Heterogeneous Photocatalysis. VIII.[1] Zinc Sulfide Catalyzed Hydrogen Formation from Water in the Presence of Sodium Formate

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A suspension of n-ZnS in aqueous sodium formate photocatalyzes formation of hydrogen (72%) and carbon monoxide (27%). The stoichiometry of the hydrogen producing reaction is determined as $HCO_2Na+H_2O=H_2+HCO_3Na$. The quantum yield at 290 nm is 0.24 mol H_2/Einstein and its wavelength-dependence parallels that of the anodic photocurrent measured photoelectrochemically. Reaction rates increase linearly with increasing light-intensity and do not change when the temperature is increased up to 70 °C. No gaseous products are formed when nonaqueous formic acid is employed instead of formate, or when ZnS is dehydrated at 250 °C before use or when CdS is substituted for ZnS. When THF or sulfur compounds are added to the solution, H_2 is the only gaseous product. The dependence of the reaction rate on formate concentration points to a Langmuir-type adsorption of formate onto the semiconductor surface, $K_{ads}=26\ M^{-1}$. In D_2O/HCO_2Na the initial rate does not change but the amount of CO increases to 60% and photocorrosion is much stronger than in H_2O; the initial isotopic composition of 85, 10, and 5% changes to 63, 30, and 7% of D_2, HD, and H_2, respectively, when 400 mL of gas has been produced. In H_2O/DCO_2Na the rate decreases by a factor of 1.3 and the amount of CO is only 15%; only H_2 but no D_2 and HD are detectable. The hole scavenger KSCN does not influence the quantum yield of hydrogen formation while the electron scavenger $NaNO_3$ induces a strong decrease and completely inhibits CO formation. Stern-Volmer analysis indicates that nitrate scavenges in addition to conduction band electrons also an intermediate CO_2^- radical. The latter has been identified by spin-trapping experiments.

Sodium formate and formic acid have been employed as reducing agents for hydrogen production from water in photoelectrochemical cells containing photoanodes like zinc oxide[1,2] and cadmium sulfide.[3-5] In addition, suspensions of semiconductor powders like titanium dioxide,[6] platinized[5] and nonplatinized cadmium sulfide (CdS/Pt),[7] and colloidal zinc sulfide[8] were recently used as photocatalysts. In this colloidal system as with unmodified CdS only carbon dioxide was reported as oxidation product while CdS/Pt induces also formation of carbon monoxide. In most cases the amount of hydrogen produced was small, no complete material balance was established and the mechanistic information is rather scarce. In the following we report on the ability of n-type zinc sulfide powder to photocatalyze the reduction of water in the presence of sodium formate on a preparative scale. The mechanism of the reaction is studied by establishing a complete material balance and by investigating the effects of temperature, light intensity, pH-value, formate concentration, deuterated substrates, and electron and hole scavengers on the reaction rate and product composition.

Results

Characterization of the Photocatalyst. Zinc sulfide was prepared from zinc sulfate and thiourea[9] in alkaline medium. The compound has to be stored under argon since otherwise zinc oxide which inhibits the photocatalytic activity, is produced upon standing at room temperature. When the precipitation of the sulfide is performed in neutral solution, the obtained powder is three times less active and photocorrodes much faster. The bulk ratio Zn:S of this sample determined by elemental analysis is 1:1 while it is 1:0.86 for the material obtained from the alkaline solution which has a surface ratio of 1:0.74 as determined by EDAX-measurements. This latter sulfide was used in all of the experiments unless otherwise stated. SEM-micrographs reveal an average particle diameter of 200 nm; the specilfic surface area as obtained from BET-measurements is 17 $m^2\,g^{-1}$. The surface ratio Zn:S drops to 1:0.47 after several hours of irradiation in the presence of formate.

Diffuse Reflectance spectra indicate a band-gap of 3.65 eV. The spectrum of a previously irradiated sample contains a shoulder at 3.2 eV and absorption extends to 3.0 eV. The shoulder appears also when small amounts of zinc powder are admixed to nonirradiated zinc sulfide. When Co^{2+} , Mn^{2+}, Fe^{2+}, or Ni^{2+} are present in about 5 mol% during the preparation, the correspondingly doped samples are inactive. In the case of Co^{2+} the spectrum contains a shoulder at 3.47 eV.

The "point of zero zeta potential" ("pzzp")[10] was determined by differential titration. A maximum is observed at pH 8±0.2 (Fig. 1).

Photoelectrochemical measurements with a zinc sulfide-covered platinum electrode afford an anodic photocurrent. The typical current-voltage curve has its onset at +0.25 and −0.45 V, and reaches a plateau at +0.8 and +0.3 V (NHE) in the absence and presence of formate, respectively. In the latter case the saturation current is 1.3 times larger than in the former. The wavelength dependence of this photocurrent is shown in Fig. 2a. It parallels the quantum yield of hydrogen formation, $\Phi(H_2)$, obtained from irradiation of a

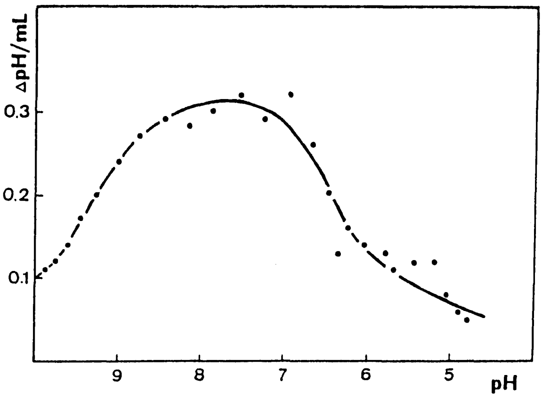

Fig. 1. Differential potentiometric titration of ZnS; see Experimental Section.

