Photocatalytic Carbon–Carbon Bond Formation with Concurrent Hydrogen Evolution on Colloidal Zinc Sulphide

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In the photocatalytic system containing colloidal ZnS, water, and organic substrates such as triethylamine, tetrahydrofuran, or methanol, oxidative carbon–carbon bond formation occurs with efficient reductive H_2 evolution, to give the dimeric products 2,3-bis(diethylamino)butane, 2,2′-bitetrahydrofuryl, or ethylene glycol, respectively.

In photocatalytic systems consisting of photocatalysts, water, and organic electron donors, that evolve H_2, selective carbon–carbon bond formation by oxidation of the electron donors would be of great interest since it could provide a method for energy conversion and storage and be synthetically significant.[1] However, there has been little study on such systems, because degradative and exergonic reactions were believed to predominate in the oxidation process. We now report on the effectiveness of colloidal ZnS for the photo-oxidative carbon–carbon bond formation linked with photoreductive H_2 evolution.

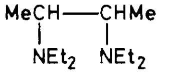
A heterogeneous mixture of an aqueous ZnS colloid and an organic substrate was deaerated and irradiated in a Pyrex vessel (>290 nm) using a high pressure mercury arc lamp as in a previous report of ours.[2] As shown in Table 1, H_2 was evolved in fairly high quantum yields and selective α-carbon–carbon bond formation occurred in the oxidation of triethylamine (TEA), tetrahydrofuran (THF), and the alcohols shown except for t-butyl alcohol. TEA afforded 2,3-bis(diethylamino)butane (**1**) with a small amount of *threo*-3-(diethylamino)butan-2-ol; THF gave 2,2′-bitetrahydrofuryl (**2**) with traces of butane-1,4-diol, 2-hydroxytetrahydrofuran, and unidentified oligomers. The major products (**1**) and (**2**) were equal mixtures of the diastereoisomeric forms. Surprisingly, the alcohols gave the vicinal diols (**3**) and the expected carbonyl compounds. t-Butyl alcohol, however, gave traces of H_2 and the β-carbon–carbon coupling product, 2,5-dimethylhexane-2,5-diol under comparable conditions.

The stoicheiometry of this photoredox process was quantitatively examined by using the methanol system. As shown in Figure 1, the colloidal ZnS kept its activity during 60 h irradiation and the total molar quantity of ethylene glycol and formaldehyde was in fair agreement with that of H_2, indicating that the electron balance was consistent and further oxidation

Table 1. Hydrogen evolution and carbon–carbon bond formation in the photocatalytic reaction using colloidal ZnS.

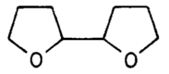
Organic substrate	Irradiation method[a]	Products[b] (mmol) [$\Phi(1/2H_2)$][c]
Triethylamine	A	H_2 (21.0) [0.27], (**1**) (12.6)[d]
Tetrahydrofuran	A	H_2 (38.7) [0.14], (**2**) (20.5)[e]
Methanol	A′	H_2 (8.69) [0.15], (**3**); $R^1 = R^2 = H$ (4.05)[f]
Methanol	B	H_2 (0.32), (**3**); $R^1 = R^2 = H$ (0.12)[g]
Ethanol	B	H_2 (0.52), (**3**); $R^1 = H, R^2 = Me$ (0.19)[h]
Propan-2-ol	B	H_2 (0.45) (**3**); $R^1 = R^2 = Me$ (0.05)[i]
t-Butyl alcohol	B	H_2 (0.05)[j]

