UV photochemical oxidation of aqueous sodium sulfide to produce hydrogen and sulfur

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Abstract

Sodium sulfide solutions were illuminated with ultraviolet light ($\lambda = 253.7$ nm) to produce hydrogen and disulfide ion in equimolar amounts. The quantum efficiency for hydrogen production was as high as 27% for a 0.5 M Na_2S solution in a batch reactor. While light intensity and sulfide concentration had a pronounced effect on reaction rate, the photochemical process was found to be pH independent within the range 8.5–13.3. A mechanism involving adsorption of bisulfide ion on the inner sleeve of the photoreactor is postulated. Elemental sulfur could be recovered from the disulfide solution via purging with H_2S and then filtering. The resulting filtrate was also photoactive, suggesting the possibility of a continuous closed cycle photochemical operation for H_2S decomposition into its constituent elements.
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1. Introduction

Hydrogen sulfide, H_2S, is commonly found in Nature as a by-product of anaerobic metabolic processes. It is also produced in large quantities through the hydrodesulfurization of crude petroleum. As a noxious, toxic gas, even at low concentrations, there is continuing interest in effective methods for its conversion to more benign substances.

There are a number of methods available for the decomposition of hydrogen sulfide to its constituent elements. One is simple thermal decomposition of hydrogen sulfide at high temperature and pressure [1–6]. Decomposition temperatures typically range from 973 to 1273 K. Even at these temperatures, yields are well below those predicted by thermal equilibrium. Another approach is electrolysis [7–11]. Hydrogen sulfide can be uptaken into $FeCl_3$ [7,11] or alkaline [8–10] solution, and then electrolyzed to evolve hydrogen at the cathode and produce sulfur at the anode. To be a high efficiency process, platinum or gold electrodes must be employed, and the anode is susceptible to passivation due to sulfur blockage, discouraging commercial application.

There are also photochemical methods for H_2S decomposition. Among these are photocatalytic and photoelectrolytic approaches [12–20]. The most commonly studied photocatalyst for this purpose is cadmium sulfide, CdS. Due to its moderate band gap ($E_g = 2.42$ eV), CdS is capable of utilizing solar radiation. However, the environmental toxicity of cadmium compounds and the tendency of CdS toward photoanodic decomposition are problems yet to be fully addressed.

In addition to the above methods, UV photochemical oxidation of sodium sulfide and reduction of water to hydrogen in aqueous solution was reported by Hara et al. [21]. The authors used a high-pressure mercury lamp as a light source and found that marked amounts of hydrogen were produced. The major advantages of this approach are that neither catalyst deactivation nor electrode passivation must be dealt with. However, the 8.9% quantum yield for hydrogen formation leaves room for further consideration of illumination source and reaction conditions.

In this work, we have studied the photochemical oxidation of sodium sulfide solution accompanied by H_2 evolution under the irradiation of a low-pressure Hg lamp. The effects of pH, concentration and light intensity were investigated. Mass balance analyses for a series of photolytic reactions involving the same sulfide solution were performed.

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2. Experimental

Reagent-grade sodium sulfide ($Na_2S \cdot 9H_2O$, Fisher) was used for the photolytic reactions. Sodium disulfide and tetrasulfide solution standards were prepared by adding stoichiometric amounts of sulfur powder (Fisher) to 0.1 M Na_2S solution and stirring several hours under moderate heat. A 60 W germicidal lamp (Atlantic Ultraviolet Corporation) was applied as a light source. The spectral output is mainly at 253.7 nm.

Fig. 1 depicts a batch reaction system for the sodium sulfide photolytic reactions. The total reactor volume was 790 ml. Prior to irradiation, the solution was purged with nitrogen for one hour. The collected hydrogen was analyzed quantitatively using a gas chromatograph installed with an MS-5A column (Ar carrier gas) and a thermal conductivity detector.

Sulfur was recovered via two methods: (1) for determination of reaction yield and stoichiometry, 1.0 M HCl solution was added to disulfide solution until pH was steady at pH = 1.00. After filtering, the sulfur powder was dried at 100 °C overnight and then weighed; (2) for the closed cycle experiments, the disulfide photolyte was purged with hydrogen sulfide overnight, dropping pH from about 13.0 to 7.4. The precipitated sulfur was then filtered, dried and weighed via the same procedure as was mentioned previously.

UV light intensity measurements were performed using an IL 1700 Research Radiometer/Photometer (International Light Inc.). To perform the photolytic oxidation of sodium sulfide at different intensities, a variable autotransformer was used to adjust the power input to the UV light.

