Catalytic and Stoichiometric Hydrogen Formation by UV Irradiation of Sodium and Zinc Sulfide

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UV irradiation ($\lambda \geqslant 248$ nm) of sodium sulfide in aqueous solution leads to hydrogen and disulfide, $\Phi(H_2) = 0.34$ at $\lambda = 254$ nm. Light absorption occurs by HS^- which affords the solvated electron and the HS radical as indicated by flash photolysis and pulse radiolysis. In the presence of formate, hydrogen evolution becomes catalytic with respect to HS^-, $\Phi(H_2) = 0.12$ at $\lambda = 254$ nm. Deuteration experiments indicate that hydrogen formation occurs partially via hydrogen atoms which abstract hydrogen from formate. The latter is finally oxidized to give carbonate. When methanol is used instead of formate, there are produced ethanol, ethylene glycol, methane, and formaldehyde in addition to hydrogen and carbonate. It is shown that the direct homogeneous photolysis of HS^- may contribute significantly to the heterogeneous zinc sulfide-catalyzed hydrogen evolution in the presence of sodium sulfide when performed in quartz vessels.

Katalytische und stöchiometrische Bildung von Wasserstoff bei der UV-Bestrahlung von Natrium- und Zinksulfid

UV-Belichtung ($\lambda \geqslant 248$ nm) von Natriumsulfid in wäßriger Lösung führt zu Wasserstoff und Disulfid, $\Phi(H_2) = 0.34$ bei $\lambda = 254$ nm. Die Lichtabsorption erfolgt durch HS^-, dessen Primärreaktion zum HS-Radikal und solvatisierten Elektron durch Blitzlichtspektroskopie und Pulsradiolyse untersucht wurde. In Gegenwart von Natriumformiat wird die Wasserstoffentwicklung katalytisch in bezug auf HS^-, $\Phi(H_2) = 0.12$ bei $\lambda = 254$ nm. Deuterierungsexperimente deuten darauf hin, daß die Wasserstoffbildung teilweise über eine Abstraktionsreaktion zwischen Wasserstoffatomen und Formiatmolekülen erfolgt. Letztere werden schließlich zu Carbonat oxidiert. Wird Methanol statt Formiat verwendet, werden zusätzlich zu Wasserstoff und Carbonat noch Ethanol, Ethylenglycol, Methan und Formaldehyd gebildet. Die direkte, homogene Photolyse von HS^- trägt beträchtlich zur heterogenen, Zinksulfid-katalysierten Wasserstoffentwicklung bei, wenn letztere in Quarzapparaturen in Gegenwart von Natriumsulfid durchgeführt wird.

Recently we have reported that UV irradiation of metal dithiolenes in the presence of reducing agents like sodium formate, tetrahydrofuran (THF), or 2,5-dihydrofuran (2,5-DHF) leads to an efficient catalytic hydrogen evolution[1]. In the case of zinc dithiolenes n-zinc sulfide is formed during the initial induction period and the catalytic reaction occurs at the semiconductor surface. Formate is oxidized to carbon dioxide, the cyclic ethers undergo a

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chemo- and regioselective dehydrodimerization[1e,f]. When the metal dithiolene contains a transition metal like molybdenum or nickel, no metal sulfide is produced and hydrogen evolution is less efficient[1d]. In this case, sulfide ions are formed during the induction period and a homogeneous catalytic reaction takes place. Accordingly, sodium sulfide and other ionic metal sulfides catalyze hydrogen evolution without a noticeable induction period. In the following we report on the mechanism of this reaction and its relevance to the heterogeneous zinc sulfide-catalyzed hydrogen evolution in the presence of sodium sulfide.

Results and Discussion

Stoichiometric Hydrogen Evolution

The absorption spectrum of aqueous sodium sulfide has a broad band at $\lambda_{max} = 230$ nm ($\varepsilon = 7.2 \cdot 10^3$ l mol^{-1} cm^{-1}) which originates from the hydrogen sulfide ion[2]. When the pH value of this solution is increased, a new weak band due to the sulfide ion appears at $\lambda_{max} = 360$ nm ($\varepsilon = 2.0 \cdot 10^2$ l mol^{-1} cm^{-1}). The band at 230 nm is typical for inorganic ions like halides, hydroxide, and sulfate and originates from a charge-transfer-to-solvent transition (CTTS)[3-5]. The same character was assigned to the weaker sulfide band[2].

