HYDROGEN FROM WATER: PHOTOCATALYTIC SPLITTING OF WATER WITH VISIBLE LIGHT?

Tom Autrey, Sotiris Xantheas, Liyu, Li, John Linehan, James Franz, Dimitris Katakis, Christiana Mitsopoulou, Zacharias Sofianos, Tom Bitterwolf.

Pacific Northwest National Laboratory
University of Athens
University of Idaho

Introduction

One of the Holy Grails of chemistry is to seek a photo-activated catalyst to split water into H\textsubscript{2} and O\textsubscript{2} using solar spectra\textsuperscript{1}. Significant effort has been undertaken by the scientific community to develop a catalyst that can catalytically split water using visible light with limited success\textsuperscript{2,3,4}. However, one exception may be the homogeneous catalyst, tris-[1-(4methoxyphenyl)-2-phenyl-1,2-ethylenodithiolenic-S,S']tungsten, reported by researchers at the University of Athens.\textsuperscript{5} A unique and highly desirable characteristic of the tris-dithiolene catalyst is its ability to form both hydrogen and oxygen from water without the need to add a consumable (sacrificial) donor.\textsuperscript{6} Water is reduced to hydrogen and oxidized to oxygen in a sequential pathway. The energy storage efficiencies of the tris-dithiolenes have been reported to range between 7-11\%, values approaching the economic break point for solar production of hydrogen. While much work has been reported on the stability and efficiency of the various derivatives and isomers of tris-dithiolenes, little is known about the important steps of the mechanism that leads to hydrogen and oxygen formation. To this end, the understanding of the mechanism for the gas formation will assist in the design of the next generation of PCC’s with the aim in increasing their efficiency.

Experimental

Synthesis and purification of PCC tris-[1-(4methoxyphenyl)-2-phenyl-1,2-ethylenodithiolenic-S,S']tungsten.

Synthesis of the PCC requires a three step two-pot procedure, Scheme 1, starting with the mixed benzoin 4-methoxybenzoin prepared according to literature procedures.\textsuperscript{7} The formation of several isomers is feasible, however in practice only 3 isomers are formed under the reaction conditions with 4-methoxybenzoin the major product (80\%). Two other isomers, the symmetric benzoin from benzaldehyde and the symmetric benzoin from 4-methoxybenzaldehyde compose the remaining balance of the material. The isomers are not isolated in this step because they are easier to separate later on a column as the tungsten complexes.

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The benzoin mixture is placed in a 3-neck round bottom (RB) flask in anhydrous dioxane. Solid P\textsubscript{2}S\textsubscript{5} was added to the dioxane solution and the RB was fitted with an argon degas inlet and reflux condenser. On the reflux condenser a hose barb was connected to Tygon tubing emerged in a solution of lead acetate (PhAc). The reaction was brought to reflux and the H\textsubscript{2}S generated was purged from the reaction solution and trapped by the PhAc. The reaction mixture was filtered through a Buchner funnel (to remove unreacted P\textsubscript{2}S\textsubscript{5}) and the resulting dioxane solution containing the thiophosphate ester is used in the next step. To the reaction mixture above was added a sodium tungstate solution (in 1 N HCl). The reaction flask is fitted with bubbler and refluxed under argon for 2.5 hr converting the red thiophosphate ester to a mixture of green tungsten complexes. After cooling to room temperature the reaction mixture was transferred to a sepratory funnel and the flask rinsed with toluene and added to sepratory funnel. Extraction with toluene yields the tungsten tris-dithiolene complexes. Brine was used to wash the toluene to break up the emulsions formed in the sepratory funnel. The aqueous wash solution no longer turned yellow all tungstate was assumed to be extracted from toluene layer. Rotary-evaporation of toluene provided the tungsten tris-dithiolene complexes for separation on silica column. A small fraction of the tungsten complex mixture from the toluene extraction was dissolved in toluene and added to the silica column for flash separation of various isomers (eluent 70/30 vol/vol cyclohexane/toluene). The third band to elute from the column is the desired unsymmetrical tungsten complex. Generally two other bands are eluted and some unidentified species sticks to the origin. Rotary evaporation of the first band off the column and a final drying under vacuum provides the desired tris-[1-(4methoxyphenyl)-2-phenyl-1,2-ethylenodithiolenic-S,S']tungsten complex as a dark green powder. The unsymmetrical complex does not crystalize like the symmetric complexes.\textsuperscript{8}

Figure 1. Photocatalyst catalyst (PCC) tris-[1-(4methoxyphenyl)-2-phenyl-1,2-ethylenodithiolenic-S,S']tungsten

Scheme 1.

