In conclusion we have shown that the built-in oxazolidinone ring turned out to be an effective way of controlling the diastereofacial approach of two side chains and the overall strategy has been successfully applied to the total synthesis of α-allokainic acid.

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Light-Induced Hydrogen and Oxygen Generation from Water with Vesicle-Stabilized Colloidal Mercury Sulfide and Sodium Metaborate

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Photochemical solar energy storage is a popular candidate as a possible source of alternative energy. We are interested in a quantum conversion, particularly hydrogen and oxygen generation from water with the vesicle-stabilized colloidal mercury sulfide and sodium metaborate. The availability of photochemical solar energy conversion using TiO_2[1-5,12] and CdS[6-13] are studied extensively and intensively. In general, the leading scientists have obtained hydrogen and oxidized product from water and the sacrificial electron donor, respectively. A photochemical system which can be returned to the original state after producing hydrogen and oxygen from water has to be established. Here, we, for the first time, report photochemical hydrogen and oxygen generation from water using vesicle-stabilized colloidal mercury sulfide particle with Rh particles and metaborate.

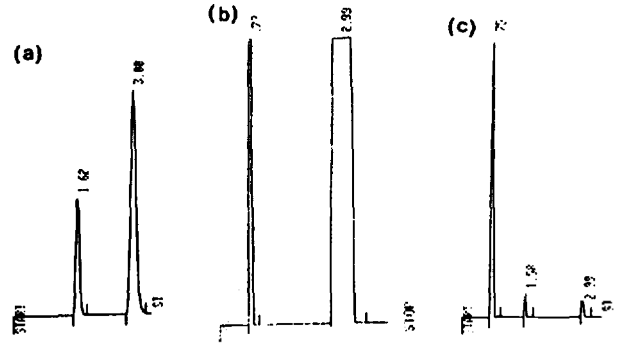


Figure 1. Gas chromatographs of air (a), H_2 diluted with nitrogen (b) and gases in vesicle-stabilized HgS system (c). Retention time (min): H_2; 0.73-0.75, O_2; 1.58-1.62, N_2; 2.99-3.00.

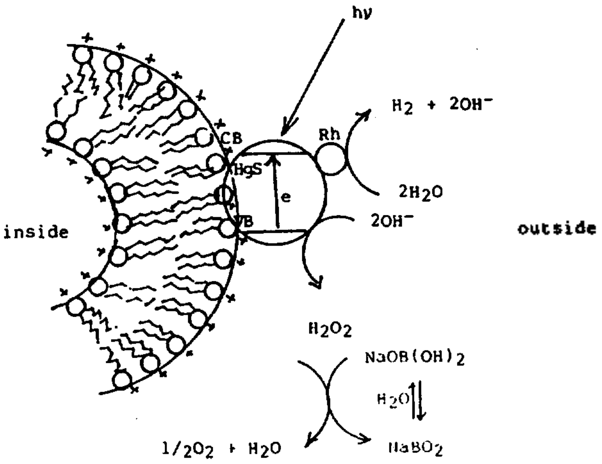
We select HgS colloidal particles instead of CdS, becuase the band gap of HgS is high enough to reduce and oxidize water. We also think metaborate can generate oxygen cyclically by reacting with hydrogen peroxide produced in the photochemical reaction of the vesicle-stabilized colloidal mercury sulfide with Rh particles. DODAB vesicle (dioctadecyl dimethyl ammonium bromide) containing HgS colloid was prepared as described previously by Fendler *et al.*[10] The vesicle was prepared by sonication of the mixture of surfactant (DODAB, 0.12 g, 2×10^{-4} moles) and water (200 m*l*, triply distilled). $HgCl_2$ stock solution (0.1 M, 1 m*l*) was added to the vesicle and then shaken thoroughly. If hydrogen sulfide gas was bubbled through the vesicle for 1 minute, the color of the vesicle turned to black. The superflous H_2S was eliminated by argon bubbling through vesicle for 2 hrs. Transmission electron microscope of absorbed HgS particles on DODAB vesicle surface confirmed that colloid particles were mainly attached on the focussed vesicle surface. The colloidal HgS formed in vesicle had a band gap of 350 nm compared to 498 nm of CdS[10].