UV irradiation ($\lambda \geqslant 248$ nm) of aqueous sodium sulfide ($\varepsilon = 62$ l mol^{-1} cm^{-1} at $\lambda = 254$ nm) results in a stoichiometric hydrogen evolution with a quantum yield of $\Phi(H_2) = 0.34$ at 254 nm (Fig. 1a). The reaction stops when 0.5 mol of H_2 per mol of Na_2S have been formed. At this time the initially colorless solution became yellow due to the formation of 0.5 mol of S_2^{2-} as determined from the absorbance at 280 nm ($\varepsilon \approx 10^3$ l mol^{-1} cm^{-1})[6].

Since no reaction occurs with light of $\lambda \geqslant 290$ nm, we conclude that HS$^-$ is the absorbing species. The overall reaction is therefore described by eq. (1) and not by the conversion $2S^{2-} + 2H_2O \rightarrow H_2 + 2OH^- + S_2^{2-}$.
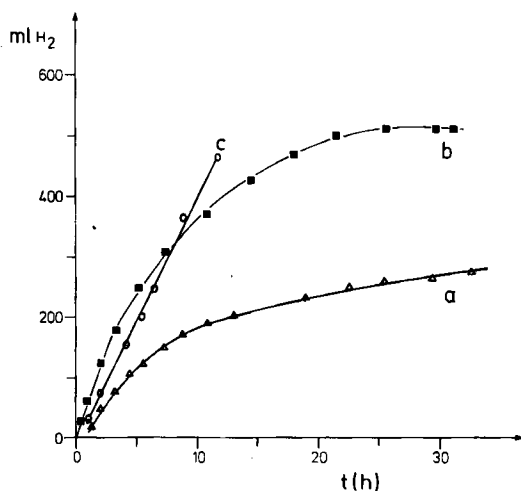

Fig. 1. Hydrogen evolution as a function of irradiation time ($\lambda \geqslant 248$ nm); (a) 0.2 M Na_2S; (b) $8.3 \cdot 10^{-4}$ M Na_2S and 0.18 M HCO_2Na; (c) $1.8 \cdot 10^{-3}$ M Na_2S in MeOH/0.1 M NaOH (1:1 v/v)

