Photochemical Water Splitting: Inorganic Dyes as Catalytic Sensitizers.

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Since the majority of today's energy demands are met by non-renewable 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. One of the reactions being considered is the splitting of water.

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \quad \Delta G = 57 \text{ kcal/mol} \]

A system that produces \( \text{H}_2 \) from water upon irradiation with visible light developed by Moradpour and co-workers as an approach to water splitting is depicted in scheme 1. The sensitizing agent in this system is \( \text{Ru(bpy)}_3^{2+} \) (bpy=2,2'-bipyridine), the excited state of which is capable of reducing methylviologen, \( \text{MV}^{2+} \), to its monocation radical, \( \text{MV}^+ \). \( \text{MV}^+ \) can react with protons on a colloidal platinum catalyst to produce \( \text{H}_2 \). The exothermic back reaction of \( \text{MV}^+ \) and \( \text{Ru(bpy)}_3^{3+} \) is prevented by an excess of EDTA, which re-reduces the ruthenium (III) complex. This is an example of a sacrificial system since EDTA is consumed as \( \text{H}_2 \) is produced.

This sacrificial system demonstrates some of the important factors to be considered in the design of water splitting systems. The sensitizing agent 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 Ru(bpy)$_3^{2+}$ is adequate, but the excited state lifetime is only on the order of 1 usec at room temperature. This short lifetime dictates that high quencher concentrations be used so production of MV$^+$ is efficient. Methylviologen is reduced in the presence of some catalysts, obviously an unwanted side reaction. Finally, the cage escape quantum yield for the Ru(bpy)$_3^{2+}$/MV$^+$. Couple has been determined to be 0.25, which becomes an upper limit on the efficiency of this system. These considerations have led to the development of new sensitizers, electron transfer agents and catalysts.

The water soluble porphyrin zinc tetrakis(4-methylpyridyl)porphyrin, (ZnTMPyP$^{4+}$), has been used as the sensitizer in a similar H$_2$ producing system. The yield of H$_2$ 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 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 quench the excited state of Ru(bpy)$_3^{2+}$ via energy transfer 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 (I) complex Cu(dpp)$_2$ (dpp = 2,9-diphenyl 1,10 phenanthroline) can also be used as the sensitizer in this scheme; it has a much broader absorbance in the visible then Ru(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 coworkers\textsuperscript{13} which utilizes the technology developed in the sacrificial systems is illustrated in scheme 3. The $\text{H}_2$ is produced in a similar fashion as in the systems described above, but with platinum deposited on colloidal $\text{TiO}_2$ as the catalyst. The $\text{O}_2$ is produced by the reaction of $\text{Ru(bpy)}_3^{2+}$, the complex after quenching, with water at $\text{RuO}_2$ deposited on colloidal $\text{TiO}_2$. Since this step is a four electron process it is kinetically limiting, and significant back reaction occurs between $\text{MV}^+$ and $\text{Ru(bpy)}_3^{3+}$. Hydrogen and oxygen are produced for about 20 hours during continuous irradiation but production stops due to the competing reaction of $\text{O}_2$ with $\text{MV}^+$ 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 $\text{H}_2$ and $\text{O}_2$ were produced in the absence of electron relay,\textsuperscript{13C} although at reduced yields. The mechanism proposed to explain this involves sensitizer molecules absorbed to the $\text{TiO}_2$ (or within a diffusion radius) that donate electrons directly into the conduction band of the $\text{TiO}_2$, that was developed to explain the photosensitization\textsuperscript{14} of electrodes by dyes. This is significant in light of the undesirable reaction of $\text{O}_2$ with $\text{MV}^+$.

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