3. Results and discussion

3.1. Reaction stoichiometry

A 0.1 M Na_2S solution was photolyzed with a 60 W low-pressure Hg lamp as shown in Fig. 1. Gas evolution commenced immediately after light exposure. Hydrogen was identified as the sole gaseous substance via gas chromatographic analysis. The reaction was monitored by measuring total gas volume evolved versus time. Hydrogen formation rates from the photolysis of sodium sulfide solution are shown in Fig. 2. After an induction period of approximately 100 min, the gas evolution curve would attain a linear slope, but ultimately become somewhat sublinear as photolysis time progressed. H_2 formation rates as high as 253 ml/h were observed. The solution would turn from colorless to yellow, indicating the formation of soluble polysulfides; no sulfur precipitation was observed during the course of the photochemical reaction.

A sodium sulfide UV-Vis spectrum at 6.25 mM concentration is shown in Fig. 3, along with prepared solutions of hydrogen sulfide, sodium disulfide (Na_2S_2), and sodium tetrasulfide (Na_2S_4). The absorption curve indicates that UV light with wavelength shorter than 280 nm can be readily absorbed by sodium sulfide. The UV-Vis spectrum for Na_2S solution after UV irradiation for 273 min is also shown in Fig. 3.
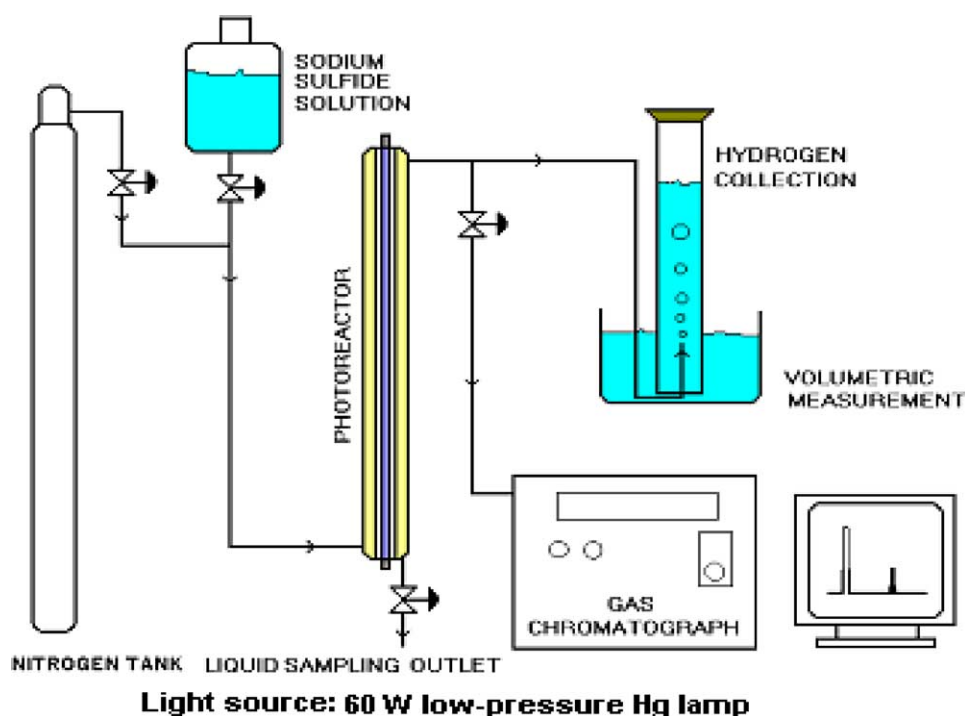

Fig. 1. Photoreactor system for photolytic decomposition of sodium sulfide (light source: 60 W low-pressure Hg lamp).
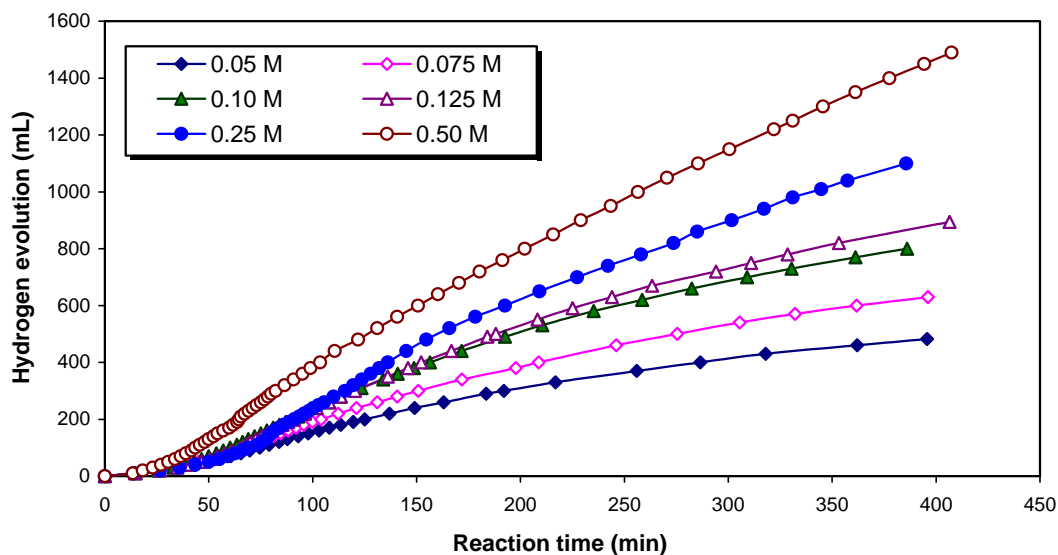
Fig. 2. Hydrogen evolved vs. irradiation time for photolysis of sodium sulfide at varying concentrations.