$$2 \ HS^- \xrightarrow{h\nu} H_2 + S_2^{2-} \tag{1}$$

$$HS^- \xrightarrow{h\nu} HS + e^-_{solv} \tag{2}$$

$$HS + HS^- \rightleftharpoons H_2S_2^- \tag{3}$$

$$H_2S_2^- \rightleftharpoons HS_2^{2-} + H^+ \tag{4}$$

$$HS_2^{2-} \longrightarrow HS^- + S^- \tag{5}$$

$$2 \ S^- \longrightarrow S_2^{2-} \tag{6}$$

Flash photolysis of aqueous sodium sulfide yields two transients which differ in absorption maxima and life times (Fig. 2). Transient A appears immediately after the laser flash and is identified as the solvated electron due to the characteristic absorption at 700 nm and its inhibition in the presence of N_2O or O_2. By analogy with the photochemistry of other simple ions[7], the primary process is formulated as photoinduced electron transfer to the solvent (eq. 2). The long-lived transient B ($\lambda_{max} = 380$ nm) appears several nanoseconds ($\geqslant 20$ ns) after the laser pulse, indicating that it is not a primary product. From pulse radiolysis of H_2S it is known that the radical HS does not absorb at 380 nm and that it is transformed into S_2^{2-} by reactions (3) – (6)[6]. Since also S^- has no absorption at this wavelength, transient B is assigned to the $H_2S_2^-/HS_2^{2-}$ species. This is supported by pulse radiolysis of Na_2S in N_2O saturated water affording a transient with the same optical properties as B (Fig. 2). In this system the OH radical, obtained from the reaction of N_2O with e^-_{solv}, oxidizes HS^- to the HS radical which then forms the $H_2S_2^-/HS_2^{2-}$ intermediate.
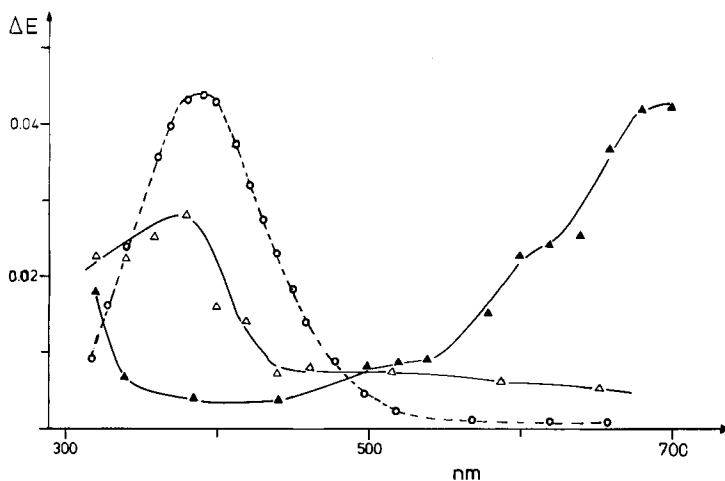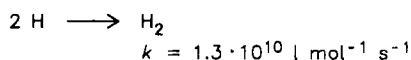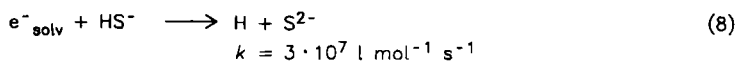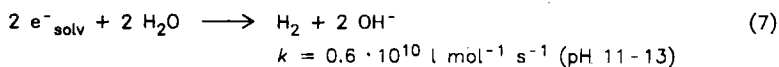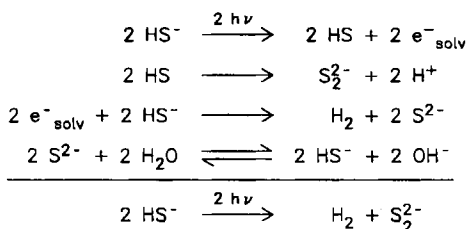

Fig. 2. Transient spectra obtained from laser flash photolysis ($\lambda_{exc} = 248$ nm, measured 20 (▲) and 500 (△) ns after the pulse in Ar-saturated solution) and pulse radiolysis (○---○, N_2O saturated) of Na_2S at pH 12

From these results, the formation of disulfide under the continous irradiation is formulated to occur via reactions $(2)-(6)$.

Hydrogen may be produced via eq. (7) and/or eq. (8) since the reactions with protons ($e_{solv}^- + H_3O^+ \rightarrow H + H_2O$, $k = 2.2 \cdot 10^{10}$ l mol^{-1} s^{-1} at pH $= 4-5$)[8] or hydrogen sulfide ($e_{solv}^- + H_2S \rightarrow H + HS^-$, $k = 1.1 \cdot 10^{10}$ l mol^{-1} s^{-1})[6] should be much slower due to their very low concentrations of 10^{-13} and 10^{-7} M at pH $= 13$, respectively. If it is assumed that the stationary concentration is $[e_{solv}^-] \leqslant 10^{-5}$ M, hydrogen formation should be faster via eq. (8) than via eq. (7). The most likely mechanism is summarized in Scheme 1 wherein the second step is an abbreviation of eq. $(3)-(6)$.

$$2\ e^-_{solv} + 2\ H_2O \longrightarrow H_2 + 2\ OH^- \tag{7}$$
$$k = 0.6 \cdot 10^{10} \text{ l mol}^{-1}\text{ s}^{-1} \text{ (pH 11-13)}$$

$$e^-_{solv} + HS^- \longrightarrow H + S^{2-} \tag{8}$$
$$k = 3 \cdot 10^7 \text{ l mol}^{-1}\text{ s}^{-1}$$

$$2\ H \longrightarrow H_2$$
$$k = 1.3 \cdot 10^{10} \text{ l mol}^{-1}\text{ s}^{-1}$$

