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UV photoinduced reduction of water to hydrogen in Na_2S, Na_2SO_3, and $Na_2S_2O_4$ aqueous solutions

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Abstract

Hydrogen was produced by ultraviolet (UV) light irradiation (>200 nm) in an Na_2S aqueous solution without photocatalysts. Water (protons) appeared to be directly reduced to hydrogen by excited electrons produced in photon absorption with sulfide ions (S^{2-}). The maximum quantum efficiency for hydrogen formation, 8.9%, was obtained in a 25 mmol dm^{-3} Na_2S solution. Marked amounts of hydrogen were produced under UV light irradiation in the aqueous solutions of ${SO_3}^{2-}$ and ${S_2O_4}^{2-}$ ions. S^{2-} ion absorption began at 290 nm, ${SO_3}^{2-}$ at 275 nm, and ${S_2O_4}^{2-}$ at 400 nm. Hydrogen hardly formed at all, however, in ${SO_4}^{2-}$, I^-, and SCN^- solutions. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Hydrogen formation; UV light irradiation; Proton reduction

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1. Introduction

Hydrogen production from hydrogen sulfide (H_2S) produced in large amounts when sulfur-containing compounds from petroleum are hydrodesulfurized is an important process from the viewpoint of hydrogen reproduction and utilization of H_2S as a hydrogen source. At present, H_2S is partially oxidized to sulfur by the Claus process. Hydrogen sulfide is decomposed into hydrogen and sulfur endothermically:

$$H_2S \rightarrow H_2 + S \qquad \Delta G^0_{298} = 8\,\mathrm{kcal\,mol^{-1}} \tag{1}$$

The bond dissociation energy (HS–H) is about 90 kcal mol^{-1}. This process has been extensively studied thermochemically and in a hybrid process, thermally and electrochemically [1–3]. The conversion efficiency of H_2S to H_2 in direct thermal decomposition is, however, only 30%, even at 1400 K [1]. H_2S was photolyzed in a gas phase under ultraviolet (UV) light (249 nm) irradiation [4]. Sulfide ions (S^{2-}), dissociation products of H_2S in solutions, is known to be oxidized easily over sulfide semiconductor photocatalysts as electron donors. Hydrogen was formed in visible-light induction from H_2S over CdS photocatalysts [5–7].

Hydrogen was produced from water under UV light irradiation in solutions of metal ions, such as Fe^{2+} [8–10], Eu^{2+} [11–13], Ce^{3+} [14], Cu^+ [15], and anions (Cl^-, Br^-, I^-) [16,17]. Hydrated electrons are proposed to have been produced by UV light absorption with iodide anions [18]:

$$I^- + h\nu \rightarrow (I^-)^* \qquad \text{excited ion} \tag{2}$$

$$(I^-)^* \rightarrow I + e^-_{aq} \qquad \text{hydrated electron} \tag{3}$$

$$H^+ + e^-_{aq} \rightarrow H \tag{4}$$

$$2H \rightarrow H_2 \tag{5}$$

The electron produced is trapped by an H^+ ion to form an H atom. We found that hydrogen could be produced by UV light irradiation (>200 nm) in an Na_2S aqueous solution without photocatalysts. This reaction appears to be due to direct water (proton) reduction to hydrogen by excited sulfide ions (S^{2-}) similar to Fe^{2+}, Eu^{2+}, and I^- ions. We report UV-photoinduced hydrogen production from water in aqueous solutions of S^{2-}, ${SO_3}^{2-}$, and ${S_2O_4}^{2-}$ ions.

