Semiconductor Photocatalysis. Part 4.[1] Hydrogen Evolution and Photoredox Reactions of Cyclic Ethers catalysed by Zinc Sulphide

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ZnS-catalysed photoredox reactions of aqueous solutions of cyclic ethers, *i.e.* tetrahydrofuran, dihydrofurans, 2,5-dimethyltetrahydrofuran, 3-methyloxetane, 1,4-dioxane, and tetrahydropyran are described. A freshly prepared ZnS suspension displays efficient and selective photocatalysis especially for furan derivatives under band-gap irradiation (>290 nm); reduction of water by the conduction band electrons generates H_2 and one-hole oxidation of the substrates leads to carbon–carbon bond formation through coupling of intermediary radicals. In the photolysis of tetrahydrofuran, oligomerization from the dimeric product (**1**) to octamer was observed with efficient H_2 evolution ($\varphi_{\frac{1}{2}H_2}$ = 0.13—0.62). Further oxidation of intermediary radicals and photoreduction of the resulting oxidation products were also confirmed; *e.g.* photolysis of 2,5-dimethyltetrahydrofuran gave exclusively the ring-opened product (**9**) with its photoreduced product, hexane-2,5-diol (**10**).

Since the critical role of the semiconductor surface in photoinduced electron-hole separation was established, photocatalytic reactions on semiconductors have been a subject of various studies during the last several years.[2] An important aspect of these studies is to establish a solar, light-harvesting process for photoproduction of compounds of higher values from abundant, low-cost materials. With regard to TiO_2 and CdS which have been extensively investigated as photocatalysts, it appears that a modification with noble metals such as Pt and RuO_2, or the coexistence of appropriate electron acceptors such as Ag^+ ion and O_2, is needed to obtain good efficiency in the net chemical reactions followed by photophysical charge separation.[3,4]

On the other hand, zinc sulphide with a large band-gap energy (3.7 eV, 335 nm) has received little attention as a candidate for light-energy conversion units until recently. It was reported to photodecompose in water through H_2 evolution,[5] and was also reported to show poor catalytic efficiency.[6] As reported previously,[1,7] however, a freshly prepared ZnS dispersion is photostable especially in the presence of appropriate electron donors and induces sustained interfacial electron transfer without noble metal modification.

On literature survey, two interesting studies were found; the suppression of photodegradation of ZnS by organic dyes[8] and the disappearance of ethyl xanthate in water by the irradiated ZnS[9] are worth noting. Recently, a number of closely related investigations have appeared in the literature. Flat band potential determination,[10] luminescence studies,[11] and photochemical reactions[12] should be mentioned.

The present report deals with interfacial photoredox reactions of a freshly prepared ZnS suspension and cyclic ether derivatives in aqueous medium. An important finding of the work is that photocatalysis of ZnS is strongly affected by the structures of ethers, and that not only one-electron redox reactions, but also two-electron redox reactions, occur without any charge relays on semiconductor ZnS.

Results and Discussion

Hydrogen Evolution.—As reported previously,[1,7] the simultaneous presence of ZnS suspension, organic substrates as electron donors, and water resulted in sustained hydrogen evolution upon u.v. irradiation (>290 nm); H_2 evolutions under 313 nm irradiation in the presence of various cyclic ethers were plotted against time and are shown in Figure 1. With some furan derivatives, except furan itself, H_2 evolved very efficiently to such an extent that bubbles of H_2 were observable under irradiation at atmospheric pressure. Furan did not serve as an electron donor for H_2 evolution in this system, although it has the lowest ionization potential (8.87 eV) of the ethers examined.[13,14]

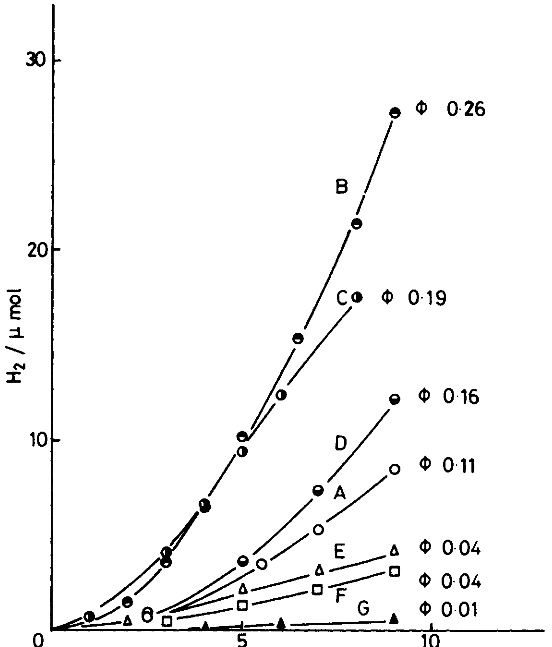


Figure 1. ZnS-photocatalysed H_2 evolution in the presence of cyclic ethers as electron donors. Conditions: see Experimental section. A, THF; B, 2,5-dihydrofuran; C, 2,3-dihydrofuran; D, 2,5-dimethyltetrahydrofuran (*cis* and *trans* mixture); E, tetrahydropyran; F, 3-methyloxetane; G, 1,4-dioxane

Photoreduction of water to hydrogen by electrons upon irradiating ZnS was established by mass spectral analysis of the hydrogen evolved in D_2O–THF and H_2O–[$^2H_8$]THF (Table 1). The hydrogen source is the bulk water and the slight HD formation can be explained by the liberation of a proton from

Table 1. ZnS-photocatalysed hydrogen evolution in the presence of deuteriated species[a]

ZnS Source (mmol)	Water	Electron donor	Irradiation time (h)	Ratio[b] D_2:HD:H_2 or D
Dried ZnS[c] (0.10)	D_2O	THF	15	84:14:3
ZnS suspension[d] (0.19)	D_2O	THF	23	86:12:2
ZnS suspension[e] (0.10)	H_2O	[$^2H_8$]THF	15	1:2:97

[a] According to method B, photolysis was carried out by using ZnS, water (7 cm^3), and electron donor (1 cm^3). [b] The ratios measured respectively by focusing *m/e* 2, 3, and 4, were averaged. [c] ZnS suspension prepared from $ZnSO_4$ and Na_2S was evaporated to dryness [d] Prepared from $ZnCl_2$ and $Na_2S{\cdot}9D_2O$. [e] Prepared from $ZnSO_4$ and $Na_2S{\cdot}9H_2O$.

