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Production of Hydrogen by Photogalvanic Cell. Part 2. pH Dependence of Alkylammonium Molybdate System

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Introduction

We have reported the photogalvanic behavior (at pH 5.2–5.4) for the aqueous alkylammonium molybdate based on the photoreduction of Mo^{VI} to Mo^{V} which is coupled with a water oxidation to hydroxyl radical [1]. The splitting of water ($H_2O \rightarrow ½H_2 + \cdot OH$) has been considered to be given in terms of the half-reactions:

$$\text{Photoanode: } Mo^{VI}=O + H_2O \xrightarrow{h\nu} Mo^{V}\text{–}OH + \cdot OH \qquad (1)$$

$$Mo^{V}\text{–}OH \rightarrow Mo^{VI}=O + H^+ + e \qquad (2)$$

$$\text{Cathode: } H^+ + e \rightarrow ½H_2 \qquad (3)$$

This is the first example producing hydrogen from water using photogalvanic effect of molybdenum compounds, although the photoreactivity is limited to ultraviolet wavelength ($\lambda < 400$ nm). When hexakis(isopropylammonium) heptamolybdate, $[NH_3Pr^i]_6[Mo_7O_{24}]$, is used as the molybdate, it has been postulated that the electrochemically active intermediate, exhibiting the photogalvanic effect, is produced by the decondensation of the one-electron photoreduced 7-molybdate to 1-molybdate [2]. To understand some of the basic aspects of photoelectrolysis, we describe here the operation of a photogalvanic cell

$$Pt|54.4\ mM\text{-}[NH_3Pr^i]_6[Mo_7O_{24}]\,||\,5N\text{-}H_2SO_4\,|Pt$$

on the variation of pH values for the anodic solution containing 54.4 mM $[NH_3Pr^i]_6[Mo_7O_{24}]$ and discuss the reason for an observable optimum pH (7–8).

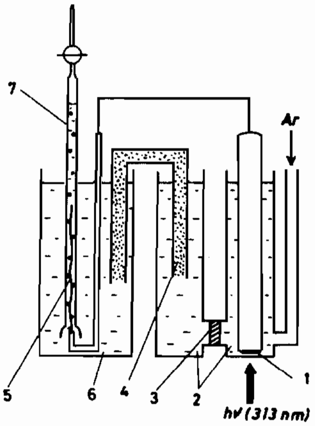

Fig. 1. Schematic drawing of the experiment cell: (1) 18 mm^2 bright Pt circular plate (anode); (2) molybdate solution at given pH; (3) glass frit; (4) KCl-agar salt bridge; (5) 50 mm long and 1 mm in diameter Pt wire (cathode); (6) 5N H_2SO_4 solution; (7) buret.

Experimental

Hexakis(isopropylammonium) heptamolybdate trihydrate was prepared and recrystallized following our procedure [2] and its structure was determined by single-crystal X-ray diffraction. 2-methyl-2-nitrosopropane was added in the spin trapping experiments. A solution of pH 6 to 8 was adjusted by Na_2MoO_4 to avoid a drastic decrease in $Mo_7O_{24}^{6-}$ concentration due to the equilibrium reaction ($Mo_7O_{24}^{6-} + 4H_2O \rightleftarrows 7MoO_4^{2-} + 8H^+$) between $Mo_7O_{24}^{6-}$ and MoO_4^{2-} [3]. Measurements of the absorbance (ϵ = 90 M^{-1} cm^{-1}) at 320 nm revealed that the concentration of $Mo_7O_{24}^{6-}$ was almost constant (54.4 mM) at these pH range. Other pH levels were adjusted by $HClO_4$ or NaOH. Continuous irradiation experiments were performed using a 500 W superhigh pressure mercury lamp in conjunction with filters. The light intensity was determined by ferrioxalate actinometry. Measurements of electrode potential and photocurrent were done by Takeda Riken Co. electrometer TR-8651. The flash photolysis experiment was carried out using a conventional flash-photolysis apparatus Xenon Corp. Model 720. X-band e.s.r. spectra were recorded on a Varian E12 spectrometer. Unless otherwise specified, all measurements were done at room temperature.

