Heterogeneous Photocatalysis, IX[1]

Zinc Sulfide Catalyzed Photoreduction of Carbon Dioxide

Horst Kisch* and Gerhard Twardzik

Institut für Anorganische Chemie der Universität Erlangen-Nürnberg,
Egerlandstraße 1, D-8520 Erlangen

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Carbon dioxide is catalytically reduced to formate in a suspension of zinc sulfide in water/2,5-dihydrofuran when irradiated ($\lambda \geq 290$ nm). Turnover rates are in the range of 1.5 monolayers CO_2/h. No reaction occurs at pH = 12, and a very slow one at pH = 3. 2,5-Dihydrofuran functions as reducing agent which is oxidized to dehydro dimers. When it is substituted by 2-propanol, no CO_2 reduction is observed. Semiconductor photocatalysis by a two-electron transfer from zinc sulfide to adsorbed hydrogen carbonate is assumed as the key step of CO_2 fixation.

The photoreduction of carbon dioxide in the presence of transition-metal complexes or semiconductors as potential photocatalysts has been investigated in connection with solar-energy conversion and organic synthesis from C_1 chemicals[3]. In the presence of semiconductor powders like $SrTiO_3$, CdS, TiO_2, and α-Fe_2O_3 the products formate, methanol, methane, and even carbon were obtained[4-8]. In addition, colloidal CdS induces the formation of small amounts of glyoxylic acid and acetic acid[9]. Usually, the yields are very low, and it is unclear whether these reactions are catalytic or assisted with respect to the semiconductor. In many cases the reducing agent was assumed to be water although the experimental evidence was rather scarce. Henglein et al. reported that the photoreduction of carbon dioxide by methanol or 2-propanol is catalyzed by colloidal ZnS[10]. Since the photocatalytic properties of the colloid usually differ from those of the powders – the dehydrodimerization of cyclic ethers[11] is not photocatalyzed by the colloid nor does the powder induce H_2 evolution from 2-propanol/water mixtures – it seemed worthwhile to test whether similar differences occur also in CO_2 reduction.

Results and Discussion

Irradiation ($\lambda \geq 290$ nm) of a suspension of ZnS powder in water/2-propanol (150:20, v/v) under a continuous purge of carbon dioxide does not afford formate. However, this is formed when 2-propanol is replaced by 2,5-dihydrofuran (RH) (Figure 1). The latter is oxidized to the dehydro dimers described recently for the same system but in the absence of carbon dioxide[11]. There is no reaction at pH = 12 and only a very slow one at pH = 3, indicating that hydrogen carbonate is the species which is reduced. These results suggest that the overall stoichiometry is according to eq. 1.

$$CO_3H^{\ominus} + 2\,RH \xrightarrow{h\nu,\ ZnS} HCO_2^{\ominus} + R-R + H_2O \qquad (1)$$

Although the reaction is rather slow, it is catalytic as indicated by the production of 1.8 mmol formate/mmol ZnS after 72 h irradiation time. The turnover rate is ca. 1.5 monolayers of CO_2/h (see Experimental). The reason for the rather low catalytic activity is partly due to the fact that the formate produced is easily reoxidized in a very efficient reaction[2]. The quantum yield of product formation is in the range of 0.001 (λ = 300 nm).

A possible mechanism involves photoexcitation of ZnS to generate an electron-hole pair trapped at the surface. The reduction potential of the trapped electron should be at ca. −1.8 V (pH = 7), the position of the conduction band edge of ZnS[12], and it is thermodynamically unlikely that $e_{tr}^{\ominus}$ will reduce $CO_3H^{\ominus}$ in a one-electron transfer since $E^{\circ}(CO_2/CO_2^{\ominus}) = -2$ V[13]. In agreement with this postulate no oxalate could be detected, the typical dimerization product of the $CO_2^{\ominus}$ radical. This parallels the results obtained with colloidal ZnS in 2-propanol/water[10], and we also assume that the reduction occurs by a two-electron transfer. The redox potential of $E^{\circ}(CO_3H^{\ominus} + 2\,H^{\oplus} + 2e^{\ominus} \rightarrow HCO_2^{\ominus} + H_2O) = -0.53$ V[14] corroborates this proposal. Due to the considerable Zn(0) character of excited ZnS[15] it seems likely that the two electrons produced by sequential two-photon absorption are trapped at the surface as zinc atoms[10] which then reduce adsorbed hydrogen carbonate. The trapped holes have a potential of ca. 1.8 V. This is positive enough to oxidize two molecules of 2,5-dihydrofuran to the radical cations which are converted into the products R–R by deprotonation and consecutive dimerization[11].