Table 2. Effect of pH on ZnS-catalysed photoreaction of THF

Buffer solution	pH initial	pH final	H_2 (mmol)	2,2′-Bitetrahydrofuryl (1) (mmol)
Phosphate	7.23	7.89	0.047	0.012
Borate	9.69	10.20	0.251	0.063
Carbonate	10.51	10.38	0.250	0.065
1N-NaOH	14		0.090	

[a] Reaction conditions: aqueous $ZnSO_4$ (0.04 mol dm^{-3}, 1 cm^3), aqueous Na_2S (0.04 mol dm^{-3}, 1 cm^3), buffer solution (5 cm^3), and THF (1 cm^3) were irradiated for 4 h according to method B.

the oxidized THF radical cation to the bulk water [equation (5)].

In the absence of any electron donors, only minute amounts of H_2 were formed as reported.[5] Degradative H_2 evolution is explained by equations (1)—(3).

$$ZnS + h\nu \longrightarrow h_{VB} + e_{CB} \qquad (1)$$

$$ZnS + e_{CB} \longrightarrow Zn^0 \qquad (2)$$

$$Zn^0 + 2H_2O \longrightarrow Zn^{2+} + 2OH^- + H_2 \qquad (3)$$

In an oxygen-purged THF system, the concentration of Zn^{2+} in the bulk solvent was invariably low over irradiation for 24 h, indicating the absence of photodegradation of ZnS.[5] The stability of the ZnS suspensions in the presence of THF was also supported by the negligible change in pH (< 1 pH unit) during the irradiation even in an unbuffered solution; the degradation was roughly estimated to be <0.1% of the ZnS suspension by assuming reactions (1)—(3).

During irradiation, slight darkening of the ZnS suspension was occasionally observed even in the presence of THF, but it disappeared soon after irradiation was stopped. This fact indicates that the darkening should be superficial. Photoinduced blackening of ZnS is well known especially in the case of crystalline ZnS, but there exists uncertainty in the explanation.[15] The observed darkening of the ZnS suspension may be explained as either due to Zn metal deposition[5] or to light-induced change in charged states of the surface defect levels just as in the case of photochromism in wide band-gap semiconductors.[16]

Recently, Henglein and Gutierrez proposed the participation of photoformed Zn metal on the efficient H_2 evolution by ZnS catalyst.[12] However, it seems to be improbable in view of the high hydrogen overvoltage of Zn, *i.e.*, the low exchange current density (i_0); log i_0 of Zn is − 10.5, which is comparable with that of Hg (− 12.3).[17] In fact, H_2 evolution was not influenced by the superficial colour change. Efficient H_2 evolution without a noble metal can be ascribed to the large and negative conduction band edge of ZnS, which may produce hydride ion or hydride species by sequential two-electron reduction of water or proton.

The effect of pH on H_2 evolution was examined only in the range from neutral to alkali region, since ZnS degrades in acidic solutions. As shown in Table 2 and Figure 2, H_2 was evolved in the pH range from 6.6 to the carbonate buffer region, but not in highly alkaline solution. It was also found that the presence of phosphate ion is responsible for a decrease in H_2 evolution at pH 7.23 in Table 2.

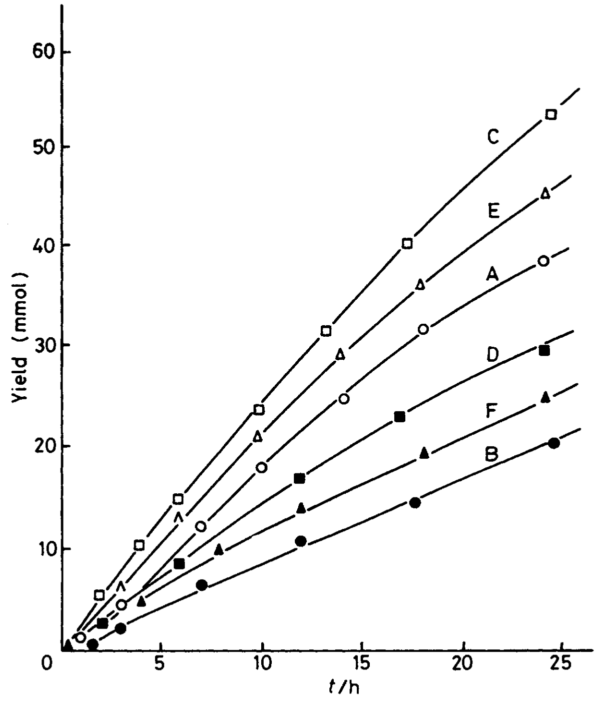


Figure 2. Effect of pH on H_2 evolution and the formation of 2,2′-bitetrahydrofuryl in the ZnS-catalysed photolysis of THF. Conditions: method C; ZnS, 5 mmol; THF, 200 cm^3; buffer solution, 200 cm^3; 100 W Hg lamp. A, H_2; B, dimer (1) in water (initial pH 6.6); C, H_2; D, dimer (1) in borate buffer solution; E, H_2; F dimer (1) in carbonate buffer solution

The quantum yields at 313 nm were determined from the slope of the linear portion of H_2 evolution in Figure 1, by assuming that two photons produce one molecule of H_2 [equation (4)]. The highest quantum yield, 0.62, was obtained

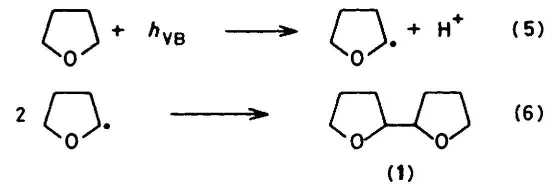
$$H_2O \rightleftharpoons OH^- + H^+ \xrightarrow{e_{CB}} 1/2H_2 \qquad (4)$$

for a carbonate buffer solution of THF under reduced pressure (see Experimental section).

