Photochemical Hydrogen-Evolution from Alkaline Solution of Alkylammonium Isopolyvanadate

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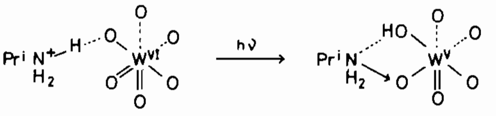
Introduction

We have reported hydrogen-evolving systems by a use of isopolyoxoanions of molybdenum and tungsten [1, 2]. H_2 evolution from water by the photoirradiation of LMCT bands in polyoxoanions can be observed in the presence of alkylammonium cations or carboxylic acids [3, 4]. U.V. irradiation of aqueous solution containing isopropylammonium polytungstates(VI) results in the redox reaction between polytungstate(VI) and water to yield W^V at the octahedron site and $\dot{O}H$. Such photoreduced polytungstates can be oxidized to the original state by coupling with water reduction to H_2 formation, since the photoreduced polytungstates exhibit an oxidation potential more negative than the reduction potential of water. It has been considered that the transfer of a hydrogen bonding proton from $[NH_3Pr^i]^+$ to a bridging oxygen atom at the octahedron site of polytungstate(VI) is preceded (eq. 1) and that $[NH_3Pr^i]^+$ serves mainly as an electron relay for the photoredox reaction (eq. 2), although it is oxidized in minor part (eq. 3) [2–5].



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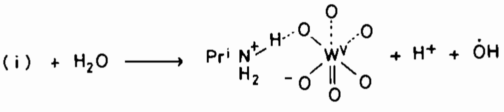

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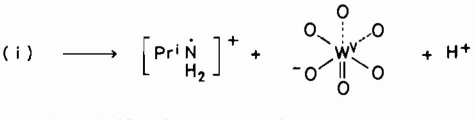

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The difficulty with the isopolytungstate system for the chemical conversion of solar energy is a lack of absorption of polytungstates such as $[W_6O_{20}(OH)]^{5-}$ and $[W_{10}O_{32}]^{4-}$ in the visible wavelength region, although $[W_{10}O_{32}]^{4-}$ exhibits a light yellow color due to an absorption maximum at 323 nm ($\epsilon = 1.35 \times 10^4$ M^{-1} cm^{-1}) in CH_3CN [6]. From this standpoint we have directed our attention to the hydrogen-evolving system by a use of polyvanadates, since solutions of polyvanadate(V) at pH < 8 are yellow-orange in color with a long shoulder sloping into the visible. This paper describes U.V.-induced H_2-evolution from solutions of isopropylammonium polyvanadate at narrow pH range around 9.5, where $[HV_2O_7]^{3-}$ is likely to be photosensitive. Photochemical H_2-generation from alcohols in the presence of the polyvanadate is also reported.

Experimental

All chemicals were of analytical grade and were used without further purification. All experiments were performed according to previous methods [1, 2]. Sample solutions at pH 9.9 were prepared by mixing 4.6 mM Na_3VO_4 and 65 mM $[NH_3Pr^i]ClO_4$ in aqueous solution. Other solution pH levels were adjusted by $HClO_4$ or NaOH. The sample solutions of 70 cm^3 were flushed with argon for 30 min to exclude oxygen and exposed to u.v. light ($\lambda > 200$ nm) from a USHIO UM-102 100 W Hg lamp fitted with a water jacket to remove i.r. irradiation. The gas evolved was conducted to a gas volumeter. Hydrogen gas was analyzed by GC (Hitachi 164 gas chromatograph equipped with a column of carbosieve S at 50 °C).

A 500 W xenon lamp served as the light source for photocurrent measurements. A bright platinum circular plate (20 mm^2 area) was used as a working electrode for photocurrent measurements. Potentiostatic photocurrent-potential curves were measured for the argon-flushed sample by a customary potentiostatic arrangement and each data point on the curve was for the maximum value for the anodic photocurrent. These measurements were done under the incidence of white light (nonfiltration) on the sample, in order to have sufficient light intensities. The measurement of the action spectrum of the photocurrent was carried out by a lock-in (NF model LI-575) technique using modulation of the light beam with 8 Hz, in conjunction with monochrometer (Nikon G-250, blaze wavelength 300 nm) and the signals obtained were corrected to constant photon flux at each wavelength.