Scheme 1

$$2\ HS^- \xrightarrow{2\ h\nu} 2\ HS + 2\ e^-_{solv}$$
$$2\ HS \longrightarrow S_2^{2-} + 2\ H^+$$
$$2\ e^-_{solv} + 2\ HS^- \longrightarrow H_2 + 2\ S^{2-}$$
$$2\ S^{2-} + 2\ H_2O \rightleftharpoons 2\ HS^- + 2\ OH^-$$
$$\overline{}$$
$$2\ HS^- \xrightarrow{2\ h\nu} H_2 + S_2^{2-}$$

However, is cannot be ruled out that some hydrogen is formed via eq. (7). In this case, Scheme 1 has to be modified by replacing the third step by eq. (7) and omitting the last step.

Hydrogen Evolution Catalyzed by HS⁻

UV irradiation of sodium sulfide in the presence of alcohols, sodium formate, THF, or 2,5-DHF leads to an efficient hydrogen evolution which is catalytic with respect to sodium sulfide (Fig. 1b). Thus, a solution of 0.1 mmol of sodium sulfide and 22.0 mmol of sodium formate in 120 ml of water affords 22.4 mmol of H_2, 0.5 mmol of CO_2 and traces of CO after 31 h irradiation time. In the liquid phase are found 22.1 mmol of carbonate and traces of oxalate. Fig. 3 shows the quantitative relation between amounts of hydrogen, oxalate, and formate as a function of the reaction time expressed as the volume of hydrogen produced. From these results the reaction is formulated according to eq. (9). The quantum yield $\Phi(H_2)$ is determined as 0.12 at $\lambda = 254$ nm. This value is obtained only when the formate

concentration is above 0.6 M while at 0.3, 0.2, and 0.005 M values of $\Phi = 0.08$, 0.07, and 0.04, respectively, are found. $\Phi(H_2)$ does not change within the experimental error of 10% when the sulfide concentration is varied from $0.5 \cdot 10^{-3}$ to $6.4 \cdot 10^{-3}$ M. In the absence of sulfide, irradiation of formate (0.6 M) at $\lambda = 254$ nm affords only traces of hydrogen, $\Phi(H_2) = 6 \cdot 10^{-4}$.
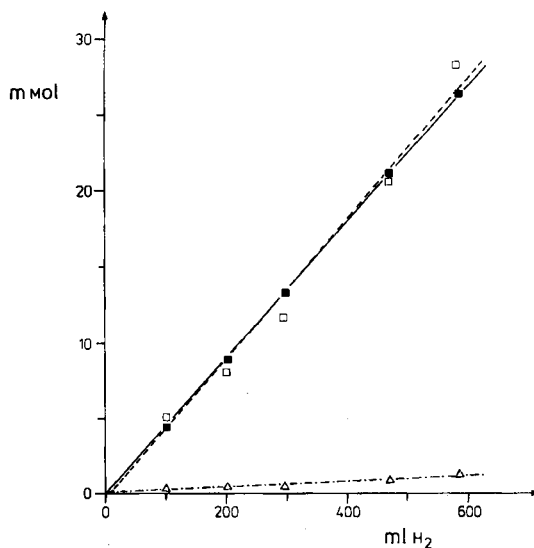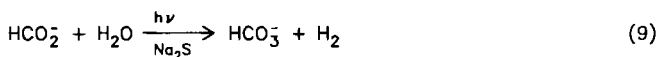
$$HCO_2^- + H_2O \xrightarrow[Na_2S]{h\nu} HCO_3^- + H_2 \qquad (9)$$

Fig. 3 Formation of hydrogen (■) and oxalate (△) and consumption of formate (□) upon irradiating ($\lambda \geqslant 248$ nm) a solution containing 0.2 mmol of Na_2S and 29.4 mmol of HCO_2Na

As in the stoichiometric reaction, excitation of HS^- produces HS and e_{solv}^- (eq. 2), and hydrogen may be formed via eq. (7) and/or eq. (8)[9]. Accordingly, electron scavengers like carbon dioxide and chloroform have an inhibitory action (Fig. 4). Surprisingly, when N_2O is used instead of carbon dioxide, only a very weak inhibition is observed. The quantum yield at $\lambda = 254$ nm changes from $\Phi(H_2) = 0.12$ (Ar) to 0.10 (N_2O). Addition of NaOH does not change the reaction rate.