No correlation was found between the quantum yields and ionization potentials of THF (9.74 eV),[13] tetrahydropyran (9.25 eV),[13] and 1,4-dioxane (9.43 eV).[13] The case is true for furan as described. These are quite unexpected, since the large and negative conduction band edge indicates that one-hole oxidation by less positive valence band hole could be rate-determining in H_2 evolution. Odaira *et al.*[18] observed the highest reactivity of THF in the photodimerization of cyclic ethers in the presence of $HgCl_2$. From these facts, the stability of intermediary radicals, in other words the ease of liberation of proton from the initially formed radical cations, should play an important role in quantum efficiency. The selective α-radical formation (see later) also supports this conclusion.

One-hole Oxidations.—As photo-oxidation products in THF systems, the dimer 2,2′-bitetrahydrofuryl (**1**) was formed with a small amount of 2-hydroxytetrahydrofuran (**2**) and butane-1,4-diol (**3**). In the absence of ZnS, there was trace formation even under irradiation by shorter wavelength light (> 254 nm); dimer formation was *ca.* 1%. The dimer (**1**) gave equimolar mixtures of diastereoisomeric forms free from other isomeric dimers derived from 3-tetrahydrofuryl radical or the rearranged dimer reported in the radical reactions of THF.[19,20]

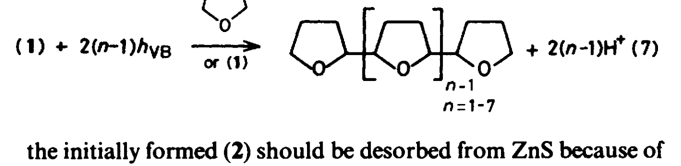
Formation of the dimer (**1**) can be explained by the coupling mechanism of 2-tetrahydrofuryl radical [equations (5) and (6)].



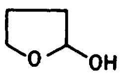
(**1**)

The stoicheiometric quantity of the dimer (**1**) was in the range 25—50% of the evolved H_2, which depended on the THF concentration but was independent of the pH of the reaction mixture (Figure 2 and Table 2). In order to clarify the stoicheiometric relationship between H_2 evolution and the oxidation products, the respective products H_2 and (**1**)—(**3**) were followed by g.l.c. under 100 W Hg arc lamp irradiation of a 50% v/v THF solution (Figure 3). γ-Butyrolactone was also detected but its formation is not shown in Figure 3, because its quantity was only a trace and was unchanged during irradiation. The dimer (**1**) and H_2 were formed constantly and had a slight tendency to level off. At the early stage of the photolysis, the two-hole oxidation product (**2**) (see later) was formed more than the dimer (**1**), but gradually decreased, while the diol (**3**) increased at the expense of (**2**). After 24 h irradiation, the stoicheiometric quantity of the diol (**3**) corresponded to *ca.* 13% of the evolved H_2 and that of the dimer (**1**) *ca.* 50%. It was also found that the isolated oil contained not only the dimer (**1**) but also unidentified oligomeric products. Therefore, the rest (37%) of the electron balance for H_2 evolution was ascribed to oxidation producing oligomeric products.

Similarly, photolysis of a dilute THF solution was monitored under comparable conditions as shown in Figure 4. H_2 Evolution was as efficient as in the concentrated system, but not always proportional to the decrease in THF. The dimer formation was far less efficient than that in the concentrated system, while the product (**2**) did not change in quantity during the irridation. The diol (**3**) was also formed but in a very small amount. Furthermore, oils were isolated (Table 3) and found to contain oligomeric products which ranged from the dimer to the octamer of THF on the basis of mass spectral analysis. These facts indicate that the dimer (**1**) once formed should be preferentially adsorbed on ZnS and then undergo successive one-hole oxidation followed by carbon–carbon bond-forming reactions to yield oligomers [equation (7)]. On the other hand,



the initially formed (**2**) should be desorbed from ZnS because of its hydrophilic property and survive in the bulk water.



(**2**)

HO(CH$_2$)$_4$OH

(**3**)

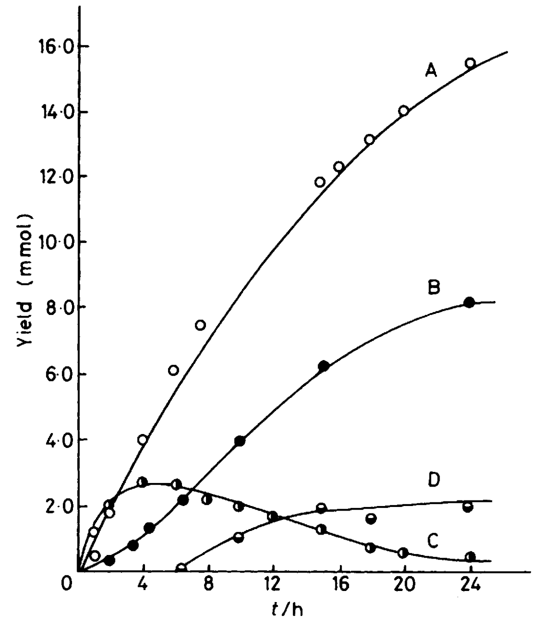


Figure 3. ZnS-catalysed photoredox reactions of aqueous 50% THF solution. Conditions: method C; ZnS, 4.3 mmol; THF, 200 cm^3; water, 200 cm^3; 100 W Hg lamp. Initial pH 6.2 (6.5 at end of irradiation). A, H_2; B, 2,2′-bitetrahydrofuryl (**1**); C, 2-hydroxytetrahydrofuran (**2**); D, butane-1,4-diol (**3**)