Oxygen Measurements. Oxygen evolved during the irradiation of the PCC is measured by chemical trapping with Cr(II). Under the reaction conditions the PCC solution is constantly purged to remove the oxygen that is formed during irradiation. This can complicate gas analysis because as the sample is purged from the reaction mixture
the gases formed from the catalytic splitting of water become diluted. However, if the oxygen is not removed by the in-situ purging the PCC catalyst will be consumed by the $O_2$ produced. In a typical experiment, the tris-dithiolene tungsten PCC sample ($10^{-5}$ M) and methyl viologen ($10^{-3}$ M) dissolved in a 80/20 v/v acetone/water mixture) is irradiated (>350 nm, 1000 W Xe lamp and continuously purged with acetone saturated nitrogen. The purge gas path is split into two paths with half directed through a control loop composed of double trap containing freshly prepared 0.02 M Cr(II) in 1N HCL and other half of the purge gas is passed through the photolysis sample and before passing through a similar double trap containing the freshly prepared 0.02 M Cr(II). If any oxygen leaks into the system the control loop will account for this background – non-catalytically generated oxygen. Under the reaction conditions the irradiation of the PCC (>350 nm 1000 W Xe lamp) produced $8.4 \times 10^{-7}$ moles $O_2$ in 3.5 hours (or 2 mL $O_2$ gas). The rate of oxygen produced is ca. $0.16 \mu L \ O_2 \ s^{-1}$.

**Hydrogen Measurements.** An in-situ photoreactor (Ace Glass Reaction assembly 7840) equipped with a Gas Chromatography (Varian microGC with TCD) was used to measure the hydrogen gas evolved during irradiation. The PCC/methylviologen sample as described above is irradiated with visible light (>350 nm) using a 450 W medium pressure mercury vapor lamp. Argon carrier gas is sparged through the reaction vessel to continuously extract the hydrogen formed from irradiation of the PCC. The purge gas is sampled by GC (TC detector) at time intervals by opening and closing a computer control valve. The temperature of the reaction vessel can be controlled with a constant temperature recirculation bath. The experimental data is stored on a PC as chromatographs for $H_2$ yield analysis.

**Results and Discussion**

The reports published by the Athens group using the photocatalyst catalyst (PCC) tris-[1-(4methoxyphenyl)-2-phenyl-1,2-ethylenedithiolene-S,S'] tungsten to split water into hydrogen and oxygen gas using visible light and no sacrificial electron donor provide some very seductive observations.

The PCC is stable in the presence of air in the dark, however if the solution is not purged during irradiation the methyl viologen radical cation is formed and the catalyst undergoes decomposition (Figure 2). Current interpretation suggests a ground state complex is formed between the PCC and electrons acceptor methylviologen (MV$^{2+}$), eq. (1). The photo-activated catalyst is believed to be a ground state complex formed between the PCC and methylviologen (MV$^{2+}$). No apparent absorption change has been observed, but this assumption is based upon the 100-fold excess MV$^{2+}$ used in the experiment. The ground state PCC/MV$^{2+}$ complex is believed to absorb the visible light and to yield the active catalyst responsible for the observed photodecomposition of water, eq. (2). The active absorption band is centered around 410 nm, with subtle shifts of a few wave numbers depending on the substituents on the dithiolenic rings. There are two possible `active centers' on the homogeneous catalyst, the metal or the sulfur atoms on the thiolene ligands. Ultraviolet irradiation destroys the catalyst while long wavelength irradiation gives no observable photochemistry. Some initial spectroscopic investigations suggest that the hydrogen gas is formed on a nanosecond time scale and that it may involve one or maybe two water molecules, eqs. (3) & (4). The oxygen gas may be formed in a subsequent bimolecular reaction leading to the regeneration of the active catalyst, eq. (5). The scheme of the proposed mechanism is as follows where M = the PCC catalyst:

$$H_2O \rightarrow M \rightarrow MV^{2+} \rightarrow H_2 + OM + MV^{2+} \rightarrow H_2 + OM + MV^{2+} \rightarrow H_2 + OM + MV^{2+} \rightarrow H_2 + OM + MV^{2+}$$