When the catalytic reaction is performed in D_2O/HCO_2^- or H_2O/DCO_2^-, the ininial hydrogen isotopic composition is 38% D_2, 60% HD, 2% H_2 and 26% H_2, 73% HD and 1% D_2, respectively (Table 1). This supports the involvement of deuterium (hydrogen) atoms which dimerize to give D_2 (H_2) or abstract hydrogen (deuterium) from formate to produce HD (Scheme 2, eq. 11). The latter process seems to be preferred over the former as indicated by the ratio of $HD/D_2(H_2)$. This step ($k = 2.6 \cdot 10^8$ l mol^{-1} s^{-1})[10] produces the CO_2^- radical which partially dimerizes to form oxalate[11,12] but predominantly reacts with HS to yield HS^-

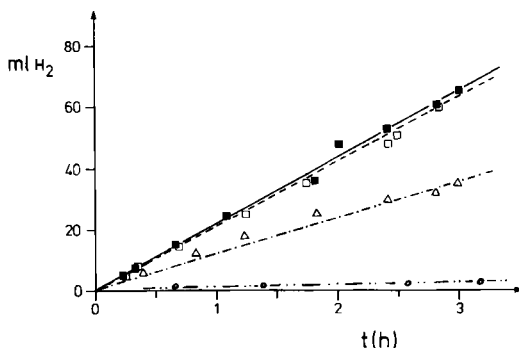Fig. 4. Hydrogen evolution as a function of irradiation time ($\lambda \geq 248$ nm); [HCO_2Na] = 0.49 M, [Na_2S] = 1.8 10^{-3} M; (■) Ar-saturated; (△) CO_2-saturated; (□) in the presence of 0.1 M NaOH, Ar-saturated; (○) in the presence of 0.34 M $CHCl_3$, Ar-saturated
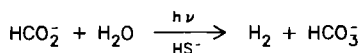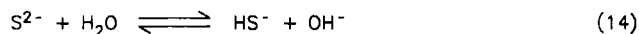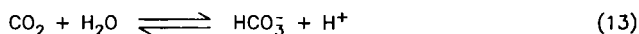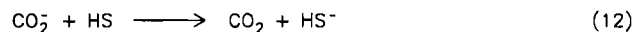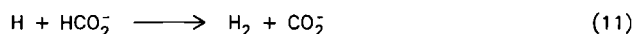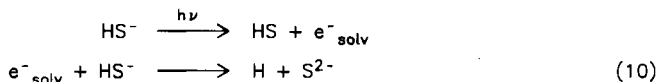
and CO_2. This step (eq. 12) regenerates the catalyst and resembles the formation of carbon dioxide instead of oxalate during pulse radiolysis of aqueous thiols ($CO_2^- + RS \rightarrow CO_2 + RS^-$)[13]. Scheme 2 summarizes a plausible reaction sequence for the case that hydrogen is formed via reduction of HS^- (eq. 10) followed by the abstraction reaction (eq. 11).

Table 1. Variation of the isotopic hydrogen composition with increasing reaction time in the catalytic system Na_2S/HCO_2Na ($\lambda \geq 248$ nm)

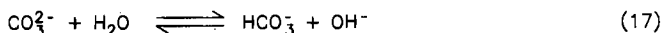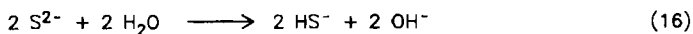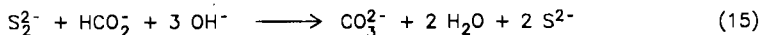| ml Gas evolved	Composition (%)			ml Gas evolved	Composition (%)		
	H_2	HD	D_2[a]		H_2	HD	D_2[b]
0−50	2.3	60.0	37.7	0−50	26.3	72.5	1.2
50−160	1.7	55.2	43.1	50−100	30.0	69.0	1.0
160−230	1.3	48.0	50.7	150−275	78.3	21.3	0.4
230−300	<1.0	39.3	60.7	275−325	86.2	13.7	0.1
300−375	1.7	17.1	81.2	325−400	92.1	7.9	0.0

[a] [Na_2S] = $3.5 \cdot 10^{-3}$ M, [HCO_2Na] = 0.3 M in D_2O. — [b] [Na_2S] = $1.7 \cdot 10^{-3}$ M, [DCO_2Na] = 0.4 M in H_2O.