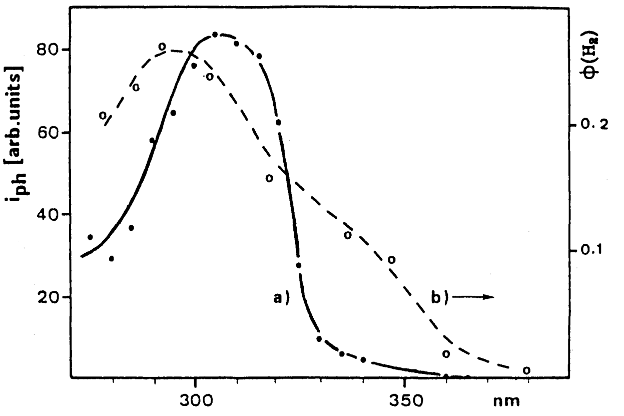

Fig. 2. Wavelength dependence of a) anodic photocurrent of a ZnS covered platinum electrode (0.5 V vs. NHE), 0.1 M K_2SO_4 and 0.015 M HCO_2Na; b) quantum yield of hydrogen formation (mol H_2/ Einstein), 8.5 mg (0.09 mmol) of ZnS suspended in 4 mL of 1.84 M aqueous HCO_2Na.

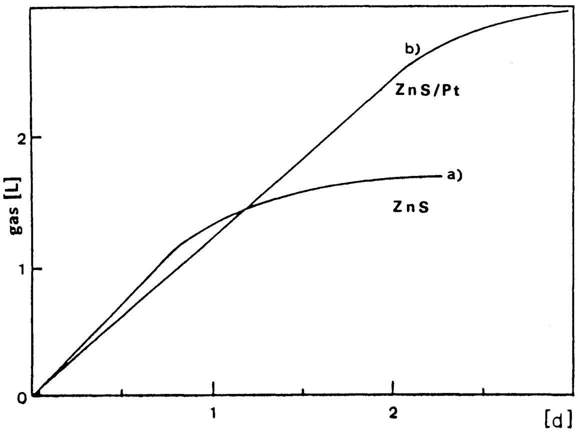

Fig. 3. Gas evolution as function of irradiation time; 40 mg (0.41 mmol) of ZnS suspended in 100 mL of 1.17 M HCO_2Na, $\lambda \geq 248$ nm; a) untreated ZnS, b) platinized ZnS or ZnS prepared in situ from $[Zn(mnt)_2](NBu_4)_2$.

zinc sulfide suspension in the presence of sodium formate. A maximum value of 0.24±0.02 mol H_2/ Einstein is measured at 290 nm. At this wavelength a slight and almost linear increase to 0.25, 0.26, 0.27, 0.28, 0.30, and 0.31 (±0.02) occurs upon decreasing the light intensity to 78, 61, 45, 32, 20, and 12% of its original value, respectively. No gas evolution is observed when zinc sulfide is replaced by cadmium sulfide prepared analogously.

Photochemical Hydrogen Evolution. Polychromatic irradiation ($\lambda \geq 248$ nm) of a suspension of zinc sulfide in aqueous sodium formate results in a catalytic gas evolution (Fig. 3) which levels off after one day but continues with a constant rate up to 2—3 days when the photocatalyst is either platinized or prepared in situ from $[Zn(mnt)_2][NBu_4]_2$, mnt^{2-}=maleonitriledithiolate.[11] The same rate is measured at 70 °C. A linear increase of the rate occurs when the relative intensity of the exciting light (λ=290 nm) is increased from 10 to 90%. Negligible amounts of gas are produced when zinc sulfide is omitted in these experiments. Depending on the reaction conditions, turnover rates are about 3000 monolayers HCO_2Na/h.[12] After irradiating 20 mg of ZnS suspended in 0.245 M HCO_2Na (1 M=1 mol dm^{-3}) for 50 min, the gas evolved contains 72% H_2, 27% CO, 0% CO_2, and 1% unidentified products. The results of a complete material balance for the gas and liquid phase are summarized in Fig. 4. From these data it follows that the ratio of carbonate to hydrogen as well as that of carbonate to formate consumed is 1 : 1, when the latter is corrected for the amounts of CO and oxalate produced. Thus, the stoichiometry of the hydrogen producing reaction is given by Eq. 1.

$$HCO_2Na + H_2O \xrightarrow{h\nu,\ ZnS} H_2 + HCO_3Na. \qquad (1)$$

Depending on the formate concentration the initial pH value of 8—9 is increased to 10—11 after irradiating for several hours. When the solution is brought first to pH 4 by addition of HCl, the pH value increases steadily and reaches a plateau at pH 10.6 after 20 min reaction time; the rate has not changed but 19% of carbon dioxide are now present in the gas phase. When an aqueous formic acid solution of the same concentration is used instead of formate, the rate becomes three times slower and the composition of the gas phase after evolution of 80 mL gas is changed to 76% CO_2. 15% H_2, 8% CO, and 1% CH_4; the aqueous phase contains now 2 mmol of formaldehyde. No gaseous products are produced when zinc sulfide is irradiated in the presence of concentrated, nonaqueous formic acid.