[a] Method A: internal irradiation at atmospheric pressure using a 100 W high pressure Hg arc lamp. Colloidal ZnS, 5 mmol; substrate, 200 cm^3; H_2O 200 cm^3; irradiation time 24 h; A′: ZnS (gelatinous), 2 mmol; substrate, 300 cm^3; H_2O, 100 cm^3. Method B: external irradiation under reduced pressure using a 300 W high pressure Hg arc lamp. ZnS (gelatinous), 0.05 mmol; substrate, 10.8 cm^3; H_2O, 1.2 cm^3; irradiation time 4 h. Colloidal ZnS was prepared *in situ* by mixing aqueous solutions of $ZnSO_4$ and Na_2S (both 0.1 M). Gelatinous ZnS was prepared by filtration of the colloidal ZnS and washing with water (*ca.* 75% H_2O). [b] Determined by a Shimadzu GC-7A gas chromatograph using the following columns: H_2, active carbon, i.d. 3 mm × 2 m; vicinal diols, Porapak Q, i.d. 3 mm × 1 m; formaldehyde, Porapak T, i.d. 3 mm × 2 m; other organics, Ucon oil 50LB 550X on Uniport (15%), i.d. 3 mm × 2 m. [c] Quantum yields determined using a hexan-2-one actinometer by assuming that two photons produce one molecule of H_2. Not corrected for light absorption by the suspended catalyst. [d] *Threo*-3-(Diethylamino)butan-2-ol also formed but not determined quantitatively. [e] Butane-1,4-diol (1.2), 2-hydroxytetrahydrofuran (0.2), and oligomers also formed but not determined quantitatively. [f] Formaldehyde (3.81) also formed. [g] Formaldehyde (0.15) also formed. [h] Acetaldehyde also formed but not determined quantitatively. [i] Acetone also formed but not determined quantitatively. [j] 2,5-Dimethylhexane-2,5-diol also formed but not determined quantitatively.

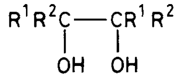


$\underset{NEt_2}{MeCH}-\underset{NEt_2}{CHMe}$

(**1**); dl, *meso*



(**2**); dl, *meso*



$R^1R^2\underset{OH}{C}-\underset{OH}{C}R^1R^2$

(**3**)

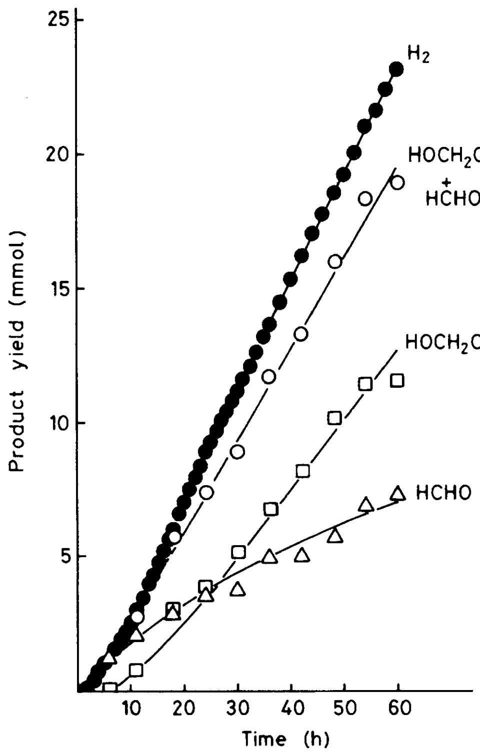


Figure 1. Product yields from band gap irradiation photolysis of a colloidal ZnS solution containing methanol (300 cm^3), water (100 cm^3), and ZnS (2 mmol).

to other products was negligible. Figure 1 also shows that the formation of ethylene glycol gradually increased and prevailed over that of formaldehyde. When a small amount of formaldehyde was added to the starting mixture and this was irradiated ethylene glycol was formed immediately. However, further investigation revealed that the ratio of the yield of ethylene glycol to that of formaldehyde varies widely with other conditions such as the concentration of methanol.

These observations are in contrast with other photocatalytic systems which evolve H_2, where degradative oxidation of the donors is predominant.[3,4] This implies that the photoexcited ZnS controls one-electron transfer from organic substrates, giving free carbon radicals through proton loss, which lead to carbon–carbon bond formation by their combination reactions[5] or by their addition reactions with carbonyl compounds formed concurrently,[6] as observed in general free radical reactions. Recently, Kisch and his coworkers[7] also reported the photocatalytic dimerization of 2,3-dihydrofuran on colloidal ZnS.

In conclusion, we have demonstrated the first example of a photoassisted process in which carbon–carbon bond formation occurs *via* free radical intermediates by utilizing semiconductor particles.

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