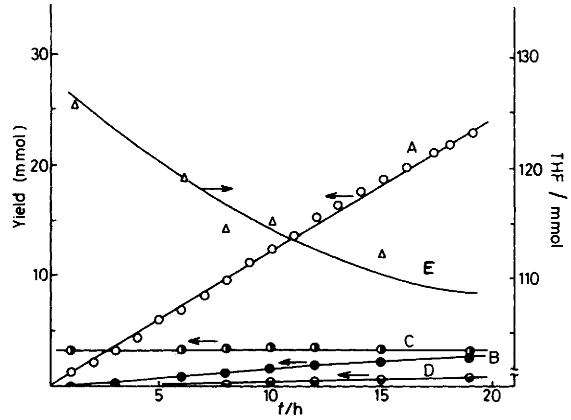
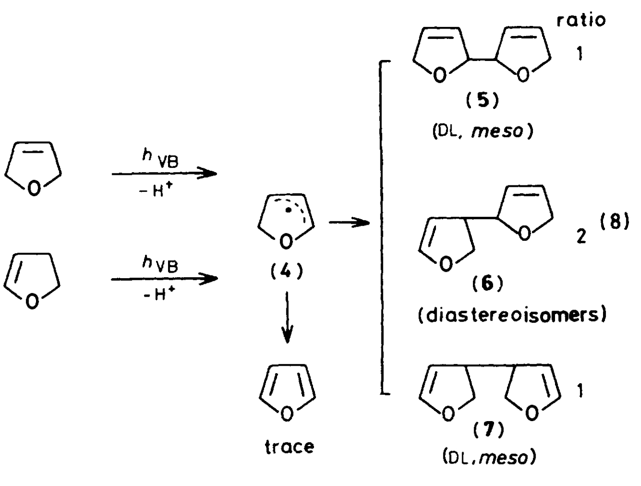


Figure 4. ZnS-catalysed photoredox reactions of aqueous dilute THF solution. Conditions: identical with Figure 3 except using ZnS (5 mmol), THF (10 cm^3), and water (450 cm^3); E, THF.

The product analysis was extended to the photolysis of 2,3- and 2,5-dihydrofuran. When their saturated water solutions were irradiated under comparable conditions, good yields of dimeric products were obtained with H_2 (Table 3). To our surprise, they were identical in i.r., ^{1}H, and ^{13}C n.m.r. spectra, as shown partly in Figures 5 and 6. On the basis of ^{1}H and ^{13}C n.m.r., they were confirmed to be isomeric mixtures of the 2,2′-dimer (**5**) (DL and *meso*), the 2,3′-dimer (**6**) (diastereoisomers), and the 3,3′-dimer (**7**) (DL and *meso*) in *ca.* 1:2:1 ratios [equation (8)].

In the case of 2,3-dihydrofuran, H_2 evolution was proportional to its disappearance within 5 h irradiation. Furthermore, the electron balance between H_2 and the oxidation products was quite consistent (Table 3), and the distillation residues were



(8)

Table 3. ZnS-catalysed photoreaction of cyclic ethers in water[a]

Cyclic ethers (g)	Reaction time (h)	H_2 evolution rate (mmol h^{-1})	Reaction products	
			H_2 (mmol)	oil (g [mmol][c])
THF 10	4	2.35	9.5	0.86 [6.1]
2,3-Dihydrofuran 15	7	3.70	23.2	3.50 [25.4]
2,5-Dihydrofuran 15	4	4.90	19.2	2.55 [18.5]
1,4-Dioxane[d]	27.7	0.37	8.8	0.56 [3.2]

[a] Photolysis was carried out using water (400 cm^3) and ZnS suspension (5 mmol) under irradiation of 300 W Hg arc lamp at pH 7.0 (Method C). [b] See Experimental section. [c] Calculated by assuming that all are dimeric products. [d] Using 1,4-dioxane (300 cm^3) and water (100 cm^3).