2. Experimental details

Reagent-grade $Na_2S{\cdot}9H_2O$, K_2S, KI, KSCN, Na_2SO_4 (Wako Pure Chemical Industries, Ltd.), Na_2SO_3 (Nakarai Chemicals, Ltd.), and $Na_2S_2O_4$ (Kokusan Chemical Works,

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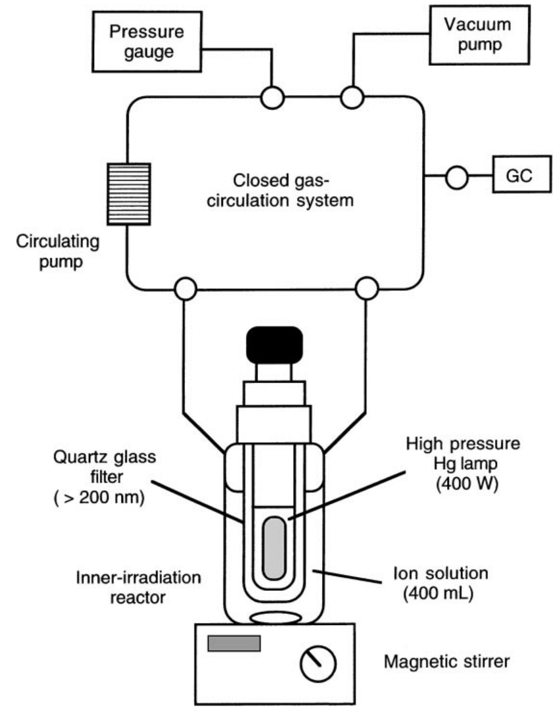

Fig. 1. Schematic diagram of equipment for photoreaction.

Ltd.) were used without any further purification for photoreactions. A known amount of these chemicals was dissolved in 400 ml of distilled water. Oxygen dissolved in the solution was eliminated in vacuum before photoreactions, which were conducted in an inner-irradiation reactor connected to a closed gas-circulation system (Fig. 1). A high-pressure Hg lamp (400 W) was the light source and a quartz glass filter was used to cut off light of <200 nm. The hydrogen produced was analyzed quantitatively using a gas chromatograph having an MS-5A column (Ar carrier) and a thermal conduction detector. UV–VIS absorption spectra of the solution were observed using a Shimadzu MPS-2000. X-ray fluorescence (XRF) spectra were measured on a Seiko Instruments Inc. SEA 2010.

3. Results and discussion

3.1. Hydrogen formation in the different ion aqueous solutions

Table 1
UV photoinduced formation in ion solutions[a]

Additive	Amount (mmol)	H_2 (μmol 20 h^{-1})
–	–	32.0
Na_2S	1.3	1560
Na_2S	3.3	3690
Na_2S	10.0	6830
K_2S	3.3	340
Na_2SO_3	3.3	3080
Na_2SO_3	6.4	5620
$Na_2S_2O_4$	3.3	3058
Na_2SO_4	3.3	33.3
KI	3.3	15.9
KSCN	3.3	13.7

[a] Light source: high-pressure Hg lamp (400 W); solution: H_2O 400 ml.

Hydrogen yields under UV light irradiation for 20 h in aqueous solutions containing 3.3 mmol of ionic compounds (8.3 mmol dm^{-3}) are shown in Table 1. A marked amount of hydrogen formed in Na_2S, Na_2SO_3, and $Na_2S_2O_4$ aqueous solutions, suggesting that the photoexcited electrons formed by UV absorption with these ions directly reduced protons to hydrogen, oxidizing ions in this process. The hydrogen yield for 20 h was 3.7 mmol for the Na_2S solution and 3.1 mmol for the Na_2SO_3 solutions. The hydrogen yield in a K_2S aqueous solution was 0.34 mmol, lower than in the Na_2S solution. Hydrogen was hardly produced at all, however, in SO_4^{2-}, SCN^-, and I^- solutions.

Jortner et al. reported that hydrogen formed under UV light irradiation in I^- aqueous solutions [17], obtaining a highly quantum yield of hydrogen, 0.25, using light at 228.8 nm in an I^- solution at pH 2 adjusted using H_2SO_4. H^+ acted as the hydrated electron scavenger, converting it to H atoms. They also used 1 mol dm^{-3} methanol as the H atom scavenger to produce molecular hydrogen from H atoms. Our reaction conditions differ from theirs in that the photoreaction was conducted in an I^- solution at neutral pH without H atom scavengers such as methanol, resulting in quite a low hydrogen yield.

