

## Photoinduced Catalytic Decomposition of Water and Tertiary Amines or Carbohydrates

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### Introduction

The use of the energy of light for producing chemicals or storable fuels is a modern and attractive field of research.

During the past few years, a large number of results have been published on the subject; the use of semi-conductors as converting agents [1–19, 22] has been particularly investigated.

Under exposure to visible light the semi-conductor provides a high electromotive force sufficient to allow redox reactions to take place, reducing an acceptor such as  $H^+$  and oxidizing a donor such as water or a selected organic material.

The present letter deals with the capability of CdS semiconductor powder to generate molecular hydrogen from water under illumination, and with the effects of addition of various organic electro-donors.

The purpose is not only to establish the optimal conditions for cathodic hydrogen evolution, but also to study the anodic cleavage of high molecular weight

organic raw materials, or biological wastes, into shorter and more useful molecules.

It appears that if the smooth anodic oxidation of products such as cellulose or lignin is able to induce their degradation into sugars or chemicals of low molecular weight, the economic advantages of such a process would be far superior to those leading only to the recuperation of hydrogen fuel.

### Experimental

Reagents of A.R. quality grade obtained from commercial sources are used without further purification.

All experiments were performed in an air-cooled 50 ml Pyrex bulb illuminated with three 125 W high pressure Hg-lamps (Philips).

In a typical run; a ten milliliter aliquot of an aqueous solution (bidistilled water), containing potassium chloride (0.1 M), the electrodonor ( $6.7 \cdot 10^{-2}$  M unless otherwise stated) and 250 mg cadmium sulphide, were deoxygenated under nitrogen (99.8% purity) and irradiated under reduced pressure (water-pump vacuum) for various times under thorough agitation.

The evolved gases were collected through a simple valve and immediately injected into the gas chromatograph (Packard Instruments, Porapak column, nitrogen as a carrier).

The semi-conductor powder was used without any specific metal-loaded catalytic preparation. The effects of deposition of cobalt, platinum or other noble metals are presently being investigated.

TABLE I. Photoinduced  $H_2$  Evolution Rates (see Experimental for Reactions Conditions).

Photosensitizer	Reducing agent	Irradiation time (h)	Average $H_2$ evolution rate <sup>a</sup> ( $\mu l h^{-1}$ )
CdS	EDTA	25	228.3 ± 26.3
CdS	TEOA	22.5	71.6 ± 1.87
CdS	DEXTROSE	22	4.34 ± 0.22
CdS	SACCHAROSE	22	2.65 ± 0.14
CdS	STARCH (700 mgr)	26	1.45 ± 0.02
none	EDTA	66.25	1.35 ± 0.04
SrTiO <sub>3</sub> <sup>b</sup>	EDTA	23	76.03 ± 2.39

<sup>a</sup>The quoted errors on average evolution rates are calculated as standard deviation for ten samples at least. V.P.C. detector was a catharometer calibrated by means of a 99.98% pure hydrogen standard. <sup>b</sup>Comparison should take differences in granulometry into account: Mean particle size SrTiO<sub>3</sub>:  $2.9 \mu m \pm 0.4$ ; CdS:  $2.1 \mu m \pm 0.3$  determined with Nano-Sizer (Coulter Electronics)-Particles may be considered as being monodisperse.

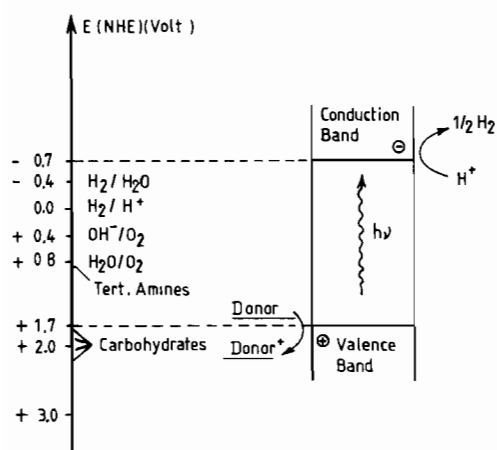
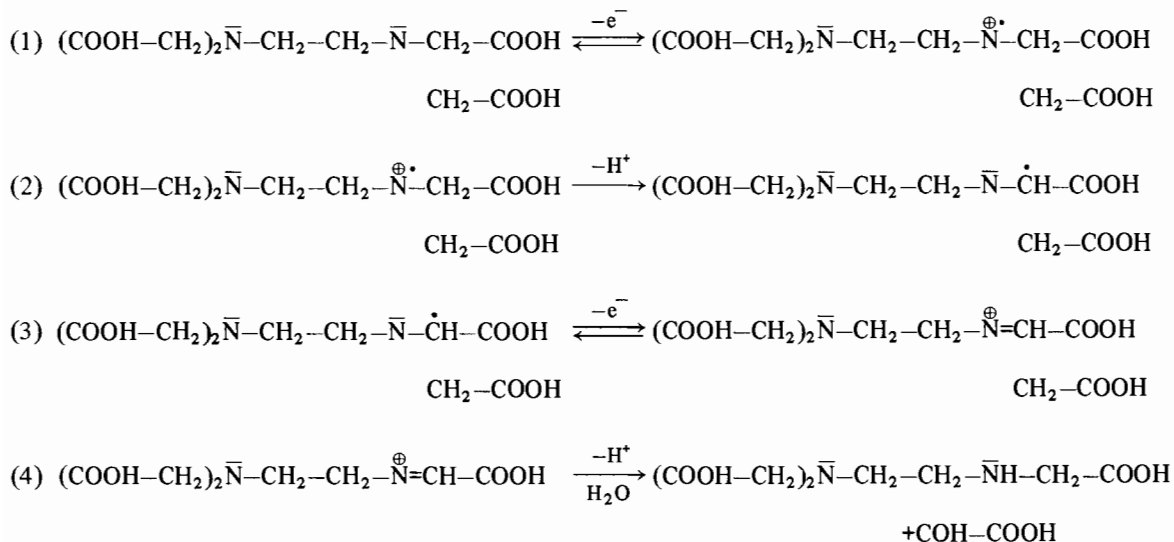


Fig. 1. Photoredox reactions with CdS semi-conductor.