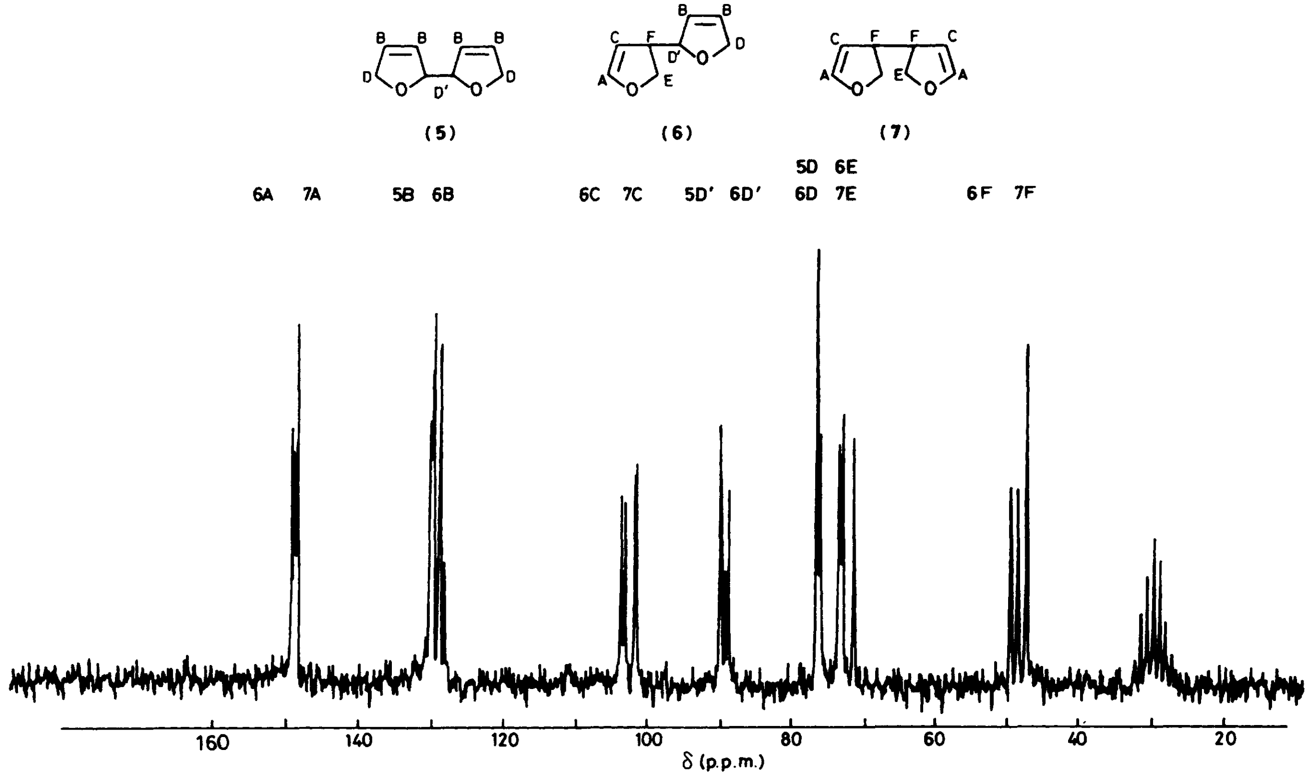
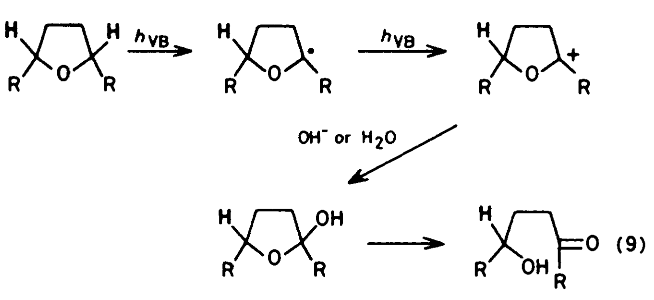


Figure 5. ^{13}C N.m.r. of the dimeric products (distillate) from 2,5-dihydrofurans (in [$^2H_6$]acetone)

small in both cases, implying that the dimerization reaction should prevail for 2,3- and 2,5-dihydrofuran. In both photolyses, a trace of furan was also detected by g.p.c. analysis. These facts can be explained as follows: the common allylic radical (**4**) should be formed through allylic hydrogen liberation after the one-hole oxidation step and coupling should occur statistically as shown in equation (8). It seems that the difference in quantum yields reflects the ease of radical formation.

With regard to the dimeric products from 1,4-dioxane, DL and *meso* forms of 2,2′-bi-1,4-dioxanyl were isolated by column chromatography. Their formation relative to H_2 was very small, implying competitive H_2 evolution due to the degradation of ZnS.[5] In fact, H_2 evolution was as slow as that in the absence of electron donors (Figure 1).

Two-hole Oxidations.—Formation of 2-hydroxytetrahydrofuran (**2**) was remarkable at the early stage of the photolysis of THF. Kisch and his group also observed the similar hydroxylation at the early stage of the ZnS-catalysed photolysis of 2,5-dihydrofuran.[7] On the other hand, when 2,5-dimethyltetrahydrofuran (*cis* and *trans* mixture) solution was irradiated under comparable conditions, 5-hydroxyhexan-2-one (**9**) was formed selectively almost in proportion to H_2 as shown in Figure 7; neither its cyclic isomer corresponding to the product (**2**)[21] nor dimeric products corresponding to the dimer (**1**) was detected. These observations suggest that oxidation of intermediary radicals, *i.e.*, two-hole oxidation, should occur exclusively to 2,5-dimethyltetrahydrofuran, yielding cationic species which should be concomitantly attacked by water or hydroxide ion to give the hydroxylated product (**8**). The resulting intermediate (**8**) should undergo ring opening to give the product (**9**) [equation (9)].



(2; R = H)
(8; R = Me)

(9; R = Me)