The colloidal HgS vesicles[14] (20 m*l*) were added to 30 m*l*-pyrex cell with a rubber stopper. Rh colloids (50 μ*l*) which were obtained by reduction of $RhCl_3$ with $NaBH_4$, and $NaBO_2$ (1 M, 50 μ*l*) were added to the 30 m*l*-pyrex cell and then degassed with argon for 30 min. When the colloidal HgS vesicles (20 m*l*) with Rh colloids were irradiated under anaerobic condition by 500 W-Xenon lamp using 0.4 M $CuSO_4\cdot5H_2O$ solution filter, hydrogen and oxygen were obtained. The gases were identified with authentic samples by G.C. The retention times of hydrogen, oxygen and nitrogen in molecular sieve column (5 A molecular sieve, 1/8 inch, 6 ft column, oven temp. 50℃) were 0.75, 1.58 and 3.00, respectively. Gas chromatographs of air, hydrogen diluted with nitrogen, and gases on HgS-metaborate system are shown in Figure 1. Some portion of the peak of retention time 1.58 (O_2) and all portion of the peak of retention time 3.0 (N_2) came from air leaking during reaction and/or injection times. The amount of hydrogen and oxygen were determined with standard lines of authentic samples and by comparing the ratio of oxygen and nitrogen of air. The amount of hydrogen and oxygen produced *vs.* irradiation time is shown in Table 1. Hydrogen and oxygen were produced continuously. Hydro-

Table 1. Amount of H_2 and O_2 Produced in HgS Colloid System with Rh and Sodium Metaborate

Irradiation time (min)	H_2 (1×10^{-7} mole)		O_2 (1×10^{-7} mole)	
	1st run	2nd run*	1st run	2nd run*
30	0.92	1.78	0	0
50	2.26		0.79	
70	2.98		0.70	
90	4.20	2.74	1.12	0.90
110	4.66		0.91	
130	4.90		2.41	
150	5.20	3.45	1.34	1.76

*After 150 min irradiation.



Scheme 1. Generation of hydrogen and oxygen from water using vesicle-stabilized HgS colloid with Rh particles, and $NaBO_2$. VB: valence band, CB: conduction band.

gen (0.5 m*l*/*l*·soln) was generated for 150 min irradiation. The vesicle solution degassed after 150 min irradiation produced hydrogen and oxygen again. Even though hydrogen generation is somewhat higher than oxygen in the first rnn, one volume of hydrogen and half volume of oxygen were produced in the second run.

No hydrogen and oxygen productions were observed without illumination. The following scheme is drawn not because we have firm conviction that it is entirely correct, but rather because it affords a rationale for the process (see Scheme 1). Light absorption leads to the promotion of an electron from the valence to the conduction band of HgS to given e^-h^+ pair[15]. Water is reduced to given hydrogen and hydroxide anion on Rh catalyst holding negative charge that is injected from the conduction band of HgS[5,9-11]. The hydroxide anion is oxidized to give hydroxyl radical[16] which in turn produces then hydrogen peroxide on electron hole of the HgS semiconductor. Oxygen probably is generated by reacting hydrogen peroxide and sodium borate which is equilibrated with sodium metaborate[17]. It is significant that hydrogen peroxide has been detected with ferrous chloride and potassium manganate solution upon irradiation of the vesicle systems. We are currently exploring the optimum conditions for the water photolysis and will report on them in due course.

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Functionalization of *p*-1,3-Diallylcalix[4]arene

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Host-guest or biomimetic chemistry[1] comprises a variety of types of investigations which attempt the *in vitro* simulation of processes that occur *in vivo*. Particularly interesting among these are reactions involving enzymes, and an important and expanding area of current investigation deals with compounds that have been called "enzyme models". Functionalization is essential to the enzyme model studies of calixarene compounds[2]. Functionalization can be carried out both