Only fully hydrated zinc sulfide photocatalyzes the reaction as demonstrated by the results summarized in Fig. 5. Dehydration in vacuo at temperatures from RT to 250 °C leads to increasing induction times and finally to an inactive zinc sulfide. DTA- and DTG-experiments for the same temperature range indicate

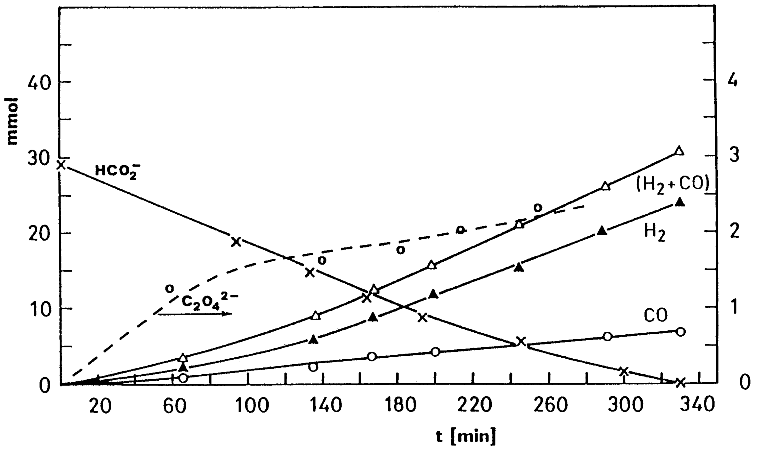

Fig. 4. Concentration changes of educt and products observed upon irradiation of 20 mg (0.2 mmol) of ZnS suspended in 120 mL of 0.245 M HCO_2Na; $\lambda \geq 248$ nm; note the different concentration range for oxalate.

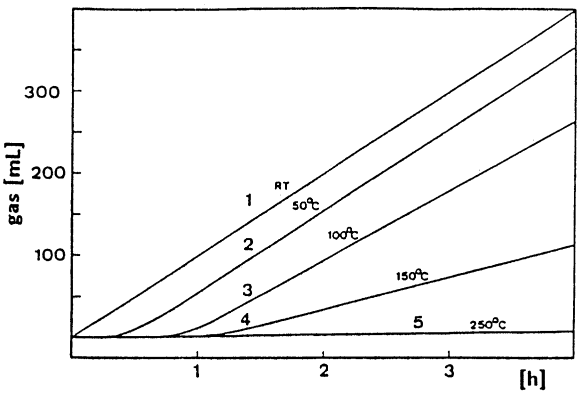

Fig. 5. Influence of dehydration conditions of ZnS on induction time and reaction rate of the gas evolution; 1—4 correspond to curves obtained with photocatalysts which were dried at 0.1 Torr for 8 h at the temperatures indicated; 30 mg (0.31 mmol) of ZnS suspended in 100 mL of 0.33 M HCO_2Na, $\lambda \geq 248$ nm.

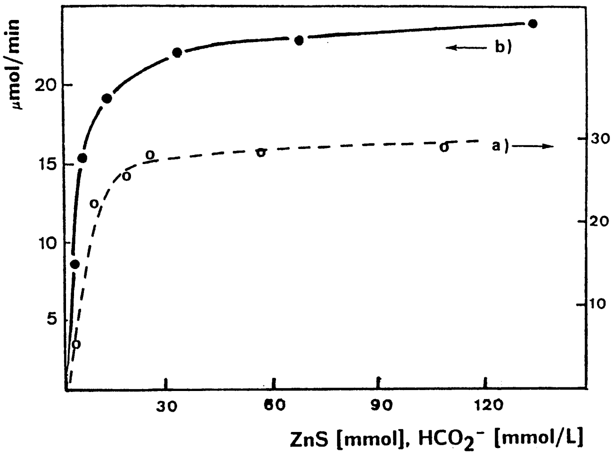

Fig. 6. Gas evolution rate measured at $t=90$ s; a) as function of amount of ZnS present in 22 mL of 0.33 M HCO_2Na; b) as function of formate concentration, 15 mg (0.15 mmol) of ZnS suspended in 22 mL of water; $\lambda \geq 254$ nm.

that the largest weight loss occurs endothermically at 50—150 °C followed by a smaller, now exothermic one at 150—300 °C.

The relative amount of carbon monoxide increases on the expense of hydrogen from 13 to 50% when the formate concentration is increased from 0.04 to 0.73 M. At a fixed concentration the relative CO content has a similar wavelength dependence as the anodic photocurrent (Fig. 2, see Experimental). Addition of THF or Na_2mnt induces a partial or almost complete suppression of CO. When zinc sulfide is generated from $[Zn(mnt)_2][NBu_4]_2$, no CO is produced at all.

Influence of Formate and Zinc Sulfide Concentrations. At a given formate concentration maximum rates are obtained when all the incoming light is absorbed by the suspended catalyst powder. In the case of the experimental conditions given in Fig. 6a, this occurs at about 15 mmol of ZnS suspended in 22 mL of aqueous formate.

At a given amount of photocatalyst the rate increases first sharply when the formate concentration is raised to about 0.015 M (Fig. 6b); thereafter a much slower acceleration occurs up to a concentration of 3 M. When these data are treated as a Langmuir isotherm[13] a plot of the reciprocal rate as function of reciprocal concentration affords a straight line from which an adsorption equilibrium constant of $K=26$ $L \cdot M^{-1}$ is obtained.

Higher formate concentrations induce a decrease of photocorrosion which may be estimated by the ratio $r_{i(2)}/r_{i(1)}$; $r_{i(1)}$ is the rate measured in the first irradiation experiment, $r_{i(2)}$ the one when the powder is filtered off and used again in a second experiment. The corresponding ratios are 0.05, 0.2, 0.26, 0.4, 0.5, 0.7, 0.8, 0.8, and 0.8 at 0.007, 0.02, 0.038, 0.06, 0.075, 0.10, 0.15, 0.25, and 0.30 M HCO_2Na, respectively. Thus, almost no photocorrosion occurs when the formate concentration is above 0.1 M.

Influence of Deuterated Substrates. When D_2O is employed, the initial rate does not change up to 50 min reaction time. But the relative amount of CO produced at that time increases to 60% as compared to 27% in the case of H_2O; in addition, photocorrosion is much stronger and leads to darkening of zinc sulfide through the formation of Zn(0) as indicated by the reduction of MV^{2+} (methylviologen). The corrosion induces a levelling off in the gas evolution curve much earlier as compared to the nondeuterated case.