The resulting spectrum is consistent with disulfide formation. Since disulfide strongly absorbed UV light shorter than 320 nm, it would act as a strong optical filter on the H_2 evolution reaction. Build-up of S_2^{2-} would then play a role in the sublinearity of H_2 evolution over long photolysis times.

Na$_2$S solution made by dissolution of the crystalline hydrate into water does not contain principally sulfide ion, S^{2-} (aq), but rather bisulfide ion, HS^- (aq), due to hydrolysis of the conjugate base:

$$S^{2-} \text{ (aq)} + H_2O \rightarrow HS^- \text{ (aq)} + OH^- \text{ (aq)}, \quad K_{eq} = 10$$
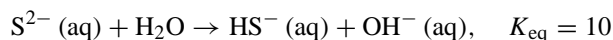
Therefore, a 0.1 M Na$_2$S solution prepared as described is nominally 0.1 M in HS^- and 0.1 M in NaOH. The dilutions of the various sulfide solutions were done with 0.1 M NaOH so as to avoid pH effects in the spectra. With this understanding, we determined that the molar absorptivity of HS^-

ion at pH 13 is 7.7×10^2 l/mol cm. With the assumption that the absorptivity coefficient can be applied to higher concentrations, the penetration depth of the UV light, excluding bleaching and mass transport effects, was only 0.26 mm at 99% absorption, much less than the annular thickness of the photoreactor.

A mass balance analysis of reaction products after a 400 min photolysis from 0.05 to 0.50 M sulfide concentration was performed: the results are shown in Fig. 4. The yields of hydrogen and sulfur were determined as measured hydrogen (or sulfur) moles divided by the total sodium sulfide moles present. It was found in each case that the sulfide photolysis reaction yielded hydrogen and sulfur in equimolar amounts, indicating that no other by-products were formed.

As a further determination of reaction stoichiometry, an exhaustive photolysis (>40 h) was performed, until
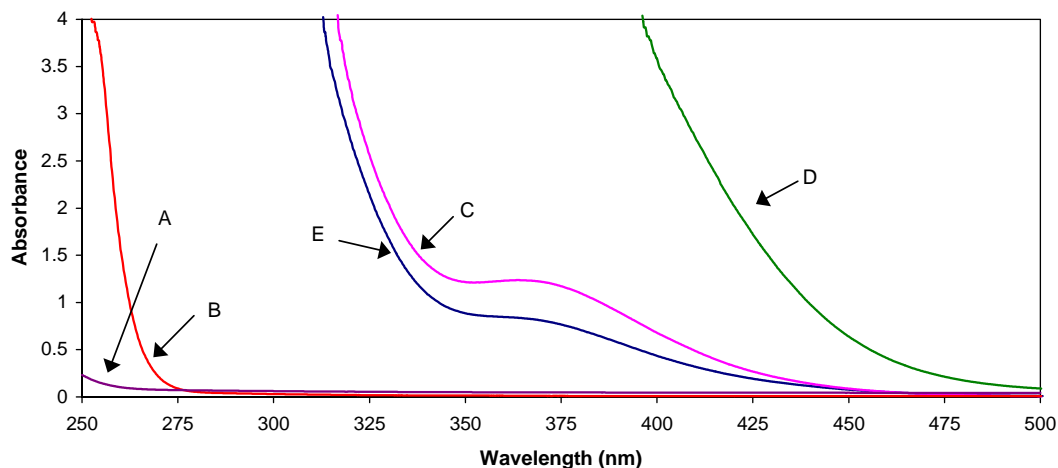

