

RECENT DEVELOPMENTS IN PHOTOCHEMICAL H₂ PRODUCTION
FROM AQUEOUS SOLUTIONS OF TRANSITION METAL IONS

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Current sources of useful energy are becoming increasingly unreliable. Many systems have been proposed to convert available energy to a more practical form. One promising choice is the conversion of sunlight to a storable form of chemical energy such as H₂.

For many years several aqueous metal solutions (Fe²⁺, Cr²⁺, Ce³⁺, Cu⁺) have been known to produce hydrogen from water upon irradiation by light [1]. In their present state, however, none of these systems are adequate since all require the use of ultraviolet light which does not penetrate the earth's atmosphere. In addition, once oxidized, the majority of metal ions become incapable of further activity until they are reduced (chemically or electrochemically). Recently, research in this area has increased, with a particular emphasis towards understanding the mechanisms of these potential hydrogen producing catalysts and thus finding ways to modify the conditions needed for efficient absorption of solar radiation. These systems may be broken down into several classes: solvated electron formation, production of metal hydrides, and polynuclear metal systems.

Chromium(II) has been found to produce H₂ and Cr³⁺ when irradiated with UV light. Ryan and Espenson [2] demonstrated that a solvated electron was generated during the photo-induced step which quickly reacted with H⁺(H₂O) to give a hydrogen atom. Subsequent reaction with Cr²⁺ yields CrH²⁺ which breaks down in acid to yield H₂. Unfortunately, this process neither uses available sunlight nor allows the Cr²⁺ to be regenerated. Hence, this system is only of interest mechanistically.

Sakharovskii [3-5] determined that Co(CN)₅³⁻ will also produce H₂ in UV light. A probable mechanism was proposed involving formation of a hydride, but very little is known about this reaction. An encouraging discovery was that the resulting Co(III) product could also be reconverted to Co(CN)₅³⁻ upon irradiation by UV light, although the results are far from clear [6].

A solution of HCl may be converted to H₂ and Cl₂ when irradiated with 254 nm light in the presence of IrCl₆³⁻ [7]. This is an example of a true cyclic process. While there is disagreement concerning the mechanism [8], the results are promising. Gray suggests that the use of IrBr₆³⁻ might allow the use of longer wavelengths during irradiation.

Some polynuclear metal systems may be the best answer to the photochemical production of hydrogen [9]. Their ability to maintain several different oxidation states and their low-lying excited states may allow a higher quantum yield of hydrogen. Mo₂Cl₈⁴⁻, which supposedly generates H₂ by a ligand to metal charge transfer

(LMCT) transition [10], has stirred interest since the LMCT transition usually requires less energy than a transition involving the production of a solvated electron (CTTS).

Polymolybdates demonstrate a photogalvanic effect. [11-13]. Upon irradiation by UV light, $[\text{NH}_3\text{Pr}]_6[\text{Mo}_7\text{O}_{24}]$ is converted to a mixed oxidation state containing one Mo(V) center. The resulting half-cell between this species and $\text{Mo}_7\text{O}_{24}^{6-}$ has a large enough potential to reduce H^+ at a platinum electrode. Polytungstates have been found to exhibit this same effect [14], with the added benefit that the required energy of irradiation is less than for the polymolybdates.

While it must be pointed out that none of these systems are as yet workable, progress is being made. The wavelengths of light required still need to be increased to match the available solar spectrum, and the quantum yields obtained so far must be increased. By using different ligands and/or modifying the metal centers, truly photocatalytic splitting of water should become possible.

References

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