

Effective Hydrogen Generation System by use of Ascorbic Acid as a Reversible Electron Donor

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Received October 9, 1980

A new hydrogen generating system was discovered, consisting of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$, methyl viologen, colloidal Pt, and ascorbic acid as a reversible electron donor. This system showed a high recycling number for each catalyst involved and a reasonable quantum yield for hydrogen production. The mechanism of the hydrogen-generating reaction is discussed.

Artificial photosynthesis is receiving special attention from chemists because of the significance of the conversion of solar energy into chemical energy.¹ From our current attempts to model photosynthesis,² one of the most important problems to be solved in the photochemical energy conversion seems to be how to avoid the thermodynamically favorable and kinetically rapid "back reaction". As reported previously³ in the model for photosynthesis of bacterial type, this serious problem was solved by connecting the charge-separation system with the electron-transport system. Next, our interest was focused on a hydrogen-producing system constructed with a reversible electron donor. In most of the hydrogen-producing systems reported, irreversible electron donors such as EDTA or triethanolamine were used,^{1,4} and the processes were less promising from a practical viewpoint.

Only a few systems are reported to be constructed with a reversible electron donor such as ascorbic acid,⁵ and the quantum yield of the H_2 generation is only 4.6×10^{-4} . We report here a much more effective H_2 -generating system consisting of ascorbic acid (AsA) as a reversible (ascorbic acid can be regenerated from dehydroascorbic acid through an appropriate photoreaction or dark reaction) electron donor, zinc meso-tetra(4-hydroxysulfophenyl)porphyrin ($\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$) as a water-soluble photocatalyst, methyl viologen (MeV^{2+}) as an electron carrier, and colloidal Pt as a hydrogen generation catalyst.^{1,c,d}

In a typical experiment, visible light ($\lambda \geq 410 \text{ nm}$) irradiation of 8 mL of aqueous solution containing $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ ($7.7 \times 10^{-5} \text{ M}$),⁶ AsA ($1.0 \times 10^{-1} \text{ M}$), MeV^{2+} ($1.0 \times 10^{-2} \text{ M}$), and Pt colloid (Pt, $1.15 \times 10^{-4} \text{ M}$), prepared according to Rampino's procedure,⁷ at 0°C leads to H_2 gas

generation at a rate of $110 \mu\text{L/h}$. After 9 h, $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ and MeV^{2+} were practically unchanged ($>99\%$), and the recycling numbers were about 143 on $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ and 96 on the Pt catalyst at this stage (i.e., more than 7150 mol of H_2 produced with the sacrifice of 1 mol of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$). At this stage the observed decrease of AsA or the increase of dehydroascorbic acid was ca. 5.6% based on iodometric titration. The yield of hydrogen evolved based on the ascorbic acid consumed was more than 95% under these conditions. The rate of H_2 generation was reduced gradually when irradiation was continued further, and it was about $80 \mu\text{L/h}$ on the average for 9-18-h irradiations. The slow decrease of the H_2 generation is presumably caused by a back electron transfer from MeV^{+} to dehydroascorbic acid which was accumulated during the irradiation. From a consideration of reduction potentials of AsA ($E_0' = 0.058 \text{ V}$) and H_2 ($E_0' = -0.421 \text{ V}$), this system represents a photochemically driven uphill conversion of ca. 20 kcal/mol. The quantum yield of hydrogen production by use of this system was 5×10^{-3} ,⁸ considerably more effective than that of the $\text{AsA-Ru}(\text{bpy})_3^{2+}\text{-Co}^{2+}$ complex system reported by Sutin et al. ($\phi = 4.6 \times 10^{-4}$).⁵ No appreciable H_2 production was observed in control experiments where one of the components is omitted: no light, no AsA, or no $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$. On the contrary, in the absence of MeV^{2+} a considerable amount of H_2 was still generated ($130 \mu\text{L}/3 \text{ h}$). But in this case almost complete degradation of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ was observed within 3 h. This rapid decomposition of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ in the absence of MeV^{2+} seems to be preceded by demetalation to $\text{H}_2\text{T}_{\text{SO}_3\text{Na}}\text{PP}$ (actually complete within 5 min), judging from the electronic spectrum change during the irradiation (disappearance of the 558-nm absorption and appearance of a 645-nm absorption). Also, the hydrogen production was directly observed from the system consisting of AsA, Pt colloid, and $\text{H}_2\text{T}_{\text{SO}_3\text{Na}}\text{PP}$ at approximately the same rate as the above system consisting of AsA, Pt colloid, and $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$, in good agreement with the mechanism proposed above. In the presence of MeV^{2+} , $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ was quite stable, and no photoinduced demetalation was observed. In the absence of Pt colloid, neither H_2 generation nor accumulation of the viologen cation radical was observed, in marked and interesting contrast to the irreversible system where viologen cation radical is accumulated even in the absence of Pt colloid.

