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EVALUATION OF THE PHOTOCHEMICAL PRODUCTION OF HYDROGEN FROM SOLAR ENERGY

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ABSTRACT

We have investigated the potential for utilizing solar energy through photochemical storage. Both water and nitrosyl chloride systems are examined. A comprehensive review of the literature led us to conclude that many major questions must be answered before photochemical energy storage becomes a viable alternate means of exploiting solar energy.

INTRODUCTION

This project was initiated to explore the potential for future utilization of solar energy through photochemical storage. The principle involved in the photochemical energy storage and utilization is straightforward. Light quanta are used as the energy source and chemically stable substances are dissociated or modified to either directly release or store energy in their chemical bonds. Compounds with high bond energies then may be reacted in a controlled fashion to release the energy stored in the bonds. A chemically "closed" system may be conceived in which no reactant or product loss is incurred. The product of a photochemical reaction may serve as a reactant that can be used in the eventual regeneration of the starting compounds. Such a photochemical system offers the advantage that, after the system is operating, energy would be gained essentially without cost (discounting maintenance and any natural degradation inherent in chemical systems). With gaseous or liquid reaction products, photochemical energy utilization could offer mobile energy generation and storage capabilities. Consequently, the energy loss normally sustained in, for example, wire transmission or storage batteries, would be eliminated.

Among the candidates for photolysis reactants, water appears to be an ideal choice. Water is inexpensive, a major resource (even in many underdeveloped nations), and has an enthalpy of 57.80 kcal/mol. This quantity of heat generated per mole of reactant is easily large enough to power a boiler or fuel cell system. Unfortunately, the maximum wavelength of light that can dissociate water is in the near ultra-violet (4000 Å). Less than 5% of the sunlight reaching the earth's surface contains its energy in wavelengths shorter than 4000 Å (see Figs. 1 and 2). The lack of sufficiently energetic photons has caused difficulties that have plagued past researchers who have attempted to photodecompose water with sunlight.

MASTER

Fig. 1. Spectral distribution of sunlight reaching earth's surface showing the maximum wavelength that will cause dissociation of water (4000 Å, 3.01 eV). (Solid curve is the solar energy distribution outside the atmosphere, dashed curve is the solar energy distribution at the earth's surface.)

Fig. 2. Fractional solar energy corresponding to various wavelengths and the maximum percentage of solar energy available at 4000 Å, the wavelength needed to photodecompose water.

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PHOTODECOMPOSITION OF WATER

Fujishima and Honda

A scheme for the photodecomposition of water was developed by the Japanese chemists, A. Fujishima and K. Honda.¹ They described the successful photodecomposition of water into hydrogen and oxygen using a sealed titanium dioxide semiconductor anode irradiated by a 500-W xenon lamp. They hypothesized that the decomposition reaction was propagated by the creation of holes in the semiconductor, reducing the free energy of oxygen evolution to below that of hydrogen production. The overall reaction is written as

Although the system successfully photolyzed water, it essentially was nothing more than a variation of electrolysis where the electric current was photoelectric in origin. This method not only inherited many of the problems of cost and efficiency that have plagued solar cell development but it did not increase the overall efficiency beyond that of the present solar cells. The quantum efficiency of 0.1 quoted by Fujishima and Honda¹ as well as a typical electrolysis efficiency of 70% limit the amount of storable energy to between 0.35 and 0.70% of the incident energy.

Heidt

An earlier photocatalysis scheme involving water was developed by Heidt in the 1950's.² Heidt's method involved the photoreduction of cerium (IV) ions and the photooxidation of cerium (III) ions. He proposed the following reaction mechanism for the photodissociation³:

The hydrogen and oxygen evolved in these reactions then can be recombined to regenerate water and yield thermal energy.

The flaw in this system was clear to Heidt when he observed that the quantum efficiencies of this photodecomposition in sunlight were too small to be considered economical, as the numerous quenching reactions involved in this system tended to decrease its efficiency.³ These factors excluded normal sunlight as a source with sufficient energy to activate the reaction.

To achieve an acceptable level of dissociation in his initial experiments, Heidt had to use a mercury lamp which generated the majority of its light at 2537 Å.

Because of the inefficiency of these schemes, the approach to this problem had to be re-examined. The 1.23-V potential necessary for the electrolysis of water was simply too large and excluded the use of 96% of the solar photons reaching sea level. Also, the low quantum efficiencies inherent in photosensitization (the use of a catalyzing agent or device) of the water dissociation reaction indicate poor prospects for any appreciable solar energy storage. Consequently, a photosensitive substance that would dissociate efficiently within the available solar spectrum had to be found. The selected photosensitive reactant would have to be a balance between quantum efficiency and thermodynamic potential.

