

JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

© Copyright 1985 by the American Chemical Society

VOLUME 107, NUMBER 6

MARCH 20, 1985

Catalytic Formation of Hydrogen and C-C Bonds on Illuminated Zinc Sulfide Generated from Zinc Dithiolenes

N. Zeug, J. Bücheler, and H. Kisch*

Contribution from the Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a.d. Ruhr, West Germany. Received August 27, 1984

Abstract: UV irradiation of bis(*cis*-1,2-dicyano-1,2-ethylenedithiolate)zinc bis(tetrabutylammonium) in aqueous tetrahydrofuran (THF) or 2,5-dihydrofuran (2,5-DHF) leads to the semiconductor *n*-ZnS which photocatalyzes an efficient H₂ evolution ($\phi_{300\text{nm}} = \geq 0.1$) coupled to a chemoselective dehydrodimerization of the cyclic ether. The reaction does not occur in pure water nor in dry ethers. *n*-ZnS, which immediately photocorrodes in pure water, becomes very stable in the presence of 2,5-DHF. 2,3-DHF and six-membered ethers do not dehydrodimerize or prevent photocorrosion. The H₂-evolution rate increases linearly with light intensity and does not change as a function of temperature (20–50 °C) or pH (4–10). In the case of 2,5-DHF, the previously unknown 2,2'-, 2,3'-, and 3,3'-dehydrodimers are formed in the ratio of 1:2:1, respectively, on analytical and preparative scales. With THF, the reaction proceeds regioselectively with the exclusive formation of the 2,2'-dihydrodimer. A complete material balance shows that no water is consumed although the initial gas phase contains more than 90% D₂ when D₂O is used. The latter value decreases with increasing turnover and is accompanied by the formation of HD and H₂. These results are compatible with the reduction of water to hydrogen by conduction band electrons. The dehydrodimers are produced by dimerization of the corresponding radicals formed most likely by hole oxidation of the cyclic ether with subsequent deprotonation. Comparison with reactions of OH[•] generated in homogeneous solution reveals a higher selectivity for the catalytic ZnS system.

UV irradiation of metal dithiolenes dissolved in aqueous solutions of tetrahydrofuran (THF) or 2,5-dihydrofuran (2,5-DHF)¹ produce catalyzed hydrogen evolution. The metal dithiolenes which are photolyzed during the initial induction period are catalyst precursors.^{1c,d} Zinc dithiolenes give rise to a very efficient catalyst system that induces the formation of hydrogen with maximum turnover numbers of 4000. In a recent communication,^{1c} we reported that in the case of bis(*cis*-1,2-dicyano-1,2-ethylenedithiolate)zinc bis(tetrabutylammonium) (**1**), the heterogeneous catalyst zinc sulfide is formed and that hydrogen evolution is coupled to dehydrodimerization of 2,5-DHF. In the growing field of semiconductor-catalyzed organic photoreactions like oxidations of amides² and olefins,^{3,4} this reaction appears to be the first known example of a large scale synthesis of a new organic compound. Only the photo-Kolbe reaction⁵ and the dehydrodimerization of the cyclopentadienyl anion⁶ also involve the formation of C-C bonds. In the following we report a study of the catalytic zinc sulfide system including a complete material balance, detailed D₂O experiments, preparative isolation of the previously unknown dehydrodimers of 2,5-DHF, and a comparison with model reactions of OH radicals generated by photolysis of hydrogen peroxide and radiolysis of water. Very recently it has been reported that the ZnS system is also capable of catalyzing the dehydrodimerization of amines and alcohols.⁷

Experimental Section

Preparative irradiations were carried out with a 120-mL quartz immersion lamp apparatus fitted with a high-pressure mercury lamp

(Philips HPK 125 W, $\lambda \geq 248$ nm). Hydrogen evolution was measured with a continuously recording gas buret,⁸ hydrogen being identified by GC and MS. In the irradiations with the 2500-W Hg-Xe high-pressure lamp (Canrad Hanovia), a cylindrical cell of 20-mL volume ($l = 2$ cm) was fitted with a stirrer, a cooling jacket, and a continuously recording 100-mL gas buret. Monochromatic irradiations at $\lambda = 254$ nm were conducted with a low-pressure mercury lamp (Gräntzel) on an optical bench incorporating a Schott WG 230 filter to remove the 185-nm Hg line. A 4-mL quartz cell mounted in the light path was fitted with a magnetic stirrer and a two-stopcock device, allowing GC determination of the total amount of H₂ present in solution and in the gas phase.⁹ Quantum yield determinations were performed on an optical bench incorporating a mercury HBO 500-W lamp (Osram), a Kratos-Schoeffel GM 252 monochromator, and an electronic actinometer calibrated with ferri oxalate.¹⁰

γ radiolyses were performed with a ⁶⁰Co-radiation source (Nuclear Engineering Ltd., irradiation unit Type LCU 2'). NMR spectra were

- (1) (a) Henning, R.; Schlamann, W.; Kisch, H. *Angew. Chem.* **1980**, *92*, 664. (b) Battaglia, R.; Henning, R.; Kisch, H. *Z. Naturforsch., B* **1981**, *36B* 396. (c) Bücheler, J.; Zeug, N.; Kisch, H. *Angew. Chem.* **1982**, *94*, 792. (d) Battaglia, R.; Henning, R.; Dinh-Ngoc, B.; Schlamann, W.; Kisch, H. *J. Mol. Catal.* **1983**, *21*, 239.
- (2) Pavlik, J. W.; Tantayanon, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 6755.
- (3) Kanno, T.; Oguchi, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1980**, *21*, 467.
- (4) Fox, M. A.; Chen, C.-C. *J. Am. Chem. Soc.* **1981**, *103*, 6757. Fox, M. A. *Acc. Chem. Res.* **1983**, *16*, 314.
- (5) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 7729; **1978**, *100*, 5985.
- (6) Fox, M. A.; Owen, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6559.
- (7) Yanagida, S.; Azuma, T.; Kawakami, H.; Kizumoto, H.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1984**, 21.
- (8) Bogdanovic, B.; Spliethoff, B. *Chem.-Ing.-Tech.* **1983**, *55*, 156.
- (9) Weeke, F.; Bastian, E.; Schomburg, G. *Chromatographia* **1974**, *7*, 163.
- (10) Amrein, W.; Gloor, J.; Schaffner, K. *Chimia* **1974**, *28*, 185.

* New address: Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, D-8520 Erlangen, West Germany

† Dedicated to O. E. Polansky at the occasion of his 65th birthday.

obtained with Bruker WH 400, WH 270, and HX 60 E instruments; GC analyses, gas phases (Hewlett-Packard 700, 4-m charcoal column: diameter 0.3–0.5 mm, 0.45 bar of Ar, 30 °C, TCD) and liquid phases (Varian 1700, 70 m of CW 20 M, 0.8–0.9 bar of H₂, 70–240 °C, 6 °C/min, FID); GC–MS coupling, Perkin-Elmer F 22 chromatograph (50 m of CW 20 M) and Finnigan MAT CH 7 mass spectrometer. For sample preparation in the case of experiments with 2,5-DHF/H₂O (1/1), the organic phase was separated in a separatory funnel, distilled under high vacuum, and dried over MgSO₄. In experiments with 2,5-DHF/H₂O (14/1), water was removed by drying with MgSO₄.

All solvents were commercially available and were used as received unless otherwise noted. 5,6-Dihydro-2H-pyran was synthesized from 3-buten-1-ol.¹¹ All solvent ratios are by volume. Peroxides, which tend to be present in cyclic ethers, were removed by column chromatography over alumina. Solutions usually were flushed with Ar for 5–10 min prior to irradiation.

Preparation of ZnS. A. Fifty milligrams (0.06 mmol) of **1** in 120 mL of 2,5-DHF/H₂O (14/1) was irradiated for 10 h by using the immersion lamp apparatus. The white precipitate formed was collected by centrifuging, washed with water, and dried in a desiccator. Elemental analyses (e.g.: C, 55.68; H, 8.32; Zn, 12.5; S, 6.2) of these samples gave inconsistent values with an average ratio of Zn/S = 1/1, while a value of 1/0.86 was found by X-ray fluorescence microanalyses. The Debye-Scherrer exposures agree with the data for cubic ZnS.¹² IR and mass spectra indicate the presence of 2,5-DHF oligomers.