Fluorescence quenching of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ with AsA or MeV^{2+} was investigated. As shown in Figure 1, 0.1 M of AsA (the same concentration used in the H_2 -generating system) only slightly (ca. 2%) quenches the $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ fluorescence. On the other hand, quenching with MeV^{2+} is remarkable, and no $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ emission was observed even at a concentration of MeV^{2+} as low as $5 \times 10^{-3} \text{ M}$.

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(8) Recently our improved system gave a much higher quantum yield, $\phi = 0.1$; the results will be reported soon.

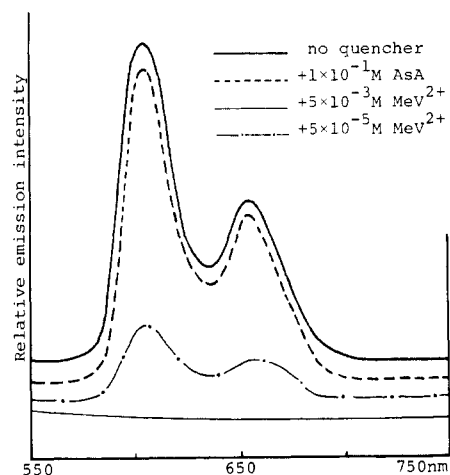


Figure 1. Fluorescence emission spectra of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ (3.3×10^{-7} M) with AsA or MeV^{2+} .

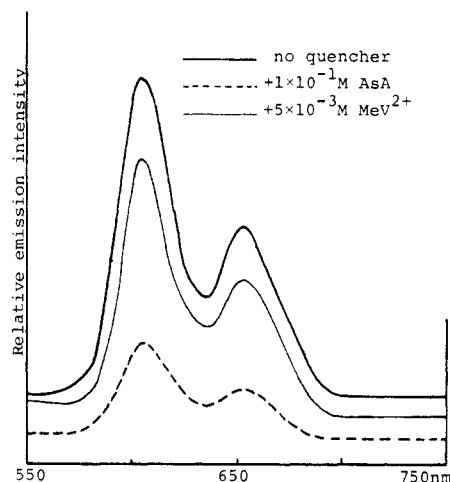
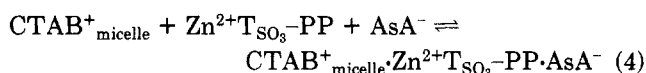
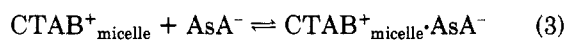
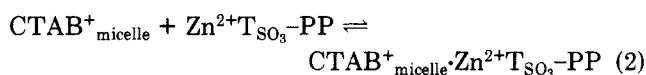
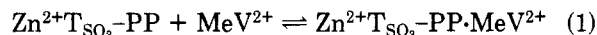


Figure 2. Fluorescence emission spectra of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ (3.3×10^{-7} M) in aqueous CTAB solution (3.3×10^{-3} M) with AsA or MeV^{2+} .

The emission of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ was quenched 75% even with 5×10^{-5} M MeV^{2+} . This remarkable quenching of the $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ seems to be due to the direct interaction between $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ and MeV^{2+} . The fluorescence quenching efficiency was dramatically changed when CTAB (3.3×10^{-3} M) was added into the solution. Methyl viologen quenching became quite inefficient in the CTAB micelle: ca. 20% with 5×10^{-3} M of the methyl viologen (ca. 1/375 times as effective as in homogeneous solution) but ca. 70% with 0.1 M ascorbic acid (ca. 35 times more effective as in homogeneous solution), as shown in Figure 2. These observed quenching characteristics may be reasonably interpreted by ion pairing. In homogeneous solution ion pairing (eq 1) may be important, leading to



efficient fluorescence quenching by MeV^{2+} ,⁹ while in the CTAB micelle, the major ion pairing should be anionic

(9) Recently Grätzel reported the formation of complexes between $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ and MeV^{2+} .^{1d}

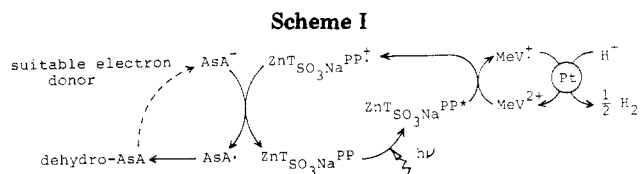


Table I. Effect of Dehydroascorbic Acid Added to $\text{EDTA-Ru}(\text{bpy})_3^{2+}\text{-MeV}^{2+}\text{-Colloidal Pt}$ System^a