The photogalvanic cell for H_2 generation is shown in Fig. 1: The anode compartment was made of two test chambers (for the KCl–agar salt bridge-immersed and irradiated solutions) connected by glass tubing 10 mm in inside diameter with a very fine glass frit. Anodic solutions were flushed with argon and irradiated at 313 nm with an intensity of 1.76×10^{-8}

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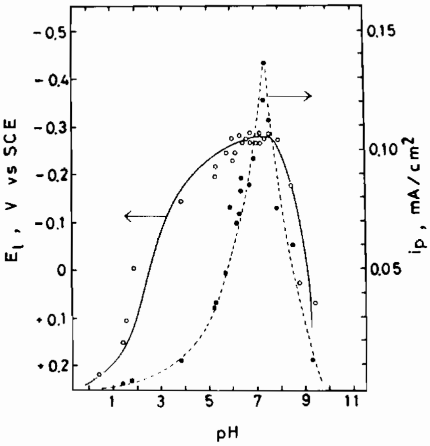

Fig. 2. Photostationary potential (E_l) and short-circuit photocurrent (i_p) as a function of anode solution pH. Photocurrent measurements were after 1 hr irradiation with 313 nm light.

E/s. cm^2. Hydrogen was analyzed by conventional GC with a Carbosieve S column.

The photocurrent-applied potential curves at given pH were measured potentiostatically according to the previous method with a light pulse of 6 ms duration and each data point on curves was for the photocurrent value just before the light is turned off under the chopped white light irradiation [1].

Results and Discussion

The photopotential of the electrode of the photogalvanic cell (Fig. 1) reached the photostationary value within several minutes of the irradiation time. The short-circuit photocurrent rose steeply within several seconds and then decreased with fast decay ($\tau \cong$ 15 min) and succeeding long term decay ($\tau \cong$ 14 hrs) during the duration of the irradiation. The photostationary potential (E_l) and the short-circuit photocurrent (i_p) at 1 hr irradiation are plotted as a function of the anodic solution pH in Fig. 2, where the most negative E_l and the highest i_p are observed around pH 7.4. The evolution of H_2 bubbles at the cathode was readily observed at pH 5–8, where E_l was more negative than the redox potential (–0.22 V *vs.* SCE at pH = –0.4) [4] of H^+/H_2. The quantum yield of the cell at optimum pH 7.4 in terms of current produced per photon added to the system was calculated to be 0.08 using i_p = 135 μA/cm^2 †. On the basis of the fact that a stoichiometric ratio for moles of electrons to moles of H_2 was close to 2:1 [1], then, quantum yield for H_2 production was calculated to be 0.04. In this case, pH gradient across the KCl-agar salt bridge supplies a voltage of approximately 8 × 59 mV = 0.472 V: 0.472 eV of a total of 1.77 eV [4] for water splitting is derived from pH gradient as an external potential source, if we assume that the nett reaction of water splitting is $2H_2O \rightarrow H_2 + H_2O_2$. 1.3 eV which was actually gained at the quantum yield of 0.08 for electron flow from 4 eV photons (λ = 313 nm) is therefore produced at an optical energy conversion efficiency [5] of 2.6%. This value is comparable to the largest value (about 2%) for the photoelectrolysis with a use of TiO_2 photoanode [6].

Quantities of ΔE_{ld} (E_l relative to the dark equilibrium potential of +0.18 V *vs.* SCE at pH 7.4) was logarithmically dependent on light intensity with a slope of 85 mV. i_p was linearly proportional to the light intensity. During the prolonged irradiation, the anodic solution at pH 7.4 changed to a brown color. Resulting solution was e.s.r. inactive at room temperature and admission of oxygen into the solution brought about a color change to colorless, suggesting that the brown solution contained a dimer of the reduced 1-molybdate probably with an octahedral di-μ-oxo structure [7]. Irradiation of the solution in the presence of 2-methyl-2-nitrosopropane in the cavity of an e.s.r. instrument immediately produced a signal of the spin adduct (g = 2.004, a = 16.0 G, a_H = 3.1–3.5 G at pH 7.4) of ·OH (or ·OOH) which resulted from the water oxidation (eqn. 1). Back reaction between the reduced molybdates and ·OH (or H_2O_2) was likely to be depressed, since most of ·OH (or H_2O_2) reacted with $Mo_7O_{24}^{6-}$ to yield peroxymolybdate (for example $Mo_7O_{26}^{6-}$) under the high concentration (54.4 m*M*) of $[NH_3Pr^i]_6[Mo_7O_{24}]$ [8]. A consumption of $Mo_7O_{24}^{6-}$ due to the reaction with ·OH (or H_2O_2) may be a factor which decreased the short-circuit photocurrent during the duration of the irradiation.