In the system DCO_2^-/H_2O the rate decreases by a factor of 1.3 and the relative CO content of the evolved gas is decreased to 15% at 50 min of irradiation time.

The product isotope effect was studied by determining the differential isotopic composition of the hydrogen produced as a function of reaction time. When D_2O is employed, the amount of total hydrogen increases on expense of CO (Fig. 7A). To obtain the changes for hydrogen only, the CO-part was subtracted. As can be calculated from the data of Fig. 7, the relative percentages of D_2, HD, and H_2 change from 85, 10, and 5 to 63, 30, and 7%, respectively, when 400 mL of gas have been produced. This decrease of the D_2 content (Fig. 7B, curve a) is not affected when D_2 is isotopically diluted by addition of 2 mol% of H_2O (curve b). When DCO_2Na is used in this latter system, almost no decrease is observed.

In the system $ZnS/H_2O/DCO_2Na$ only H_2 and no HD or D_2 is detectable even when the concentration of DCO_2Na is as high as 0.72 M.

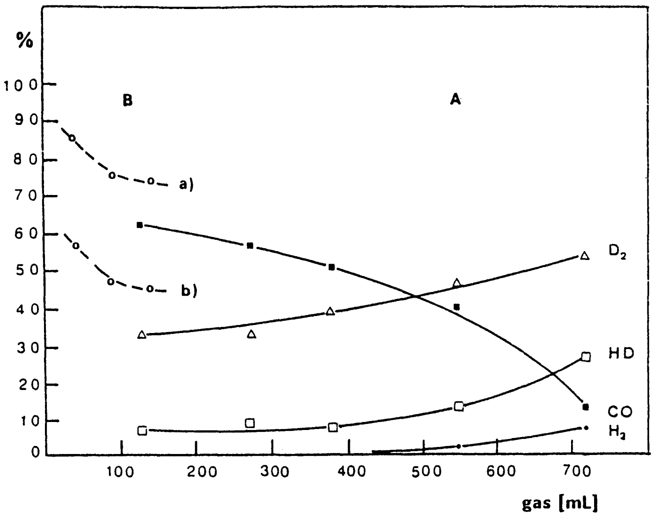

Fig. 7. A) ——: Differential isotopic composition of total gas phase, and B) ----: D_2-content relative to total amount of hydrogen gas as function of gas evolved; 20 mg (0.21 mmol) of ZnS suspended in 100 mL (5.5 mol) of D_2O, A): 0.44 M HCO_2Na, B): a) 0.29 M HCO_2Na, b) as in a) but 2 mL (0.11 mol) of H_2O were added.

Effect of Scavengers for Radical, Holes and Electrons. When the system $ZnS/H_2O/HCO_2Na$ is illuminated in the presence of (4-pyridyl-1-oxide)-1-*N*-*t*-butylnitrone (POBN) an intermediate CO_2^- radical is detected through the ESR spectrum of the corresponding spin adduct. No evidence for an adduct of the OH radical could be found. These findings agree with the results of Harbour and Hair.[14]

Addition of dissolved zinc, cadmium, nickel, or manganese(II) chlorides in amounts slightly above equimolar with respect to ZnS results in a complete inhibition of the gas evolution. With sodium nitrate which scavenges electrons in a diffusion-controlled process[15] (Eqs. 2 and 3).

$$NO_3^- + e^-_{aq} \longrightarrow NO_3^{2-} \quad (2)$$

$$NO_3^{2-} + H_2O \longrightarrow NO_2^- + OH + OH^- \quad (3)$$

The quantum yield of hydrogen formation, $\Phi^\circ(H_2)$= 0.24, decreases linearly with the scavenger concentration. However, at 0.008 M nitrate a plateau is observed which persists up to 0.03 M (Fig. 8a).

Thereafter a further decrease of $\Phi(H_2)$ occurs (Fig. 8b) and at a concentration equal to that of formate, 1.84 M, it has dropped to 0.01. The ratios $\Phi^\circ(H_2)/\Phi(H_2)$ are plotted in Stern-Volmer diagram for both concentration ranges in Fig. 8. The inhibiting effect of nitrate is accompanied by a decrease of the CO content which becomes zero at 0.008 M where $\Phi(H_2)$ is still 0.12.

To test how hole scavengers influence the hydrogen formation, KSCN was added to the suspension of zinc sulfide in 0.033 M HCO_2Na. The quantum yield of 0.22 is changed only ($\Phi(H_2)$=0.26) when the thiocyanate to formate ratio reaches 2.8 : 1. It increases further to 0.28 when this ratio is 11 : 1. The product of hole-scavenging, $(SCN)_2^-$, λ_{max}=470 nm could not be detected spectrophotometrically. No hydrogen is formed when the system $ZnS/KSCN/H_2O$ is illuminated in the absence of formate.

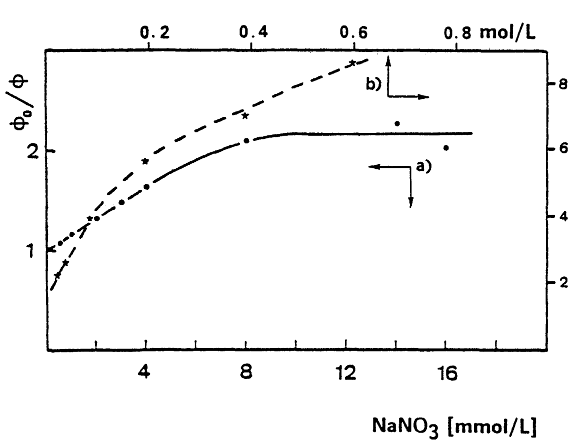

Fig. 8. Stern-Volmer plot for the inhibition of hydrogen formation by $NaNO_3$; 8.5 mg (0.089 mmol) of ZnS suspended in 4 mL of 1.83 M HCO_2Na containing different amounts of nitrate; λ=290 nm.