Fig. 3. UV-Vis spectra of various sulfur species. (A–D) 6.25 mM solutions of H_2S, HS^-, S_2^{2-}, and S_4^{2-}, respectively. (E) 0.1 M NaHS solution after a 273 min photolysis.
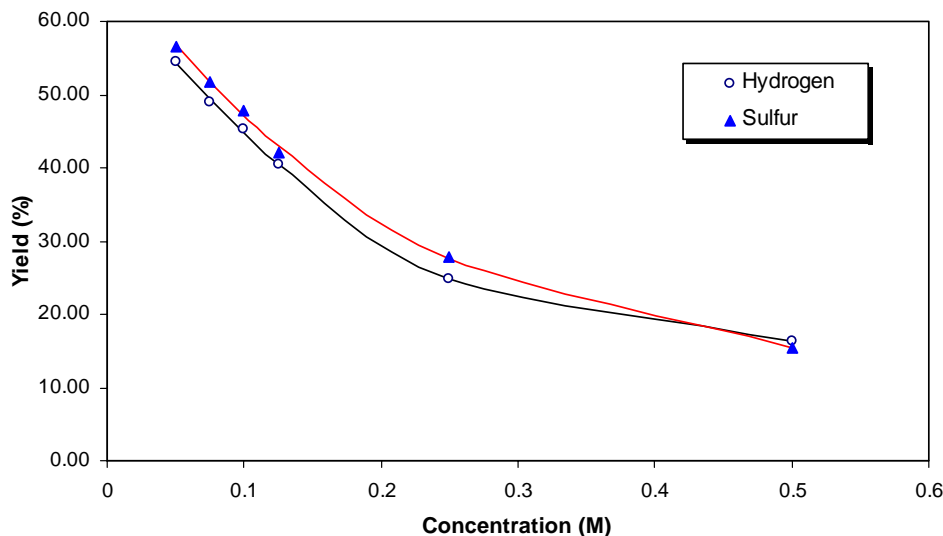
Fig. 4. Hydrogen and sulfur yields for the photolysis of sodium sulfide at different concentrations (6 h photolysis).

H_2 evolution ceased. The amount of H_2 produced after 42.6 h was 960 ml, corresponding to 0.043 mmol of gas. In comparison, 0.079 mmol S as HS^- were initially present. If S_2^{2-} was the only sulfur-containing product, H_2 production could not have exceeded 50% of the total S initially present, due to the stoichiometry associated with

$$2HS^- \rightarrow H_2 + S_2^{2-}.$$
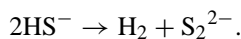
For the lowest sulfide concentrations, yields just exceed 50% of theory. Therefore, some small amounts of tetrasulfide may have formed. Either way, disulfide and tetrasulfide ions were found to readily release their zerovalent sulfur upon pH decrease.

The polysulfide ions not only function as an optical filter, but may also compete with hydrogen evolution for reducing equivalents [12,13]:

$$2e^- + S_2^{2-} \rightarrow 2S^{2-}, \quad \text{instead of}$$

$$2e^- + 2H_2O \rightarrow H_2 + 2OH^-.$$
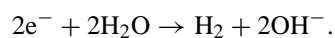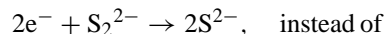
In future work, it would be of interest to separate the roles these two loss mechanisms play.

3.2. Hydrogen formation as a function of intensity

Hydrogen formation as a function of UV light intensity was investigated. The results are shown in Fig. 5, where the volume of H_2 obtained during a 6 h photolysis has been plotted versus light intensity in mW/cm^2. In general, hydrogen formation rates increased with increasing light input. The intensity dependence was sublinear; an exponential curve with exponent approximately 0.75 could be fitted to the data. The steady decay in quantum efficiency at higher intensities likely corresponds to increasing diffusion
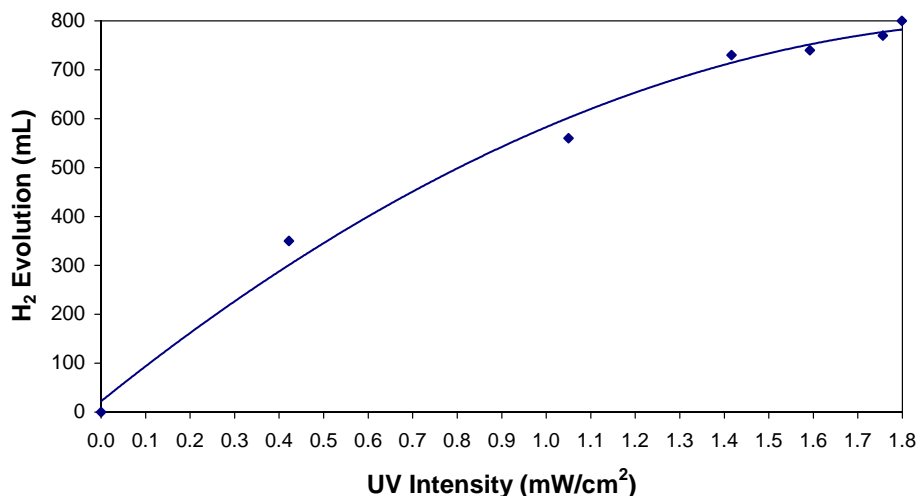