**Figure 2.** Visible absorption spectra of $10^{-5}$ M PCC, $10^{-5}$ M MV$^{2+}$ complex in 80/20 acetone/water before and after irradiation. The absorbance due to the green PCC complex with an absorbance maximum at 686 nm is replaced by the methylviologen radical cation (MV$^{+}$) complex when the solution is not purged during the irradiation.

The chemical trapping oxygen measurements carried out in Athens are convenient for testing a variety of tris dithiolene metal complexes or various electron acceptors/relay agents, however, a direct measure of hydrogen gas production is highly desirable. With this goal, a direct measure of hydrogen gas and the constraint of constantly removing the oxygen formed under irradiation, an in-situ photoreactor/detector was designed and assembled in the Environmental Molecular Sciences laboratory at PNLL. The reactor couples a photoreaction vessel with a GC detector. Purge gas is constantly swept the vessel and analyzed with a thermal conductivity detector. Figure 3 shows some preliminary results of our efforts to measure $H_2$ gas in-situ. The yield of hydrogen increases with irradiation time to a maximum and levels off. However, and most importantly when the light is turned off the $H_2$ yield drops rapidly to zero. This process was repeated on the subsequent day and the same results were observed, $H_2$ formation under irradiation – no $H_2$ when the light is turned off.

While the tungsten tris-dithiolenes may have the potential to provide a cheap alternative source to platinum there are still some technical challenges to overcome to make the PCC catalyst become economically viable. The catalyst is not soluble without a co solvent. While the organic solvent acetone is not consumed it would be far

![Ground State Spectra of PCC/MV2+](image-url)
Substituted complexes $\text{W}(\text{S}_2\text{C}_2\text{H}_3)\text{S}(\text{S}_2\text{C}_2\text{H}_3\text{HPh})$, $\text{W}(\text{S}_2\text{C}_2\text{H}_3)\text{S}(\text{S}_2\text{C}_2\text{HPhO})$ and $\text{W}(\text{S}_2\text{C}_2\text{HPhO})$ as well as the $\text{MV}^{2-}-\text{W}(\text{S}_2\text{C}_2\text{H}_3)$ complex (Figure 4). The calculations were performed at the HF and DFT (B3LYP) levels of theory. Preliminary computational results suggest that the hydrogen may be formed at the sulfur center adjacent to the tungsten metal.

**Conclusions**

CW Irradiation of the tungsten-tris-dithiolene/methylviologen complex with visible light leads to the formation of H$_2$ gas. Technical issues to overcome are solubility of the catalyst in water or co-solvent and metal impurities that can destroy the tris-dithiolene catalyst. Elucidation of the mechanistic pathways will provide insight into the design of more efficient catalysts. This preliminary work provides a confirmation of the formation of H$_2$ gas from water from visible light irradiation. The water source must be carefully deionized to remove trace metal elements that lead to catalyst poisoning. Photo-induced electron transport mediated through methyl viologen to yield a mixed valence metal dimer complex intermediate ($M^{n+}-\cdots-M^{n-}$) should be considered as a potential active H$_2$ generating species (i.e., PCC$\cdots$MV$\cdots$PCC$^-$). The dithiolene ligand is extensively delocalized in 3-dimensions resulting in a nonplanar (3-dimensional) aromaticity that involves the mixing of sigma and pi bonds. Molecular hydrogen formation either within the dithiolene ligand or at the metal center is possible.

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**References**

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Figure 3. Visible irradiation (>350 nm) of tungsten tris-dithiolene complex/MV2+ complex in aqueous acetone solution. Flow rate argon purge gas 30 mL/min. H$_2$ yield as a function of time measured by GC with a TCD. Light turned off after 12.5 hr irradiation.

Computational Efforts. We have initiated first principles electronic structure calculations on the structures of simply and triply

Figure 4. Lowest energy conformation of tris-1,2-ethylene-dithiolenic –S,S' tungsten methyl viologen complex.