Discussion

Hydrogen Formation. From the experiments presented above, the following mechanism is proposed for the hydrogen producing reaction (Eqs. 1 and 4—9). For the sake of simplicity, photophysical processes,

$$H_2O + {}^{\square}ZnS \rightleftarrows H_2O_{ad} \tag{4}$$

$$HCOO^- + {}^{\square}ZnS \rightleftarrows HCOO_{ad}^- \tag{5}$$

$$ZnS \overset{h\nu}{\rightleftarrows} ZnS(e_{tr}^-, h_{tr}^+) \tag{6}$$

$$h_{tr+} + HCOO_{ad}^- \longrightarrow HCOO_{ad} \tag{7}$$

$$HCOO_{tr} + H_2O_{ad} \longrightarrow CO_2 + H_3O_{ad}^+ + e_{tr}^- \tag{8}$$

$$2\,e_{tr-} + 2\,H_2O_{ad} \longrightarrow H_2 + 2\,OH_{ad}^- \tag{9}$$

$$HCOO_{ad} + H_2O_{ad} \longrightarrow H_3O_{ad}^+ + COO_{ad}^- \tag{10}$$

$$COO_{ad}^- \rightleftarrows CO_2^- \tag{11}$$

$$2\,CO_2^- \longrightarrow C_2O_4^{2-} \tag{12}$$

$$2\,CO_2^- + 2\,H^+ \longrightarrow CO + CO_2 + H_2O \tag{13}$$

adsorption equilibria and the hydration of CO_2 are omitted unless they are of special importance. This is the case for the adsorptions of water and formate (Eqs. 4 and 5) as indicated by the influences of ZnS dehydration and formate concentration on the reaction rate. The long induction times observed when ZnS is dehydrated at temperatures from RT to 100 °C (Fig. 5) point to a rehydration of the surface during this initial reaction stage. At temperatures above 100 °C the removal of physisorbed water is accompanied by loss of chemisorbed water resulting in the formation of ZnO. This is corroborated by ESCA-spectra exhibiting O1s binding energies of 532.2, 531.6, and 530.4 eV for samples dehydrated at 0.1 Torr and RT, 150 and 300 °C, respectively.[16)] Thus, to observe hydrogen formation the surface of ZnS has to be covered with physisorbed water, different to TiO_2 where the presence of surface OH groups is sufficient.[17)] This finding agrees with the failure of nonaqueous formic acid to undergo the same reaction.

The adsorption equilibrium of formate (Eq. 5) is supported by the dependence of the rate on the formate concentration (Fig. 6b). The obtained curve is best rationalized by assuming that it is equivalent to a Langmuir adsorption isotherm. The corresponding equilibrium constant, 26 $L\,mol^{-1}$, agrees well with values measured for the adsorption of other efficient reducing agents.[18)] Since the adsorption properties may depend on the surface charge of the catalyst, the "pzzp" was measured. It is found at pH 8±0.2 and indicates a weak acidic surface for the ZnS employed throughout this study. The linear changes of formate and hydrogen concentrations with reaction time are further evidence for a surface reaction. Parameter-free plots of these data[19)] indicate the presence of a zero order reaction. The n-type semiconducting character of the zinc sulfide employed is corroborated by the anodic photocurrent measured both with a slurry or with a ZnS-powder electrode. The increase of the saturation current by a factor of 1.3 when formate is present, is due to "current-doubling",[20)] suggesting that a reaction intermediate can inject an electron into the conduction band. The strong decrease of the photocurrent at wavelengths shorter than 300 nm points to enhanced surface recombination due to the shorter penetration length of the absorbed light.[21a-c)] The slight increase of $\Phi(H_2)$ at low light intensity most likely is due to reduced surface recombination.[21d)] Further evidence that the n-type character is necessary for photocatalytic action stems from the observation that powders with a slight excess of zinc are better catalysts than those with a 1 : 1 ratio of zinc to sulfur. Additional support is the fact that the action spectrum of hydrogen evolution parallels that of the photocurrent.

The photogenerated electron-hole pair in ZnS (Eq. 6) has Zn(0) and S(0) character[22)] and therefore photocorrosion is an efficient process in the absence of electron and hole scavengers.[23)] Formate prevents anodic corrosion to Zn(II) and S(0) since only a very small amount of dissolved Zn(II) is formed which does not increase during the reaction. At a limiting formate concentration the corrosion is almost completely suppressed and the powder may be used a second time without decrease in catalytic activity.

The possibility that in the polychromatic irradiations part of the hydrogen originates from HS^-,[24)] can be excluded since in that case HD should be a major part of the gas phase when D_2O is employed. However, this occurs only at pH 14 where the hydrogen composition changes to 15, 40, and 4% as compared to 85, 10, and 5% of D_2, HD, and H_2, respectively, at pH 9. At the high pH value part of the ZnS has dissolved by formation of DS^- which photocatalyzes a homogeneous hydrogen formation.[24)]

The oxidation of adsorbed formate (Eq. 7) is thermodynamically feasible since the hole in the valence band has a redox potential of about 1.8 V (NHE) at pH 7[25)] while E° (CO_2^-, H^+/HCO_2^-) is 1.0 V.[26)] Other hole scavengers like thiocyanate do not induce hydrogen evolution.