Scheme 2

$$HS^- \xrightarrow{h\nu} HS + e^-_{solv}$$

$$e^-_{solv} + HS^- \longrightarrow H + S^{2-} \tag{10}$$

$$H + HCO_2^- \longrightarrow H_2 + CO_2^- \tag{11}$$

$$CO_2^- + HS \longrightarrow CO_2 + HS^- \tag{12}$$

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \tag{13}$$

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^- \tag{14}$$

$$HCO_2^- + H_2O \xrightarrow[HS^-]{h\nu} H_2 + HCO_3^-$$

The large amounts of $D_2(H_2)$ initially formed may be produced via Scheme 1 followed by reaction steps[14] according to eq. (15)−(17). As in the stoichiometric reaction, a slightly modified scheme would apply when hydrogen is formed via eq. (7) instead of eq. (10), (11).

$$S_2^{2-} + HCO_2^- + 3\ OH^- \longrightarrow CO_3^{2-} + 2\ H_2O + 2\ S^{2-} \tag{15}$$

$$2\ S^{2-} + 2\ H_2O \longrightarrow 2\ HS^- + 2\ OH^- \tag{16}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \tag{17}$$

The decrease of HD and concomitant increase of $D_2(H_2)$ with reaction time (Table 1) is explainable by the rate decrease of the hydrogen abstraction (eq. 11) with increasing consumption of formate[15]. Similar, this step explains also the dependence of the quantum yield of the formate concentration since maximum scavenging occurs only when $[HCO_2Na] \geqslant 0.6$ M.
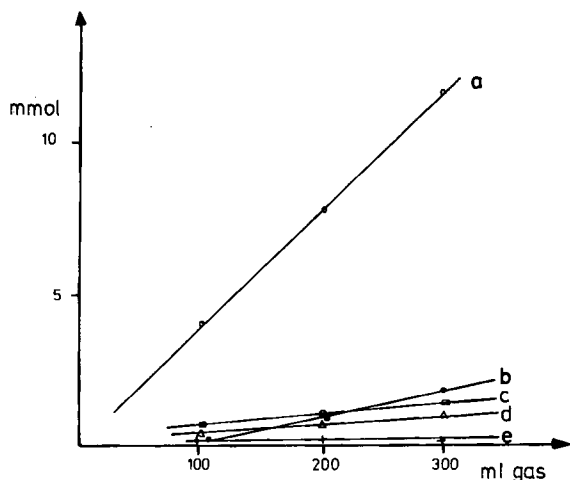

Fig. 5. Product development as function of evolved gas during the irradiation of Na_2S in $MeOH/H_2O$; experimental conditions as in Fig. 1c; H_2(a), EtOH (b), ethylene glycol (c), methane (d), formaldehyde (e)

According to the proposed mechanism, other scavengers for hydrogen atoms should also induce a catalytic reaction. When methanol is used in neutral water in the presence of 17 mg of sodium sulfide, about 80 ml of hydrogen are produced after 8 h irradiation time. In alkaline solution (pH 13) the reaction is much faster (Fig. 1c) and after the evolution of 640 ml of gas 26.6 mmol of H_2 and 1.8 mmol of CH_4 are found in the gas phase and 3.3 mmol of EtOH, 1.5 mmol of ethylene glycol, 0.4 mmol of formaldehyde, and 4 mmol of carbonate in the liquid phase. The formation of these products as function of the amount of gas evolved is shown in Fig. 5 for an alkaline solution (pH 13). The amounts of H_2 and CH_4 are not

significantly changed by lowering the pH to 12.5 while those of ethanol and ethylene glycol are decreased by the factors 0.05 and 0.2, respectively. Contrary, the amount of formaldehyde increases by a factor of 50.

