Production of Hydrogen by Photochemical Splitting of Water Using Diammonium Tetrathiomolybdate as Photocatalyst

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Synopsis. Hydrogen gas is generated at the cathode when the anode compartment of a photogalvanic cell anode/$(NH_4)_2MoS_4$(aq, satd.)//5 M HCl (aq)/cathode is illuminated. The photocurrent generated rises slowly with time and reaches a limiting value. A mechanism is suggested involving the conversion of Mo(VI) to Mo(V) and the formation of OH radicals, as evidenced by development of paramagnetism on irradiation. Although the photocatalyst is susceptible to hydrolysis, it can be easily regenerated by passing H_2S.

Transition metal complexes are known to sensitize photodissociation of water to produce hydrogen, a potential fuel. Recently[1] it has been shown that hexakis-(alkylammonium)heptamolybdate catalyzes the photochemical splitting of water, but the efficiency of the system is very low since the photocatalyst absorbs in the UV region only. Herein is described the photogalvanic generation of hydrogen gas using diammonium tetrathiomolybdate as the photocatalyst. This compound absorbs in the visible region (λ_{max}=467.3 nm)[2] and, therefore, may be more effective from the standpoint of solar energy utilisation.

Experimental

$(NH_4)_2MoS_4$ was synthesized by following the method available in the literature[3] and was characterized by analytical, as well as spectral data.[2] The IR spectra were measured as KBr pellets using a Perkin Elmer 597 IR spectrophotometer and the UV-visible spectra were measured using a Perkin Elmer Hitachi 200 model instrument. The photocatalyst was preserved in the dark and always a freshly prepared solution was used. The photogalvanic cell consisted of two half-cells connected by a KCl-agar salt bridge. A saturated solution of $(NH_4)_2MoS_4$ was used as the photoactive anolyte and a 5 M HCl solution as the dark catholyte. A Pt-foil or a carbon rod (obtained from a flashlight dry cell) was used as the anode. The cathode was a Pt-wire which was subsequently replaced by platinized Pt and Cu wires. The H_2 gas generated at the dark cathode was collected in an inverted microburette over the cathode wire. The solutions of different pH were prepared from reagent grade NH_4Cl and NH_4OH.

The anode compartment was illuminated by a 1 kW halogen lamp, heating effect being minimised[4] by placing a saturated solution of Na_2SO_4 contained in a 10 cm thick cell, in between the compartment and the light source. The short circuit current was measured by using a Keithley model 616 digital electrometer. A Guoy type magnetic balance was used to measure the paramagnetic susceptibility generated on irradiation of the $(NH_4)_2MoS_4$ solution. A 15% (w/v) aqueous solution of $NiCl_2$, $6H_2O$ was used as the callibrant.

Results and Discussion

The photogalvanic cell can be represented as follows: anode/$(NH_4)_2MoS_4$ (aq, satd.)//5 M HCl/cathode.

On irradiation of the anode compartment hydrogen is generated at the cathode. The amount of hydrogen generation depends on the anode and cathode materials. Effect of changing the cathode material (Table 1) clearly reflects the relative ease of hydrogen evolution on platinized Pt, bright Pt, and Cu as determined by the respective overvoltage. Platinized Pt is known to be a better electrocatalyst than bright Pt for this reaction, whereas Cu is much inferior. However, the increase in the rate of hydrogen production on replacing a Pt-foil by a carbon rod of approximately the same surface area (*ca.* 7.5 sq. cm) can arise due to two different reasons: (i) Difference in the catalytic activities of carbon and Pt for the anode reaction, (ii) the active surface area of carbon may be much greater than the measured 'apparent' surface area due to its somewhat porous nature. This question is sorted out later. The quantum efficiencies of hydrogen production, as given in Table 1, are not monochromatic values and hence, can be considered as the lower limits of actual efficiencies under the given conditions. These values are based on the number of average photons in the visible range received by the anolyte solution which is measured by Reinecke's salt actinometry.[5] The quantum yield of its photoaquation has been assumed to be 0.3 over the entire visible region of the spectrum.[5]