The Stern-Volmer diagram (Fig. 8) indicates that nitrate scavenges two different species. When the first plateau is reached, $\Phi(H_2)$ is lowered by 50% and CO formation is completely inhibited. This indicates that CO and the half amount of hydrogen are formed through a common intermediate. This is unlikely to be CO_2^- since in the radiolysis experiments the G-value for H_2 is not increased when ZnS is introduced into the solution containing this radical. It is therefore more likely that the adsorbed formate radical[27)] injects an electron into the conduction band (Eq. 8)[28)] and that this process is completely inhibited by 0.008 M nitrate. At this concentration and up to 0.03 M $NaNO_3$ formate can supply only one electron for the reduction of water (Eq. 9). At this low scavenger concentration it is unlikely that nitrate could compete with adsorbed water for the trapped electron. This seems to occur only at higher concentrations (Fig. 8).

In the absence of nitrate part of the formate radical forms carbon monoxide and oxalate (Eqs. 10—13). The latter product is predominantly obtained when CO_2^- is generated in homogeneous solution.[29] The low oxalate yield of 7% may suggest that 14% of the radicals escape to the solution. However, it cannot be excluded that the dimerization occurs between adsorbed molecules.

The interfacial electron transfer to water (Eq. 9) may occur via a surface state at −0.45 V (NHE), pH 7, as suggested by the onset of the photocurrent in the photoelectrochemical experiments. In the absence of formate a surface state is located at +0.25 V and accordingly no hydrogen evolution is observed. As in the colloidal systems Zn(0) formed by cathodic photocorrosion in competition with Eq. 9, may facilitate the electron transfer. Apparently, platinization does not accelerate this latter process, since the rate is not changed, but rather inhibits photocorrosion. Therefore the original catalytic activity is conserved much longer than in the case of non-platinized ZnS (Fig. 3).

Carbon Monoxide Formation. The fact that addition of THF or Na_2mnt decreases the CO formation suggests that a fully solvated intermediate is involved. In addition, the method of ZnS preparation is also important since no CO is produced when ZnS is synthesized from a zinc dithiolene. Furthermore, CO formation is also wavelength-dependent, having a maximum at 310 nm. Finally, the CO content increases when the concentrations of formate or hydroxide are increased and when D_2O is used instead of H_2O. These findings resemble the complicated situation reported for the electrochemical oxidation of formate, where the amount of CO produced depends on concentration, current density, and diffusion layer thickness.[30] By analogy we therefore assume that in the present system CO is formed via a disproportionation (Eq. 13), $\Delta G°=-2.6$ eV.[26] The decrease of CO formation upon use of DCO_2Na is in agreement with the now more difficult deprotonation step (Eq. 10).

From the catalytic thermal decomposition of formic acid it is known that dehydrogenation occurs predominantly at metal surfaces while dehydration is favored at MgO and ZnO.[31] This may rationalize the observation that platinized ZnS induces a decrease of the CO content by 60% as compared to the non-platinized catalyst. The diminishing amounts of CO with increasing irradiation time may therefore be caused by the concomitant formation of Zn(0) through photocorrosion (Fig. 7A).

Deuterated Substrates. The linear dependence of rate on light intensity suggests that only one photochemical step is involved in product formation. Since no thermal activation energy is observable, the rate is determined by the intensity of the light absorbed. Accordingly, D_2O induces no change of rate while a small isotope efffect of 1.3 is measured when HCO_2Na is replaced by DCO_2Na. This indicates an influence of reaction steps according to Eq. 8 and Eq. 10 in which C–D (C–H) bond breaking occurs. When the amount of CO is subtracted or when CO formation is inhibited by addition of Na_2mnt, the product isotope effect in $ZnS/HCO_2Na/D_2O$ exactly parallels the one observed in the system ZnS/2,5-dihydrofuran/D_2O.[11] The increasing amounts of HD and H_2 are due to the formation of H_2DO^+ in reaction step according to Eq. 8. In the absence of adsorption effects the amount of D_2, HD, and H_2 should be statistically related to the mole fraction $x_H=H/(H+D)$. A calculation[32] shows that for $x_H=0.02$, as given for the experimental conditions of Fig. 7B, curve b, one expects 95% D_2, 5% HD, and negligible amounts of H_2. However, the experimental values of 58% D_2, 33% HD, and 9% H_2 are very different but fit exactly if it is assumed that $x=0.25$. This behavior is found for all the isotopic compositions determined at different reaction times and suggests that the mole fraction at the surface is about ten times larger than in solution. This may result from the better adsorption of HCO_2Na as compared to H_2O[33] and therefore D_2O. Further evidence stems from the addition of H_2O to the system $ZnS/D_2O/HCO_2Na$. The rate of D_2 decrease does not change although x_H in solution increases from 0.05 (curve a) to 0.07 (curve b, Fig. 7B). The fact that even in the presence of 0.72 M DCO_2Na in H_2O no D_2 or HD can be detected, is in agreement with the large excess of H_2O ($x_H \approx 1$) and therefore no deuterated gas should be formed. Assuming that the concentration of DCO_2Na may be ten times larger, one should find 10% HD.

Experimental

All ZnS-suspensions were sonicated for 5 min prior to irradiation in Ar-saturated solutions. Volumes of 100—120 mL were irradiated in an immersion lamp apparatus equipped with an inner quartz tube ($\lambda \geq 248$ nm) and a high-pressure mercury lamp (Philips HPK 125 W), volumes of 22 mL in a cylindrical quartz cell with a 2500 W Hg-Xe lamp (Canrad Hanovia, $\lambda \geq 254$ nm); the evolved gases were continuously recorded.[11] Quantum yields were measured using a specially designed 4 mL quartz cuvette which allowed the GC-determination of dissolved and gaseous hydrogen.[11] The intensity of the exciting light was lowered with the help of metal gauze filters of different mesh size; under the experimental conditions as described in Fig. 2 the rate increases from 1 to 1.7, 2.7, 3.6, 4.5, 5.5, and 7.6 μmol h^{-1} when the intensity of the absorbed light ($\lambda=290$ nm) is increased from 10 to 22, 33, 45, 60, 75, and 98%, respectively. See Ref. 11 for further details.