By analogy with the formate system, hydrogen may be formed partially via eq. (18) ($k = 1.56 \cdot 10^6$ l mol^{-1} s^{-1})[10] producing a hydroxymethylene radical. Dimerization affords ethylene glycol while disproportionation leads to methanol and formaldehyde[11,12]. Hydrogen formation via the reaction $e_{solv}^- + CH_3OH + H_2O \rightarrow H_2 + CH_2OH + OH^-$ is unlikely due to the small value[10] of $k \leqslant 4 \cdot 10^2$ l mol^{-1} s^{-1}. Methane and ethanol are probably produced by the reaction of methyl radicals with methanol and the hydroxymethylene radical, respectively. The methyl radical may be formed via $e_{solv}^- + CH_3OH \rightarrow CH_3 + OH^-$ as observed in pulse radiolysis experiments[11].

$$H + CH_3OH \longrightarrow H_2 + CH_2OH \tag{18}$$
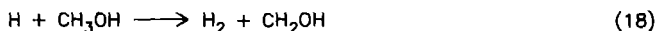
The regeneration of the catalyst most likely occurs by the reaction of formaldehyde with S_2^{2-} to give HS^- and HCO_2^- [14,16]. In more alkaline solutions this would be favoured due to the higher reducing power of formaldehyde. In addition, formaldehyde may disproportionate in this basic medium to yield formate and methanol. Accordingly, less formaldehyde is observed in the reaction at the higher pH value. The formate produced accounts for the higher hydrogen evolution rate in alkaline solution and for the formation of carbonate.

Zinc Sulfide-Catalyzed Hydrogen Evolution

The observation that irradiation of sodium sulfide induces a stoichiometric and catalytic hydrogen evolution through excitation of HS^- at $\lambda \geqslant 248$ nm, is of
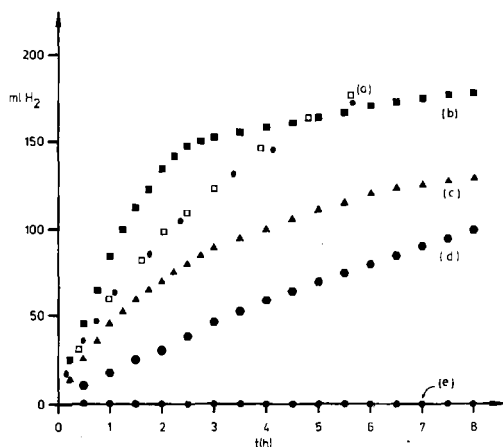

Fig. 6. Hydrogen evolution observed upon irradiation of (a) 100 ml of 0.2 M Na$_2$S in the absence ($\bullet$) and presence ($\square$) of 1.0 mmol of ZnS, $\lambda \geqslant 248$ nm. (b) 90 ml of a solution containing 0.08 M Na$_2$S, 0.1 M Na$_2$SO$_3$ and 1.0 M NaOH in the presence (b) and absence (c) of 4 mmol ZnS, $\lambda \geqslant 248$ nm; (d) and (e): as (b) and (c), respectively, except that irradiation was performed with light of $\lambda \geqslant 290$ nm

relevance to zinc sulfide catalyzed photoreactions. Firstly, HS^- is formed in the reductive photocorrosion of colloidal zinc sulfide[17]. Secondly, sodium sulfide has been used as reducing agent in zinc sulfide-catalyzed hydrogen formation[18]. In the latter reaction, sulfide is oxidized to disulfide and the net reaction corresponds to the stoichiometric photolysis of HS^- (eq. 1). Since zinc sulfide absorbs only light of the wavelength $\lambda \leqslant 340$ nm, irradiation conditions have to be carefully selected to prevent the hydrogen sulfide reaction. This is illustrated by a series of irradiations performed with the commonly employed high-pressure mercury lamp (Fig. 6).