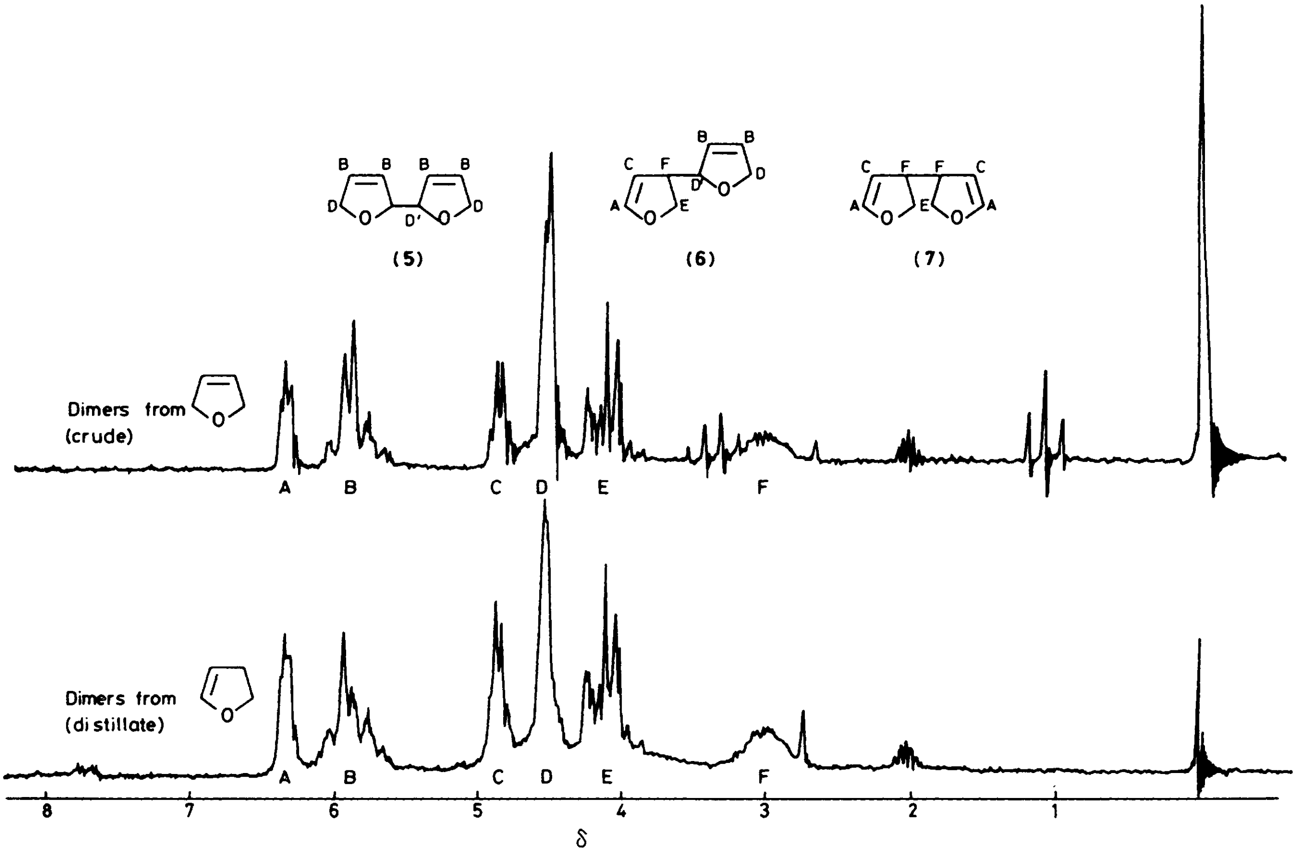


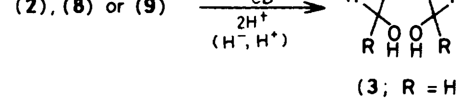
Figure 6. ^{1}H N.m.r. (60 MHz) of the dimeric products from dihydrofurans (in [$^2H_6$]acetone)

Selective two-hole oxidation of 2,5-dimethyltetrahydrofuran can be rationalized as follows; the radical must be subject to further oxidation by another hole, since it is stabilized by hyperconjugation of the methyl group and dimerization is sterically inhibited. In addition, it should become more oxidizable because of the electron-donating properties of the methyl group.

Kirsch *et al.* proposed the participation of hydroxyl radical in the formation of hydroxylated products,[7] but it would be plausible only at the early stage of the reaction, because reduction of the adsorbed O_2 by the conduction band electron is conceivable producing hydroxyl radical through superoxide anion radical.[22] The induction phenomena observed in the H_2 evolution (Figure 1) may be due to the reduction of the adsorbed O_2.[23]

Two-electron Reductions.—As shown in Figures 3 and 7, butane-1,4-diol (**3**) and hexane-2,5-diol (**10**) were formed as minor products. Their formation had induction periods and was followed by production of the two-hole oxidation products (**2**) and (**9**). However, the diols (**3**) and (**10**) were not detected when the products (**2**) and (**9**) were respectively irradiated without ZnS suspension under comparable conditions. These facts eliminate a mechanism involving ketyl radicals.

Since ZnS has a large and negative conduction band edge [E_{CB} −1.74 V *versus* s.c.e. (pH 1)],[10] the diol formation may be rationalized in terms of sequential two-electron transfer from the conduction band to the adsorbed hydroxylated intermediates (**2**), (**8**) or their ring-opened products (**9**) [equation (10)]. Their adsorption onto the surface of ZnS may facilitate simultaneous reduction without any electron relay systems.[24] As was proposed for efficient H_2 evolution, reduction by hydride ion cannot be ruled out at present. Recently, two-electron reduction products were detected spectroscopically in TiO_2-catalysed photolysis.[2b,25] Further studies on photoreduction of organic compounds on ZnS are in progress.[26]



(10)

(3; R = H)
(10; R = Me)

Conclusions.—This study has revealed that a freshly prepared dispersion of fine ZnS particles is stable towards u.v. irradiation in oxygen-purged systems and shows efficient catalytic activities

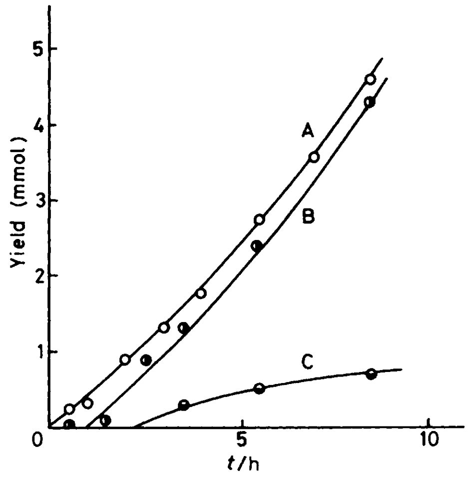


Figure 7. ZnS-catalysed photoredox reactions of aqueous 2,5-dimethyltetrahydrofuran solution. Conditions: method C; ZnS, 5 mmol; the furan (*cis* and *trans* mixture), 15 g; water, 400 cm^3; 100 W Hg lamp. A, H_2; B, 5-hydroxyhexane-2-one (**9**); C, hexane-2,5-diol (**10**)

