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ZINC SULFIDE-CATALYZED PHOTOCHEMICAL CONVERSION OF PRIMARY AMINES TO SECONDARY AMINES

Shozo YANAGIDA,* Hirotoshi KIZUMOTO, Yoshiteru ISHIMARU,
Chyongjin PAC, and Hiroshi SAKURAI†

Chemical Process Engineering, Faculty of Engineering,
Osaka University, Yamadaoka, Suita, Osaka 565
†Nara Technical College, Yata-cho, Yamatokoriyama 639-11

Nonmetallized ZnS catalizes efficiently the photochemical conversion of primary amines to secondary amines with liberation of ammonia under irradiation of the UV light of λ>290 nm. The conversion is interpreted as due to the two-hole-oxidation of primary amines to Schiff bases and their two-electron-reduction to secondary amines by the photogenerated electrons in ZnS.

Recently, photocatalytic reactions over irradiated semiconductors have been extensively applied to a variety of reactions, and the applications to organic syntheses have received prominent attention and interest.1) In such photocatalytic systems, semiconductor powders have often been modified with noble metals such as platinum in order to intercept recombination of the photogenerated electron-hole pair by facilitating reduction processes.2) If H_2 is present in systems, however, noble metals on photocatalysts can catalyze thermal reduction through chemisorption of H_2. When hydrogen and noble metal can coexist in the semiconductor system, it is difficult to appreciate the photoreduction by electrons in the conduction band of semiconductors. On the other hand, ZnS was recently found to act as an efficient photocatalyst without noble metal modification.3-5) Since ZnS has the conduction band edge which is very negative(-1.74 V vs. SCE(pH 1)),6) the irradiated ZnS should reveal a strong reducing power. With these in view, we continued further studies on photoredox reactions catalyzed by ZnS and have now found that ZnS induces the efficient photocatalytic conversion of primary amines to secondary amines through photoreduction of Schiff bases in the absence of noble metal modification.

Under cooling in ice water, a nitrogen purged suspension of freshly prepared ZnS(5 mmol) in an aqueous solution(400 cm^3) of ethylamine(50 v/v%) was irradiated through a Pyrex filter with a 100 W high-pressure mercury arc lamp as in our previous report.3b) As shown in Fig. 1, diethylamine was formed increasingly with H_2 after an apparent induction period, while H_2 evolution had a tendency to level off. In a diluted reaction system consisting of 10 cm^3 of ethylamine and 400 cm^3

of water, the constant evolution of H_2 was confirmed and diethylamine was detected only after 6 h irradiation(Fig. 1). These results indicate that ZnS-catalyzed photoreduction should occur competitively to water and to a certain organic intermediate leading to diethylamine. In other word, photoreduction by conduction band electrons(e_{CB}) should occur to water ($H_2O \rightleftharpoons OH^- + H^+ \xrightarrow{e_{CB}} \frac{1}{2}H_2$) until reducible intermediates accumulate enough in the reaction system.

Similar conversion of primary amines to secondary amines was recently reported in an irradiated TiO_2/Pt system;$^{7)}$ Schiff bases were proposed to be intermediates to secondary amines and the secondary amine formation was explained due to the catalytic reduction of the Schiff bases by the platinum and the photogenerated hydrogen in the reaction system. The qualitative analysis by a quadrupole mass spectrometer revealed that ammonia was formed at the early stage of the reaction and increased as the reaction proceeded. Liberation of ammonia indicates that ethylamine should be oxidized by valence band hole(h_{VB}), giving ethylimine followed by hydrolysis to acetaldehyde. The aldehyde once formed could react with excess ethylamine, yielding N-ethylideneethylamine;

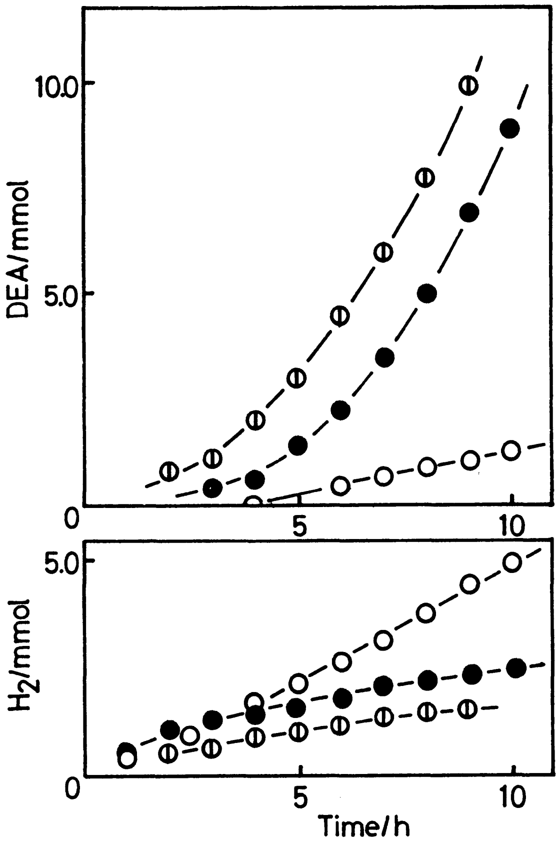

Fig. 1. Formation of diethylamine(DEA) and H_2 by irradiation of ZnS-dispersed aqueous solutions of ethylamine(ZnS, 5 mmol). ● ethylamine, 200 cm^3; H_2O, 200 cm^3. ○ ethylamine, 10 cm^3; H_2O, 400 cm^3 ⦶ ethylamine, 200 cm^3; H_2O, 200 cm^3; acetaldehyde, 0.5 cm^3.