Results and Discussion

H_2 evolution from the sample solution was observed within the range 8–10.5 only, reaching a maximum at 9.5 as shown in Fig. 1(A). During the photolysis the colorless solutions turned brown, due to the accumulation of photoreduced vanadate

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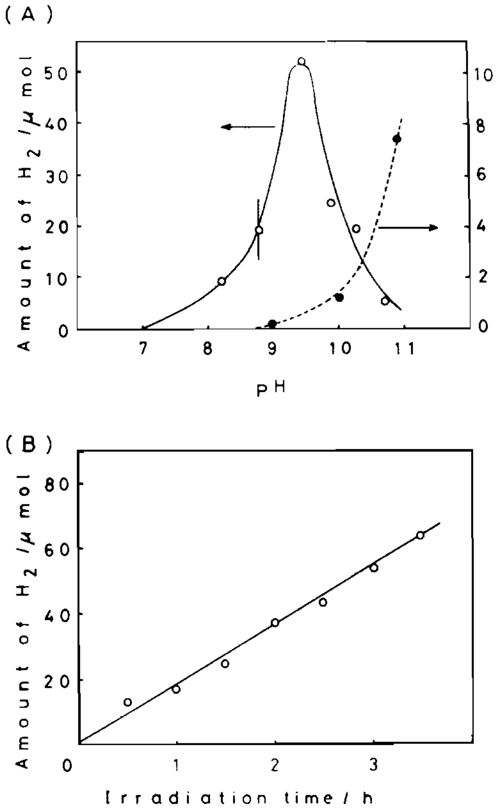

Fig. 1. Amount of H_2 at room temperature as functions of solution pH (A) and irradiation time (B). Aqueous solutions (70 cm^3) were exposed to $\lambda > 200$ nm light. —○—: 4.6 m*M* in total V^V and 65 m*M* $[NH_3Pr^i]ClO_4$, - - ● - - -: 65 m*M* $[NH_3Pr^i]ClO_4$. Yield measurements in (A) were after 3 h of the photoreaction. pH of the sample solution for (B) was 9.5.

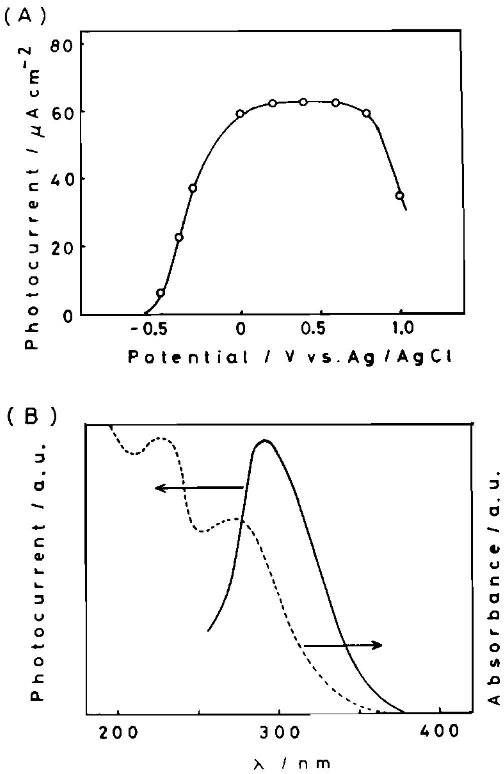

Fig. 2. Potential dependence (A) and action spectrum (B) of anodic photocurrents. Sample solutions (25 cm^3 at pH 9.5) contained 4.6 m*M* in total V^V and 65 m*M* $[NH_3Pr^i]ClO_4$ in H_2O. Action spectrum (———) was measured at $U_{Ag/AgCl}$ = 0.5 V and absorption spectrum (- - - -) of the solution was shown in (B) for comparison.

(probably $V \rightarrow IV$).† In the absence of vanadates, H_2 formation due to the photolysis of $[NH_3Pr^i]ClO_4$ was observed and was significant at high alkalinity of pH > 10.5 (Fig. 1(A)). The H_2 evolution in strongly alkaline solutions demonstrates the photochemical dehydrogenation of NH_2Pr^i (pK_a = 10.6 [7] for $[NH_3Pr^i]^+$) [8]. Amount of H_2 evolved in the polyvanadate system at pH 9.5 increased linearly with the irradiation time (Fig. 1(B)). The quantum yield of H_2 formation was estimated to be about 0.002 for 254-nm light irradiation.