3.2. Ion solution UV absorption spectra

Fig. 2 shows UV absorption spectra of ion solutions. Na_2S solution absorption starts at 290 nm and Na_2SO_3 solution absorption at 275 nm. $S_2O_4^{2-}$ ions absorb the photons at less than 400 nm (Fig. 2). This UV light absorption induced the photoreduction of water. K_2S solution absorption with a yellow color started at 500 nm. The S_2^{2-} ion solution absorbs visible and UV light at 500 nm, similar to the K_2S

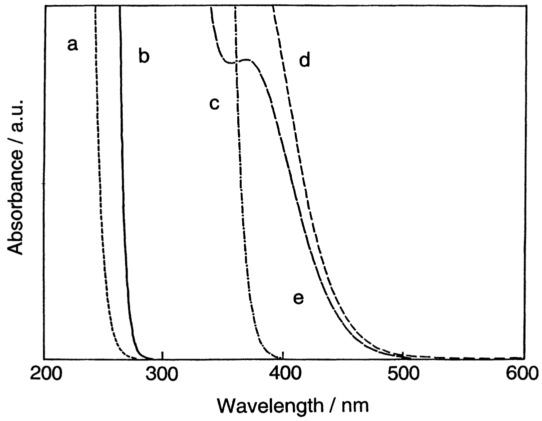

Fig. 2. Absorption spectra of ion aqueous solutions: (a) Na_2SO_3; (b) Na_2S; (c) $Na_2S_2O_4$; (d) K_2S; and (e) Na_2S aqueous solution after the photoreaction.

solution. K_2S solution absorption in the visible light region is due to potassium disulfide (K_2S_2) and polysulfide such as K_2S_4 present in K_2S as impurities. The Na_2S solution changed from colorless to yellow after the reaction (Fig. 2, line e). This absorption spectrum agrees fairly well with that of the $S_2{}^{2-}$ solution, suggesting the formation of disulfide ions $S_2{}^{2-}$ (or polysulfide ions) due to S^{2-} ion oxidation in the Na_2S solution after the photoreaction.

3.3. Hydrogen formation in Na_2S and Na_2SO_3 solutions

For 3.3 mmol of the Na_2S, K_2S, Na_2SO_3, and $Na_2S_2O_4$ solutions, over 3 mmol of hydrogen, which is the equivalent amount of ions, was produced in 20 h of irradiation (Fig. 3). The initial rate of hydrogen formation depends strongly on the type of ion — 1.9 mmol h^{-1} for Na_2S and 0.88 mmol h^{-1} for Na_2SO_3. Hydrogen formed in the $Na_2S_2O_4$ solution at 0.63 mmol h^{-1} and in the K_2S solution at 0.026 mmol h^{-1}.

We studied the effect of Na_2S concentration on hydrogen formation — 3.1 mmol dm^{-3} for 1.25 mmol of Na_2S, 8.3 mmol dm^{-3} for 3.3 mmol of Na_2S, and 25 mmol dm^{-3} for 10 mmol of Na_2S (Fig. 4). The hydrogen yield increases with increasing Na_2S concentration. As mentioned above, disulfide ions ($S_2{}^{2-}$) formed in the Na_2S solution after the photoreaction, suggesting the presence of the following reaction path:

$$2S^{2-} + 2H_2O + h\nu(2\text{photons}) \rightarrow S_2^{2-} + 2OH^- + H_2 \quad (6)$$

This reaction also occurred in hydrogen formation on a CdS photocatalyst in an Na_2S aqueous solution [19] in which the maximum hydrogen yield is expected to be half the amount of S^{2-} ions. Hydrogen yield, however, exceeds half the amount of S^{2-} ions — 6.8 mmol of hydrogen formed after 23 h in the solution containing 10 mmol of S^{2-} ions, and 3 mmol of hydrogen formed after 20 h in the 3.3 mmol S^{2-} ion solution (Table 1 and Fig. 4). 1.7 mmol of hydrogen, exceeding the amount of S^{2-} ions formed in the 1.3 mmol S^{2-} solution. These results suggest the presence of other hydrogen formation reaction paths from S^{2-} ions. No sulfur precipitated in the solution after the photoreaction, showing that sulfur was not concerning the reaction.

