Water Splitting by Photoirradiation of Alkylammonium Polytungstates in Homogeneous Solutions and Detectable Paramagnetic Species

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Introduction

In studies on water photolysis by alkylammonium polytungstates, it has been described that the photoexcitation of aqueous solutions of pentakis(isopropylammonium) hydrogenhexatungstate $[NH_3Pr^i]_5[W_6O_{20}(OH)]$ leads to hydrogen evolution from water in the presence of Pt catalysts. Based on the results of the photo-electrochemistry of the polytungstate and polymolybdate systems [1–3], the reaction mechanism of the water splitting has been discussed and summarized by following reaction scheme:

$$W^{VI}{=}O + H_2O \xrightarrow{h\nu} W^{V}{-}OH + {\cdot}OH \quad (1)$$

$$W^{V}{-}OH \rightarrow W^{VI}{=}O + \tfrac{1}{2}H_2 \quad (2)$$

In order to obtain some evidence for the above reaction scheme, we have measured esr spectra of the isopropylammonium polytungstate solutions at various pH levels. This paper describes the water photolysis by a use of alkylammonium polytungstate without the help of a Pt catalyst as a simpler method of water splitting, in addition to the detection of hydroxyl radicals (·OH) and two distinct W^V species on photo-irradiation. Acidic aqueous solutions of the polytungstate, which exhibit the photoabsorption ($\epsilon_{350} \approx 10^2$ M^{-1} cm^{-1}) at $\lambda > 320$ nm, seem to be promising from the point of view of the water photolysis by solar energy. Furthermore, the photochemistry of polyoxometalate enables us to understand the photochemical process at the oxide semiconductor–electrolyte interface in the molecular level, if we consider that the charge-transfer complex (I) formation in the alkylammonium polymetalate systems [4] corresponds to the appearance of the photogenerated hole (on the oxygen atom) at the interface by oxygen to metal charge–transfer excitation.

Experimental

Sample solutions of isopropylammonium polytungstate were prepared by mixing 0.16 *M* Na_2WO_4 and 0.64 *M* $[NH_3Pr^i][ClO_4]$ in water, the solution pH being adjusted by $HClO_4$. Prolonged photoirradiation and measurement of the hydrogen quantum yield were carried out as previously described [1]. 254-nm light was obtained from an USHIO SUV–110 OL 110 W Hg lamp with filters. Other monochromatic light-irradiation experiments were carried out using a 500-W superhigh pressure mercury lamp in conjunction with filters. Light intensities were measured using a potassium ferrioxalate actinometer. The evacuation of solutions was done by several freeze-pump-thaw cycles to 10^{-4} torr. Mass spectroscopy was performed with a use of a Hitachi M80 G.C./mass spectrometer. Carbosieve S column (at 50 °C, Ar carrier) was used to separate the gaseous content over the photolyte. ESR spectra were recorded using a Varian E-12 X-band spectrometer equipped with a 100 K-Hz field modulation unit.

Samples for the spin trapping method were prepared in the dark, under nitrogen. In order to remove the colored impurity from the spin-trapping agent 5,5-dimethylpyrroline-1-oxide (DMPO) purchased from Aldrich, sample solutions containing DMPO were shaken with activated charcoal and were filtered through glass wool prior to photolysis. This purification procedure tends to remove a small amount (~10%) of the spin trap itself. In a typical experiment, sample solutions containing DMPO (~0.1 *M*) and isopropylammonium polytungstate was transferred to a quartz capillary esr tube and was then photolyzed in the cavity of the spectrometer. In the dark, sample solutions gave exceedingly weak signals with DMPO, which were not sufficient to interfere with any of the experiments [5]. The detection of W^V species in the photolyte was carried out at 77 K.

Results and Discussion

Aqueous (usually deaerated) solutions of isopropylammonium polytungstate were irradiated with UV light of $\lambda > 200$ nm. Hydrogen formation was rapidly noticeable at various pH levels of 7 to 1. There was no change in solution pH for each of various pH solutions: at least within 30 hrs of the irradiation time.