B. According to ref 13, NaOH was added to 0.1 mol of ZnSO₄ × 7H₂O in 200 mL of H₂O until the precipitated zinc hydroxide dissolved as zincate. A solution of 0.2 mol of thiourea in 200 mL of H₂O was then added and the resulting mixture slowly heated to 80 °C. All solutions were purged with argon during the procedure. After 1 h at 80 °C, the solution was allowed to cool, and the precipitated ZnS was washed to neutrality and dried under argon atmosphere for several hours.

Induction Period and Thermal Stability for 1/THF/H₂O. A solution of **1** (4.5×10^{-5} M) in 4 mL of THF/H₂O (1/1) was irradiated at $\lambda = 254$ nm. The absorbance of **1** at $\lambda = 380$ nm and the amount of H₂ (by GC) were measured after 5, 10, 15, and 25 min. H₂ formation started only after 10 min, the time after which the absorbance of **1** had decreased by 90% from its initial value. No change in absorbance occurred in experiments ($\lambda \geq 248$ nm) with a continuous N₂O purge or in the dark after refluxing for 2 h in THF/H₂O or 2,5-DHF/H₂O, respectively.

Synthesis and Characterization of 2,5-DHF Dehydrodimers 2–4. Fifty milligrams (0.06 mmol) of **1** was dissolved in 120 mL of 2,5-DHF/H₂O (14/1) and irradiated for 42 h in the immersion lamp apparatus producing 2.7 L (0.12 mol) of H₂. A GC spectrum showed seven major peaks corresponding in order of increasing retention time, to 2,3-DHF, furan, and 2–4. In addition, the following compounds could be detected if peroxides and oxygen were present in the solution: 3-buten-1-ol,^{14a} 2-hydroxytetrahydrofuran,^{14b} 5H-furan-2-one,^{14c} and 2-(4'-(2'-hydroxytetrahydrofuryl))-2,5-dihydrofuran.¹⁵

Vacuum distillation yielded a fraction consisting of 2–4 with a boiling point of 35–40 °C: 0.1 torr, 13 g, 96% purity as determined by GC, 90 mmol. Anal. Calcd for C₈H₁₀O₂: C, 69.56; H, 7.25; O, 23.19. Found: C, 69.71; H, 7.00; O, 23.08. Preseparation by medium-pressure liquid chromatography (Lobar Si 60 LiChroprep, 40–63 μ m, size B, reciprocating pump, Duramat, Chemie und Filter GmbH, Heidelberg, CH₂Cl₂ analytical grade as eluting agent) yielded the dehydrodimers in the sequence **4**, **3**, **2**. Two hundred milligrams of the mixture 2–4 was used per single run and fractionated into three main fractions. After 23 runs, 1 g of **2**, 1 g of **4**, and 2 g of **3** were obtained. The separation of **2** into the diastereomers **2a** and **2b** and of **4** into **4a** and **4b** was performed by preparative GC (10% OV 101 on Chromosorb P, 60–80 mesh, 6-m length, 10-mm diameter, 550 mL of N₂/min, 100 °C). In the case of **3**, separation into the diastereomers was not possible. Due to the O₂ and H₂O sensitivity of **3** and **4**, samples for NMR analyses were degassed by three freeze-pump-thaw cycles and sealed in vacuo. The mass spectra of 2–4 are almost identical except for some small differences in relative intensities: **2a**, 138 (M⁺, confirmed by chemical ionization), 69 (100), 41 (25), 39 (10). GC analyses using 124 m of the chiral phase TFA-L-Asp-bis(cyclohexyl) ester ($T = 115$ °C 1.6 bar of H₂, FID) gave one peak for **2a** and two for **2b**. Two peaks were also observed for **3**, each showing

a weak splitting while only one peak was found for **4a** and **4b** even with a chiral-phase length of 224 m.

An alternative method for the separation of **2** is as follows: 13 g (90 mmol) of the distillation fraction containing 2–4 (see above) was dissolved in a small amount of H₂O. After addition of 8 mL (94 mmol) of H₂O₂ (30%, without stabilizer), the solution was stirred for 1 h at 50 °C and extracted 5 times with 100-mL portions of CH₂Cl₂. The solvent was evaporated at reduced pressure and the residue separated by molecular distillation: the first fraction (50 °C evaporator temperature, 5 torr) consisted of 2.5 g of **2** (18 mmol, 96% purity) and the second one (50 °C, 0.001 torr) of 3.6 g of 2-(4'-(2'-hydroxytetrahydrofuryl))-2,5-dihydrofuran¹⁵ (23 mmol, 80% purity).

Blank Experiments. A. 2,5-DHF/H₂O (120 mL) (14/1) was irradiated for 90 h in the immersion lamp apparatus, producing 400 mL of gas (GC: 35% H₂, 57% CO, 8% C₃H₆ + C₃H₄). GC–MS analysis of the liquid phase showed the presence of 12 major components consisting predominantly of ring-opened products such as 3-buten-1-ol,^{14a} recombination products of a dihydrofuryl radical with a ring-opened DHF radical (MS: 140, 122, 69, 41, 27), and products without a dihydrofuran ring (MS: 142). The dehydrodimers 2–4, furan, 2,3-DHF, and THF are present only as minor components.

B. Four milliliters of 2,5-DHF/H₂O (1/8) was irradiated in a quartz cell for 1 h at $\lambda = 300$ nm (500-W HBO high-pressure Hg lamp, Kratos-Schoeffel GM 252 monochromator). GC analyses gave no indication of H₂ and dehydrodimer formation. If this experiment is repeated in the presence of 1 mg (0.006 mmol) of ZnS, 2–4 and small amounts of furan and 2,3-DHF are formed. The reaction does not occur in ZnS/H₂O or ZnS/2,5-DHF.

Irradiation of 1 in THF/H₂O. Fifty milligrams (0.06 mmol) of **1** was dissolved in 120 mL of THF/H₂O (1/1) and irradiated in the immersion lamp apparatus for 20 h, affording 150 mL of gas (GC: 93% H₂). GC–MS analysis of the organic phase showed two main peaks, representing more than 80% of the products formed. Both peaks give rise to the same MS with a weak M⁺ at 142 and the typical fragments of the THF ring at 71 (100), 43 (42), 27 (17) mass units. They are identified as meso and racemic 2,2'-bitetrahydrofuran by comparison with authentic material.¹⁶ There is no evidence (GC) for the formation of 2,3'- or 3,3'-dehydrodimers (see also radiolysis of H₂O/THF).

Time Dependence of Product Formation. In a standard experiment as described for the synthesis of 2–4, 0.584 g of *n*-undecane was added as the internal standard prior to irradiation. Samples for GC analyses were withdrawn from the liquid (0.5 mL) and gas phase (50 mL) at the intervals indicated in Figure 2. The irradiation was stopped after 23 h: response factors relative to standard, 1.52 (2–4); 1.65 (2,3-DHF); 1.60 (furan) and (2,5-DHF).

Inhibition by ZnCl₂. In a standard experiment as described for the synthesis of 2–4, 0.399 g of *n*-dodecane was added as the internal standard. Samples for GC (0.2 mL) were withdrawn after 2-, 4-, and 5-h irradiation time and contained 6.5, 17, and 24 mmol of H₂ and 6, 16, and 22.5 mmol of 2 + 3 + 4, respectively. Subsequent addition of 40 mg (0.2 mmol) of ZnCl₂ resulted in complete inhibition of product formation as indicated by GC analyses after 7-, 9-, and 11-h irradiation time. The effect is due to Zn²⁺ since no inhibition occurs with NaCl.¹⁷

Temperature Dependence. Two milligrams (0.02 mmol) of ZnS was suspended in 4 mL of THF/H₂O (1/1) and equilibrated for 5 min at the appropriate temperature before irradiating at $\lambda = 254$ nm. No difference in the rates of H₂ formation was observed when carrying out the experiment at 20, 30, 40, and 50 °C.