Fig. 5. Evolved hydrogen as a function of light intensity (0.10 M Na_2S; 6 h photolysis).

control limitation of the reaction. The quantum yield of hydrogen formation, $\Phi(H_2)$, could be calculated as follows [21]:

$$\Phi(H_2) = \frac{2\nu(H_2)}{J} \times 100\%$$

where $\nu(H_2)$ is hydrogen formation rate (mol/min) and J the total number of photons input per minute (einstein/min).

As would be expected for a batch reactor, net quantum yield varied as a function of irradiation time. The general trend was for net quantum yield (total H_2 evolved/total light absorbed) to reach its maximum value at 100–150 min and then gradually decline. This was interpreted as an interplay between the build-up of H_2 partial pressure inside the photoreactor early in the experiment versus the build-up of UV light-absorbing disulfide ion at longer times. Quantum yield was also found to be concentration dependent. In general, the quantum yield was higher for higher concentrations. The highest quantum efficiency achieved was 27% for a 0.5 M Na$_2$S solution. The annular thickness of the photoreactor (12 cm) was considerably greater than the penetration depth of the UV radiation at 99% absorption (<1 mm), and so the concentration effect cannot be explained in terms of proportional amounts of photons absorbed.

3.3. H_2 formation as a function of pH

Another informative experiment from a mechanistic perspective was the pH dependence shown in Fig. 6 for a 0.1 M Na$_2$S solution. The pH was adjusted from its initial value (13.3) by dropwise addition of 1.0 M HCl. Hydrogen evolution from the photolytic system was then monitored at successively lower pH values. The lower end of the pH range terminated at 8.5, as it represented the threshold below which H$_2$S evolution would commence, thus compromising the background concentration of reduced sulfur species present.

It was seen that H_2 formation rates did not significantly change with pH. This would imply that the rate-determining step does not involve protonation, reaction with hydroxide ion, or other pH-dependent interactions.

The consistency of reaction rate over the above pH range can be understood by considering the distribution of sulfide species as a function of pH. With a first acid dissociation constant on order of 10^{-7} and a second dissociation constant of $\sim 10^{-15}$, a wide range is created where bisulfide ion is the predominate species. Within the pH range 8.0–13.5, bisulfide ion accounts for greater than 90% of the sulfide species present. Therefore, reaction rate was constant over the stated pH range because nearly the same concentration of HS$^-$ reactant was present in each case.

3.4. HS$^-$ concentration dependence—mechanistic implications

From Fig. 2 it is apparent that increasing HS$^-$ concentration correspondingly increases the rate of H_2 generation. A rough comparison of final H_2 volumes for the various HS$^-$ concentrations suggests a sublinear dependence. The overall mechanism must then reflect this behavior.

The simplest mechanism would be one where an excited state bisulfide species forms an excimer with a ground state bisulfide ion, which reorganizes into diatomic hydrogen and disulfide ion:

$$HS^- + h\nu \rightarrow HS^{-*}$$
$$HS^{-*} + HS^- \rightarrow [(HS)_2]^{-*} \rightarrow H_2 + S_2^{2-}$$
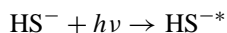
This mechanism fulfills the pH independence criterion discussed previously, but the apparent rate law would be second order with respect to bisulfide ion, instead of something less than unity.