## Results and Discussion

Table I shows the photoinduced hydrogen evolution rates. These experiments were conducted with a large excess of electrodonor, as compared with the total amount of  $\text{H}_2$  evolved, in order to keep the concentration constant during the reaction.

To avoid changes in activity, the ionic strength was kept constant because of the presence of potassium chloride.



Only very small traces of oxygen were detected in the evolved gases. Therefore the amount of amine or carbohydrate consumed can be correlated with the amount of  $\text{H}_2$  evolved. The absence of oxygen is due to surface overvoltage causing a kinetic hin-

drance when no specific evolution catalyst (such as  $\text{RuO}_2$ ) is present.

As shown in Fig. 1, tertiary amines, ethylenediaminetetraacetic (EDTA) and triethanolamine (TEOA) are liable to be oxidized, because of their redox potential which is high [20] in comparison with the positive hole potential of cadmium sulphide semi-conductor [13].

Carbohydrates on the other hand would give rise to poor yields, because their mobility and oxidation potential [11] are both low.

The experimental results are in good agreement with the thermodynamic and kinetic predictions.

## Scheme of Reaction Mechanism

Studies on oxidation of tertiary amines in aqueous solution [23–25] show the formation of a secondary amine and an aldehyde *via* hydrolysis of an iminium salt.

The primary products of the oxidation of TEOA should be diethanolamine and glycolaldehyde [20]; EDTA degradation probably follows the same scheme. EDTA is however unsymmetrically substituted and dealkylation of the tertiary into a secondary amine must take neighbouring functional groups into account. The carboxylic function should indeed favour both a deprotonation of the radical cation [2] and a hydrolysis of the iminium salt [4]. This is thought to explain the higher (3.1) oxidation rate for EDTA than for TEOA.

As to carbohydrates, further investigations will be made bearing in mind that a gaseous oligosaccharide radical cation decomposes into monosaccharide by glycosidic cleavage, as observed by mass spectroscopic experiments [21]. With carbohydrates, lower

positive hole potential semi-conductors ( $\text{Nb}_2\text{O}_5$ ,  $\text{TiO}_2$ ,  $\text{SrTiO}_3$ ) should preferentially be used for thermodynamic reasons, although an illumination as shorter wavelengths is required.

New approaches appear to be quite promising, not only for the purpose of hydrogen production from wastes but also for the revalidation of processing of otherwise worthless biochemicals.

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### References

- 1 G. Campet and M. P. Dare-Edwards, *Nouv. Journ. de Chimie*, **4**, 8/9, 501 (1980).
- 2 J. B. Goodenough, 'Advances in Chemistry Series', n. 186, Solid State Chemistry (1980).
- 3 M. P. Dare-Edwards and A. Hamnett, *J. Electroanal. Chem.*, **105**, 283–290 (1979).
- 4 S. Anderson and E. Constable, *Nature*, **280**, 5273, 571 (1979).
- 5 A. Hamnett and M. P. Dare-Edwards, *J. Phys. Chem.*, **83**, 3280 (1979).
- 6 T. Kawai and T. Sakata, *Nature*, **286**, 474–475 (1980).
- 7 T. Kawai and T. Sakata, *Nature*, **282**, 283–284 (1979).
- 8 T. Kawai and T. Sakata, *Chem. Phys. Lett.*, **72**, 1, 87–89 (1980).
- 9 T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Comm.*, 694–695 (1980).
- 10 M. Calvin, *Photochem. Photobiol.*, **23**, 425–444 (1976).
- 11 T. Kawai and T. Sakata, *Chem. Lett.*, 81–84 (1981).
- 12 S. Sato and J. M. White, *Chem. Phys. Lett.*, **72**, 83–86 (1980).
- 13 H. Gerscher, *Pure Appl. Chem.*, **52**, 2649–2667 (1980).
- 14 M. P. Dare-Edwards, A. Hamnett and J. B. Goodenough, *J. Electroanal. Chem.*, **119**, 109–123 (1981).
- 15 H. P. Maruska and A. K. Ghosh, *Solar Energy*, **20**, 443–458 (1978).
- 16 H. Gerscher, *J. Electroanal. Chem.*, **82**, 133–143 (1977).
- 17 B. Krautler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 7, 2239–2240 (1978).
- 18 B. Krautler and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 23, 7729–7730 (1977).
- 19 S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 14, 4667–4675 (1977).
- 20 M. Kirch, J. M. Lehn and J. P. Sauvage, *Helv. Chim. Acta*, **62**, 4, 1345–1384 (1979).
- 21 T. Radford and D. C. Dejongh, 'Biochemical Application of Mass Spectrometry', 294–310, Wiley Interscience, New York.
- 22 J. M. Lehn, J. P. Sauvage and R. Ziessel, *Nouv. J. Chim.*, **4**, 11, 623–627 (1980).
- 23 S. G. Cohen, A. Parola and G. H. Parsons Jr., *Chem. Rev.*, **73**, 141 (1973).
- 24 S. G. Cohen and R. J. Baumgarten, *J. Am. Chem. Soc.*, **87**, 2996 (1965).
- 25 P. J. Smith and C. K. Mann, *J. Org. Chem.*, **34**, 1821 (1969).