Quantum Yield. ZnS (8.5 mg, 8.7×10^{-5} mol) was suspended in 5 mL of 2,5-DHF/H₂O (14/1) and irradiated at $\lambda = 300$ nm. H₂ was determined after 30 min by GC; $\phi = 0.1$ mol H₂/einstein. This value was reproducible within $\pm 10\%$.

Intensity Dependence. In order to prevent potential precipitation of ZnS at the front window of the irradiation cell, a mirror was placed above a vertically mounted 120-mL irradiation flask (Hg–Xe lamp apparatus, cooling jacket, magnetic stirring, and continuously recording gas buret). The mirror furnishes a vertical light beam which strikes the top window not in contact with the solution. Fifteen milligrams (0.018 mmol) of **1** dissolved in 100 mL of 2,5-DHF/H₂O (1/1) was irradiated until the H₂ rate became constant. Light attenuators were placed above the front window.

pH Dependence. 1/THF/H₂O. Two milliliters of a 2.02×10^{-4} M stock solution of **1** in THF was mixed with 2 mL of the aqueous solution of known pH (pH was adjusted with HCl or NaOH, respectively) and irradiated ($\lambda = 254$ nm) in the 4-mL quartz cell. To ensure measurement of the H₂ rate beyond the induction period, the solution was preirradiated

(11) Leopold, R.; Michael, A. *Fortschr. Teerfarbenfabrikationen Industriezweige* **1931**, 16, 139. Hanschke, E. *Chem. Ber.* **1955**, 88, 1053.

(12) "Powder Diffraction Standards"; Swanson, H. E., Ed.; National Bureau of Standards, Joint Committee on Powder Diffraction Standards: Washington, DC, 1976.

(13) Kurian, A.; Suryanarayana, C. V. *J. Appl. Electrochem.* **1972**, 2, 223.

(14) (a) EPA/NIH Mass Spectral Data Base, p 19. (b) Friedman, L.; Long, F. A. *J. Am. Chem. Soc.* **1953**, 75, 2832. (c) Baggett, N.; Barker, S. A.; Foster, A. B.; Moore, R. H.; Whiffen, D. H. *J. Chem. Soc.* **1960**, 4565.

(15) Zeug, N. Doctoral Dissertation, University of Dortmund, 1983.

(16) We thank Dr. H.-P. Schuchmann for a small sample of 2,2'-bitetrahydrofuran.

(17) Bücheler, J.; Kisch, H. unpublished results.

for 30 min, and the H_2 value was taken during the next 30 min.

ZnS/THF/ H_2O . This was prepared as described above but 2 mg (0.02 mmol) of ZnS was used and H_2 was measured after the first 30 min.

Solvent Dependence. Irradiations were performed with the Hg-Xe lamp apparatus by using 5 mg (0.05 mmol) of ZnS or 8.3 mg (0.01 mmol) of **1** in 20 mL of solvent mixture.

ZnS/10 mL of Solvent/10 mL of H_2O . After 2-h irradiation, no H_2 was detected in the case of 2,3-DHF, tetrahydropyran, 2,3-dihydro-4H-pyran and 1,4-dioxane. Strong corrosion of ZnS (darkening) was usually observed within in the first 5 min. 5,6-Dihydro-2H-pyran induced H_2 formation which ceased after 50 min. This was accompanied by a darkening of the ZnS. To obtain maximum H_2 -evolution rates, the amount of THF and 2,5-DHF had to be at least 9% (v/v).

1/Solvent/2,5-DHF/ H_2O . In the following systems, GC analyses revealed the formation of H_2 and **2-4** and gave no indication of the presence of dimers containing at least one 1,4-dioxyl or tetrahydrofuryl ring: 1,4-Dioxane/2,5-DHF/ H_2O = 10/1/9 and 35/1/2 (10- and 20-h irradiation, respectively); THF/2,5-DHF/ H_2O = 10/1/9 (10-h irradiation).

Material Balance. 2,5-DHF was saturated with triply distilled water at 0 °C under an argon atmosphere. The water content was determined to be 8.84% (w,w) by GC analysis with MeOH (Merck p.a., GC: 0.05% H_2O) as the internal standard (Hewlett-Packard II, 2 m of Poropak-Q, 80–120 mesh, column T = 120 °C, injection block T = 150 °C, 4 mL of He/min, TCD; response factor for H_2O , 0.951). Of the stock solution 90.67 g was transferred into the irradiation vessel which had been carefully dried in an oven. **1** (40 mg, 0.048 mmol) was then added, and Ar flushing was not carried out before irradiation (immersion lamp apparatus) in order to prevent loss of material.

After irradiation, 14.675 g of MeOH was added as an internal standard. This caused a homogenization of the two-phase system formed during the reaction. H_2O and **2-4** (*n*-tetradecane as standard) were determined as described above; H_2 was measured volumetrically and corrected for standard conditions and purity (GC).

For a second experiment, 2,5-DHF was saturated with water at 20 °C, resulting in a water content of 9.78% (w,w).

The following results were obtained in experiment 1 (experiment 2): irradiation time 18 h (36 h), 0.051 mol of H_2 (0.115 mol) formed, 0.046 mol of **2-4** (0.102 mol) formed, 0.097 mol of 2,5-DHF (0.214 mol) consumed, and 0.445 ± 0.002 mol of H_2O (0.654 ± 0.001) before and 0.445 ± 0.002 mol of H_2O (0.656 ± 0.003) after irradiation.

Time Dependence of Isotopic Gas-Phase Composition. Following is the standard experiment as described for the synthesis of **2-4**. The D_2O used (Merck, Uvasol) contained 99.75% D, the 2,5-DHF about 0.1% (GC) H_2O . For each gas analysis, the irradiation was interrupted at the time intervals indicated in Figure 4, and a sample was withdrawn into an evacuated flask (50 mL) which was cooled with liquid N_2 during the subsequent MS measurement. Before the irradiation was continued, the solution and reaction vessel, including the buret, were flushed with Ar to remove all hydrogen.

Test for Isotopic Exchange of 2,5-DHF with D_2O . Fifty milligrams (0.06 mmol) of **1** was dissolved in 112 mL of 2,5-DHF (dried over molecular sieve 4 Å), and then 8 mL (0.44 mmol) of D_2O was added. Irradiation was interrupted after formation of 1.1 L (0.05 mol) of H_2 . GC-MS analysis of the liquid phase gave no evidence for the incorporation of D into **2-4**, 2,5-DHF, 2,3-DHF, or furan.

Photolysis of H_2O_2 in 2,5-DHF/ H_2O . A mixture of 112 mL (1.5 mol) of 2,5-DHF and 8 mL of aqueous H_2O_2 (=71.7 mmol; 30%, Merck p.a., without stabilizer) was irradiated in the immersion lamp apparatus (8 h). Samples of the solution were withdrawn after 30, 60, 90, 120, 180, 300, and 480 min. **2-4** and 3-hydroxytetrahydrofuran were analyzed by GC, and H_2O_2 was determined by titanyl sulfate.¹⁸ 3-Hydroxytetrahydrofuran was isolated by first evaporating 2,5-DHF in vacuo, followed by bulb-to-bulb distillation of the residue under high vacuum. The distillate was separated by preparative GC (10% OV 17 on Chromosorb P, 60–80 mesh, 6 m/10 mm column, 500 mL of N_2 /min, 100 °C); 1H NMR and IR correspond to ref 19.