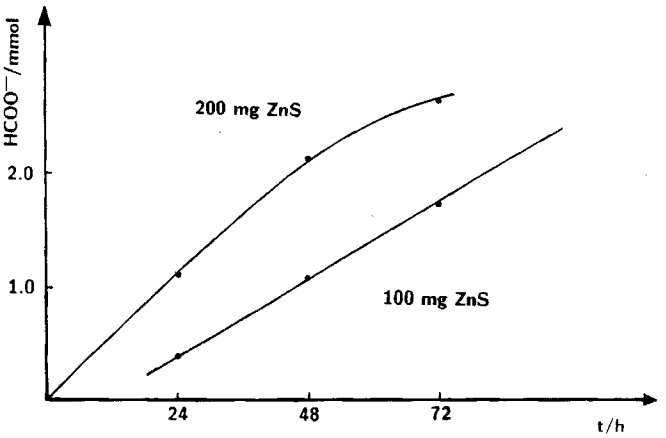

Figure 1. Formation of formate upon irradiating ($\lambda \geq 290$ nm) a suspension of ZnS in water/2,5-dihydrofuran under a constant purge of carbon dioxide

The failure of 2-propanol to function as reducing agent in the powder system further supports the general difference in the chemical selectivity of powder and colloidal semiconductor photocatalysts. If this originates in the more positive potential for 2-propanol

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vs. 2,5-dihydrofuran oxidation [$E(Me_2CHOH/Me_2COH)$ = 1.8 V[10] vs. $E(RH/R^{\bullet} + H^{\oplus}$ = 1.6 V)[11]] it suggests that the valence band of the powder is cathodically shifted with respect to that of the colloid. Whether this or different adsorptive properties of the colloid and powder surface towards the two reducing agents are the dominating factors, cannot be decided at the present.

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Experimental

ZnS was prepared by hydrolysis of thiourea in the presence of zinc sulfate at 80°C; the specific surface area of the resulting powder, as determined by B. E. T. measurements, was 100 m^2/g[16]. – 2,5-Dihydrofuran was heated at reflux for 1 h with maleic anhydride[17] before distillation, b.p. 65–66°C. – 2-Propanol (Merck; p.a.) was used as received.

A suspension of 200 mg (2.05 mmol) of ZnS in water/2,5-dihydrofuran (150 ml:20 ml) was sonicated under CO_2 atmosphere. The consecutive irradiation was performed for 24, 48, and 72 h under a constant CO_2 purge in a pyrex standard immersion-lamp apparatus[11] using a 150-W (Z1, Heraeus, Original Hanau) high-pressure mercury lamp ($\lambda \geq 290$ nm). The organic phase was extracted with $CHCl_3$, and the dehydro dimers were identified by GLC[11]. 5 ml of 1.0 M KNO_3 was added to the aqueous phase as internal standard, followed by filtration through a Millipore filter (0.2 μm pore size). 20 μl of the resulting solution was injected into the ion chromatograph (column: ET 250/8/4 NUCLEOSIL 10 Anion II; Knauer HPLC Pump 64; elution agent: 0.002 M potassium hydrogen phthalate at pH = 4, 2 ml/min, 110 bar; UV detection at λ = 254 nm; calibrated with 0.01 M HCO_2Na and 0.01 M KNO_3). Irradiations in the presence of 100 mg of ZnS or 2-propanol were conducted analogously. The pH dependence was studied by adding prior to sonication 0.1 M HCl or NaOH to adjust the pH value to pH = 3 and 12, respectively.

The turnover number was calculated under the assumption that one monolayer[18] of CO_2 consists of 10^{14} molecules/cm^2; since 0.1 g of ZnS with specific surface area of 100 m^2/g was employed and 1.8 mmol of CO_2 was reduced within 72 h, 1.5 monolayers of CO_2/h had to be consumed. The quantum yield was estimated by comparison of the rates of hydrogen evolution and formate formation measured under identical conditions in the systems zinc sulfide/water/2,5-dihydrofuran (Φ = 0.1)[11] and zinc sulfide/water/2,5-dihydrofuran/carbondioxide, respectively.

CAS Registry Numbers

ZnS: 1314-98-3 / CO_2: 124-38-9 / 2,5-dihydrofuran: 1708-29-8 / formate: 71-47-6

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