$$CH_3CH_2NH_2 \xrightarrow[-2H]{2h_{VB}} CH_3CH{=}NH \xrightarrow[-NH_3]{H_2O} CH_3CH{=}O \xrightarrow[-H_2O]{CH_3CH_2NH_2} CH_3CH{=}NCH_2CH_3$$

In fact, in similar treatment of an aqueous propylamine(50 v/v%) solution, a small amount of N-propylidenepropylamine was detected by glc analysis(ASC-L 3 m glass column(Nishio Ind. Co. Ltd), Shimadzu GC-7AF). In this case, dipropylamine(4.3 mmol) was formed with 3.8 mmol of H_2 after 10 h irradiation.

Taking into account these facts, acetaldehyde(0.5 cm^3) was added into an aqueous solution(400 cm^3) of ethylamine(50 v/v%) and the mixture was irradiated under the same conditions. Surprisingly, hydrogen evolution was suppressed and diethylamine was formed more smoothly as shown in Fig. 1. When propionaldehyde instead of acetaldehyde was added and irradiated in a similar manner, ethylpropylamine was mainly formed, whereas diethylamine was undetected even after 10 h irradiation.

Furthermore, N-propylidenpropylamine was attempted to reduce to dipropylamine in the ZnS-aqueous ethylamine system.8) N-Propylidenepropylamine was immediately converted into N-propylideneethylamine by an exchange reaction between the amines in the dark and ethylpropylamine was produced exclusively by irradiaion as was observed by addition of propionaldehyde to the same reaction system. These reducions never occur without irradiation, suggesting that Schiff bases should undergo two-electron-reduction by conduction band electrons(e_{CB}), giving dialkylamines;

$$RCH{=}NCH_2R \ + \ 2e_{CB} \ + \ 2H^+ \longrightarrow (RCH_2)_2NH$$

It should be remarked that a dimeric product at the α-carbon, e.g., 2.3-diaminobutane from ethylamine, was not detected even in the small quantity of residue obtained after separating water as benzene azeotrope. This fact is in contrast to the oxidative α-coupling reactions observed for triethylamine and diethylamine.3b,9) It seems that one-hole-oxidation intermediates, i.e., aminyl radicals(CH_3CH_2NH) or α-amino radicals(CH_3CHNH_2) should readily undergo further oxidation, leading to N-ethylideneethylamine through formation of ethylimine and/or acetaldehyde. The carbinolamine[$CH_3CH(OH)NHCH_2CH_3$] and aminal[$CH_3CH(NH_2)NHCH_2CH_3$], precursors of N-ethylideneethylamine,10) are also conceibable as reducible intermediates, as the aminal intermediates are sometimes proposed to be hypothetical intermediates in the reductive conversion of primary amines to secondary amines.11) However, since ZnS has a hydrophobic character, Schiff bases would be preferentially adsorbed on the surface of ZnS and readily undergo reduction by the conduction band electrons in ZnS. This interpretation may also be supported by the fact that diethylamine is produced efficiently in the dilute system.

The quantum yields for the present photoreaction have not yet been determined because of the rather long induction period for the formation of secondary amines. However, the total quantity of the photoproduced diethylamine and H_2 was almost the same with that of the H_2 generated in the water photoreduction using diethylamine as an electron donor under the comparable condition.12) This obsevation means the highly efficient photoreduction of Schiff bases rather than water or H^+.

It is wellknown that aryl-N-alkylimines are photoreduced in hydrogen donating solvents by a chemical sensitization mechanism.13) However, the present reactions never occur in the absence of ZnS. In conclusion, we have demonstrated that efficient photoreduction occurs to organic substrates in aqueous systems by utilizing nonmetallized semiconductor particles.14)

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8) N-Ethylideneethylamine was attempted to photoreduce to diethylamine by using methanol or hydrogen in methanol as electron donors under the ZnS-photocatalyzed system, but was unsuccessful. The failure may be attributable to the instability of the Schiff base in the reaction systems.

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10) It is wellknown that carbinolamines are intermediates to Schiff bases from aldehydes and primary amines. "The chemistry of Open-chain Organic Nitrogen Compounds," ed by P. A. S. Smith, W. A. Benjamin, Inc. New York, (1965), Vol. 1, p. 299.

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12) The apparent quantum yield for H_2 production in this system was determined to be 0.27 for 313 nm light by assuming that two photons produce one molecule of H_2.10)

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14) It was recently reported that UV(λ=310 nm) irradiation of a dilute solution of Methyl Orange and colloidal TiO_2(10^{-4} mol dm^{-3}) leads to the photoreduction to a hydrazine derivative. G. T. Brown and J. R. Darwent, J. Chem. Soc., Faraday Trans. 1, 80, 1631(1984).

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