γ Radiolyses. A. Triply distilled H_2O (760 g, 42.2 mol) and 35.5 g (0.49 mol) of THF were mixed in an irradiation vessel. After purging with N_2O for 30 min, the solution was subjected to γ irradiation under steady N_2O bubbling (in order to convert e_{aq}^- in OH^- ; dose = 7.6 Mrad). The solution was then extracted 6 times with 100-mL portions of CH_2Cl_2 , and the solvent was removed under atmospheric pressure. GC-MS analysis of the residue revealed the presence of four product peaks in the

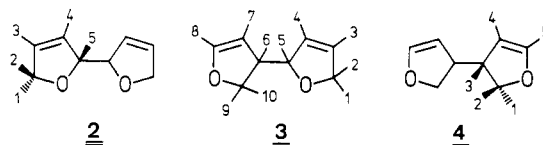


Figure 1. Dehydrodimers **2-4**.

ratio of 5:5:1:1. The corresponding MS data are 142 (M^+), 84 (3), 71 (100), 43 (45), 27 (16) for **1** and **2** and 142 (M^+) (8), 83 (7), 71 (100), 43 (45), 27 (12) for **3** and **4**. Peaks 1 and 2 are identified as two diastereomers of 2,2'-bitetrahydrofuran and **3** and **4** as two diastereomers of 2,3'-bitetrahydrofuran.

B. Determination of the G Value for Formation of **2-4.** Solutions of 6.79×10^{-5} mol of 2,5-DHF in 10 mL of N_2O -saturated triply distilled water were irradiated for 3, 10, 15, and 20 min, respectively (dose rate = 6.77 krad/min). Quantitative determination of **2-4** was performed by GC (70-m CW 20 M, 0.8 bar of H_2 , 3 min, 60 °C iso, 60–160 °C, 4 °C/min, FID; internal standard, 1-butanol): G -value $G(\mathbf{2-4}) = 0.92$ (theoretical 2.5).¹⁵

C. One hundred grams (5.5 mol) of triply distilled H_2O , 1 g (11.4 mmol) of 1,4-dioxane, and 60 mg (0.86 mmol) of 2,5-DHF were irradiated as described in section A (dose = 150 krad). No evidence for **2-4** was obtained by GC analysis (45-m OV 101 FS(c) 83, 0.6 bar of H_2 , 60–240 °C, 6 °C/min, FID).

D. Seven hundred grams (38.8 mol) of triply distilled water, 34 g (0.39 mol) of 1,4-dioxane, and 1 g (14.3 mmol) of 2,5-DHF were irradiated and worked up as in A (7.6 Mrad). GC-MS analysis (95 m of SF 96, 1.2 bar of N_2 , 8 min, 60 °C iso, 60–200 °C, 4 °C/min, FID) revealed the presence of five product peaks. The corresponding MS data are as follows: peak 1, 86 (60), 58 (40), 30 (100); **2** or **3**, 158(8), 127 (8), 115 (6), 96 (82), 87 (100), 83 (82), 71 (30), 70 (50), 57 (32), 42 (66), 43 (50), 31 (44), 27 (44); **4** or **5**, 174 (4), 143 (5), 130 (6), 112 (5), 99 (8), 87 (100), 73 (18), 59 (12), 43 (34), 31 (46). Peaks 1 and **4/5** are identified as 1,4-dioxene and two diastereomers of bi-1,4-dioxane, respectively, by comparison with ref 20. Peaks **2/3** show fragments typical for dioxyl and tetrahydrofuryl groups and most likely are two diastereomers of a tetrahydrofuryl-1,4-dioxane.

Results and Discussion

Identification of the Photocatalyst. UV spectroscopy reveals that in the reaction of system **1**/THF/ H_2O or **1**/2,5-DHF/ H_2O ($\lambda_{irr} = 254$ nm), hydrogen evolution starts only after about 90% of **1** has been photodecomposed. Filtration of the resulting suspension through a millipore filter (0.2- μ m pore size) gives a solution which lacks any catalytic activity and a white powder insoluble in organic solvents. The latter contains cubic zinc sulfide and a polymer of the cyclic ether which may be responsible for the stability in strong alkaline suspensions. This ZnS is an efficient photocatalyst for hydrogen evolution, reaching maximum turnover numbers of 4000 (moles of H_2 /mole of **1**) in the system H_2O /2,5-DHF.^{1d} The *n*-type semiconducting character of [ZnS] has been confirmed by photoelectrochemical experiments.²¹ ZnS prepared according to method B (see Experimental Section) catalyzes the same reaction; however, its catalytic activity ceases after 15 h while [ZnS] from **1** remains active for several days^{1d} (see also Figure 2). A long induction period is observed if ZnS is dehydrated at 150 °C (0.1 torr) before use.

Formation of [ZnS] from **1** is contingent on the presence of both 2,5-DHF (or THF) and water. This reaction is only efficient if **1** is irradiated in the high-energy absorption band ($\lambda_{irr} = 267$ nm) rather than in the lower energy one ($\lambda_{irr} = 366$ nm).^{1d} The wavelength dependence parallels the photoionization²² of **1**, and it is likely that the first step in the conversion of **1** to [ZnS] is a photoinduced electron transfer to the solvent. In accord with this, the electron scavenger N_2O inhibits the photodecomposition

(20) MS Computer Data Bank, Max-Planck-Institut für Kohlenforschung, Mülheim a.d. Ruhr.

(21) Sprünken, R.; Bücheler, J.; Kisch, H., unpublished results. In THF/ H_2O the onset of the anodic photocurrent is located at -0.6 V vs. NHE; the difference to the flat band potential (-1.64 V at pH 7 in H_2O vs. NHE)^{24a} of Al-doped ZnS indicates charge recombination via a surface state in the case of the ZnS powder used in this study. See also: Becker, W. G.; Bard, A. J. *J. Phys. Chem.* 1983, 87, 4888.

(22) Fernandez, A.; Görner, H.; Kisch, H. *Chem. Ber.*, submitted for publication.

(18) Eisenberg, G. M. *Ind. Eng. Chem., Anal. Ed.* 1943, 15, 327.

(19) The Sadtler Standard Spectra, Sadtler Research Laboratories, Philadelphia, NMR-Spectra No. 20423 M. Infrared Grating Spectra No. 34754 K.

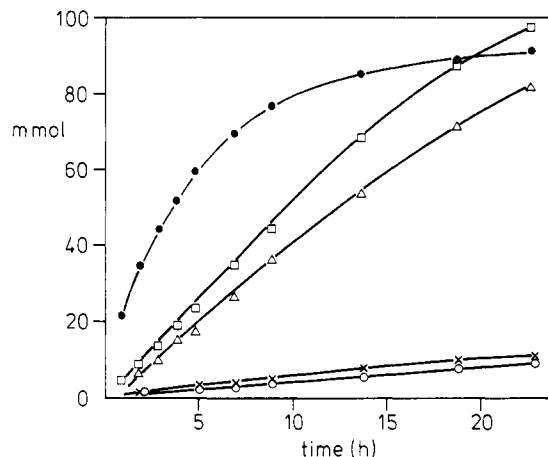


Figure 2. Formation of hydrogen (\square), dehydrodimers **2-4** (Δ), furan (\times) and 2,3-dihydrofuran (\circ) as a function of irradiation time; **1** = 5×10^{-4} M in 120 mL of 2,5-DHF/ H_2O (14/1) (v/v); $\lambda_{\text{irr}} \geq 248$ nm; (\bullet) hydrogen formation by using 20 mg (0.2 mmol) of ZnS instead of **1**.

1. No metal sulfides are formed with the analogous cadmium and mercury dithiolenes under the same experimental conditions.¹⁷

In contrast to its photosensitivity, **1** is thermally stable if oxygen and solvent peroxides are absent. Refluxing of **1** for 2 h in 2,5-DHF/ H_2O does not result in any decomposition.

Isolation and Structure of 2,5-DHF Dehydrodimers 2-4. During the catalytic photoreaction, THF and 2,5-DHF are dehydrodimerized to 2,2'-bitetrahydrofuran and 2,2', 3,3'-, and 2,3'-bidi-hydrofuranes, respectively. Similar dimers have been described in the case of THF²³ but are novel for 2,5-DHF. In a minor reaction path (about 10%), 2,5-DHF is transformed to furan and 2,3-DHF.

A mixture of the regioisomers (**2/3/4** = 1:2:1, Figure 1) is obtained (13 g in a typical experiment) by distillation of the reaction mixture after irradiation. Subsequent treatment of the distillate with H_2O_2 leads to hydroxylation of **3** and **4** at the vinylic groups, causing a drastic change in the boiling point of the components. After distillation, **2** can be separated into pure meso (**2a**) and racemic (**2b**) forms by preparative GC. All three regioisomers can be isolated in gram quantities by medium-pressure liquid chromatography. Figure 2 shows that the sum of the mole quantities of the solvent products (**2-4**, furan, and 2,5-DHF) equals the amount of hydrogen produced.