[dehydro AsA], M	H_2 production, μL	
	after 4.5 h	after 9 h
0	440 \pm 40	1120 \pm 100
1×10^{-4}	225	560
1×10^{-3}	105	210
1×10^{-2}	27	28

^a $\text{EDTA}\cdot 2\text{Na}^+$, 5×10^{-2} M; $\text{Ru}(\text{bpy})_3^{2+}$, 1×10^{-4} M; $\text{MeV}^{2+}\text{Cl}_2$, 5×10^{-3} M; colloidal Pt/PVA, 1.2×10^{-4} g-equiv/L; total volume of the solution, 5 mL.

reagent-cationic micelle complexation, which markedly enhances the significance of $\text{Zn}^{2+}\text{T}_{\text{SO}_3}\text{-PP}\cdot\text{AsA}^-$ quenching (eq 4) but retards MeV^{2+} quenching.

From the observation mentioned above it is evident that the first photoinduced charge separation in the present system occurs between $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}^*$ and MeV^{2+} to produce $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}^{\cdot+}$ and $\text{MeV}^{\cdot+}$. From the preliminary experiment, $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}^{\cdot+}$ generated by careful chemical oxidation with bromine was reduced by aqueous AsA solution to reproduce $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ immediately and almost quantitatively. Thus, 3 mL of a 1×10^{-4} M aqueous solution of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ was treated with an excess amount of a dichloromethane solution of bromine to produce an aqueous solution of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}^{\cdot+}$ showing a broad absorption at 500–750 nm, which was very close to the absorption of $\text{ZnTPP}^{\cdot+}$ reported by Fajer et al.¹⁰ By the addition of 50 μL of 1.0×10^{-1} M AsA into the solution, $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ was regenerated within a few seconds as ascertained by the characteristic absorption at 558 nm. The amount of regenerated $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ was 90% based on the $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ initially used. Since catalytic H_2 generation from reduction of H^+ with $\text{MeV}^{\cdot+}$ in the presence of suitable redox catalysts is well-known, a simple mechanism can be postulated for the photocatalyzed H_2 generation (Scheme I). Interestingly, replacement of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ by $\text{Ru}(\text{bpy})_3^{2+}$, a well-known and widely used photocatalyst, caused a remarkable decrease of the efficiency of H_2 generation (<5 $\mu\text{L}/9$ h) partly because of the rapid back electron transfer either from $\text{Ru}(\text{bpy})_3^{2+*}$ or $\text{MeV}^{\cdot+}$ to dehydroascorbic acid (see Table I).

In summary, the system reported here is one of the most effective photochemical energy storage systems from the following three viewpoints: (1) no irreversible consumption of the electron donor,¹¹ (2) reasonably high quantum yield, (3) no significant degradation of photocatalysts.

Experimental Section

Materials. The photocatalyst $\text{H}_2\text{T}_{\text{SO}_3\text{Na}}\text{PP}$ was prepared as described by Fleischer et al.⁶ and was converted to the zinc complex according to Herrmann's procedure.⁶ Methyl viologen was synthesized by methylation of 4,4'-dipyridyl with methyl iodide, and the resultant pyridinium iodide was converted to the corresponding chloride by treatment with Ag_2O followed by HCl. The pyridinium chloride was recrystallized twice from ethanol.

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(11) Recently, the authors found a very efficient and economical (even for H_2 production) electron donor for the generation of AsA, which will be described soon.

Colloidal Pt supported on poly(vinyl alcohol) ($n = 1500$) was prepared according to Rampino's procedure.⁷

Hydrogen Generation. In a typical photochemical hydrogen producing experiment, 8 mL of an aqueous solution containing $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ (7.7×10^{-5} M), AsA (1.0×10^{-1} M), MeV^{2+} (1.0×10^{-2} M), and Pt colloid (Pt, 1.15×10^{-4} M) was placed in a 10-mL test tube and was carefully deaerated by flushing with N_2 . The test tube was then closed, and into the tube was introduced 1.00 mL of Ar as an internal standard with a syringe through a rubber seal. The tube was irradiated, with ice cooling, with a National RF-110 V 500-W tungsten lamp. A filter to cut off light below 430 nm (Toshiba VY 43) was used. After irradiation a small amount of gas present in the tube was removed by use of a 50- μL microsyringe through a rubber seal, and the amount of hydrogen produced was determined by gas chromatography (Shimadzu GC-3BT) with a molecular sieve 13X column (Yanagimoto MFG Co. Ltd.) with N_2 as carrier gas at room temperature. Control experiments were carried out in a similar manner.

Quantum Yield Determination. The quantum yield was determined for 428 \pm 30-nm irradiation, selected by simultaneous application of a Toshiba T-44 cut off filter and an aqueous crystal violet solution (0.25 mM). A ferrioxalate (0.15 M) chemical actinometer was employed to measure photon quanta.