Anodic photocurrent-applied potential curve at pH 9.5 is shown in Fig. 2(A) where the onset potential, corresponding to the redox potential for the photoreduced vanadate, is likely to be situated at the potential more negative than –0.5 V *vs.* Ag/AgCl. The decrease in the photocurrent at $U_{Ag/AgCl} > 0.8$ V is due to the oxygen quenching of the photoreduced vanadate, which is the electrochemically active species [1, 2]. The maximum photocurrent for the photocurrent-potential curve at each solution pH exhibited the optimum at pH of about 9.5, which was observed for the rate of the H_2 evolution, too (Fig. 1(A)). Considering that the anodic photocurrent was due to the electron ejection from the photoreduced vanadate at the Pt electrode, the similarity of the pH dependence between the H_2 evolution and the anodic photocurrent suggests that the oxidation of the photoreduced vanadate can be coupled with the water reduction. Action spectrum of the anodic photocurrent at $U_{Ag/AgCl}$ = 0.5 V was shown in Fig. 2(B) where the absorption spectrum was added for comparison. The spectral distribution of the photocurrent showed a maximum around 290 nm with a shoulder sloping into the near-ultraviolet. The action spectrum is similar to the absorption spectrum calculated for $[HV_2O_7]^{3-}$, since the principal species around pH 9.5 are $[HVO_4]^{2-}$, $[HV_2O_7]^{3-}$, and $[V_3O_9]^{3-}$ [9, 10] and the absorption spectra of these three species are quite different, showing λ_{max} = 270,

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† We could not observe any e.s.r. signals due to V(IV) in the photolyte of pH 9.5 at 77 K. U.v. irradiation of the sample solution (pH 9.5) in the presence of phenyl-t-butylnitrone as a spin trap resulted in the formation of nitroxide radicals (a_N = 15.0 G, a_H = 3.4 G), probably due to $\dot{O}H$ adducts.

290, and 280 nm for $[HVO_4]^{2-}$, $[HV_2O_7]^{3-}$, and $[V_3O_9]^{3-}$, respectively [11]. Therefore, it seems to be plausible to assume that the photoreducible vanadate leading to H_2 evolution is $[HV_2O_7]^{3-}$. The possibility of photosensitive mononuclear vanadate $[HVO_4]^{2-}$ may be excluded by the small degree of stabilization of the photogenerated hole at oxygen atom. In metaloxoanions there is sharing of the metal d_π orbitals among the oxygens. On LMCT photoexcitation, such d_π electrons may move toward the positive hole on the oxygen atom because of the latter's attraction and the repulsion set up by the relative preponderance of the negative charge on the V^{IV} atom. This leads to the stabilization of the hole generated on the oxygen atom and its degree will increase with the condensation of VO_4 due to increasing delocalization of d_π electrons [4].

From the fact that H_2 is photochemically evolved at pH 9.5, the redox potential of the photoreduced species should be more negative than the reduction potential of water, –0.83 V *vs.* Ag/AgCl. Unfortunately, attempts to measure the anodic photocurrent at the potential more negative than –0.5 V *vs.* Ag/AgCl failed, due to the significance of the cathodic current arising from the reduction of water at Pt electrode in the dark. High negativity of the redox potential for the photoreduced vanadate may be inferred by the electrochemical reduction which occurs at the potential more negative than the reduction potential of water, although we have no details on the reaction mechanism. Cyclic voltammetry (scan rate 100 mV s^{-1}) of the solution (at pH 9.5) containing 4.6 m*M* in total V^V and 65 m*M* $[NH_3Pr^i]ClO_4$ revealed two successive irreversible reduction waves around –1.4 and –1.7 V *vs.* Ag/AgCl, using a hanging mercury drop electrode.

H_2 evolution from alcohol by the photoexcitation of the vanadate was also observed: U.V. ($\lambda \geq 330$ nm) irradiation of solutions (10 cm^3 at pH 9.5) containing 4.6 m*M* in total V^V in H_2O/MeOH = 5/1 (v/v) brought about H_2 evolution with a rate of 9.1×10^{-4} cm^3 h^{-1} at room temperature. This indicates that the photoreduced vanadate produced by the photoredox reaction between the vanadate and MeOH can be oxidized by a coupling with the water reduction to H_2 formation, as discussed about the decatungstate system [6].

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