Another possibility would be for the excited state bisulfide ion to interact with water in a multi-step mechanism:
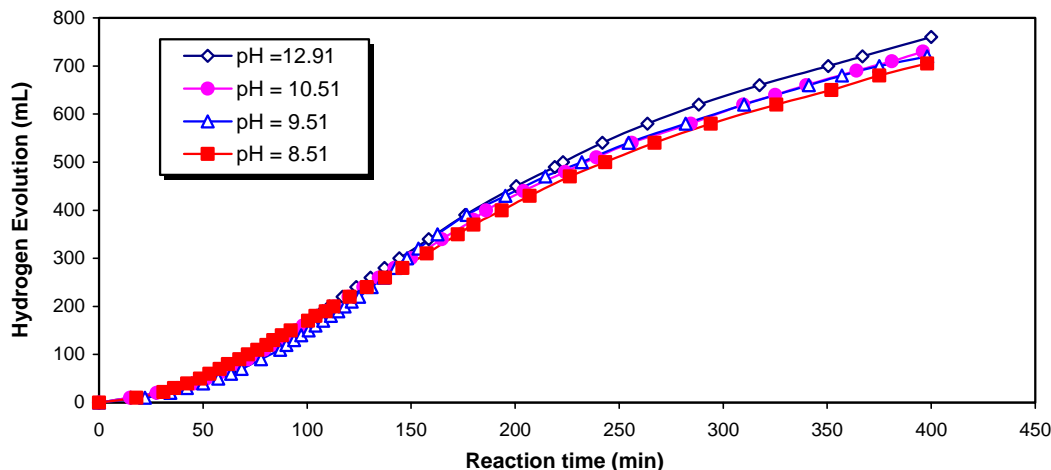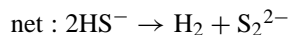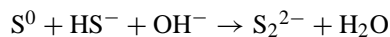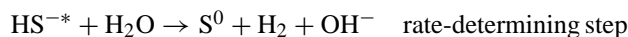

Fig. 6. Hydrogen evolution versus reaction time for various pH values (0.10 M Na$_2$S).

$$HS^- + h\nu \rightarrow HS^{-*}$$

$$HS^{-*} + H_2O \rightarrow S^0 + H_2 + OH^- \quad \text{rate-determining step}$$

$$S^0 + HS^- + OH^- \rightarrow S_2{}^{2-} + H_2O$$

$$\text{net}: 2HS^- \rightarrow H_2 + S_2{}^{2-}$$
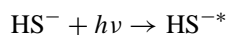
This mechanism also fulfills the pH criterion, provided the rate-determining step can be considered unidirectional, i.e., negligible back reaction. The rate law with respect to HS^- is improved with respect to the former mechanism in that only a linear dependence would be expected, but it is still not consistent with the experimental data.

The final H_2 volume obtained from a 0.5 M Na_2S solution in Fig. 2 was roughly three times that obtained with 0.05 M Na_2S, strongly suggesting a square root dependence. Indeed, the best power law fit to a plot of H_2 volume after a 6 h reaction period versus Na_2S concentration gave an exponent of 0.447 and an $R^2 = 0.996$. Hara et al. made essentially the same observation for HS^- photolysis when they showed a linear relationship between quantum efficiency and square root of concentration [21]. However, it is difficult to conceive of a mechanism that is consistent with a square root dependence on HS^-. Bisulfide ion would have to exist in equilibrium with a species that is first order in the rate-determining step, but is squared with respect to HS^- in the equilibrium expression.

Another way of rationalizing a sublinear dependence is to consider adsorption. A reaction controlled by adsorption would follow the basic expression

$$\text{rate} = k\theta = k\left[\frac{K_{ads}C_b}{1 + KC_b}\right],$$

where k is the fundamental rate constant, θ the fractional surface coverage of the adsorbing species, K_{ads} the equilibrium constant for adsorption, and C_b is its bulk solution concentration. In our case, a mean rate could be determined by final H_2 volume divided by reaction time, and the species of interest is HS^-. The expression would be

$$\frac{V_H}{t} = k'\left(\frac{K_{ads}[HS^-]}{1 + K_{ads}[HS^-]}\right),$$

where V_H is final H_2 volume, t the reaction time, and k' is a modified rate constant including a conversion from moles to volume, plus an area factor to include the annular area of the photoreactor. The expression for k' is

$$k' = \frac{RTAkt}{P},$$

where R is the ideal gas constant, T the absolute temperature, A the area of the inner annular sleeve of the photoreactor, and P the pressure. Rearranging terms, one obtains the expression

$$[HS^-] = \frac{V_H}{K_{ads}(k' - V_H)}.$$

Values of K and k' were chosen to make a best fit with the data. A plot of total H_2 volume after a 6 h photolysis at 1.8 mW/cm^2 as a function of HS^- concentration is shown in Fig. 7, along with a fitted curve based on $K_{ads} = 7.3$ M^{-1} and $k' = 1700$ ml. Using values $T = 295$ K, $A = 1216$ cm^2, $t = 6$ h, and $P = 1.0$ atm, the fundamental rate constant at the stated intensity is 2.7 nmol/cm^2 s.