The measurement of the short circuit current, with and without illumination, is more convenient and can provide more quantitative information regarding the mechanism of the overall process. The results are presented in Table 2. Apparently, the greater 'true' surface area of carbon seems to explain the increased efficiency of hydrogen production. Since the ratios of the dark and photo current densities of Pt and carbon are observed to be nearly the same, the effect appears not due to any difference in their catalytic activities. The data in Table 2 are based on apparent surface areas. However, a slow rise of the photocurrent to a limiting

Table 1. Effect of cathode and anode material on the rate of hydrogen generation

Anode	Cathode	Light intensity / E h^{-1}	Volume of H_2 / cm^3 h^{-1}	Quantum efficiency
Pt-foil	Bright Pt	4.8×10^{-4}	0.06	0.011
	Platinized Pt	4.8×10^{-4}	0.1	0.019
Carbon rod	Bright Pt	1.3×10^{-3}	0.25	0.017
	Platinized Pt	1.3×10^{-3}	0.5	0.034
	Copper	1.3×10^{-3}	Negligible	—

Table 2. Short circuit current densities with and without illumination

Anode	Short circuit current density/μA cm^{-2}		
	Dark	Illuminated	Photo
Pt-foil	2.0	12.0	10.0
Carbon rod	16.0	96.0	80.0

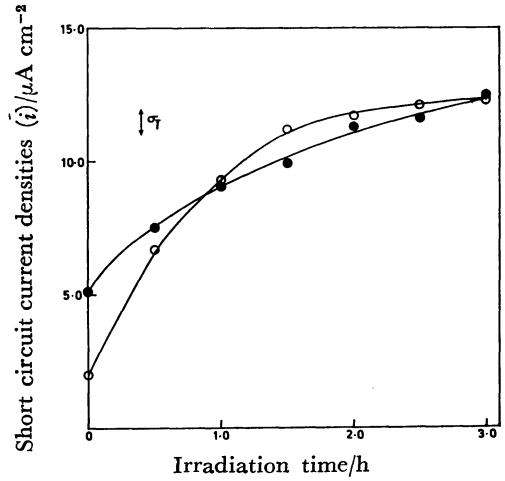

Fig. 1. Rise of short circuit current densities with irradiation time in solutions of pH 8 (○) and pH 10 (●).

value (Fig. 1) seems to indicate a competitive step in the overall reaction mechanism and a consequent slow build up of electroactive material in the anode compartment.

Following Yamase and Ikawa,[1] a sequence of steps, somewhat analogous to those in molybdate system, may be proposed:

(1) $(MoS_4)^{2-} \xrightarrow{h\nu} [(MoS_4)^{2-}]^*$

(2) $[(MoS_4)^{2-}]^* + H_2O \rightarrow (MoS_3SH)^{2-} + \cdot OH$

(3) $(MoS_3SH)^{2-} + \cdot OH \rightarrow (MoS_4)^{2-} + H_2O$

anode (4) $(MoS_3SH)^{2-} \rightarrow (MoS_4)^{2-} + H^+ + e$

cathode (5) $H^+ + e \rightarrow 1/2\, H_2$.

This sequence assumes the step (3) to be competitive with the anode reaction. Once a steady state concentration of $(MoS_3SH)^{2-}$, in which Mo is in its +5 oxidation state as against +6 state in $(MoS_4)^{2-}$, is reached the photocurrent attains its limiting value. The main water-splitting reaction according to the above mechanism is seen to be

$$H_2O \rightarrow \cdot OH + H^+ + e.$$

Carbon is known to be a better heterogeneous catalyst than Pt[6] for the combination of ·OH radicals leading to the formation of H_2O_2 and O_2 successively as follows:

$$\cdot 2HO \rightarrow H_2O_2 \rightarrow H_2O + 1/2\, O_2.$$

Consumption of ·OH radicals in this way should indirectly favour the anode reaction and thus, may be partly responsible for the observed higher efficiency of carbon than Pt apart from the surface area consideration.

