The Photolysis of Bis(cyclopentadienyl)molybdenum Oxide in Water. The Catalytic Production of Hydrogen.

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Prepared for Publication in Angewandte Chemie

Photocatalytic production of hydrogen from water has been a long term goal of inorganic photochemistry. Previous research efforts can be summarized in terms of four methods that will decompose water in hydrogen and oxygen. They include the use of simple metal salts, metal complexes, intermolecular electron transfer with sensitizers, and photoelectrochemical methods. Early studies centered around intermolecular electron transfer with sensitizers although catalytic cycles were difficult to complete because sacrificial agents had to be used to maintain the reaction. The recent application of photoelectrochemical methods offers considerable promise, especially with photosensitive dye containing cells. Complementary use of metal complexes, however, appears to be particularly effective for two reasons: (a) many metal complexes can photocatalyze the decomposition of water; and (b) ligand design offers the potential of modifying metal complexes to achieve catalysis. Nevertheless there are few well characterized metal complexes that will photochemically produce hydrogen from water. We report here the photocatalytic synthesis of hydrogen and peroxide from water by bis(cyclopentadienyl)molybdenum oxide.
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May 15, 1992

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The Photolysis of Bis(cyclopentadienyl)molybdenum Oxide in Water. The Catalytic Production of Hydrogen**


Photocatalytic production of hydrogen from water has been a long term goal of inorganic photochemistry. Previous research efforts can be summarized in terms of four methods that will decompose water into hydrogen and oxygen. They include the use of simple metal salts, metal complexes, intermolecular electron transfer with sensitizers, and photoelectrochemical methods.

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[**] We are thankful to the University of California UERG Fund (WCK, JIZ) The National Science Foundation, Science and Technology Center, Quest (GDS), and the Office of Naval Research (GDS, WCK and JIZ) for partial support of this work. We also thank Professor Glyn Pritchard for use of his high vacuum line and Professor Henry Offen for the use of his photolysis equipment. Discussions with Professor Dr. Dennis Mitchell, Department of Chemistry, Los Angeles City College, and Dr. Hermann A. Mayer, Anorganische Chemische Institute, University of Tubingen, are greatly appreciated.
Early studies centered around intermolecular electron transfer with sensitzers\textsuperscript{[1n]} although catalytic cycles were difficult to complete because sacrificial agents had to be used to maintain the reaction. The recent application of photoelectrochemical methods offers considerable promise, especially with photosensitive dye containing cells\textsuperscript{[1u]}. Complementary use of metal complexes,\textsuperscript{[1s]} however, appears to be particularly effective for two reasons a) many metal complexes can photocatalyze the decomposition of water and b) ligand design offers the potential of modifying metal complexes to achieve catalysis. Nevertheless there are few well characterized metal complexes that will photochemically produce hydrogen from water\textsuperscript{[1s]}. We report here the photocatalytic synthesis of hydrogen and peroxide from water by bis(cyclopentadienyl)molybdenum oxide.\textsuperscript{[2a,b]}

Continuous irradiation of \((\text{C}_5\text{H}_5)_2\text{Mo}=\text{O}\) in water with a 450 W medium mercury pressure lamp gives hydrogen gas and peroxide. No oxygen gas can be detected during the photolysis\textsuperscript{[3]} which is very unusual since irradiation of the complex in strictly organic solvents gives considerable oxygen gas.\textsuperscript{[2a]}

The mole ratio of hydrogen produced during photolysis to \(\text{C}_2\text{Mo}=\text{O}\) is greater than one, hence the molybdenum system behaves as a catalyst. A T.O. of approximately 2 is observed after 81 hr of photolysis or T.O./hr= 0.02. During the photolysis, a brown red solid, \([\text{C}_2\text{Mo}(\text{O})_2\text{Mo}(\text{O})_2]_2\)\textsuperscript{[4]} slowly deposits, which was identified by infrared comparison with an authentic sample. When the deposited solid was separated from the original photolysis solution, washed with freshly degassed water and re-suspended in degassed water, hydrogen production continued at a reduced rate. An authentic sample suspended in water did not produce hydrogen gas, however. In order to trace the oxygen atom presence, the photolysis of \(\text{C}_2\text{Mo}=\text{O}\) in 95\% \(\text{H}_2^{18}\text{O}\) was studied. Collection of the gas above the reaction mixture after 4 hr of photolysis with a 1000 W mercury lamp showed only the presence of hydrogen. No \(^{18}\text{O}_2\) above the background was detected in the mass spectrometer.\textsuperscript{[5]} This suggests that \(\text{H}^+\) is reduced to \(\text{H}\) in the photolysis process and the oxygen atom in water is oxidized from
the -2 state to the -1 state. Thus hydrogen appears as $\text{H}_2$ gas and oxygen as $\text{H}_2\text{O}_2$ or $\text{OOH}^-$.[6,7,8] Photolysis of specific polyoxomolybdates and tungstates can generate species that will give peroxide.[9] Evidently the peroxide species slowly degrades the catalyst. To test this hypothesis, $\text{Me}_3\text{P}$ was added to the photolysis mixture to scavenge the peroxide and thus prevent destruction of the $\text{Cp}_2\text{Mo}=\text{O}.\text{H}_2\text{O}$.[2a] Photolysis proceeded for 12 hr with a total production of 90 μ moles of hydrogen from 45 μ moles of catalyst with a T.O. of 2 and a T.O./hr of 0.16 which is ten times the previous result without the addition of $\text{Me}_3\text{P}$. The $\text{Me}_3\text{P}=\text{O}$ formed was identified by $^{31}\text{P}$ NMR and $^1\text{NMR}$ spectroscopy,[10] The following diagram depicts the essential parts of the reaction,