The structures of **2-4** are established on the basis of analytical and spectral data and from independent syntheses by photolysis of H_2O_2 /2,5-DHF and radiolysis of H_2O /2,5-DHF (vide infra). Detailed NMR analyses¹⁵ (Table I, Figure 3) reveal that the 2,5-DHF rings of **2-4** are planar while the 2,3-DHF rings are puckered. This agrees with the literature data on 2,5-DHF²⁴ and 2,3-DHF.^{25,26}

Material Balance and Experiments with D_2O . The complete material balance shows that no water is consumed during the reaction and 1 mol of H_2 is formed per 2 mol of 2,5-DHF reacted. However, if D_2O is used, the initial gas phase contains more than 90% D_2 . Prolonged irradiation leads to a decrease of D_2 with concomitant increase of HD and H_2 , the isotopic composition being dependent on the initial D_2O concentration (Figure 4). Since the water content remains constant, the hydrogen liberated from the cyclic ether is used in the regeneration of water, leading finally to the observed changes in the isotopic composition of the gas phase. No incorporation of deuterium into 2,5-DHF and the products derived from it occurs.

Table I. ^1H and ^{13}C NMR of **2-4**^a

2a	^1H NMR δ 4.61 (dddd, H^1 , $J_{12} = -12.8$, $J_{13} = 1.6$, $J_{14} = -2.4$, $J_{15} = 5.6$ Hz), (dddd, H^2 , $J_{23} = 1.6$, $J_{24} = -2.5$, $J_{25} = 3.9$ Hz), 5.98 (dddd, H^3 , $J_{34} = 6.1$, $J_{35} = -2.1$ Hz), 5.85 (dddd, H^4 , $J_{45} = 1.2$ Hz), 4.69 (m, H^5 , $J_{55} = 5.3$ Hz) ^{13}C NMR: δ 76.17 (OCH_2), 89.58 (OCH), 127.9 and 129.05 ($\text{C}=\text{C}$)
2b	^1H NMR δ 4.61 (dddd, H^1), 4.58 (dddd, H^2), 5.99 (dddd, H^3), 5.74 (dddd, H^4), 4.76 (m, H^5) ^{13}C NMR δ 75.99 (OCH_2), 88.96 (OCH), 127.44 and 129.33 ($\text{C}=\text{C}$)
3a	^1H NMR δ 4.60 (m, H^1), 4.60 (m, H^2), 5.97 (dddd, H^3), 5.78 (dddd, H^4), 4.66 (m, H^5), 3.04 (m, H^6), 4.86 (dd, H^7), 6.38 (dd, H^8), 4.25 (dd, H^9), 4.22 (dd, H^{10})
3b	^1H NMR δ 4.60 (m, H^1), 4.60 (m, H^2), 6.02 (dddd, H^3), 5.73 (dddd, H^4), 4.76 (m, H^5), 3.20 (m, H^6), 4.94 (dd, H^7), 6.35 (dd, H^8), 4.20 (dd, H^9), 4.14 (dd, H^{10})
4a	^1H NMR δ 4.07 (dd, H^1), 4.23 (dd, H^2), 3.00 (m, H^3), 4.88 (dd, H^4), 6.37 (dd, H^5)
4b	^1H NMR δ 4.04 (dd, H^1), 4.28 (dd, H^2), 3.05 (m, H^3), 4.87 (dd, H^4), 6.36 (dd, H^5)

^a Measured at 400 (^1H) and 270 (^{13}C) MHz in CD_2Cl_2 with TMS as internal standard; in compounds **2a**, **2b**, **4a**, and **4b**, the corresponding hydrogens in the two rings are chemically and magnetically equivalent; coupling constants for **2a** were derived from the calculated spectrum.¹⁵

Comparison with Reactions of OH Radicals in Homogeneous Solution. The structure of **2-4** and the change in the differential isotopic composition of the hydrogen evolved point to the intermediacy of OH and cyclic ether radicals. H abstraction from 2,5-DHF would afford the allylic dihydrofuryl radical (R^\bullet). When D_2O is used, regeneration of water would lead to HOD and, as the reaction proceeds, also to H_2O . The obtained isomeric ratio of **2-4** (1:2:1) can be explained by the statistical dimerization of R^\bullet . In order to gain further evidence for the possible involvement of OH radicals, these were generated in H_2O /2,5-DHF by two methods.

Photolysis of H_2O_2 in H_2O /2,5-DHF produces the expected dehydrodimers **2-4** in a ratio of 1:2:1 (yield: 70%), as well as 3-hydroxytetrahydrofuran (20%) which is formed by addition of OH $^\bullet$ to 2,5-DHF followed by H abstraction. This product is not present in the ZnS-catalyzed reaction.

Radiolysis of H_2O /2,5-DHF also yields **2-4** in a ratio of 1:2:1, although in a lower yield (30%) due to preferred formation of high molecular-weight products. The latter process may be induced by addition of R^\bullet to 2,5-DHF in analogy to the free radical polymerization of olefins. 3-Hydroxytetrahydrofuran is not detected among the reaction products.

This difference in product yield between the two methods of generating OH $^\bullet$ is due to the much lower concentration of OH $^\bullet$ and resultant R^\bullet in the radiolysis experiment.¹⁵ This disfavors dimerization and disproportionation as compared to polymerization.

Radiolysis of H_2O /THF yields 2,2'- and 2,3'-bitetrahydrofuran in the ratio of 5:1, respectively. This agrees well with the value of 11:1 reported for the ratio of α - to β -tetrahydrofuryl radicals in the reactions of OH $^\bullet$ with THF.²⁷ Assuming the same rate constants for α and β abstraction, this ratio should be twice that of the product ratio. Note that the ZnS-catalyzed photoreaction regioselectively affords the 2,2'-dehydrodimer without traces of the 2,3'-isomer.

Radiolysis, in water, of a mixture of 1,4-dioxane and 2,5-DHF (1,4-dioxane in excess) yields the expected dioxane dehydro dimers and cross products, consistent with the high rate constants for reaction of OH $^\bullet$ with these ethers.¹⁵ In contrast, when 1,4-dioxane/2,5-DHF mixtures with an even higher ratio of the former are employed in the ZnS-catalyzed system, only **2-4** are formed.

The nature and ratio of the products in the homogeneous systems strongly support intermediate tetrahydrofuryl and dihydrofuryl radicals in the ZnS-catalyzed photoreaction. The observed differences suggest that the ether radicals are not pro-

(23) Kondo, H.; Suzuki, H.; Takeda, K. *J. Pharm. Soc. Jpn.* **1935**, 55, 741.

(24) Korver, P. K.; Van der Haak, P. J.; Steinberg, H.; De Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1965**, 84, 129.

(25) Barfield, M.; Spear, R. J.; Sternhell, S. *J. Am. Chem. Soc.* **1971**, 93, 5322.

(26) Ueda, T.; Shimanouchi, T. *J. Chem. Phys.* **1967**, 47, 5018. Green, W. H. *J. Chem. Phys.* **1969**, 50, 1619. Durig, J. R.; Li, Y. S.; Tong, C. K. *J. Chem. Phys.* **1972**, 56, 5692.

(27) Eibenberger, J.; Schulte-Frohlinde, D.; Steenzen, S. *J. Phys. Chem.* **1980**, 84, 704.