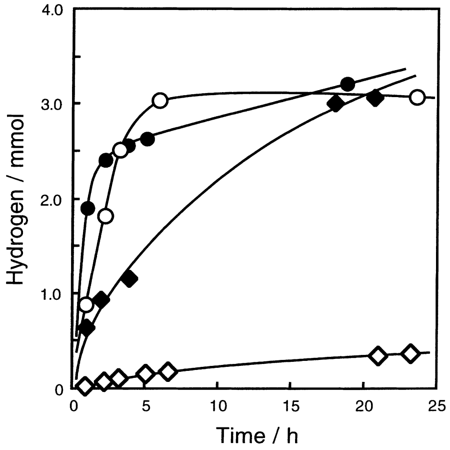

Fig. 3. Hydrogen formation under UV light irradiation (>200 nm) in aqueous solutions containing ionic compounds: (●) Na_2S; (○) Na_2SO_3; (◆) $Na_2S_2O_4$; and (◇) K_2S.

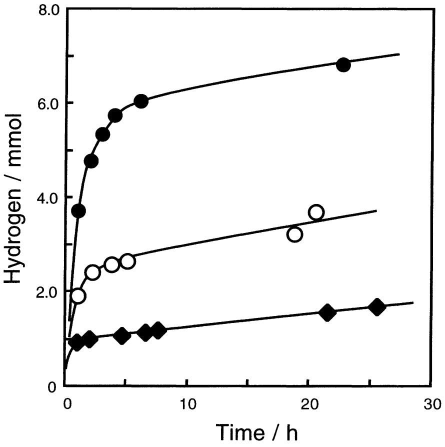

Fig. 4. Hydrogen formation under UV light irradiation (>200 nm) in Na_2S aqueous solutions: (◆) Na_2S 1.3 mmol; (○) 3.3 mmol; and (●) 10 mmol.

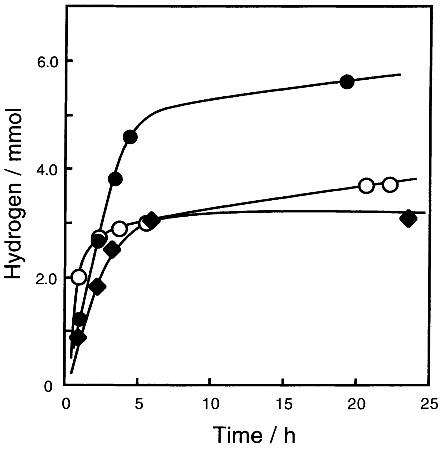

Fig. 5. Hydrogen formation under UV light irradiation (>200 nm) in Na_2SO_3 aqueous solutions: (◆) Na_2SO_3 3.3 mmol; (○) Na_2SO_3 3.3 mmol and Na_2S 3.3 mmol; and (●) Na_2SO_3 6.4 mmol.

The rate of hydrogen formation is high at the beginning of the reaction and decreases markedly after 5 h of irradiation, independent of the Na_2S concentration (0.029–0.047 mmol h^{-1}) as shown in Fig. 4, due to the decreased S^{2-} concentration and increased $S_2{}^{2-}$ concentration in solutions. Increasing $S_2{}^{2-}$ concentration leads to $S_2{}^{2-}$ reduction which competes with the H^+ reduction to hydrogen — the reduction potential of $S_2{}^{2-}$ at pH 13 is −0.37 V and H^+ is –0.56 V versus NHE [20]. This increased $S_2{}^{2-}$ concentration that decreases the rate of hydrogen formation was also seen in hydrogen formation on a CdS photocatalyst in an Na_2S aqueous solution [19]. The hydrogen yield in a K_2S solution was much lower than that in an Na_2S solution (Table 1 and Fig. 2) due to the presence of disulfide ions in K_2S.