When a solution containing 0.2 M Na_2S is irradiated in a quartz vessel ($\lambda \geqslant$ 248 nm), the rate of hydrogen evolution does not change whether zinc sulfide (1.0 mmol) is present or not (Fig. 6a). This indicates that hydrogen formation originates from the stoichiometric photolysis of HS^-. The homogeneous reaction contributes only to about 50% when the hydrogen sulfide concentration is diminished by increasing the pH, and when the fourfold amount of zinc sulfide is used (Fig. 6b,c)[19]. No contribution of the direct photolysis is observed when the irradiations are conducted in a solidex glas vessel ($\lambda \geqslant 290$ nm).

Experimental

All materials were analytical grade and used as received from commercial sources. All experiments were performed in aqueous solutions which were flushed with argon or nitrogen (10 − 15 min) prior to irradiation unless otherwise stated. A solution 0.22 M in Na_2S contains H_2S, HS^-, and S^{2-} in the concentrations of $1.1 \cdot 10^{-7}$, 0.04, and 0.18 M, respectively.

Laser flash photolysis and pulse radiolysis were conducted as described previously[20]. In the latter experiment the OH radical is formed by the reaction $e^-_{solv} + N_2O + H_2O \rightarrow N_2 + OH + OH^-$[11].

Standard irradiations were conducted with solutions of 120 ml in an immersion-lamp apparatus made from quartz ($\lambda \geqslant 248$ nm) or solidex glas ($\lambda \geqslant 290$ nm) using a high-pressure mercury lamp (Philips HPK 125 W). Hydrogen was recorded volumetrically and identified by GC and MS as reported[10].

Quantum yield determinations were performed with a low-pressure mercury lamp ($\lambda = 254$ nm, $I_0 = 9.5 \cdot 10^{-8}$ Einstein/s) as described recently[10]. The concentration of Na_2S was 0.2 M and $3 \cdot 10^{-3}$ M in the stoichiometric and catalytic reaction, respectively. In the inhibition experiments an N_2O-saturated solution (0.02 M) containing 0.49 M HCO_2Na was employed. Chloroform was passed over silica before used as inhibitor in an experiment as described in Fig. 4 except that 3.5 ml of $CHCl_3$ was added before irradiation; dichloromethane formed by the reactions $CHCl_3 + e^-_{solv} \rightarrow Cl + CHCl_2$ and $CHCl_2 + HCO_2^- \rightarrow CH_2Cl_2 + CO_2^-$[21] was identified by GC.

Quantitative determinations were performed by the following methods: GC (46 m Carbowax 20 M) for ethylene glycol and ethanol using n-octanol and 1-propanol as internal

standards, respectively; HPLC (Iono-spher 4.6 × 250 mm, elution agent: 0.04 M K_2HPO_4 in water, 90 at, 1.8 ml/min, detector: refractometer) for formate and oxalate. Formaldehyde was determined by colorimetry[22], carbonate and oxalate gravimetrically.

CAS Registry Numbers

THF: 109-99-9 / 2,5-DHF: 1708-29-8 / ZnS: 1314-98-3 / Na₂S: 1313-82-2 / H₂O: 7732-18-5 / H₂: 1333-74-0 / HCO₂Na: 141-53-7 / DCO₂Na: 3996-15-4 / D₂O: 7789-20-0 / CH₃OH: 67-56-1 / CHCl₃: 67-66-3 / NaOH: 1310-73-2 / CO₂: 124-38-9 / EtOH: 64-17-5 / oxalate: 338-70-5 / ethylene glycol: 107-21-1 / methane: 74-82-8 / formaldehyde: 50-00-0

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$CO_3^{2-} + 2H_2O + 2e^- \rightarrow HCO_2^- + 3OH^-$, $E° = -0.95$ V;
$S_2^{2-} + 2e^- \rightarrow 2S^{2-}$, $E° = -0.51$ V.

[15] Due to the very low H₂S concentration (see Experimental) it seems unlikely that the process $CO_2^- + D_2S \rightleftharpoons DCO_2^- + DS$ contributes significantly. This type of exchange was observed with thiols instead of H₂S[13d].

[16] $HCO_2^- + 2H_2O + 2e^- \rightarrow CH_2O_{aq} + 3OH^-$, $E° = -1.14$ V[14].

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