in photoredox reactions of furan derivatives without noble metals or charge relay modifications.[26] The important results are as follows. (1) The highly reducing power of irradiated ZnS is adequately explained by the conduction band edge which is very negative. (2) The efficient and selective photo-oxidation by the valence-band holes (h_{VB}) may be ascribed to less oxidative valence band edge [E_{VB} 1.92 V *versus* s.c.e. (pH 1)]; oxidation of substrate occurs even in dilute systems, because oxidation of water does not compete with it. (3) Photoredox reactions on irradiated ZnS are strongly influenced by the structure of electron donors which may correlate with the stabilities of intermediary radicals rather than their ionization potentials.

Experimental

General Methods.—M.p.s and b.p.s are uncorrected. ^{1}H N.m.r. spectra were recorded on JEOL JNM-PS100 or JNM-PMX60 spectrometers and ^{13}C n.m.r. spectra on a JEOL JNM-FX60S spectrometer with trimethylsilane as internal standard. Unless stated otherwise, $CDCl_3$ was used as solvent. Mass spectra were measured at 70 eV with a Hitachi RMU-6E mass spectrometer, u.v. spectra with a Hitachi 220A spectrophotometer, and i.r. spectra with a Hitachi 260-10 spectrophotometer. G.l.c. analyses were carried out using an active carbon column (i.d. 3 mm × 2 m) on a Shimadzu GC-3BT for H_2 and Ucon oil 50LB column (15% Uniport B, i.d. 3 mm × 3 m) on a Shimadzu GC-7AF for organic compounds.

Starting Materials.—All materials except 3-methyloxetane are commercially available and were used after distillation. 3-Methyloxetane was a gift from Daisel Chemical Industries, Ltd.

Preparation and Characterization of ZnS *Suspensions.*—Unless stated otherwise, ZnS suspensions were preared *in situ* by mixing equal amounts of aqueous solutions (0.1 mol dm^{-3}) of $ZnSO_4 \cdot 7H_2O$ (Wako Pure Chemicals, GR grade) and $Na_2S \cdot 9H_2O$ (Wako Pure Chemicals, GR grade) at room temperature (20—25 °C). The final pH of solutions was 5.5—8.5. The optical absorption spectrum of the supernatant solution of the ZnS suspension showed a sharp rise toward the u.v. below 340 nm and the onset agrees with the 3.7 eV band gap of ZnS.

Reaction Methods.—(A) Equimolar amounts of the above mentioned $ZnSO_4$ and Na_2S solutions (0.5 cm^3 each), an organic substrate (0.2 cm^3), and doubly distilled water (3 cm^3) were placed in a 4 cm^3 cuvette cell with a stopcock. Adjustment of the pH was made by addition of aqueous NaOH (1 mol dm^{-3}) or H_2SO_4 (1/2 mol dm^{-3}) solution when necessary. The mixture was purged with argon, closed off at atmospheric pressure, and irradiated at room temperature (*ca.* 20 °C) by 313 nm light. U.v. spectrophotometry confirmed that the 313 nm light was completely absorbed. The inner gas was analysed by g.l.c.

(B) Equimolar amounts of the above mentioned $ZnSO_4$ and Na_2S solutions, an organic substrate, and doubly distilled water were placed in a 30 cm^3 Pyrex tube equipped with a three-way stopcock. After pH adjustment, the mixture was sonicated for 3 min, purged with argon gas, evacuated, placed near a 300 W high-pressure Hg arc lamp, and then irradiated at room temperature with vigorous stirring. After irradiation (>290 nm), the internal pressure was brought to atmospheric pressure by injecting water into the reaction tube. The gas produced was analysed by g.l.c. and mass spectroscopy.

(C) In a *ca.* 1 dm^3 Pyrex vessel aqueous $ZnSO_4$ solution (50 cm^3) and Na_2S solution (50 cm^3) were mixed. Unless stated otherwise, doubly distilled water (100 cm^3) and an organic substrate (200 cm^3) were successively added under stirring. A 100 or 300 W high-pressure Hg arc lamp with a Pyrex filter was inserted in the vessel, and the mixture was purged with argon and irradiated at room temperature. The generated gas was monitored by trapping it over water with a gas burette.

Quantum Yield Determination.—The light quantity (7 × 10^{-9} einstein s^{-1}) was measured using a hexan-2-one actinometer and corrected occasionally with an Eppley thermopile. According to method A, the H_2 evolved was plotted against the irradiation time as shown in Figure 1. The slope of the linear portion was measured to give the quantum yield.

For the quantum yield for H_2 evolved in an evacuated THF solution buffered with a carbonate buffer, method B was employed. The mixture of carbonate buffer solution (7 cm^3) involving ZnS suspension (0.8 mmol) and THF (1 cm^3) was frozen and degassed three times and irradiated by 313 nm light (2.3 × 10^{-8} einstein s^{-1}) for 4 h. The value, 0.62, was obtained by averaging three runs.

Isolation of Products.—The reaction mixture obtained by method C was filtered to remove ZnS and was extracted with diethyl ether (3 × 100 cm^3). The extracts were combined, dried (Na_2SO_4), and concentrated at atmospheric pressure. For the isolation of butane-1,4-diol (**3**), water was removed as the benzene azeotrope and the resulting benzene solution was condensed under reduced pressure giving the diol (**3**).