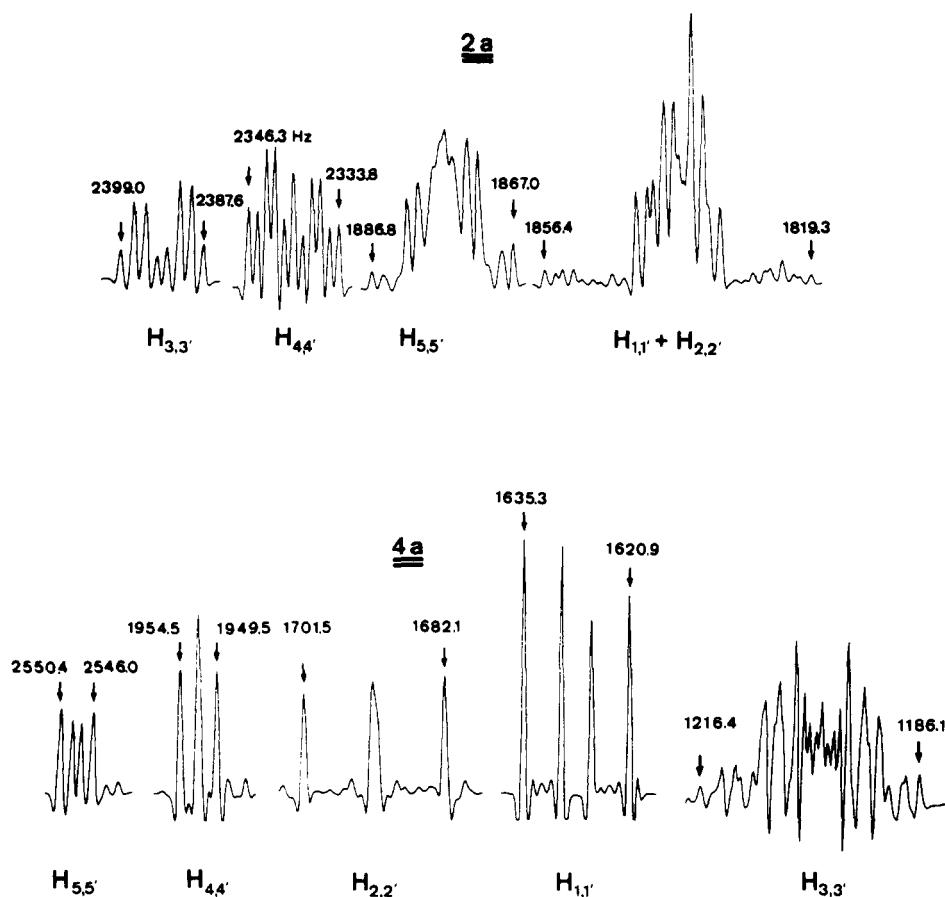


Figure 3. ^1H NMR spectra (400 MHz) of **2a** and **4a**.

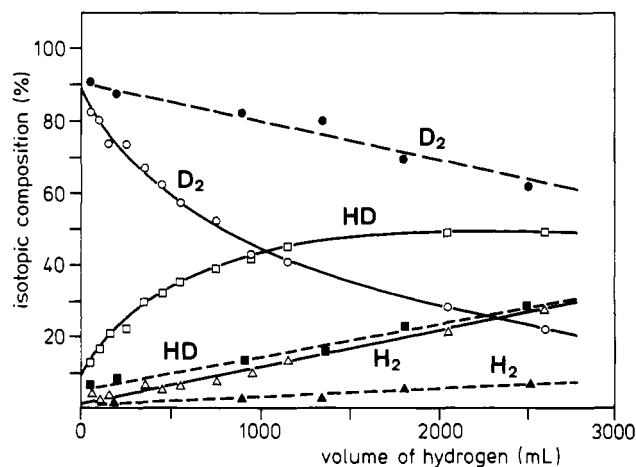


Figure 4. Differential isotopic hydrogen composition as a function of turnover; $1 = 5 \times 10^{-4}$ M; in a solvent mixture of (a) (—) 8 mL (0.44 mol) of D_2O and 112 mL (1.5 mol) of 2,5-DHF, and (b) (---) 60 mL (3 mol) of D_2O and 60 mL (0.81 mol) of 2,5-DHF; $\lambda_{\text{irr}} \geq 248$ nm.

duced via an OH radical. However, when this species is adsorbed at the surface, it may show a modified selectivity, and this pathway cannot be excluded.

Chemoselectivity of C-C Bond Formation. Further evidence for the high selectivity of the ZnS photocatalyst stems from the investigation of other ethers. While the reaction occurs with the five-membered THF and 2,5-DHF, no dehydrodimers or hydrogen are observed with 2,3-DHF and the six-membered tetrahydropyran, 2,3-dihydro-4H-pyran, and 1,4-dioxane. In all the latter cases and also with acyclic ethers,^{1d} photocorrosion of ZnS occurs within the first few minutes of illumination. Since only 50 mL of H_2 is formed from 5,6-dihydro-2H-pyran as compared to 2–3 L in the case of 2,5-DHF, it is concluded that allylic stabilization of the intermediate radical does not dominate the reaction. The

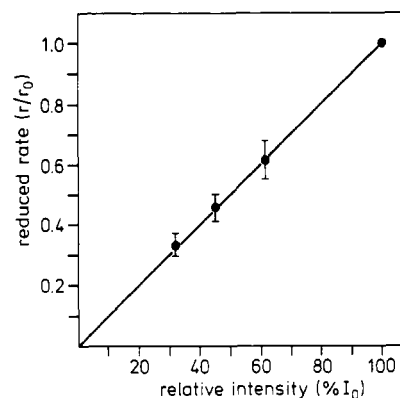


Figure 5. Intensity dependence of hydrogen evolution rate (r_0 = rate at the maximum intensity I_0); $1 = 1.8 \times 10^{-5}$ M in 2,5-DHF/ H_2O (1/1) (v/v); $\lambda_{\text{irr}} \geq 254$ nm.

rate of H_2 evolution from $\text{H}_2\text{O}/2,5\text{-DHF}$ is about 10 times faster than that from $\text{H}_2\text{O}/\text{THF}$.

Quantum Yield and Influence of pH, Light Intensity, and Temperature on Reaction Rate. The linear dependence of the hydrogen evolution rate on the light intensity indicates that generation of electrons and holes is the only photochemical step involved in product formation (Figure 5). The quantum yield ϕ_{H_2} (300 nm) of 0.1 as measured for the ZnS/ $\text{H}_2\text{O}/2,5\text{-DHF}$ system is a lower limit since no correction has been made for light loss due to reflection from the ZnS particles.

The influence of changing pH in the THF/ H_2O system is summarized in Figure 6. The H_2 -evolution rate does not change significantly from pH 4–10 for both types of zinc sulfides. The rate decreases above pH 10 in the case of ordinary ZnS is due to its dissolution. Contrary, [ZnS] generated from **1** does not dissolve, and a rate increase is observed. A similar acceleration by high hydroxide concentration has been reported for Pt/ TiO_2

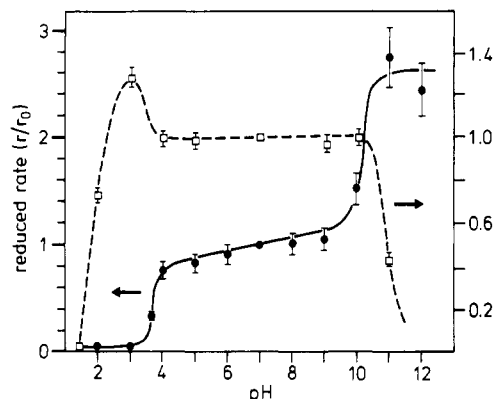
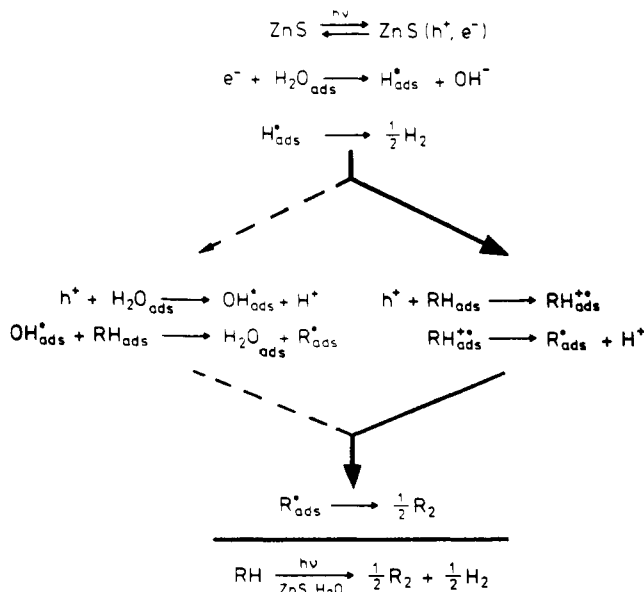


Figure 6. Hydrogen evolution rate (r_0 = rate at pH 7) as function of the apparent pH in THF/H₂O (1/1) (v/v); (—) 1.01×10^{-4} M of **1** (---) 2 mg (0.02 mmol) of ZnS suspended in 4 mL of the solvent mixture $\lambda_{\text{irr}} = 254$ nm.

