Photochemical Water Splitting: Inorganic Dyes as Catalytic Sensitizers.

Edward B. Flint Literature Seminar March 14, 1985

Since the majority of today's energy demands are met by nonrenewable resources, interest in solar energy has been increasing. However, there are many problems associated with sunlight as an energy source. Conversion of visible light into storable energy occurs in plants as photosynthesis, but has proven difficult in artificial systems. Many chemical and physical transformations have been tested as energy storage processes, including semiconductors (solar cells), biomass and chemical reactions.¹ One of the reactions being considered is the splitting of water.

 $H_2 0 \longrightarrow H_2 + 1/2 0_2 \Delta G = 57 \text{ kcal/mol}$

A system that produces H_2 from water upon irradiation with visible light developed by Moradpour and co-workers² as an approach to water splitting is depicted in scheme 1. The





sensitizer in this system is $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}(\operatorname{bpy}=2,2'-\operatorname{bipyridine})$, the excited state of which is capable of reducing methylviologen, $(\operatorname{MV}^{2^+})$, to its monocation radical, MV^+ $(\operatorname{MV}^{2^+}=1,1'-\operatorname{dimethyl}-4,4'-\operatorname{dipyridinum}$ dication). MV^+ can react with protons on a colloidial platinum catalyst to produce H₂. The exothermic back reaction of MV and Ru(bpy)₃^{3^+} is prevented by an excess of EDTA, which rereduces the rutheneium (III) complex. This is an example of a sacrificial system since EDTA is consumed as H₂ is produced.

This sacrificial system demonstrates some of the important factors to be considered in the design of water splitting systems. The sensitizer should absorb over a significant region of the visible spectrum so as much energy as possible is captured. The lifetime of the excited state should be long enough to allow efficient quenching by the electron relay. The electron relay should be stable in the presence of the catalyst, and the cage escape quantum yield, the ratio of quenching of the sensitizer excited state to the rate of production of the reduced electron relay, should be high so as little energy as possible is wasted.

The visible absorbance of $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$ is adequate, but the excited state lifetime is only on the order of 1 usec³ at room temperature. This short lifetime dictates that high quencher concentrations be used so production of MV. is efficient.⁴ Methylviologen is reduced in the presence of some catalysts,⁵ obviously an unwanted side reaction. Finally, the cage escape quantum yield for the Ru(bpy)₃^{3*}/MV. Couple has been determined to be 0.25,⁶ which becomes an upper limit on the efficiency of this system. These considerations have led to the development of new sensitizers, electron transfer agents⁷ and catalysts.⁸

The water soluble porphyrin zinc tetrakis(4-methylpyridyl)porphyrin, $(ZnTMPyP^{+})$, has been used as the sensitizer in a similar H₂ producing system.⁹ The yield of H₂ produced per photon absorbed is improved in this system compared to the ruthenium system for several reasons. The longer lifetime of the excited state, 665 usec vs 1 usec, improves the quenching efficiency, and the improved cage escape efficiency, equal to almost one in this case, means that every absorbed photon results in a reduced MV in solution. The catalyst used in this study was not the best, so the maximum possible efficiency was not obtained.

Sasse and Mau^{10} introduced another modification to this system that improved the yield of H_2 by increasing the cage escape efficiency. In this case an energy transfer step is added between the excited state sensitizer and the electron carrier, as shown in scheme 2. The 9-anthracenecarboxylate anion, (AC), can



Scheme 2

quench the excited state of $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$ via energy transfer¹¹ and then, in the excited state reduce, methylviologen. The cage escape yield of AC approaches one with both the sensitizer and the electron relay. A copper (1) complex $\operatorname{Cu}(\operatorname{dpp})_2$ (dpp = 2,9diphenyl 1,10 phenanthroline)¹² can also be used as the sensitizer in this scheme; it has a much broader absorbance in the visible then $\operatorname{Ru}(\operatorname{bpy})_3^2^+$, which improves efficiency. The major disadvantage of the energy transfer process is its increased complexity: the added components are not stable in the presence of the catalyst. While these systems are valuable in finding useful components for the reduction of water their limited utility must be kept in mind: sacrificial oxidants are being used irreversibly. Water splitting developed by Gratzel and coworkers¹³ which utilizes the technology developed in the sacrificial systems is illustrated in scheme 3. The H_2 is produced in a similar fash-



ion as in the systems described above, but with platinum deposited on colloidial TiO_2 as the catalyst. The O_2 is produced by the reaction of $Ru(bpy)_3^{3+}$, the complex after quenching, with water at RuO_2 deposited on colloidial TiO_2 . Since this step is a four electron process it is kinetically limiting, and significant back reaction occurs between MV⁺ and $Ru(bpy)_3^{3+}$. Hydrogen and oxygen are produced for about 20 hours during continuous irradiation, but production stops due to the competing reaction of O_2 with MV⁺ and the degradation of other components. The catalytic components in this scheme are not stable in the presence of the products.

