Technical Papers

Conversion of Sunlight into Chemical Energy Available in Storage for Man's Use[1]

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We have been able to establish that the key reactions in the simple photochemical process proposed by one of us (*1*, *2*) can take place concurrently in a water solution of cerous and ceric ions—namely, the production of hydrogen gas by that part of the light absorbed by the cerous ions thereby oxidized to ceric ions, and oxygen gas by that part of the light absorbed by the ceric ions thereby reduced to cerous ions. The net result of the two reactions is the photochemical decomposition of water into its elements, resulting in a gain in total chemical energy at the expense of the energy of the light absorbed by the system without the loss of any of the cerium or acid employed in the process. It has also been established that the process can be brought about by sunlight. The discovery of the photochemical oxidation of cerous to ceric ions was made by L. J. Heidt and M. E. Smith (*3*). They suggested that hydrogen was produced by the reaction, and this has been found to be the case (*1*).

No attempt was made in the experiments reported here to determine the main reaction or the details of the mechanisms of the reactions in the system or the efficiency of the process, or to collect all the gas produced or to carry out the process under the most favorable conditions. Work on these problems, especially the last one, in sunlight is under way.

The apparatus employed is shown in Fig. 1. Extreme care was taken to ensure that the system was gas-tight and that the results were not due to leakage of air, oxygen, or hydrogen into it. The dark reactions were found to be negligible. Light in the near ultraviolet of 2536 A was employed in Expts 1 and 2 for reasons stated elsewhere (*1*), and sunlight was employed in Expts 3 and 4.

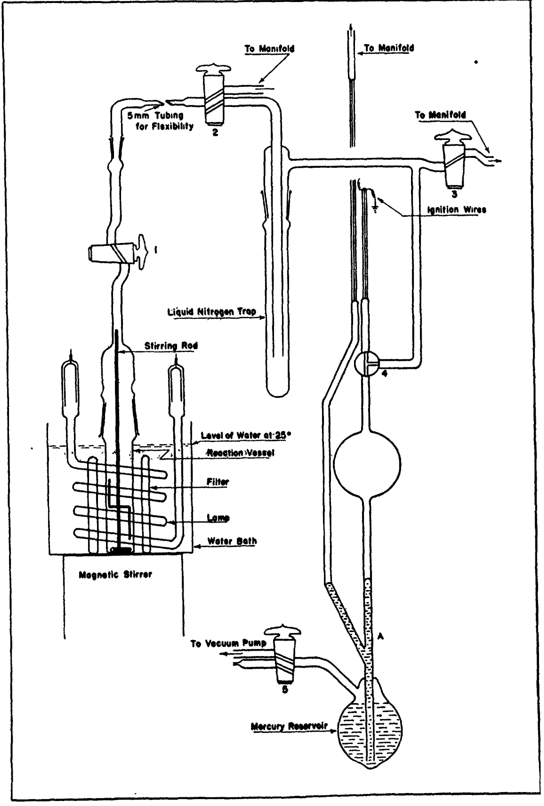

FIG. 1.

The lamp, filter, and reaction vessel were made of the best quality of clear fused quartz; the lamp and filter were similar to equipment described elsewhere (*4*). The reaction mixture was stirred continuously while being evacuated or irradiated. The gas originally in the solution was removed largely by opening stopcocks 1 and 2 to the manifold until the equilibrium pressure of the gas, other than water, from the solution was less than 10^{-5} mm. About 1 ml water was distilled off during this operation. Stopcock 1 was then closed, and the solution was irradiated after it had been established that there were no leaks in the system. Meanwhile the system up to 1 was pumped down to less than 10^{-5} mm and, when cut off from the pumps, held to 10^{-4} mm overnight. The gas produced by photolysis was transferred to the capillary containing the ignition wires by closing 3, opening 2 to this part of the system, then opening one for only 30 sec in order to let some of the gas out of the reaction vessel without an objectionable amount of water; the water was caught in the cold trap. Stopcock 1 was then closed, and 4 was turned through 180°, after which the mercury level in *A* was raised to 4. The noncondensable gas remaining between 1 and 4 was gathered for the most part into the capillary by turning 4 counterclockwise through 90°, lowering the mercury to its original position, then turning 4 clockwise 90° and again raising the mercury level to 4. The last sequence of operations was repeated several times while the level of the mercury in *A* was always above the side arm connected to the manifold. The mercury was then raised through 4, and the pressure of the gas in the capillary was taken as the difference between the heights of the mercury in this and the adjacent similar capillary connected to the manifold. The gas was ignited by a spark of short duration (about 0.1 sec) between the ignition wires; the spark was produced by means of a Tesla coil. Experiments

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showed that this treatment did not change the amount of gas when hydrogen, oxygen, or dry air alone was present.