Emission Spectra. The emission spectra from $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ in nondegassed aqueous solutions were recorded with a Union FS-301 high-sensitivity fluorescence spectrometer. In water were dissolved $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ (3.3×10^{-7} M) and an appropriate quencher

(AsA or MeV^{2+}), and the solution was irradiated at the maximum absorbance of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ (422 nm). The emission intensities were monitored from 550 to 750 nm. No correction was necessary, since MeV^{2+} , AsA, or CTAB shows no appreciable absorption in the visible region. The relative intensities of the emission at 607 nm relative to the $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ emission in the absence of the above quencher (100%) are as follows. In the absence of CTAB: 5×10^{-1} M MeV^{2+} , negligible; 5×10^{-5} M MeV^{2+} , 24; 1×10^{-1} M AsA, 98. In the presence of 3.3×10^{-3} M CTAB: 5×10^{-3} M MeV^{2+} , 75; 1×10^{-1} M AsA, 29.

Reaction of Chemically Generated $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}^{\cdot+}$ with AsA. An aqueous solution of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ (3 mL, 1×10^{-4} M) was rapidly stirred with an excess amount of bromine dissolved in dichloromethane. The violet $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ solution turned to green and the generation of $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}^{\cdot+}$ was confirmed with a broad absorption of 500–750 nm (disappearance at 558 nm) by electronic spectrum. After the addition of 50 μL of 0.1 M AsA to the solution of the cation radical, the color of the solution turned to slightly turbid violet within a few seconds, and $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ was regenerated, judging from the electronic spectrum and other characteristic spectra. From the absorption at 558 nm the amount of regenerated $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ amounted to 90%, based on the $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$ initially used.

Registry No. AsA, 50-81-7; $\text{ZnT}_{\text{SO}_3\text{Na}}\text{PP}$, 42712-11-8; $\text{MeV}^{2+}\text{Cl}_2^-$, 1910-42-5; Pt, 7440-06-4; H_2 , 1333-74-0; $\text{Ru}(\text{bpy})_3^{2+}$, 15158-62-0; $\text{EDTA}\cdot 2\text{Na}^+$, 139-33-3.

1-Pentene Hydroformylation Catalyzed by Polymer-Bound Ruthenium Complexes

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Received October 23, 1980

Polymer-bound ruthenium hydroformylation catalysts were prepared by reacting diphenylphosphinated styrene-1% divinylbenzene resins with $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ under a carbon monoxide atmosphere. Resins with 29% and 5% ring-substitution loading levels of phosphine were prepared, and resins with P/Ru ratios of 3.1, 6.7, and 11.3 were made with the 29% phosphine loading. These resins functioned as 1-pentene hydroformylation catalysts and were compared to the homogeneous use of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ as the catalyst. No olefin isomerization occurred. The resin catalysts with P/Ru ratios of 3.1 and 6.7 at 29% loading gave higher n/b aldehyde selectivities (3.5–3.8) than the homogeneous catalyst when employed at P/Ru ratios of 20 but not as high as was achieved by using $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ in molten PPh_3 (5.1). The n/b selectivity was discussed in terms of the equilibrium between (polymer- PPh_2) $_2\text{RuH}_2(\text{alkene})(\text{CO})$ and polymer- $\text{PPh}_2\text{RuH}_2(\text{alkene})(\text{CO})_2$ within the resin matrix where phosphine loading, P/Ru, ligand mobility, and swelling play contributing roles. The novel 1,1'-bis(diphenylphosphino)ferrocene ligand induced higher n/b selectivities than PPh_3 in homogeneous Ru-catalyzed reactions.

Extensive studies of olefin hydroformylation¹ have been conducted by using cobalt² and rhodium³ complexes as catalysts. Ruthenium complexes have been far less extensively studied.¹ Wilkinson et al. examined the activity of several ruthenium phosphine complexes,⁴⁻⁶ using 1-hexene as the substrate in benzene at 120 °C and 1400 psi. $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$, $\text{RuH}(\text{NO})(\text{PPh}_3)_3$,

and $\text{RuH}_4(\text{PPh}_3)_3$ were found to be effective catalysts. Hexene conversions ranged from 79 to 88% and the normal to branched aldehyde ratios (n/b) varied from 2.0 to 2.9. Products from competing hydrogenation or isomerization reactions (i.e., alkanes, internal alkenes) were not observed. The recovered metallic species in each case was $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, suggesting the same active species could have operated in each case. Wilkinson proposed $\text{RuH}_2(\text{CO})_2\text{PPh}_3$ was the active catalytic species.

We have previously employed polymer-supported cobalt and rhodium complexes for hydroformylation catalysts.⁷⁻¹⁵

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