ZnS was prepared as reported.[9,11] When prepared in neutral solution, refluxing was done for 1 h. The powders obtained should be kept under Ar at normal pressure to avoid formation of ZnO which inhibits catalysis. Aged samples can be regenerated by the removal of ZnO through treatment with 50% (w/w) HOAc for 0.5 h at 50 °C followed by carefully washing to neutrality with deoxygenated water. When CdS was prepared by the same procedure, no gas evolution occurs under identical irradiation conditions. Doped samples were precipitated from the alkaline solution in the presence of 5 mol% of the corresponding metal sulfates.

Platinization was performed by a slight modification of the procedure described by Bard et al.;[34] 2 g of ZnS were suspended in 100 mL of EtOH/H_2O and brought to pH 5 with acetate buffer; after addition of 0.5 mol% $H_2PtCl_6x6 \cdot H_2O$ and 30 min sonication the suspension was irradiated for 5 h. The grey powder was washed three times with deoxygenated water and dried 24 h at ambient conditions.

SEM experiments were performed with the Scanning Electron Microscope S 150 Cambridge-Instruments which contained an EDAX analysator model 711. For sample preparation some drops of a previously sonicated suspension of 10 mg of ZnS in 22 mL of H_2O were pasted on a glass slide and dried at about 10 Torr for 12 h. Evaporation of Au, Pd, or graphite onto the ZnS-particles did not improve the contrast of the micrographs.

Diffuse Reflectance spectra were measured against $BaSO_4$ (Weißstandard, Merck) as a reference using the double-beam spectrophotometer MIT-20, Bruins Instruments, München. The samples were diluted with $BaSO_4$ by grinding for 30 min in a ball-mill. For evaluation of the band-gap,[35] $[F(R_\infty)h\nu]^2$ was plotted as a function of $h\nu$, the energy of the exciting light; $F(R_\infty)$=Kubelka-Munk function; the straight line obtained, in accordance with an allowed transition,[36] intersects the abscissa at 3.67±0.03 eV.

Determination of "pzzp". 1 g (10.3 mmol) of ZnS were suspended in 0.5 L of triply distilled water and sonicated for 20 min. The solution was first brought to pH 10 by adding 0.1 M KOH and than titrated with 0.01 M HNO_3 in 1 mL portions. 1 min after each addition the pH value was measured with an Ingold glas electrode. When 0.5 and 3 g of ZnS were used, the maximum was steeper and more flat, respectively, due to the different buffer capacity of the suspension. The maxima occured in all three cases at pH 8±0.2.

Photoelectrochemical Experiments. On an optical bench the light from an Osram HBO 200 W lamp passed through a Kratos GM 100-3 monochromator and rotating sector onto a standard photoelectrochemical cell;[37] working electrode (WE): platinum (2×2 cm), counter electrode: platinum wire, connected with the WE-compartment via an agar-agar salt bridge saturated with K_2SO_4; reference electrode: $Hg/HgSO_4$; potentiostat: Bank Elektronik, Potentio-Galvano-Scan, Wenking PGS 77; voltage scanner: Bank Elektronik, Voltage Scan Generator, Wenking VSG 72. In the slurry method[37] 25 mg of ZnS were suspended in 50 mL 0.1 M K_2SO_4; although the platinum flag was oriented parallel to the light beam, it showed a small photocurrent in the absence of ZnS which was subtracted from the value obtained with the slurry. The ZnS-covered WE was prepared by precipitating ZnS at least two times in the presence of the platinum flag. The resulting ZnS-electrode was shortly dried under Ar at ambient conditions, dipped into 20% HOAc, washed neutral with deoxygenated, triply distilled water and dried again under Ar. SEM-micrographs revealed the presence of particles with diameters of 100—200 nm. A Lock-in-Amplifier (PAR 42) was necessary to observe a reproducible photocurrent. In all cases the results compared well with those obtained in the slurry method. The absolute value of the photocurrent was in the range of 4 and 0.5 μA for the slurry and ZnS/Pt-elctrode, respectively. Attempts to adapt one of the published deposition procedures[38] were not successful. For the measurement of the wavelength dependence the lamp spectrum was calibrated with a photodiode (Hamamatsu S780-8BQ).

Material Balance. In the experiment described in Fig. 4 the irradiation was interrupted after every 70 mL of gas produced; the gas was withdrawn into two evacuated flasks, one was analyzed by GC, the other by MS.[11] At the same intervals 5 mL of the solution were withdrawn and carbonate was removed by acidification with 0.01 M HCl; the evolved CO_2 was gravimetrically determined through absorption in 2 M NaOH and precipitation as barium carbonate; the remaining solution was brought to pH 8 by addition of dilute NaOH and carefully evaporated to dryness below 150 °C; the residue was redissolved in 10 mL of H_2O by sonicating for 20 min, ZnS was removed with the help of a millipore filter (0.2 μm), and 20 μL of this solution were used to determine formate and oxalate by HPLC (Chromopak Ionospher tmA 4×250 mm, mobile phase: 0.025 M sodium salicylate adjusted to pH 4 with HOAc, differential refractometer for detection).

Influence of pH Value. Instead of 4.4 g (0.07 mol) of HCO_2Na, 3 g (0.07 mol) of HCO_2H were employed in the presence of 50 mg (0.51 mol) of ZnS suspended in 120 mL of H_2O; formaldehyde was determined colorimetrically;[29] traces of MeOH were detected by GC. When 50 mg of ZnS were suspended in nonaqueous HCO_2H, no gas evolution occurred upon irradiation. The glass electrode was inserted directly into the immersion lamp apparatus for continuous measurement of pH changes.