PHOTODECOMPOSITION OF NITROSYL CHLORIDE

Marcus and Wohlers

Working in the early 1960's, Marcus and Wohlers⁴ developed methods for the photolysis of gaseous nitrosyl chloride. Nitrosyl chloride is a common corrosive agent formed in aqua regia according to the equation⁴:

The energy released by the dissociation of nitrosyl chloride⁴ is 9 kcal/mol; however, the energy available for storage⁵ is only 4.8 kcal/mol.

At room temperature, nitrosyl chloride is in measurable equilibrium with its dissociation products, NO and Cl₂. The longest wavelength effective in the dissociation of nitrosyl chloride is about 6370 Å. As Figs. 3 and 4 show, about 30% of the sun's energy is available for the dissociation of nitrosyl chloride. The photodissociation of nitrosyl chloride⁵:

Fig. 3. Spectral distribution of sunlight reaching earth's surface showing the maximum wavelength that will cause dissociation of nitrosyl chloride, NOCl (6370 Å, 1.95 eV). (Solid curve is the solar energy distribution outside the atmosphere, dashed curve is the solar energy distribution at the earth's surface.)

Fig. 4. Fractional solar energy corresponding to various wavelengths and the maximum percentage of solar energy available at 6370 Å, the wavelength needed to photodecompose nitrosyl chloride, NOCl.

proceeds at an appreciable rate in the gaseous phase with a quantum yield of 2.⁶ In the liquid phase a solar furnace is required to give an average quantum yield of 0.023.⁵ With the use of a flow system in the furnace, quantum efficiencies have reached 0.224.⁵

All the work of Marcus and Wohlers was done with a solar furnace.* The average focal flux of Marcus and Wohlers' mirror was 4.16×10^{-3} einstein/min⁵ compared to an average unfocused flux of $\sim 3.5 \times 10^{-5}$ einstein/min/cm² at the earth's surfaces. A quartz reaction chamber was suspended at the furnace focal point and nitrosyl chloride in carbon tetrachloride was introduced. In their first photolysis systems, the reaction mixture was stagnant; the nitric oxide bubbled up through the solution and escaped, while the chlorine remained dissolved in the carbon tetrachloride. A flow system was then designed to allow the constantly moving liquid to impinge on a splash plate. This permitted the nitric oxide to escape more readily from solution, increasing the quantum efficiency tenfold.

From these experiments, Marcus and Wohlers confirmed that the major quenching reaction in any nitrosyl chloride system would be the back reaction of the newly liberated nitric oxide and the chloride radical. Therefore, to increase the practicality of a system employing nitrosyl chloride, a more efficient means of separating the reaction products had to be found.

Silver Chloride Improvements

To improve upon the work of Marcus and Wohlers, a material was needed that was able to absorb either the chlorine or the nitric oxide molecule and then release it on demand. The troublesome, efficiency-limiting back reaction thus might be controlled. Simplicity in the separation system was essential to prevent the large cumulative energy losses that are potentially present in multistep processes. Silver appeared to be an ideal element for such purposes. Using gaseous nitrosyl chloride as the reactant, the chlorine liberated by its dissociation might react with a thin layer of silver on the walls of the reaction chamber, forming silver chloride. Silver chloride is an attractive

* The solar furnace is a parabolic mirror that focuses sunlight on a single point.

material for photochemical energy storage because it is not water soluble and thus is easy to handle. It is also sensitive to light up to 4050 Å in wavelength; consequently, it undergoes some spontaneous photodecomposition in sunlight. The silver chloride might be photodecomposed at a later time to regenerate the chlorine and elemental silver.⁷ The reactions below illustrate this overall process.

We investigated a hypothetical solar energy system using the storage potential of silver and nitrosyl chloride. In this hypothetical system, nitrosyl chloride gas would be first admitted into an evacuated, conical-walled, flat-topped reaction vessel. The walls of the vessel would be lined with a fine layer of silver metal. As sunlight shined through the transparent container top, the nitrosyl chloride would be dissociated. The photochemically liberated chlorine atoms (or molecules) then could react with the silver metal. Heat generated by the formation of the silver chloride would be collected from the outside of the reaction vessel. Next, light would be blocked out to prevent the dissociation of any of the newly formed silver chloride. The reaction vessel would be evacuated to remove the nitric oxide and unreacted nitrosyl chloride. To dissociate the silver chloride, sunlight would be readmitted. The silver metal would be left on the chamber walls, ready for another cycle, and the chlorine gas would be pumped away. Finally, the nitric oxide and chlorine thus produced would be fed into a reaction chamber where they would reform NOCl. The energy liberated from the formation of NOCl would be collected.