In order to find the reason for the optimum pH 7.4 of anodic solution, the photocurrent-applied potential (*vs.* SCE) behavior at given pH was measured. Typical results are shown in Fig. 3. The relaxation time of about 20 ms [1] for the photocurrent signal was almost independent on solution pH, suggesting that the lifetime of the electrochemically active species was scarcely influenced by pH. Anodic photocurrent onset from the photocurrent-applied potential curves, which corresponds to the value of the standard redox potential ($E^\circ_{Mo^{VI}/Mo^{V}}$) for the electrochemically active species, represents the approximately linear pH dependence with a slope of about –59 mV/pH as shown in the insert of Fig. 3. At pH $\geqslant$ 9 the electrochemically active species was scarcely formed, since Raman spectra of the solutions at pH $\geqslant$ 9.0 exhibited only three bands at 898, 833, and 310 cm^{-1} due do nonphotoactive MoO_4^{2-}. This explains why there was no significant operation of the photo-

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† Intrinsic value of the quantum yield may be higher since corrections for the amount of light absorbed were not made.

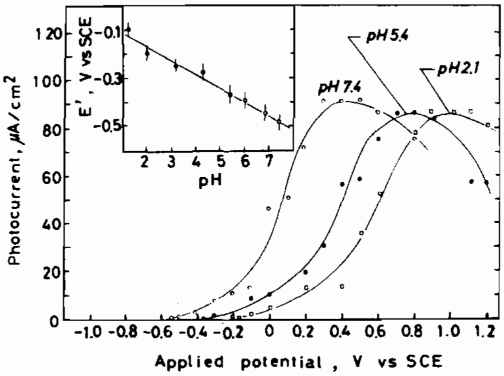

Fig. 3. Influence of applied potential on photocurrents for different pH-value (= parameter). The resulting potential onset (E′) for the photocurrent in dependence on the pH is shown in the insert.

galvanic cell at anodic solution pH $\geqslant$ 9. Therefore, the observation of the most negative E_1 at pH 7.4 (Fig. 2) can be explained by pH dependences of the redox reaction (eqn. 2) for the electrochemically active species and the equilibrium reaction between 7- and 1-molybdates in the dark. As shown in Fig. 3 the maximum photocurrent in photocurrent-applied potential curves occurs near the redox potential ($E^\circ_{O_2/H_2O}$ = 0.985 – 0.06 (pH) volt *vs.* SCE) [4] for the water oxidation to oxygen, because of the oxygen-quenching of the electrochemically active species at anodic polarization higher than $E^\circ_{O_2/H_2O}$ [1]. This suggests that the value of the reorganization energy for the electrochemically active species is more than 1 eV corresponding to the difference between $E^\circ_{O_2/H_2O}$ and $E^\circ_{Mo^{VI}/Mo^V}$ [9]. In flash photolysis experiments the first intermediate with broad absorbance at the near ultraviolet-visible wavelength range was converted into the second species (λ_{max} = 500 nm) with a first order reaction of $\tau \cong 10^{-4}$ s irrespective of pH ($\leqslant$8). Qualitative observations indicated that the yield of the intermediate formation was maximized at pH 5.4. Based on the assumption that an electron transfer can only occur between both donor and acceptor electronic energy states having equal energy [9], therefore, a steep increase of i_p with increasing pH $\leqslant$ 7.4 (Fig. 2) was considered to result from increasing overlaps of distribution functions between H^+ (acceptor) and electrochemically active species (donor) due to the shift of $E^\circ_{Mo^{VI}/Mo^V}$ to the negative side.

We extend the photogalvanic photoelectrolysis to other polyanions such as tungstate and vanadate [10]. In investigating H_2 evolution by isopropylammonium salts of these polyanions we found that H_2 was formed as expected and we noticed that the pH range favoring H_2 formation was at pH 7–10.

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