We therefore propose a mechanism that is a modification of the water-based mechanism above, involving adsorption of bisulfide ion, which photodecomposes into adsorbed sulfur and hydrogen. The sulfur is solvated via formation of polysulfide ion, and the adsorbed H-atoms pair up to evolve H_2 gas:
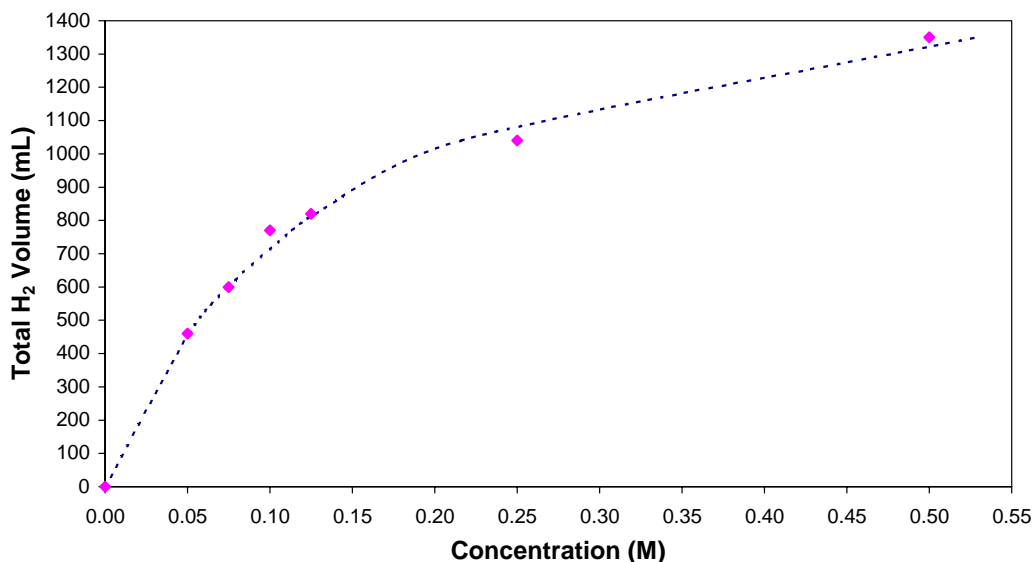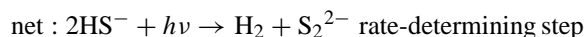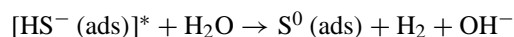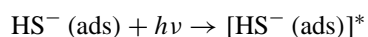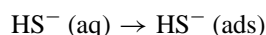

Fig. 7. Dependence of evolved hydrogen on bisulfide concentration (6 h photolysis; 1.8 mW/cm^2 light intensity).
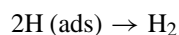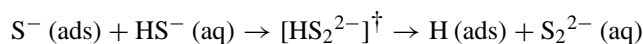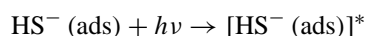
Table 1
Mass balance for hydrogen sulfur during cyclic photochemical reactions

Sample number	Time (min)	pH		Hydrogen evolved		Sulfur produced	
		Initial	Final	ml	mol	g	mol
First run	2560	13.12	12.98	960	0.0429	0.97539	0.0304
Second run	1579	7.74	12.23	1875	0.0837	2.68256	0.0837
Third run	1575	7.98	12.33	1874	0.0837	2.67783	0.0835
Fourth run	1560	7.67	12.05	1980	0.0884	2.83106	0.0883

$HS^- \text{ (aq)} \rightarrow HS^- \text{ (ads)}$

$HS^- \text{ (ads)} + h\nu \rightarrow [HS^- \text{ (ads)}]^*$

$[HS^- \text{ (ads)}]^* + H_2O \rightarrow S^0 \text{ (ads)} + H_2 + OH^-$

$S^0 \text{ (ads)} + HS^- + OH^- \rightarrow S_2^{2-} + H_2O$

net : $2HS^- + h\nu \rightarrow H_2 + S_2^{2-}$ rate-determining step

This mechanism would also address the sublinear intensity dependence. While it is unclear at this point whether adsorption precedes light absorption or vice versa, in either case, increasing light intensity would ultimately deplete the population of reactive species in a surface-controlled reaction, bringing on a mass transport-limited condition.

The above mechanism presumes that reaction between $(HS_{ads}^-)^*$ and water is quite rapid, on order of the excited state lifetime of bisulfide ion, which is likely 10^{-8} to 10^{-9} s. It may be that bisulfide ion itself can undergo an intramolecular charge transfer to produce an adsorbed hydrogen atom and a partially oxidized sulfide ion, ultimately resulting in disulfide:

$HS^- \text{ (ads)} + h\nu \rightarrow [HS^- \text{ (ads)}]^*$

$[HS^- \text{ (ads)}]^* \rightarrow H \text{ (ads)} + S^- \text{ (ads)}$

$S^- \text{ (ads)} + HS^- \text{ (aq)} \rightarrow [HS_2^{2-}]^\dagger \rightarrow H \text{ (ads)} + S_2^{2-} \text{ (aq)}$

$2H \text{ (ads)} \rightarrow H_2$

Further experimentation will be necessary to decipher between the various adsorbed bisulfide mechanisms.