The quantum yield of H_2 evolution by 254-nm light irradiation at pH 7 was 0.05. The 313- or 365-nm light irradiation did not result in significant H_2 evolution, since $[W_6O_{20}(OH)]^{5-}$ as a predominant species at pH 7 exhibited little photoabsorption

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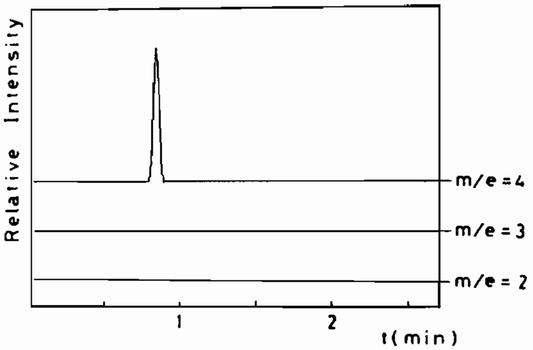

Fig. 1. Relative intensity of ion current for gas (D_2, HD, or H_2) over the photolyte obtained with GC/MS.

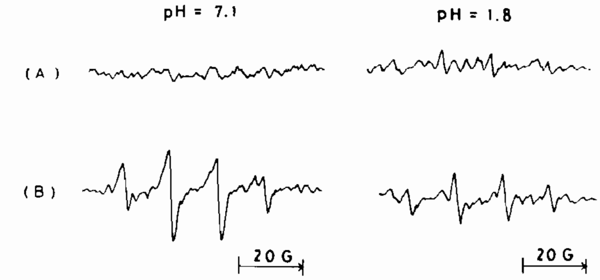

Fig. 2. Typical esr spectrum of •OH spin adducts of DMPO for samples at pH 7.1 and 1.8. (A) in the dark. (B) under photoirradiation.

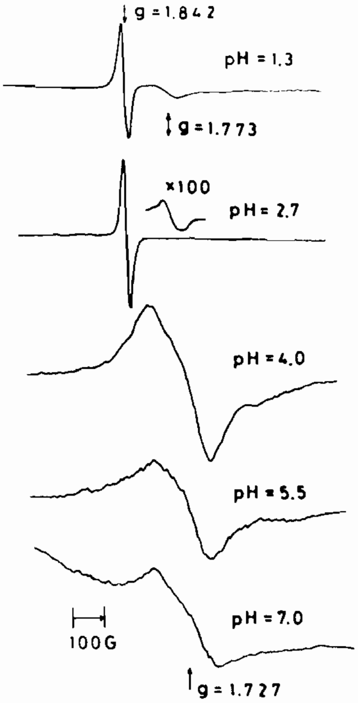

Fig. 3. Esr spectra (77 K) of photolytes of isopropylammonium polytungstates at pH 1.3, 2.7, 4.0, 5.5 and 7.0.

at the wave-length region of $\lambda > 300$ nm [1, 2]. The quantum yield of 0.05 is about three times higher than that (0.017) in the presence of the colloidal Pt, which has been described previously [1]. Lowering of the quantum yield in the presence of colloidal Pt is mainly caused by an absorbance of the colloidal Pt itself and we conclude that, for the polytungstate aqueous solution system, colloidal Pt is not necessarily essential for the H_2 evolution from water. The H_2 evolution from water was demonstrated by using D_2O for the same kind of experiment: white crystals of isopropylammonium tungstate, probably as 12-tungstate*, were isolated from the aqueous solution at pH 6–7 and dissolved in D_2O. The photoirradiation of the D_2O solution (pH 7.1) containing 1.4% isopropylammonium polytungstate brought about 100% of D_2 as the composition of the gas evolved. The reconstructured ion current chromatogram in the G.C.-mass spectroscopic analysis obtained is shown in Fig. 1, where the gas evolved contains neither HD nor H_2.