Further evidence in support of the said mechanism is obtained by following the change in the magnetic property of an aqueous solution of $(NH_4)_2MoS_4$ on irradiation. On exposure to light the solution develops paramagnetism as expected if Mo(V) species and OH· radicals are produced, which reaches a limiting value after 1.5 h (Fig. 2). The striking similarity of the rise in photocurrent and growth of paramagnetism with time places the validity of our tentative reaction scheme on a firmer basis. The % conversion of $(MoS_4)^{2-}$ has been calculated from the experimental paramagnetic susceptibility measurements of the irradiated solution and the theoretically computed values for $(NH_4)_2MoS_3SH$ and ·OH taking into consideration the 'spin only' magnetic moments. The decay curves obtained after switching off the light source are also identical in pattern. However, while the photogenerated paramagnetism disappears almost completely within one and a half hour or so, much longer time, even overnight, is necessary for the short circuit current to return to its initial *i.e.*, dark value. Admittedly, at present we are unable to account for this observation quantitatively.

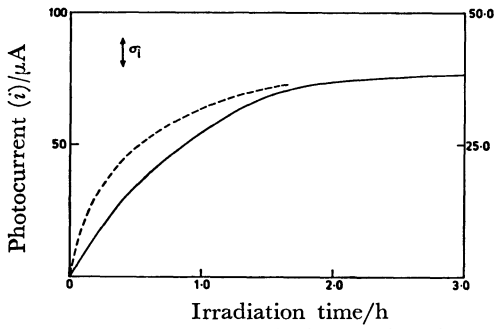

Fig. 2. Rise of photocurrent (solid curve) and growth of paramagnetism (dotted curve) with irradiation time.

All the above experiments were performed in solutions of pH around 8 as the photocatalyst is stable in alkaline solutions only. However, $(NH_4)_2MoS_4$ undergoes a slow hydrolysis in aqueous solution according to the following reaction where stepwise replacement of S atoms by O atoms occurs.

$$(NH_4)_2MoS_4 + nH_2O \rightarrow (NH_4)_2MoO_nS_{4-n} + nH_2S\ [n=1,2,3,4]$$

A part of the resulting H_2S may dissolve and dissociate to give HS^- and S^{2-} ions. Although the dissociation constants are very small in acid solutions (1.1×10^{-7} and 1×10^{-4} respectively) these may increase appreciably with the increase in pH of the solution. Thus, the redox couple H_2S/S may be established at higher pH as S has a tendency to dissolve in alkaline solution, containing excess of S^{2-}, forming polysulphides. The redox potential of the reaction

$$2H^+ + S + 2e \rightarrow H_2S$$

at pH 7 is 0.14 V.[6] We have observed that at pH 10 the dark short circuit currents have appreciably higher values leading to some amount of hydrogen production even in the dark. This seems possible in view of the negative Nernst potential calculated for the couple H_2S/S at these higher pH values. However, the photoeffect remains essentially of the same nature (Fig. 1). Due to this slow hydrolysis, occasional 'reactivations' by passing H_2S has been found to be necessary to use $(NH_4)_2MoS_4$ as a catalyst for photodissociation of water over long periods of time.

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References

1) T. Yamase and T. Ikawa, *Inorg. Chim. Acta*, **37**, L 529 (1979) and relevant references therein.

2) E. Diemann and A. Mueller, *Coord. Chem. Rev.*, **10**, 79 (1973).

3) G. Kruss, Leibigs. *Ann. Chem.*, **225**, 29 (1884).

4) S. Marks, *Solar Energy*, **25**, 255 (1980); D. R. Biswas, *ibid*, **19**, 99 (1977).

5) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).

6) D. J. G. Ives and G. J. Janz, "Reference Electrodes," Academic Press (1961).