Scheme I



and SrTiO₃.²⁸ No change in H₂-evolution rate is detected between 20 and 50 °C for the system THF/H₂O.

Mechanism. From these results, a simplified mechanism is outlined in Scheme I. Ultra band gap excitation ($E_g = 3.7$ eV¹⁷) generates an electron-hole pair which is efficiently trapped at the surface if THF or 2,5-DHF is present. ZnS, which decomposes upon irradiation in pure water,²⁹ becomes surprisingly stable in the presence of these cyclic ethers. This stabilization is a very selective process since structurally related compounds, i.e., 2,3-dihydrofuran and six-membered ethers, neither prevent photodecomposition nor undergo dehydrodimerization. The trapped electrons reduce water to hydrogen as demonstrated by the inhibiting effect of electron scavengers like N₂O, SF₆,^{1d} and Zn²⁺. After production of the initial 100 mL of gas, corresponding to a water turnover of 1%, the D₂ content has decreased already by 8%. This indicates that the trapped electrons reduce HOD or HOH much faster than D₂O. A kinetic isotope effect of $k_{\text{H}}/k_{\text{D}} = 5$ is obtained by simulating the change in the isotopic hydrogen composition.³⁰ Values of 2–7 were observed in the electrochemical

reduction of water at different electrodes.³¹ Efficient H₂ evolution occurs in the ZnS system without the presence of a noble metal catalyst which is necessary for TiO₂ and CdS.³² This is probably due to the stronger reducing power of the conduction band electrons in ZnS and the catalytic effect of traces of metallic zinc as recently observed for colloidal ZnS.³³ It is known that the darkening of zinc sulfide powder upon irradiation is due to the formation of elemental zinc.^{29,33} Values of -1.8^{34a} and -1.0 V^{34b} vs. NHE have been reported for the conduction band edge of ZnS at pH 7. Thus, the reduction of water ($E_0 = -0.41$ V) by the conduction band electrons is exoergic by at least 0.6 eV.

The valence band edge of ZnS at pH 7 has been located at 1.82^{34a} and 2.7 V^{34b} vs. NHE. Comparison with the standard potentials for the oxidation of water ($\text{H}_2\text{O} \rightleftharpoons \text{OH}^{\bullet} + \text{H}^+ + e^-$, 2.4 V)³⁵ and the cyclic ether ($\text{RH} \rightarrow \text{R}^{\bullet} + \text{H}^+ + e^-$; THF, 2.0; 2,5-DHF, 1.6 V³⁶)³⁷ reveals that the oxidation of the ether is thermodynamically favored. This is corroborated by the tenfold rate increase when 2,5-DHF is substituted for THF as the reducing agent. If the holes instead would oxidize water, this step is expected to be rate determining, and variation of the ether should have a rather weak influence.³⁸ However, the rate increase above pH 10 points to a possible oxidation of hydroxide ions. Although unlikely, a direct oxidation of water can therefore not completely be excluded.

The absence of a notable thermal activation energy in the system THF/H₂O indicates that hole scavenging by the ether is not a rate-determining reaction step. It rather suggests that THF is involved in the primary photoprocesses by changing the ratio of recombination to trapping of the charge carriers at the zinc sulfide surface. The constant reaction rate in the range of pH 4–10 is compatible with this assumption. In the other mechanistic possibility, the rate should decrease since the flat band potential shifts cathodically with increasing hydroxide concentration.^{34a}

Irrespective of the mode of formation of the cyclic ether radicals, their involvement is well established by isolation and identification of the dimers 2–4 as well as small amounts of disproportionation products. Neglecting the latter, the overall reaction consists of dehydrodimerization of the cyclic ether. It is endothermic by 13 kcal/mol in the case of THF³⁹ and was proposed as a potential system for the conversion of light into chemical energy.

The fact that only 2–4 but no 2,2'-ditetrahydrofuran is formed when THF is present in a tenfold excess over 2,5-DHF points to selective adsorption and/or a specific adsorbate structure⁴⁰ for the unsaturated ether. This and the absence of a correlation between reaction efficiency and ionization potential⁴¹ suggest that

(30) The kinetic scheme incorporates the formation of $\text{ZnS}(e^-, h^+)$, its reaction with H₂O, HOD and D₂O to H_{ads} and D_{ads} , and the recombination to H₂, D₂, and HD.¹⁵

(31) Krumbiegel, P. "Isotopieeffekte"; Akademie-Verlag Berlin, 1970; p 108.

(32) See, e.g.: "Energy Resources through Photochemistry and Catalysis"; Grätzel, M., Ed.; Academic Press: 1983.

(33) (a) Henglein, A.; Gutierrez, M. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 852. (b) Henglein, A.; Gutierrez, M.; Fischer, Ch.-H. *Ibid.* **1984**, *88*, 170.

(34) (a) Measured with an Al-doped ZnS single crystal electrode: Fan, F.-R.; Leempoel, P.; Bard, A. J. *J. Electrochem. Soc.* **1983**, *130*, 1866. (b) Estimated from work function and band gap energy: Tributsch, H.; Bennett, J. C. *J. Chem. Tech. Biotechnol.* **1981**, *31*, 565.

(35) Zamaraev, K. I.; Parmon, V. N. *Catal. Rev.-Sci. Eng.* **1980**, *22*, 261.

(36) (a) Estimated according to ref 33b by using $E_0(\text{H}^+/\text{H}^{\bullet}) = -2.1$ V and the C–H bond dissociation energies^b of 4.1 (THF) and 3.7 (2,5-DHF) eV. (b) "Chemical Bonds and Bond Energy", Sanderson, R. T., Ed.; Academic Press: 1976.

(37) Comparison with the oxidation potentials of THF and 2,5-DHF is less reliable since the latter is unknown and the former may be at about 1.8 V vs. NHE: Weinberg, N. J. *Chem. Educ.* **1983**, *60*, 270.

(38) In homogeneous solution the rate constant for H abstraction by OH[•] is 4.3×10^9 and 9×10^9 M⁻¹ s⁻¹ for THF and 2,5-DHF, respectively.¹⁵

(39) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.

(40) The influence of adsorbate structures on chemical selectivity was reported for platinum-catalyzed oxidations of aromatic compounds; Hubbard, A. T. *J. Mol. Catal.* **1983**, *21*, 211 and references cited therein.

(41) Ionization potentials (eV): 2,3-DHF (8.5); 2,5-DHF (9.14); 1,4-dioxane (9.42); 5,6-dihydro-2H-pyran (9.45); THF (9.70). We appreciate the measurement of the PE spectra by A. Landers. See also: Kimura, K.; et al. "Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules"; Japan Scientific: Tokyo, Halsted Press: New York, 1981.

(28) Van Damme, H.; Hall, W. K. *J. Am. Chem. Soc.* **1979**, *101*, 4373. Wagner, F. T.; Somorjai, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 5494; *Nature (London)* **1980**, *285*, 559. Fang, S.-M.; Chen, B.-H.; White, J. M. *J. Phys. Chem.* **1982**, *86*, 3126.

(29) (a) Schleede, A. *Chem. Ber.* **1923**, *56*, 386. (b) Shionoya, S. *J. Chem. Soc. Jpn.* **1950**, *71*, 461. (c) Platz, H.; Schenk, P. W. *Angew. Chem.* **1936**, *49*, 822. (d) Schleede, A.; Herter, M.; Kordatzki, W. *Z. Phys. Chem.* **1923**, *106*, 386.

the chemoselectivity is governed by adsorption phenomena.