We have pointed out the polytungstate exhibiting the maximum of the photoresponse around 345 nm in the study on the photogalvanic current, which was observed for solutions of pH < 3 and which was distinguished from $[W_6O_{20}(OH)]^{5-}$ [2]. The quantum yield of H_2 evolution by 365-nm light irradiation at pH 2 was about 5×10^{-4}. 254-nm light excitation in this case brought about no significant H_2 evolution, because of the absence of $[W_6O_{20}(OH)]^{5-}$ in the solution of pH 2.

In order to confirm the formation of hydroxyl radicals (•OH) formation in the polytungstate system, the spin trapping by a use of DMPO as a spin trap was examined for its effectiveness in trapping •OH in water. The photoirradiation of isopropylammonium polytungstate solutions at various pH levels in the presence of DMPO resulted in the 1:2:2:1 line spectra in esr, exhibiting $a^N = a^H = 15.0$ G and g = 2.007 as shown in Fig. 2. The spectrum is comparable to that attributed to the •OH spin adduct of DMPO [5], indicating that the photo-induced formation of •OH for the isopropylammonium polytungstate solution occurs at various acidities.

Frozen solutions of the photolyte at various pH acidities showed esr signals due to W^V at 77 K. A broad singlet (ΔH_{ms} *ca.* 200 G) esr signal around g = 1.72–1.73 was observed for the photolytes of pH ⩾ 4, whereas a relatively narrow singlet ($\Delta H_{ms} = 20$ G)

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*X-ray crystal structural determination is currently in progress.

signal of g = 1.842 was observed for the photolytes of pH < 3. The signal intensity increased with the duration of the photolysis without appearance of the hyperfine structure. Typical results are shown in Fig. 3. At pH ⩾ 8 there was no observable esr signal at 77 K. As can be seen from Fig. 3, the spectra are similar in g-value and ΔH_{ms} for the photolytes at pH levels higher than 4. Each of the spectra for pH < 3 is also similar but a new weak signal of g = 1.773 with $\Delta H_{ms} \approx 60$ G appears and its intensity ratio to g = 1.842 signal increases with an increase in the acidity. The water photoelectrolysis using a photogalvanic cell, Pt|alkylammonium polytungstate solution‖5N-H_2SO_4|Pt, occurred as a result of the photoabsorption of two distinct polytungstates of $[W_6O_{20}(OH)]^{5-}$ and unknown species (X): the former was observed at pH ⩾ 4 and the latter at pH < 3 [2]. In conjunction with the dependence of the photochemical H_2-evolution from water on solution pH and the wavelength of the incident light, it is likely that paramagnetic species of g = 1.72–1.73 and 1.842 arise from the photoreaction of $[W_6O_{20}(OH)]^{5-}$ and X, respectively. Solutions of tetrakis(tetrabutylammonium) decatungstate $[Bu_4N]_4[W_{10}O_{32}]$ in acetonitrile show a maximum ($\epsilon \approx 10^3$ M^{-1} cm^{-1}) at 325 nm in the absorption spectrum [6]. $\lambda > 350$ nm-light photolysis of this solution (1 m*M* $[Bu_4N]_4[W_{10}O_{32}]$) gave a single esr line of g = 1.842 with ΔH_{ms} = 20 G at 77 K, in good agreement with the esr spectrum for the photolyte at pH < 3 (Fig. 3). The addition of water into the solution resulted in no change of g value or ΔH_{ms} for the esr spectrum of the photolyte. Furthermore, $\lambda > 350$ nm-light exposure in the presence of water (CH_3CN/water > 9, v/v) and colloidal Pt led to H_2 evolution. The presence of colloidal Pt in this case was essential for H_2 evolution from water. These results [7] suggest that X species leading to H_2 evolution at pH < 3 may be associated with $[W_{10}O_{32}]^{4-}$.

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