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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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**R.J. Flesher, C. Creaser, V.I. Srdanov, G.D. Stucky  
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**The Photolysis of Bis(cyclopentadienyl)molybdenum Oxide in Water. The  
Catalytic Production of Hydrogen\*\***

By Robert J. Flesher\*, Colin Creaser<sup>≠</sup>, Vojislav I. Srdanov\*, Galen D. Stucky\*, Jeffrey  
I. Zink\* William C. Kaska\*

Photocatalytic production of hydrogen from water has been a long term goal of inorganic photochemistry<sup>[1a-z]</sup>. 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<sup>[1a,d,h]</sup>, metal complexes<sup>[1a,b,m]</sup>, intermolecular electron transfer with sensitizers<sup>[1a,z]</sup>, and photoelectrochemical<sup>[1u]</sup> methods.

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Early studies centered around intermolecular electron transfer with sensitizers<sup>[1a]</sup> 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<sup>[1a]</sup>. Complementary use of metal complexes,<sup>[12]</sup> 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<sup>[1a]</sup>. We report here the photocatalytic synthesis of hydrogen and peroxide from water by bis(cyclopentadienyl)molybdenum oxide.<sup>[2a,b]</sup>

Continuous irradiation of  $(C_5H_5)_2Mo=O$  in water with a 450 W medium mercury pressure lamp gives hydrogen gas and peroxide. No oxygen gas can be detected during the photolysis<sup>[3]</sup> which is very unusual since irradiation of the complex in strictly organic solvents gives considerable oxygen gas.<sup>[2a]</sup>

The mole ratio of hydrogen produced during photolysis to  $Cp_2Mo=O$  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,  $[Cp_2Mo(O)_2Mo(O)_2]_2$ ,<sup>[4]</sup> 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  $Cp_2Mo=O$  in 95%  $H_2^{18}O$  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  $^{18}O_2$  above the background was detected in the mass spectrometer.<sup>[5]</sup> This suggests that  $H^+$  is reduced to 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 H<sub>2</sub> gas and oxygen as H<sub>2</sub>O<sub>2</sub> or OOH<sup>-</sup>.<sup>[6,7,8]</sup> Photolysis of specific polyoxomolybdates and tungstates can generate species that will give peroxide.<sup>[9]</sup> Evidently the peroxide species slowly degrades the catalyst. To test this hypothesis, Me<sub>3</sub>P was added to the photolysis mixture to scavenge the peroxide and thus prevent destruction of the Cp<sub>2</sub>Mo=O.H<sub>2</sub>O.<sup>[2a]</sup> 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 with out the addition of Me<sub>3</sub>P. The Me<sub>3</sub>P=O formed was identified by <sup>31</sup>P NMR and <sup>1</sup>H NMR spectroscopy,<sup>[10]</sup> The following diagram depicts the essential parts of the reaction,

insert Scheme 1

- [1] a) D. J. Cole-Hamilton, D.W. Bruce, in Comprehensive Coordination Chemistry, (Ed. G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon Press, 1987, 6, p.487, and references therein. This is a description of water splitting; b) U. Kolle, M. Gratzel, Angew. Chem. Int. Ed. Engl. 1987, 26, 567; c) T. Ymase, T. Kawa, Inorg. Chem. Acta. 1980, 45, L 55; d) S. Leutwyler, E. Schumacher, Chimia, 1977, 31, 475; e) A. Harriman, J. Chem. Soc. Faraday Trans. 2 1986, 2267; f) P. A. Jacobs, J. B. Uytterhoevan, H.B. Beyer, J. Chem. Soc. Chem. Comm. 1977, 128; g) A. Harriman, G. Porter, J. Chem. Soc. Faraday Trans. 2 1982, 78, 1937; h) K. Tennakone, A. H. Jayatissa, W. Wijerantne, J. Chem. Soc. Chem. Comm. 1988, 497; i) K. Sayama, A. Tanaka, K. Domen, K. Maruya, T. Ohishi, J. Phys. Chem. 1991, 95, 1345; j) G. Gard, T. L. Brown, J. Am. Chem. Soc. 1982, 104, 6340; k) G. Calzaferri, L. Forss, W. Sphani, Chemie in Unser Zeit, 1987, 21, 161; l) J. R. Darwent, M. D. Douglas, A. Harriman, G. Porter, M-C Richaux, Coord. Chem., Rev., 1982, 44, 83; m) L. Salsini, M. Pasquali, M. Zandomenighi, C. Festa, P. Leoni, D. Braga, P. Sabatino, J. Chem. Soc. Dalton Trans. 1990, 2007; n) J. M. Lehn, J.P. Sauvage, R. Zissel, Nouveau J. de Chemie, 1980, 4, 355; o) K. Sakai, K. Matsumoto, J. Mol. Catalysis 1990, 62, 1, and references therein; p) E.