Product Analysis.—*Products from THF.* 2,2′-Bitetrahydrofuryl (**1**) had, b.p. 80—90 °C at 17 Torr (kugelrohr) (Found: C, 67.2; H, 10.0. Calc. for $C_8H_{14}O_2$: C, 67.6; H, 9.9%), $\nu_{max.}$ 1 100 cm^{-1} (CH_2OCH_2), δ_H (60 MHz) 1.5—2.1 (8 H, m) and 3.6—4.0 (6 H, m), δ_C (15 MHz) 81.2, 80.8 (>CHO), 67.9 (CH_2O), 28.6, 27.7, 26.0, and 25.0 (>CH_2), *m/z* 141 (M^+ −1, 26%) and 71 (100). G.l.c. analysis at the column temperature, 120 °C, showed two peaks of equal areas due to the DL and *meso* forms. Quantitative g.l.p.c. analysis was carried out by the same column using methyl octanoate or benzyl alcohol as internal reference. 2-Hydroxytetrahydrofuran (**2**), butane-1,4-diol (**3**), and γ-butyrolactone were characterized by direct comparison of the g.l.c. retention volumes with those of the authentic samples.

The mass spectrum of the distillation residue showed peaks at *m/z* 211 (3*M* − 1), 279 (4*M* − 3), 281 (4*M* − 1), 349 (5*M* − 3), 351 (5*M* − 1), 417 (6*M* − 5), 419 (6*M* − 3), 486 (7*M* − 6), 489 (7*M* − 3), and 559 (8*M* − 3), indicating the formation of *n*-mers. Its i.r. spectrum indicated the presence of carbonyl groups.

Products from 2,3- *and* 2,5-*dihydrofuran*. The products were identical by i.r., ^{1}H, and ^{13}C n.m.r., b.p. 84—86 °C at 12 Torr (Found: C, 69.1; H, 7.3. Calc. for $C_8H_{10}O_2$: C, 69.5; H, 7.3%). The ^{1}H n.m.r. spectra of the concentrated ether extract (derived from 2,5-dihydrofuran) and the distillate (derived from 2,3-dihydrofuran) and the ^{13}C n.m.r. spectrum of the distillate (derived from 2,5-dihydrofuran) are shown in Figures 5 and 6, respectively, with the signal assignments. In ^{13}C n.m.r., the signals at lowest magnetic field were assigned to the carbon A of the diastereoisomers (**6**) and the signal at highest magnetic field to the carbon F of the 3,3′-dimer (**7**) (DL and *meso*). The ratio of their height was almost 1:1, indicating that the ratio (**6**):(**7**) is 2:1. Similarly, the signals assigned to 5D′ and 6D′ are almost equal in height, suggesting that the ratio (**5**):(**6**) is 1:2. Accordingly, the ratio (**5**):(**6**):(**7**) was estimated to be 1:2:1. The area ratios of the signals assigned to protons A—F in the ^{1}H n.m.r. of the crude product from 2,5-dihydrofuran (Figure 5) were found to be 10:23:10:34:18:9, which were approximately equal to the calculated ratios (A:B:C:D:E:F = 1:2:1:3:2:1) on the basis of the (**5**):(**6**):(**7**) ratio of 1:2:1.

The α-hydroxylated dimeric products, which were reported by Kirsch *et al.* in the photolysis of 2,5-dihydrofuran,[7] were not detected in our freshly isolated crude products as demonstrated by the absence of signals at δ 5.5 (Figure 5). It appears that they should be analysed immediately after isolation, because they are cyclic derivatives of vinyl ether and are subject to attack of water or polymerization through protonation. In fact, we observed that they gradually became viscous on standing at room temperature.

Products from 2,5-*dimethyltetrahydrofuran* (cis *and* trans *mixture*). 5-Hydroxyhexan-2-one (**9**) had b.p. 50 °C at 8 Torr (Found: C, 62.4; H, 10.5. Calc. for $C_{16}H_{12}O_2$: C, 62.0; H, 10.4%), $\nu_{max.}$ 3 420 (OH) and 1 710 cm^{-1}, (CO) δ_H (100 MHz) 1.2 (3 H, d, *J* 6 Hz, C*H*$_3$CHOH), 1.3—2.1 (3H, m, OH, C*H*$_2$C*H*OH), 2.2 (3 H, s, CH$_3$CO), 2.33 (2 H, t, *J* 7 Hz, COCH$_2$), and 3.3—4.1 (1 H, m, CH$_3$C*H*OH), *m*/*z* 98 ($M^+ - H_2O$, 39%) and 83 (100). Hexane-2,5-diol (**10**) was characterized by the g.l.c. retention volume of an authentic sample.

Products from 1,4-*dioxane*. Chromatography on activated alumina with 1:1 petroleum (b.p. 40—60 °C)–diethyl ether as eluant yielded the *meso* form of 2,2′-bi-1,4-dioxanyl and then the DL form was eluted with diethyl ether. The *meso* form, m.p. 157.0—158.0 °C (from diethyl ether) (lit.,[27] 157.5—158 °C) (Found: C, 55.2; H, 8.2. Calc. for $C_8H_{14}O_4$: C, 55.2; H, 8.1%), $\nu_{max.}$(KBr) 1 110 cm^{-1}, δ_H (100 MHz) 3.2—4.1 (br), δ_C (15 MHz) 66.5 (C-5, C-6), 68.6 (C-3), and 74.8 (C-2) p.p.m., *m*/*z* 174 (M^+, 6%) and 87 (100). The DL form had m.p. 132.0—133.0 °C (from acetone) (lit.,[27] 133.5—134.0 °C) (Found: C, 54.9; H, 8.1. Calc. for $C_8H_{14}O_4$: C, 55.2; H, 8.1%), δ_C (15 MHz) 66.4 (C-5, C-6), 68.4 (C-3), and 74.7 (C-2) p.p.m., $\nu_{max.}$ (KBr) 1 110 and 1 100 cm^{-1}. The mass and ^{1}H n.m.r. spectra were identical with those of the *meso* form.

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