

COMMUNICATIONS

LETTERS

Hydrogen Generation from Vesicles with Ru Catalyst on the Wall

Yong-Tae Park

Department of Chemistry, Kyungpook National University, Taegu, 635, Korea (Received January 4, 1983).

Vesicles were made with didodecyltrimethylammonium bromide and ruthenium complex with two long tail as sensitizer. In order to attach the Ru catalyst to the wall of these cationic vesicles, $K_2RuCl_5 \cdot H_2O$ was added and then reduced by adding $NaBH_4$. Hydrogen was produced when the vesicle solution with electron donor (phenothiazine derivative, PHT, and ferrous chloride, pH=2.51) was irradiated with blue light. The quantum yield of hydrogen production was 3.3×10^{-4} . Blank test showed that every component is necessary for the reaction. Thus chemical energy could be stored in this system.

Within recent years, substantial research effort has been expended in photochemical conversion of solar energy. A central theme in this area has been the search and development of a working model whereby H_2O is decomposed into H_2 and O_2 ¹. Since water is transparent to solar radiation in the visible and UV ($\lambda < 200nm$) region, direct photolysis of water with solar radiation is not possible². Reaction must be carried out, therefore, utilizing sensitizer(S) and oxidation(D)/reduction(A) catalysts which can carry out the reactions depicted in the following scheme (Figure 1).

In several homogeneous system of ruthenium bipyridine complex as a sensitizer and methyl viologen as an electron acceptor, hydrogen was generated from water by light³. However the forward reaction is limited by back thermal reaction. Thus artificial devices that mimic the photosynthetic pathway were considered^{1,4}. In order to retard the back reaction, microemulsion or vesicle systems were used^{4,5}.

In this communication we devised the attachment of catalyst on the wall of vesicle like membrane in the plant and examined the storage of solar energy with this system.

Ruthenium complex with two tails [(N,N-di-(1-hexadecyl)-2, 2'-bipyridinium-4, 4'-dicarboxamide)-bis(2, 2'-bipyridine)-ruthenium perchlorate⁶, 0.5 mg, 4.0×10^{-7} moles], didodecyltrimethylammonium bromide (Eastman, 12.6mg, 2.7×10^{-5} moles) and water (5 ml) were placed in a test tube. The mixture was vortex-stirred, heated to boiling, then vortex-stirred again until the ruthenium complex had dissolved. The opalescent suspension was cooled to room temperature. $K_2RuCl_5 \cdot H_2O$ (Alfa, 1 mg, 2.7×10^{-6} moles) was added. The salt dissolv-

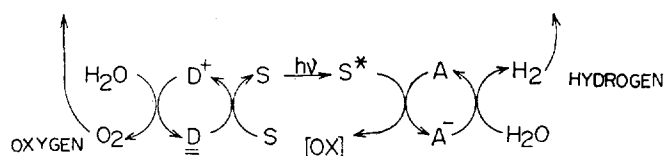


Figure 1. Schematic of photosensitized electron transport process.

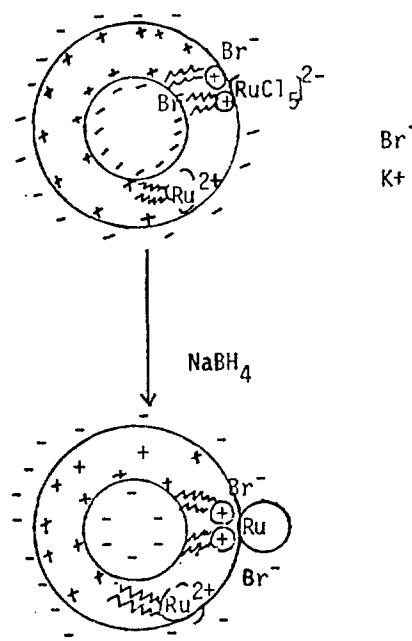


Figure 2. Ru-coated vesicle.

ed easily. Aqueous sodium borohydride (0.44M, 20 μ l) was introduced while the suspension was stirred. The solution was brought to boiling for 1-2 sec and vortex-stirred for a while, then cooled to room temperature. The addition of borohydride caused the color of the suspension to change from orange to grey-brown, its turbidity was apparently unaffected. To see the difference between ruthenium with vesicles and without vesicles, blank solution (without surfactant) was prepared. Both sample were centrifuged (cylindrical type, full RPM) for 5 min. Some of "Ru" in the sample without vesicles settled to the bottom of the tube, and was easily resuspended. No settl-

ing was apparent in the vesicle sample (see Figure 2).

The vesicle solution (2.5 ml) was taken in a cuvette (see Figure 3) and the visible absorption spectra were recorded. After deaeration with Ar gas, the solution was irradiated with blue light (440 to 550 nm) for two hours. In order to adjust pressure in the cuvette, 0.5 ml of Ar was introduced by gas tight syringe and then a portion of the gas (0.5 ml) was taken. The gas was analyzed by gas chromatograph. No hydrogen was produced. A phenothiazine derivative HCl salt (3.3 mg 8.5×10^{-6} moles) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.7 mg, 8.3×10^{-6} moles) were introduced in the cuvette. After deaeration with Ar

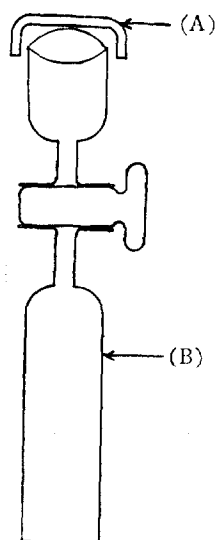


Figure 3. Reaction cuvette; (A) rubber stopper (B) uv-cuvette.

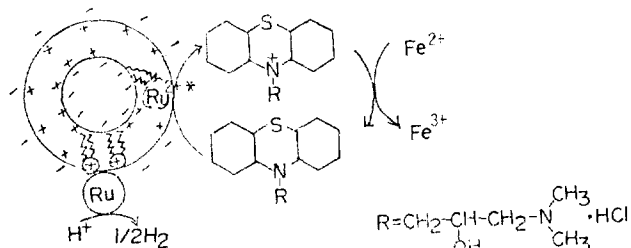


Figure 4. Photoinduced reaction on vesicle.

gas the solution was irradiated with blue light for two hours. Hydrogen ($28 \mu\text{l}$, $\phi = 3.3 \times 10^{-4}$) was produced. After deaeration again, the solution was irradiated for another 2 hours. It gave $13 \mu\text{l}$ of hydrogen. The solution of reaction cuvette was transferred to test tube and then pH of the solution was measured by pH meter (U. S. A. Chemtrix 60A). It was 2.51. As a blank test, a vesicle suspension was prepared as above but without phenothiazine derivative. When the solution was irradiated for 2 hours, no hydrogen was produced. Without FeCl_2 , no hydrogen was produced. This implies that both phenothiazine and ferrous chloride are mandatory at the hydrogen generation system (see Figure 4)

Since the reductive quenching of ruthenium bipyridine complex (Ru^{2+}) in the presence of amines was known,^{7,8} the excited ruthenium complex would be quenched by phenothiazine derivative (PHT) reductively. Since the reduced ruthenium complex (Ru^+) has potential to reduce proton to hydrogen,⁷ hydrogen is generated by catalyst of Ru on the wall of vesicles (see Figure 4). The oxidized PHT^+ oxidizes Fe^{2+} to Fe^{3+} . Thus the chemical energy is stored in the reaction.

References

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