3.5. Cyclical system operation

As was mentioned in the experimental section, it was found that addition of acid to a disulfide ion solution would shift the equilibrium back toward bisulfide ion and free sulfur:

$S_2^{2-} \text{ (aq)} + H^+ \text{ (aq)} \rightarrow HS^- \text{ (aq)} + S^0.$
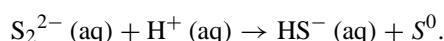
As an acidic gas, H_2S can supply the acid equivalents necessary to shift the equilibrium toward the products:

$S_2^{2-} \text{ (aq)} + H_2S \text{ (aq)} \rightarrow S \text{ (s)} + 2HS^- \text{ (aq)}.$
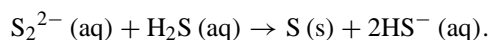
This realization offers the possibility of a closed cycle process, where the photolyte is returned to a scrubber unit for uptake of H_2S and precipitation of sulfur. The sulfurous suspension can then be filtered and fed back to the photoreactor.

To investigate this possibility, a 0.05 M sodium sulfide aqueous solution with total volume of 1500 ml was selected as an initial input solution. After being exposed to UV light for 44 h until no further hydrogen evolution was observed, the solution was then removed under nitrogen atmosphere and purged with hydrogen sulfide gas overnight until pH decreased to 7.80. Sulfur, which precipitated during the H_2S-purging, was then filtered out and the resulting clear yellow solution was again photolyzed. This process was repeated two more times. A determination of the mass balance on hydrogen evolved and the precipitated sulfur is shown in Table 1.

Several important observations can be made from these results. First, the photolytic oxidation of bisulfide ion to polysulfide (first run) with concomitant H_2 evolution can eventually be driven to completion. The molar amount of H_2 produced (0.043 mol) is slightly greater than half the total moles of sulfur present (0.075 mol) in the reactor, as expected for principally disulfide formation. Second, H_2S is unable to drive the sulfur precipitation reaction to completion. This was qualitatively apparent simply by observing that the filtrate still possessed some measure of yellow coloration. The sulfur collected from the photolyzed solution after purging with H_2S is around 71% based on H_2 yield, the balance remaining as disulfide ion in solution (pH = 7.80). Because H_2S is a weak acid ($pK_{A1} = 7.0$), a substantial excess is required to lower pH to the point where disulfide ion will decompose. Third, photolysis runs subsequent to the initial one had a higher hydrogen formation rate (1.2 ml/min average) despite the presence of light-absorbing S_2^{2-} ion in the solution. This was due at least in part to the increase in the analytical concentration of sulfide species in the reactor resulting from purging with H_2S in the previous step. Fourth, sulfur collection in the latter trials is close to 100% compared to hydrogen evolved. Once the disulfide background has been set up, any increase in disulfide concentration and sulfur content due to photochemical reaction can be quantitatively recovered. This lends strong support to the possibility of a closed cycle system.

4. Conclusion

Sulfide ions, principally bisulfide, could be photochemically oxidized under UV light to produce sulfur, complexed mainly as disulfide ion, while water was reduced to produce

hydrogen in a complementary redox process. This was accomplished without catalysts to be deactivated or electrodes susceptible to passivation and corrosion. The quantum yields of the H_2 evolution reaction using a low-pressure mercury lamp were as high as 27%, higher than other photolytic systems. By matching the UV light input to flow rate in a circulating system, the quantum efficiencies could likely be further increased.

Elemental sulfur could be recovered from the disulfide solution via purging with H_2S and then filtering. The resulting filtrate was also photoactive, suggesting the possibility of a continuous closed cycle photochemical operation for H_2S decomposition into its constituent elements.

Gas evolution rates changed very little as a function of pH, suggesting a pH-independent mechanism, at least in the range where HS^- is the predominate species:

$$2HS^- + h\nu \rightarrow H_2 + S_2{}^{2-}$$
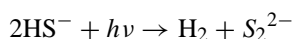
In contrast, the ability to precipitate sulfur from disulfide solution was dependent on the acidic character of H_2S:

$$S_2{}^{2-}\,(aq) + H_2S\,(aq) \rightarrow S\,(s) + 2HS^-\,(aq)$$
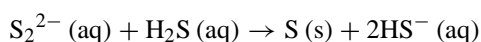
A sublinear dependence of H_2 evolution as a function of incident light intensity and sulfide concentration, along with the high absorbance of concentrated sulfide solution, suggested that an adsorption mechanism was at play.

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