Thermoanalyses. Differential Thermal Analysis (DTA) in the range from RT to 500 °C affords a minimum at 110 and a maximum at 320 °C. Differential Thermal Gravimetry (DTG) of 71 mg ZnS gave the following weight losses: 2.32 (50—150), 0.68 (150—310), 1.5 (310—400), and 0.6 mg (400—470 °C).

Wavelength Dependence of CO Formation. From irradiation of a suspension of 10 mg (0.1 mmol) of ZnS in 4 mL of 1.83 M HCO_2Na a gas phase with the following CO content was obtained: 7, 42, 25, 20, and 7% at 320, 310, 290, 280, and 254 nm, respectively.

Influence of Solutes on Product Composition. Upon additon of 20% (v/v) of THF or 50 mg (0.258 mmol) of Na_2mnt to the system 20 mg (0.21 mmol) ZnS/100 ml of 0.29 M HCO_2Na the CO content decreased by 30% or 95%. No CO is detected when ZnS prepared in situ from $[Zn(mnt)_2)][NBu_4]_2$[11] was employed in the above experiment. As compared to the original, nondeuterated case, the CO content was doubled in the system ZnS/HCO_2Na/D_2O while it was decreased to half of its original value when ZnS/DCO_2Na/H_2O was employed.

Influence of Formate Concentration on Photocorrosion. Due to strong adsorption of MV^+ onto ZnS it was not possible to use this method[40] for quantitative determination of Zn(0) produced. As a rough estimate we used the ratio of the initial reaction rates $r_{i(2)}/r_{(1)}$ measured at 90 s reaction time; 50 mg (0.52 mmol) of ZnS suspended in 100 mL of H_2O were irradiated at the given formate concentrations;

after 10 min, $r_{i(1)}$ was taken from the gas evolution curve; the catalyst was then filtered off and irradiated a second time at the same formate concentration to obtain $r_{i(2)}$; see Results section.

Influence of Deuterated Substrates. Each of the isotopic compositions given in the following is an average from three samples; the determination was performed with the spectrometer CEC MS 103-C which was calibrated with the three dihydrogen isotopes. The values (mol%) of H_2, HD, D_2, and CO for Fig. 7B are: curve a) 1.0, 3.6, 3.1, 64.4; 2.2, 6.7, 28.1, 63.0; 1.5, 9.8, 27.7, 61.0; curve b) 2.9, 11.4, 20.3, 65.4; 4.9, 13.7, 17.2, 64.3; 5.2, 15.0, 16.6, 63.3; curve c) 1.8, 16.1, 40.0, 42.1; 2.2, 16.1, 39.9, 41.9; 2.4, 17.3, 40.3, 40.0 at 50, 100 and 150 mL gas evolved, respectively. The composition of the hydrogen gas (D_2, HD, H_2) is 85, 10, 5; 80, 16, 4; 74, 23, 6; 71, 28, 3; and 63, 30, 7% at 50, 100, 150, 250, and 400 mL of total gas evolved, respectively.

The possibility that the photoexcited ZnS may catalyze an isotopic exchange between hydrogen gas and D_2O was excluded by the result of the following experiment: A suspension of 30 mg (0.31 mmol) of ZnS in 100 mL of D_2O containing 3 g (44 mmol) of HCO_2Na was irradiated under H_2 which was permanently bubbled through the suspension with the help of a circulating pump and a 2 L reservoir. When 60 mL gas were formed, only D_2 and CO but no HD were detected by MS. To exclude a deuterium exchange between H_2O and DCO_2Na, the experiment described above was performed by adding 2 g (111 mmol) of H_2O and replacing HCO_2Na by 1 g (14.5 mmol) of DCO_2Na. After evolution of 150 mL gas, ZnS was removed by centrifugation and the filtrate evaporated to dryness; IR-analysis of this solid residue gave no evidence for the presence of HCO_2Na. In the system ZnS (20 mg, 0.21 mmol)/H_2O (100 mL)/DCO_2Na (5 g, 072 M) no HD or D_2 could be detected after 600 mL of gas produced (92% H_2, 8% CO).

For measurement of the kinetic isotope effect a suspension of 8.5 mg (0.087 mmol) of ZnS in 4 mL of H_2O or D_2O containing 0.1 g (1.47 mmol) of HCO_2Na or 0.101 g (1.47 mmol) of DCO_2Na was irradiated with a low-pressure mercury lamp (λ=254 nm) and the amount of gas evolved after 2 min, it contained only very small amounts of CO, was determined by GC; these values were taken as the initial rates. In the system ZnS/HCO_2Na the rates in D_2O and H_2O were identical, in ZnS/H_2O the rate was lowered by a factor of 1.3 when DCO_2Na was employed instead of HCO_2Na.

Influence of Scavengers. The system ZnS (10 mg, 0.1 mmol)/HCO_2Na (0.1 g, 1.4 mmol)/H_2O (50 mL) was placed in a flat cell and irradiated for a few minutes ($\lambda \geq 330$ nm) in the presence of POBN in the cavity of the ESR spectrometer (Varian E-6-X-band). The observed signal (a_H=3.3, a_N=1.53 G) is in accordance with the literature.[41] No signal was observed when the systems HCO_2Na/POBN or ZnS/POBN were irradiated. Attempts to scavenge OH-radicals either with POBN or with 5,5-dimethyl-1-pyrroline-*N*-oxide, which affords a longer lived spin adduct, failed.

Radiolysis Experiments. 0.1 M HCO_2Na in the absence and presence of ZnS was bubbled with N_2O for 30 min followed by γ-radiolysis for 30 min (dose rate=6.77 krad min^{-1}, ^{60}Co-radiation source, Nuclear Engineering Ltd. "Irradiation Unit, Type LCU 2") and the total amount of H_2 was determined by GC.[11] The following *G*-values were obtained: G_H=0.92 (without ZnS), 1.08 (with ZnS, with stirring), and 0.90 (with ZnS, without stirring).

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