A significant observation about this system is that H_2 and O_2 were produced in the absence of electron relay, ^{13C} although at reduced yields. The mechanism proposed to explain this involves sensitizer molecules absorbed to the TiO₂ (or within a diffusion radius) that donate electrons directly into the conduction band of the TiO₂, that was developed to explain the photosensitization¹⁴ of electrodes by dyes. This is significant in light of the undesireable reaction of O_2 with MV⁺.

References

- a) C. Kutal "Photochemical Conversion and Storage of Solar Energy" J. Chem. Ed. 1983, 60, 882-7.
 - b) "Photochemical Conversion and Storage of Solar Energy," Connolly, J. S. (ed.) Academic Press, New York, 1981.
- P. Keller, A. Moradpour, E. Amouyal, H. Kagan "Hydrogen Production by Visible-Light using Viologen-Dye Mediated Redox Cycles" <u>Nouv. J. Chim. 1980</u>, 4, 377-84.

- 3) O. Johansen, A. Launikonis, A. W.-H. Mau, W. H. F. Sasse "Light-Induced Electron-Transfer Reactions Involving the Tris(2,2'-bipyridine)ruthenium Dication and Related Complexes 1." Aust. J. Chem. <u>1980</u>, 33, 1643-8.
- 4) E. Amouyal, B. Zidler, P. Keller, A. Moradpour "Excited State Electron-Transfer Quenching by a Series of Water Photoreduction Mediators." Chem. Phys. Letts. <u>1980</u>, 74, 314-7.
- 5) O. Johansen, A. Launikonis, J. W. Loder, A. W.-H. Mau, W. H. F. Sasse, J. D. Swift, D. Wells "Solar Reduction of Water 1." Aust. J. Chem. <u>1981</u>, 34, 981-91.
- 6) S.-F. Chan, M. Chou, C. Creutz, T. Matsubara, N. Sutin. "Mechanism of the Formation of Dihydrogen from the Photoinduced Reactions of Poly(pyridine)ruthenium(II) and Poly-(pyridine) rhodium(III) Complexes" J. Amer. Chem. Soc. <u>1981</u>, 103, 369-79.
- 7) P. A. Lay, A. W.-H. Mau, W. H. F. Sasse, I. I. Creaser, L. R. Gahan, A. M. Sargeson. "Cobalt Cage Complexes as Electron-Transfer Agents in the Photoreduction of Water. <u>Inorg. Chem.</u> <u>1983</u>, <u>22</u>, 2347-9.
- 8) a) I. Okura, S. Nakamura, N. Kim-Thuan, K.-I. Nakamura. "Kinetics and Mechanism of Methyl Viologen Reduction and Hydrogen Generation by Visible Light with Tris(2,2'bipyridine)ruthenium Dication." J. Mol. Catal. <u>1979</u>, 6, 261-7.
 - b) P.-A. Brugger, P. Cuendet, M. Gratzel. "Ultrafine and Specific Catalysts Affording Efficient Hydrogen Evolution from Water under Visible Light Illumination." J. Amer. Chem. Soc. <u>1981</u>, 103, 2923-7.
- 9) A. Harriman, G. Porter, M.-C. Richoux "Photosensitized Reduction of Water to Hydrogen using Water-soluble Zinc Porphyrins" J. Chem. Soc. Faraday Trans. <u>1981</u>, 77, 833-44.
- 10) O. Johansen, A. W.-H. Mau, W. H. F. Sasse "Highly Efficient Photoreduction of Water using Energy Transfer." <u>Chem. Phys.</u> Letts. <u>1983</u>, 94, 113-7.
- 11) O. Johansen, A. W.-H. Mau, W. H. F. Sasse "The 9-Anthracene carboxylate Anion as a Sensitizer for the Photoreduction of Water" Chem. Phys. Letts. <u>1983</u>, 94, 107-12.
- 12) A. Edel, P. A. Marnot, J. P. Sauvage "Photochemical Reduction of Water via Energy Transfer from a Copper(I) Complex." Nouv. J. Chim. <u>1984</u>, 8, 495-9.
- 13) a) J. Kiwi, M. Gratzel "Colloidal Redox Catalysts for Evolution of Oxygen and for Light Induced Evolution of Hydrogen from Water" <u>Angew. Chem. Intl. Ed. 1979</u>, <u>18</u>, 624-6.

- b) J. Kiwi, E. Borgarello, E. Pelizzetti, M. Visca, M. Gratzel "Cyclic Water Cleavage by Visible Light: Drastic Improvements of Yield of H₂ and O₂ with Bifunctional Redox Catalysts." Angew. Chem. Intl. Ed. <u>1980</u>, 19, 646-8.
- c) E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca, M. Gratzel. "Sustained Water Cleavage by Visible Light" J. Amer. Chem. Soc. <u>1981</u>, 103, 6324-9.
- 14) A. Vante, V. Ern, P. Chartier, O. Dietrich-Buchecker, D. McMillin, P. Marnot, J. P. Sauvage. "Spectral Sensitization of Semiconductors by Copper(I) Complexes in Photoelectrochemical Systems." Nouv. J. Chim. 1983, 7, 3-5.

1