insert Scheme 1


[3] The mass spectra were measured with a fabricated quadruple mass spectrometer which used an Auxum monitoring system. Most mass spectrometers have a high m/e=2 background. Hence only measurements with internal standards are reliable measurements of H₂, or He. The measured m/e ratios were extrapolated to zero time of sample because of the large discrimination introduced by preferential
pumping of H₂ under molecular flow[7]


[5] Reactions performed in D₂O showed only D₂ gas. In order to trace the oxygen atom an IR analysis was made of the red-brown solid which precipitated during the photolysis. The material prepared according to the literature[4] and the material collected from the photolysis compared exactly by infrared. The sample prepared in H₂¹⁸O showed ν Mo=O bonds at 701 735, 611, 641 compared to 913 and 868 cm⁻¹. This suggests that the oxygen atom may remain attached to the molybdenum during the photolysis and cause catalyst degradation.


[8] The exact nature of Cp₂Mo=O in water is not clear, although it may well be as 
Cp₂Mo(OH)⁺OH⁻ since the pH of the compound in water is 9. Previous work has shown that Cp₂MoCl₂ undergoes rapid chloride aquation in water with no M-C₃H₅ protonolysis over weeks at pH 7.6[9]


[10] The presence of hydrogen peroxide or metal peroxo species in water photolysis is known[12,13,14]

[11] The ³¹P chemical shift of Me₃P=O was observed at +55.1 ppm in the D₂O sample. An authentic sample of Me₃P in D₂O showed a resonance at δ -62. [15] When O₂ was introduced and the sample allowed to stand, the δ -62 peak disappeared and a peak at δ +55.1 appeared.[16] In organic solvents the δ of Me₃P=O is 36.2 and in MeOH it is at + 45.4 ppm. The chemical shift of Me₃P in D₂O with a trace of H₂O₂ showed a peak at δ +55.1.

Experimental Procedure. A pale pink water (D$_2$O) solution (degassed) four times by freeze thaw methods before photolysis) of Cp$_2$Mo=O, 45 µ moles, was photolyzed for a total of 81 hr by placing the sample in an evacuated quartz tube in the beam of a 450 W Medium pressure mercury lamp. A total of 69.53 µ moles of hydrogen gas was collected from the reaction system by Toepler pumping every four hr. The reaction vessel was cooled in liquid nitrogen and the evolved gas was passed through a liquid nitrogen cooled trap. The gas was measured three times in a calibrated volume at three different pressures to check for homogeneity. An average of the three values was used in calculating the total amount of gas evolved. The turn over frequency of 1.54 or approximately 2 with a T.O./hr of 0.02 is observed. Blank experiments of Cp$_2$Mo=O in D$_2$O without photolysis gave no D$_2$ gas. D$_2$O without the presence of Cp$_2$Mo=O also gave no D$_2$ gas after photolysis.
Reason for Submitting this report as a Rapid Communication to Angewandte Chemie

Oil and coal have been the most dominant fuels for society for more than a century and a half. Both of these materials have their limitations in terms of decreasing availability and environmental concerns. In recent years, the ability to handle and use hydrogen as a fuel has increased greatly. What remains is to find a cheap reliable source for hydrogen from the abundant raw material, water. Inorganic photocatalysis with transition metal complexes has been a major focus of research for making new materials that will accelerate the generation of hydrogen from water. In this paper we report an instance where catalytic synthesis of hydrogen from water with the assistance of a well defined organometallic complex with no sacrificial donors. Only one metal atom is used for the formation of hydrogen and peroxide. Very few well defined single molecular systems are known to photolytically effect the cleavage of water. This special molecular oxide which photochemically releases oxygen in organic solvents and then changes its behavior by releasing hydrogen in water is a system that warrants further development. As such it represents an instance of general technical interest. Therefore we submit it for consideration as a publication in Angewandte Chemie.
Scheme 1

Cp₂Mo=O H₂O

hv

H₂

Cp₂Mo peroxide

peroxide
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