Irradiation with sunlight of the solution in the evacuated reaction vessel was accomplished by disengaging the ground-glass joint just above stopcock 1 after the latter had been closed and by placing the reaction vessel and auxiliary equipment for stirring in a clean place in direct sunlight. The gas produced by sunlight was determined after reassembling the apparatus at the ground-glass joint and evacuating and degassing the apparatus before opening stopcock 1.

The results of these experiments are given in Table 1.

TABLE 1*

Expt	$HClO_4$	$Ce(ClO_4)_3$	$Ce(ClO_4)_4$	A	10^8 B	C	10^8 D
1	2.6	0.14	0.002	0.03	0.8	28	0.8
2	2.6	0.14	0.002	0.02	2.0	34	2.0
3	2.5	0.08	< 0.0001	65†	0.64	28	0.59‡
4	2.5	0.08	< 0.0001	120†	1.0	35	0.91

* Evidence for the photochemical production of a mixture of hydrogen and oxygen gases in Expts 1 and 2 by light of 2536 A and in Expts 3 and 4 by sunlight absorbed by a mixture of cerous and ceric ions in aqueous perchloric acid. The concentrations are formal values in moles/liter of solution. The volume of the solution irradiated was 30 ml in every case. A represents, in units of 6×10^{23}, the quanta of light of 2536 A absorbed, except in Expts 3 and 4; B, moles of noncondensable gas collected in the ignition chamber; C, the pressure in mm Hg at which the noncondensable gas was ignited; D, the decrease produced in the moles of noncondensable gas by the ignition. The experiments were carried out at 25° C.

† Hours in sunlight.

‡ The noncondensable gaseous residue was found to be hydrogen.

The gaseous product of the photolysis is believed to be a mixture of hydrogen and oxygen, because the amount of noncondensable gas decreased significantly when the mixture was ignited by a spark, whereas similar treatment of hydrogen or oxygen alone produced no significant change in the amount of gas; these gases are produced by the photochemical oxidation and reduction of cerous and ceric perchlorates, respectively, when photolyzed separately in dilute aqueous perchloric acid (*1, 2*).

Subsequent photolysis of the solutions employed in Expts 1 and 2 produced a solute that browned the solutions and a gas that was mainly oxygen. The photochemical production of hydrogen may be restored in the following way. The ceric ions can be decomposed thermally at a measurable rate above 30° into cerous ions, with the simultaneous production of oxygen (*3*). This leaves to the light that can be absorbed by the cerous ions the principal task of converting the cerous ions into ceric ions, with the simultaneous production of hydrogen. This method would increase the photochemical efficiency of the net reaction and use the longer wavelengths of sunlight to supply the heat for the thermal reaction and to establish a temperature gradient by means of which the liquid can be circulated. It also makes possible the production of the hydrogen and oxygen in separate parts of the system, where they can be collected largely free from one another.

References

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Separation of Synnematin into Components A and B by Paper Chromatography

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Synnematin, an antibiotic produced by *Cephalosporium salmosynnematum* (*1*), was first described by Gottshall, Roberts, and Portwood in 1949 (*2*). The *in vitro* spectrum of synnematin and the results of some *in vivo* tests were presented by Gottshall *et al.* in 1951 (*3*).

It is the purpose of this report to present evidence that crude culture filtrates of *C. salmosynnematum* contain at least two active components, which will be designated as synnematin A and B, and to present preliminary data about the chemical composition of synnematin B. Brief descriptions are included for the method of production and separation of one of these active components (synnematin B). The detailed description of suitable fermentation media and methods of production and purification of synnematin will be presented in a later report.

Antibiotic activity as expressed below was measured by the *S. typhimurium* serial dilution assay described by Gottshall *et al.* in 1951 (*3*).

The following fermentation medium was used in this study: cornmeal 4%; soya bean meal 4%; ammonium sulfate 0.1%; calcium carbonate 1%; with a pH of 7.4 before autoclaving. The use of this medium has resulted in antibiotic activities of 400 *S. typhimurium* u/ml in shake flasks and 300 u/ml in 30-liter stirred jars.

Several recovery procedures have been used:

1) Aluminum oxide adsorption from culture filtrate containing an equal volume of acetone, followed by elution with water, phosphate buffer, or akaline methanol.

2) Countercurrent extraction from culture filtrate with butanol, plus 15% methanol, and subsequent removal of the active material in a water layer formed by the addition of xylene or benzene.

3) Solvent precipitation of inactive material, followed by removal of the antibiotic in a small volume of water thrown down by the addition of another solvent to the filtrate.

The procedure which has given the most satisfactory results is precipitation of the culture filtrate with 3