Conclusion. The results presented above demonstrate that a semiconductor catalyst may be photogenerated from a coordination complex and that it is efficiently stabilized in water by addition of an organic compound. In the case of cubic *n*-ZnS, stabilization is linked to catalytic H₂ evolution and chemoselective dehydrodimerization of cyclic ethers. This selectivity may be considered to be due to specific adsorption of the ether onto the ZnS photocatalyst. In addition it was shown that the formation of D₂ does not provide prime evidence for the consumption of water in sa-

crificial hydrogen-producing systems.

Acknowledgment. We are indebted to Dr. J. Preut for the Debye-Scherrer measurements, to Dr. H. Leitch, Dr. B. Reimann, and Prof. C. von Sonntag for helpful discussions, and to W. Schlamann and H. Gruen for valuable technical assistance.

Registry No. 1, 18958-61-7; 2 (isomer 1), 94731-60-9; 3 (isomer 1), 94731-61-0; 3 (isomer 2), 94731-63-2; 4 (isomer 1), 94731-62-1; 4 (isomer 2), 83044-27-3; 2,5-DHF, 1708-29-8; THF, 109-99-9; ZnS, 1314-98-3.

Kinetic Evidence for the Formation of the Carbene Anion Radical (EtO₂C)₂C^{•-}¹

Dean A. Van Galen, Mark P. Young, M. Dale Hawley,* and Richard N. McDonald*

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506. Received October 26, 1984

Abstract: The electrochemical reduction of (EtO₂C)₂C=N₂ (**1**) has been studied in *N,N*-dimethylformamide and acetonitrile at temperatures as low as -64 °C in order to obtain kinetic evidence for the intermediacy of the carbene anion radical (EtO₂C)₂C^{•-}. In the absence of an added proton donor, reaction of the anion radical (1^{•-}) that is formed by the slow, one-electron reduction of **1** obeys the first-order rate law $-d[1^{\bullet-}]/dt = k[1^{\bullet-}]$, where $k = 8 \pm 2 \text{ s}^{-1}$ at -38 °C, and gives (EtO₂C)₂CH⁻ as the principal product. A coulometric *n* value of 1 is obtained for the reduction of **1** in aprotic media. In the presence of an excess of the electroinactive proton donor benzoic acid, guanidinium perchlorate, or (CF₃)₂CHOH, reaction of electrogenerated 1^{•-} obeys the first-order rate law $-d[1^{\bullet-}]/dt = 2k[1^{\bullet-}]$, where *k* is the same as that in aprotic media, and affords (EtO₂C)₂CH₂ as the final product. The coulometric *n* value for the reduction of **1** under protic conditions is 2. A scheme is proposed in which the carbene anion radical that is formed by the rate-determining loss of N₂ from 1^{•-} undergoes hydrogen-atom abstraction in aprotic media or protonation followed by reduction by unreacted 1^{•-} in the presence of an added proton donor.

Dissociative electron attachment to diazoalkanes (R₂C=N₂) has been shown to be a convenient and ready method for the preparation of carbene anion radicals (R₂C^{•-}) in the gas phase.² Whether or not reductive elimination of N₂ from diazoalkanes can be used successfully to prepare carbene anion radicals in the condensed phase is less clear. Our initial claims for the formation of carbene anion radicals^{3,4a} in the condensed phase have been refuted,^{5,6} in part because of our erroneous assignments of the anodic peaks for Ph₂C=N₂^{6,8} and FI=NNNN=FI^{•-} (FI =

9-fluorenylidene)^{4b} to Ph₂CH⁻ and fluorenylidene anion radical, respectively.

Recent demonstrations^{6,8} that several electrogenerated diazoalkane anion radicals can be observed directly at reduced temperature suggest that kinetic studies might be used successfully to demonstrate carbene anion radical intermediacy. In order to focus on the kinetics of the diazoalkane anion radical reaction, we sought a diazoalkane for study that does not afford the corresponding azine as a product. Previous studies of Ph₂C=N₂³ and FI=N₂^{4a} have shown that azine formation occurs by one or more electron-transfer-induced chain reactions and that the occurrences of these chain reactions greatly increase the complexity of the electrochemical model. Accordingly, we restricted our search for a suitable R₂C^{•-} precursor to those diazoalkanes that give anion radicals which afford hydrocarbons rather than azines as final products and which have relatively low proton and hydrogen-atom affinities. Because these data are unavailable for R₂C=N₂^{•-}, we have used instead as guides the proton affinity for R₂CH⁻ and whether or not R₂C=N₂ forms non-azine products upon photolysis. Diethyl diazomalonate was selected for detailed study because its p*K*_a of 16⁹ is low compared to most methylene carbon acids and because it gives only non-azine products upon photolysis in pentane.¹⁰

Results and Discussion

Cyclic Voltammetry. The cyclic voltammetric reduction of diethyl diazomalonate (**1**) was studied as a function of scan rate, temperature, and effect of added proton donors, solvent, and supporting electrolyte. In the absence of an added proton donor at 22 °C, the cyclic voltammogram at a glassy carbon electrode

(1) "Abstracts of Papers", Midwest Regional Meeting of the American Chemical Society, Lawrence, KS, Nov. 3, 1983; American Chemical Society: Washington, DC. "Abstracts of Papers", 187th National Meeting of the American Chemical Society, St. Louis, MO, April 11, 1984; American Chemical Society: Washington, DC, 1984; ORGN 0169.

(2) (a) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491-4698. (b) Zittle, P. F.; Ellison, G. B.; O'Neil, S. V.; Lineberger, W. C.; Reinhardt, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 3731-3732. (c) McDonald, R. N.; Chowdhury, A. K.; McGhee, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 4112-4116.

(3) (a) McDonald, R. N.; January, J. R.; Borhani, K. J.; Hawley, M. D. *J. Am. Chem. Soc.* **1977**, *99*, 1268-1270. (b) McDonald, R. N.; Triebe, F. M.; January, J. R.; Borhani, K. J.; Hawley, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 7867-7872. (c) Triebe, F. M.; Barnes, J. H.; Hawley, M. D.; McDonald, R. N. *Tetrahedron Lett.* **1981**, *22*, 5145-5148.

(4) (a) McDonald, R. N.; Borhani, K. J.; Hawley, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 995-996. (b) Herbranson, D. E.; Theisen, F. J.; Hawley, M. D.; McDonald, R. N. *J. Am. Chem. Soc.* **1983**, *105*, 2544-2549.

(5) (a) Bakke, J. M.; Bethell, D.; Galsworthy, P. J.; Handoo, K. L.; Jackson, D. J. *Chem. Soc., Chem. Commun.* **1979**, 890-891. (b) Parker, V. D.; Bethell, D. *Acta Chem. Scand., Sect. B* **1980**, *B34*, 617-618. (c) Bethell, D.; Galsworthy, P. J.; Handoo, K. L. *J. Chem. Soc., Chem. Commun.* **1980**, 534-536. (d) Parker, V. D.; Bethell, D. *Acta Chem. Scand., Sect. B* **1981**, *B35*, 691-699.

(6) (a) Parker, V. D.; Bethell, D. *Acta Chem. Scand., Sect. B* **1981**, *B35*, 72-74. (b) Bethell, D.; Parker, V. D. *J. Chem. Soc., Perkin Trans. 2* **1982**, 841-849.

(7) Wright, R. E.; Vogler, A. *J. Organometal. Chem.* **1978**, *160*, 197-205.

(8) Van Galen, D. A.; Young, M. P.; Hawley, M. D. *J. Electroanal. Chem.* **1984**, *175*, 53-65.

(9) (a) Terekhova, M. I.; Petrov, E. S.; Mesyats, S. P.; Shatenshtein, A. I. *Zh. Obshch. Khim.* **1975**, *45*, 1529-1533. (b) Professor Fred Bordwell, Northwestern University, private communication, January 3, 1980.

(10) Doering, W. von E.; Knox, L. H. *J. Am. Chem. Soc.* **1956**, *78*, 4947-4950.