Difficulties in this system were revealed as our investigation proceeded. First, chlorine will not react efficiently with silver except at highly elevated temperatures.⁸ However, under the conditions required for the efficient reaction with chlorine, nitrosyl chloride itself may react directly with silver. Next, the efficient decomposition of silver chloride can be accomplished only with copious quantities of photons of 4000 Å or less in wavelength.⁸ Because only 5% of the total sunlight energy is in this region, the decomposition of a thin layer of silver chloride could be too slow or too incomplete to be practical. Finally, if an extremely thin layer of silver were used to

improve the rate of the subsequent decomposition of silver chloride, the collection of the minor amounts of heat liberated by the silver reacting with the chlorine would be a formidable task. In addition, designing a practical recombination chamber for the nitric oxide and chlorine will be difficult because of the extremely corrosive nature of the gases and the low heat of reaction per mole of gaseous product.

CONCLUSION

Before such a system for the photodecomposition of materials to produce energy can be pursued further, answers to many questions must be found. Some of the most pressing include: Under what conditions will silver react with chlorine and nitrosyl chloride? Is the efficiency of nitrosyl chloride dissociation altered by the presence of silver metal? How efficiently and how quickly does silver chloride dissociate in light (quantum yields⁹ range from 152 to 0.20)? How thick a layer of silver chloride would allow complete dissociation by sunlight? Finally, if it becomes necessary to heat the reaction chamber to cause the reaction, could the nitrosyl chloride be dissociated simply with heat?*

The field of photochemical energy storage as an alternative means of solar energy utilization is a poorly studied area. Although the particular methods discussed here may never be viable means of energy production, the field of photochemistry is too vast to be discounted by this limited analysis.

* A more recent system, hypothesized by Prengle and Sun¹⁰, suggested that a photochemical generator be used to additionally heat the steam produced in a fossil fuel power plant. The system would use solar heat to decompose methanol or ammonium hydrogen sulfate. Prengle and Sun are optimistic about the engineering feasibility of the ammonium hydrogen sulfate system. Their figures indicate that the cycling of 3.8 tons of sulfate would generate 1 MW of electric power.¹⁰

REFERENCES

1. A. Fujishima and K. Honda, *Nature* 238, 37 (1972).
2. L. J. Heidt and A. F. McMillan, *Science* 117, 75 (1953).
3. L. J. Heidt in *Solar Energy Research*, F. Daniels and J. Duffie, Eds. (University of Wisconsin Press, Madison, Wisconsin, 1955), pp. 203-219.
4. R. J. Marcus and H. C. Wohlers, *Solar Energy* 5, 44 (1961).
5. R. J. Marcus and H. C. Wohlers, in *Proc. U.N. Conf. New Sources of Energy, Rome, Aug. 21-31, 1961* (United Nations, New York, New York, 1963), Vol. 1, pp. 187-195.
6. C. F. Goodev and S. Katz, *Proc. R. Soc. London* A172, 432 (1928).
7. C. A. Jacobson, *Encyclopedia of Chemical Reactions* (Reinhold Publ. Co., New York, New York, 1956), p. 143.
8. R. Gutmacher, Lawrence Livermore Laboratory, private communication (1975).
9. F. Seitz, *Rev. Mod. Phys.* 23, 338 (1951).
10. W. H. Prengle and C. Sun, *Solar Energy* 18, 561 (1976).

BIBLIOGRAPHY

1. P. G. Ashmore and M. S. Spencer, *Trans. Faraday Soc.* 55, 1868 (1959).
2. A. Fujishima and K. Honda, *J. Chem. Soc. Japan (Kogyo Kagaku Zasshi)* 72, 108 (1969).
3. A. Fujishima and K. Honda, *J. Chem. Soc. Japan* 74, 355 (1971).
4. A. Fujishima, E. Sugiyoma, and K. Honda, *Bull. Chem. Soc. Japan* 44, 304 (1971).
5. A. Fujishima and K. Honda, *Prod. Res. (Seisen Kankya)*, 22, 478 (1970).
6. L. J. Heidt, *Sol. Energy* 11, 123 (1967).
7. D. Kop, and H. C. Thomas, *J. Am. Chem. Soc.* 71, 3047 (1949).
8. R. J. Marcus, *Trans. Conf. Use of Solar Energy: The Scientific Bases*, Tucson, Arizona, Oct. 31-Nov. 1, 1955 (University of Arizona Press, Tucson, Arizona, 1956), Vol. 4, Ch. 18.
9. R. J. Marcus, and H. C. Wohlers, *Proc. U.N. Conf. New Sources of Energy*, Rome, Aug. 21-31, 1961 (United Nations, New York, New York, 1963), Vol. 6, pp. 393-399.
10. R. J. Marcus and H. C. Wohlers, *Solar Energy* 4, 1 (1960).
11. R. J. Marcus, and H. C. Wohlers, *Solar Energy* 5, 21 (1961).
12. J. A. Leermackers, and H. C. Ramsperger, *J. Am. Chem. Soc.* 54, 1837 (1932).
13. S. Levine, H. Halter, and F. Mannis, *Solar Energy* 2, 11 (1958).
14. O. S. Nenwirth, *J. Phys. Chem.* 63, 17 (1959).
15. S. W. Paleocrassas, *Solar Energy* 16, 45 (1974).

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