]_6[Mo_7O_{24}]$ solution at pH 7|Pt [2]. It is important to emphasize that the photoreduction of Mo^{VI} to Mo^V is coupled with a water oxidation to a hydroxyl radical formation and that the electrochemically active species coordinates a hydroxide group to the Mo^V center [2, 8]. In extending the idea obtained for the polymolybdate system to the polytungstate one, it is possible to say that the work reported here offers a simple method of a water-splitting reaction, as given by the scheme of Fig. 3. In conjunction with the results [8] of the solution photochemistry of $[NH_3Pr^i]_6[Mo_7O_{24}]$, we consider that the blue species formation in the polytungstate system occurs via electrochemically active species and competes with the H_2 evolution reaction on the colloidal Pt. Prolonged irradiation (10 hr) of the sample solution to $\lambda > 200$ nm light brought about formation of a small amount of CO_2. This suggests an attack of ·OH on the NH_3Pr^i cation, resulting in oxidative decomposition. Studies of the oxidation process of ·OH are in progress, to obtain a better understanding of the process involved in this type of water photolysis.

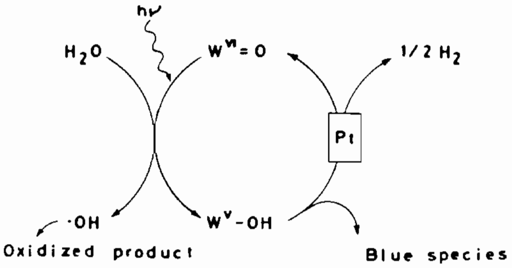

Fig. 3. Processes involved in the water photolysis.

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