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- [2] a) N. D. Silawe, M.Y. Chiang, D. R. Tyler, Inorg. Chem. 1985, 24, 4219; Photolysis of  $Cp_2Mo=O$  in organic solvents with various phosphines gives no  $R_3P=O$ ; b) N. D. Silawe, M. R. M. Bruce, C. E. Philbin, D. R. Tyler, Inorg. Chem. 1988, 27, 4669; c) M. L. H. Green, A. H. Lynch, M. G. Swanwick, J. Chem.Soc. Dalton Trans. 1972, 1445.
- [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  $H_2$ , or He. The measured  $m/e$  ratios were extrapolated to zero time of sample because of the large discrimination introduced by preferential

pumping of H<sub>2</sub> under molecular flow<sup>[7]</sup>

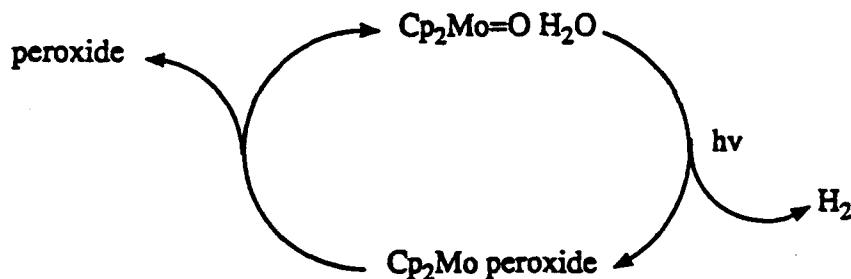
- [4] G. J. S. Adam, M. L. H. Green, J. Organomet. Chem. 1981, 208, 299.
- [5] Reactions performed in D<sub>2</sub>O showed only D<sub>2</sub> gas. In order to trace the oxygen atom an IR analysis was made of the red-brown solid which precipitated during the photolysis. The material prepared according to the literature<sup>[4]</sup> and the material collected from the photolysis compared exactly by infrared. The sample prepared in H<sub>2</sub><sup>18</sup>O showed  $\nu$  Mo=O bonds at 701 735, 611, 641 compared to 913 and 868 cm<sup>-1</sup>. This suggests that the oxygen atom may remain attached to the molybdenum during the photolysis and cause catalyst degradation.
- [6] a) E. Papaconstantinou, Chem. Soc. Rev., 1989, 18, 1; b) T. Yamase, Inorganica Chimica Acta. 1981, 54 L165; c) *ibid*; 1982, 64, L155; d) B. Kraut, G. Ferraudi, J. Chem. Soc. Dalton Trans. 1991, 2063.
- [7] S. Leutwyler, E. Schumacher, Chimia 1977, 31, 475.
- [8] The exact nature of Cp<sub>2</sub>Mo=O in water is not clear, although it may well be as Cp<sub>2</sub>Mo(OH)<sup>+</sup>OH<sup>-</sup> since the pH of the compound in water is 9. Previous work has shown that Cp<sub>2</sub>MoCl<sub>2</sub> undergoes rapid chloride aquation in water with no M-C<sub>3</sub>H<sub>5</sub> protonolysis over weeks at pH 7.6<sup>[9]</sup>
- [9] L. Y. Kuo, M. G. Kanatzidis, T. J. Marks, J. Am. Chem. Soc., 1987, 109, 57
- [10] The presence of hydrogen peroxide or metal peroxo species in water photolysis is known<sup>[12,13,14]</sup>
- [11] The <sup>31</sup>P chemical shift of Me<sub>3</sub>P=O was observed at +55.1 ppm in the D<sub>2</sub>O sample. An authentic sample of Me<sub>3</sub>P in D<sub>2</sub>O showed a resonance at  $\delta$  -62. <sup>[15]</sup> When O<sub>2</sub> was introduced and the sample allowed to stand, the  $\delta$  -62 peak disappeared and a peak at  $\delta$  +55.1 appeared.<sup>[16]</sup> In organic solvents the  $\delta$  of Me<sub>3</sub>P=O is 36.2 and in MeOH it is at + 45.4 ppm. The chemical shift of Me<sub>3</sub>P in D<sub>2</sub>O with a trace of H<sub>2</sub>O<sub>2</sub> showed a peak at  $\delta$  + 55.1.
- [12] a) K. Kalyanasundaram, M. Gratzel, E. Pellizzeti, Coord. Chem. Rev. 1986, 69, 57;

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- [15] Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis, (Ed. J. G. Verkade, L. D. Quin), 1987 VCH, Inc. Florida, USA.
- [16] F. Seel, H. J. Bassler, Z. Anorg. Allg. Chemie 1976, 423, 67.
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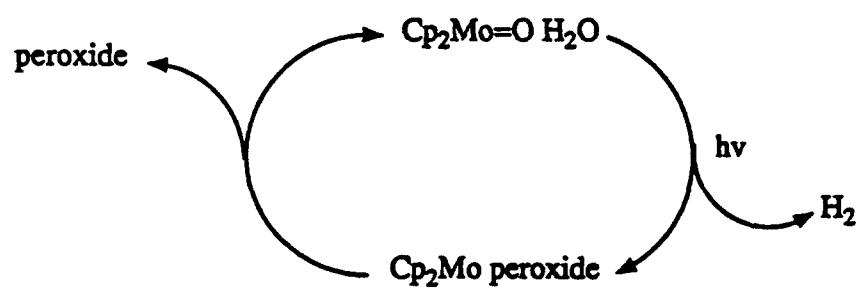
*Experimental Procedure.* A pale pink water ( $D_2O$ ) solution (degassed) four times by freeze thaw methods before photolysis) of  $Cp_2Mo=O$ , 45  $\mu$  moles, was photolyzed for a total of 81 hr by placing the sample in an evacuated quartz tube in the beam of a 450 W Medium pressure mercury lamp. A total of 69.53  $\mu$  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  $Cp_2Mo=O$  in  $D_2O$  without photolysis gave no  $D_2$  gas.  $D_2O$  without the presence of  $Cp_2Mo=O$  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

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