The hydrogen yield also increases with increasing Na_2SO_3 concentration, similar to the Na_2S solution (Fig. 5),

Table 2
Quantum yield of hydrogen formation in S^{2-} and $SO_3{}^{2-}$ solutions

Ion	Concentration ($mol\,dm^{-3}$)	$v(H_2) \times 10^{-3}$ ($mol\,h^{-1}$)	$J \times 10^{-3}$ ($Es^{a}\,h^{-1}$)	$\Phi(H_2)$ (%)
S^{2-}	3.1	0.92	83.7[b]	2.2
	8.3	1.90		4.5
	25.0	3.72		8.9
$SO_3{}^{2-}$	8.3	0.88	53.4[c]	3.3
	16.0	1.24		4.6

[a] Einstein.
[b] Calculated from Hg lines of 290–200 nm.
[c] Calculated from Hg lines of 275–200 nm.

with 5.6 mmol of hydrogen produced by irradiation for 19 h in a 6.4 mmol of Na_2SO_3 solution, suggesting that water was reduced to hydrogen by the photoexcited electrons of $SO_3{}^{2-}$ ions. Hydrogen was also formed using a CdS photocatalyst in an Na_2SO_3 aqueous solution [19]:

$$SO_3{}^{2-} + H_2O + h\nu \rightarrow SO_4{}^{2-} + H_2 \qquad (7)$$

$$2SO_3{}^{2-} + 2H_2O + h\nu \rightarrow S_2O_6{}^{2-} + 2OH^- + H_2 \qquad (8)$$

Similar reactions would occur by directly photoexciting $SO_3{}^{2-}$ ions with UV light without photocatalysts.

Hydrogen also formed for both S^{2-} and $SO_3{}^{2-}$ ions on a CdS photocatalyst in an aqueous solution [19]:

$$S^{2-} + SO_3{}^{2-} + 2H_2O + h\nu \rightarrow S_2O_3{}^{2-} + 2OH^- + H_2 \qquad (9)$$

The hydrogen yield was dramatically increased by adding Na_2S to the Na_2SO_3 solution in the photocatalytic system, but not in our system. The hydrogen yield after 20 h in 3.3 mmol of Na_2SO_3 solution with 3.3 mmol of Na_2S added was 3.7 mmol, and the initial rate of hydrogen formation increased to 2.0 $mmol\,h^{-1}$.

3.4. Quantum yield of hydrogen formation

The quantum yield of hydrogen, $\Phi(H_2)$, is calculated as follows:

$$\Phi(H_2) = \frac{2v(H_2)}{J \times 100} \qquad (10)$$

where $v(H_2)$ is the hydrogen formation rate ($mol\,h^{-1}$), i.e., the yield of hydrogen for 1 h, and J is the total number of photons irradiated for 1 h (Einstein h^{-1}). J is obtained from the total light intensity of Hg lines from 200 to 290 nm for the $S_2{}^{2-}$ solution and 200 to 275 nm for the $SO_3{}^{2-}$ solution because 290 nm is the onset of absorption for the S^{2-} solution and 275 nm is that for the $SO_3{}^{2-}$ solutions (Fig. 2). Table 2 shows the $\Phi(H_2)$ in the S^{2-} and $SO_3{}^{2-}$ solutions. The $\Phi(H_2)$ increased with increasing S^{2-} and $SO_3{}^{2-}$ ion concentrations. The maximum $\Phi(H_2)$, 8.9%, was obtained in the 25 $mmol\,dm^{-3}$ S^{2-} solution. $\Phi(H_2)$ for the 8.3 $mmol\,dm^{-3}$ $SO_3{}^{2-}$ solution is 3.3% and that for the 16 $mmol\,dm^{-3}$ $SO_3{}^{2-}$ solution is 4.6%. The relationship between $\Phi(H_2)$ and ion concentration is shown in Fig. 6, with a half-order dependence seen.

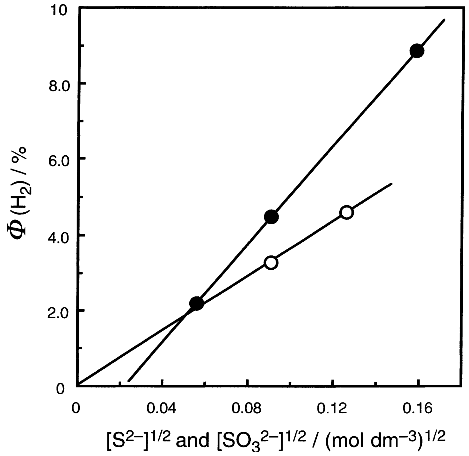

Fig. 6. Quantum yield of hydrogen $\Phi(H_2)$ vs. half-order of ion concentrations: (●) Na_2S; and (○) Na_2SO_3.

3.5. Hydrogen formation in the $Na_2S_2O_4$ solution

The hydrogen formation under UV light irradiation in 3.3, 10, and 30 mmol of $S_2O_4{}^{2-}$ ion solutions (the concentration is 8.3, 25, and 75 $mmol\,dm^{-3}$, respectively) is shown in Fig. 7. An equivalent amount of hydrogen, 3.1 mmol, was produced after 20 h in 3.3 mmol of the $S_2O_4{}^{2-}$ solution. The hydrogen yield decreased, however, with increasing $S_2O_4{}^{2-}$ concentration — 2.2 mmol of hydrogen was produced in the solution containing 10 mmol of $S_2O_4{}^{2-}$ ions and 0.9 mmol in that containing 30 mmol. A marked white precipitate formed in the high-concentration $S_2O_4{}^{2-}$ solution after the photoreaction; XRF indicates that the precipitate was sulfur, suggesting that $S_2O_4{}^{2-}$ ions decomposed into sulfur under irradiation:

$$S_2O_4{}^{2-} + h\nu \rightarrow S + SO_4{}^{2-} \qquad (11)$$

This reaction occurred preferentially with increasing $S_2O_4{}^{2-}$ concentration, decreasing the hydrogen yield.

As mentioned above, hydrogen formed markedly under UV light irradiation in S^{2-}, $SO_3{}^{2-}$, and $S_2O_4{}^{2-}$ solutions. Hydrogen was produced hardly at all, however, in the $SO_4{}^{2-}$

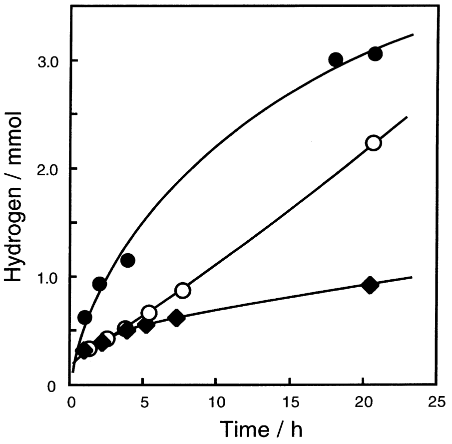

Fig. 7. Hydrogen formation under UV light irradiation (>200 nm) in $Na_2S_2O_4$ aqueous solutions: (●) $Na_2S_2O_4$ 3.3 mmol; (○) 10 mmol; and (◆) 30 mmol.

solution (Table 1). Sulfate ion cannot reduce water to hydrogen because it is the most oxidative ion of sulfur.

4. Conclusions

We found that hydrogen was produced by UV light irradiation (>200 nm) in aqueous solutions containing S^{2-}, $SO_3{}^{2-}$, and $S_2O_4{}^{2-}$ ions without photocatalysts. Water as a proton source appeared to be directly reduced to hydrogen by excited electrons produced in photon absorption with sulfide ions (S^{2-}). The absorption spectrum suggested that disulfide ions ($S_2{}^{2-}$) were produced by S^{2-} oxidation after the photoreaction. Absorption of S^{2-} ions (Na_2S) started at 290 nm, that of $SO_3{}^{2-}$ ions at 275 nm, and that of $S_2O_4{}^{2-}$ ions at 400 nm. The quantum efficiency for hydrogen formation $\Phi(H_2)$ was 8.9% for a 25 mmol dm^{-3} S^{2-} solution and 4.6% for a 16 mmol dm^{-3} $SO_3{}^{2-}$ solution. Hydrogen formed hardly at all, however, in $SO_4{}^{2-}$, I^-, and SCN^- aqueous solutions.

Acknowledgements

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