PHOTOCHEMICAL EFFECTS OF SUNLIGHT

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ABSTRACT The importance of sunlight in bringing about not only photosynthesis in plants, but also other photochemical effects, is reviewed. More effort should be devoted to photochemical storage of the sun's energy without the living plant. There is no theoretical reason to believe that such reactions are impossible. Ground rules for searching for suitable solar photochemical reactions are given, and a few attempts are described, but nothing successful has yet been found. Future possibilities are suggested. Photogalvanic cells which convert sunlight into electricity deserve further research. Eugene Rabinowitch has been an active pioneer in these fields.

It has been my privilege to be associated directly or indirectly with Eugene Rabinowitch in several of his many projects, including photosynthesis, uranium chemistry, the founding and continuing publication of the *Bulletin of the Atomic Scientists,* and the photochemical effects of sunlight. In all of these he has shown vision, good judgment, and a spirit of service.

I am glad to have been assigned the photochemical effects of sunlight for review and discussion of future possibilities. The subject is a large one. It includes:

(*a*) Photosynthesis (1), which is discussed here by others and which is the basis of all plant and animal life and the source of all human food and fuel.

(*b*) Protection against excessive bacterial damage.

(*c*) Purification of waste products.

(*d*) Photodegradation of paints, plastics, and chemical products.

(*e*) Contribution to the formation of smog.

(*f*) Production on human skin of vitamin D and sunburn (2).

(*g*) Direct photochemical use of sunlight.

The future possibilities for the direct use of the sun's energy are great (3). There have been several incentives for research on the direct use of sunlight. Our fossil fuels, on which our civilization is completely dependent, will not last indefinitely. Many of the developing nations need more mechanical and electrical power, and although they have little coal, gas, and oil, they do have abundant sunshine. Then came the need for solar batteries for exploration of outer space, and now we have the urge to reduce pollution caused by the burning of our fuel. Photochemical applications of solar energy have the advantages that they are not limited by the Carnot efficiency of heat engines $(T_2 - T_1)/T_2$ and do not need high temperatures. Moreover, the chemical photoproducts can be stored much more easily than heat or power can be stored. On the other hand, the sunlight is intermittent, and it is of such low intensity that very large areas are required. Large areas of any material are expensive. Moreover, the infrared half of the sun's radiation does not have enough energy per photon to bring about ordinary chemical reactions.

Photochemistry was in the hands of physical chemists for the first quarter of the present century. Then the chief activity passed to the biochemists and the photobiologists, and recently the organic chemists have taken a keen interest in it. At present, the environmentalists are deeply involved in it. More basic research is needed as is evidenced by our need to know how seriously the proposed use of supersonic transport planes might reduce the protective ozone layer by reaction with water vapor or nitrogen oxides and increase seriously the concentration of ultraviolet light reaching the earth's surface.

Photochemical research does not involve highly specialized techniques and expensive apparatus, and it can be readily carried out in laboratories which cannot afford to buy nuclear reactors and wind tunnels. In 1956, the National Academy of Sciences–National Research Council appointed a committee on Photochemical Storage of Solar Energy charged with the responsibility of encouraging research which might ultimately lead to new ways of using solar energy directly as light. The committee membership included L. J. Heidt, Eugene Rabinowitch, R. S. Livingston, and Farrington Daniels, and we attempted to lay down ground rules for suitable solar photochemical reactions and organized a symposium which was published (4). The question was asked, "Are there no photochemical reactions activated by sunlight, other than the all-important photosynthesis with chlorophyll?" and the point was made that "there is no theoretical reason to exclude the possibility of energy-storing photochemical reactions produced by sunlight which would not require a living plant and good agricultural soil."

Now it is 15 years later, and we have not yet found a successful man-made reaction for converting sunshine into suitable photochemical products. The challenge still remains, but there is still no reason to believe that it is an impossible challenge. Very little effort has been devoted to it.

The committee pointed out (4) that although most photochemical reactions are exothermic, the only photochemical reactions of practical use are endothermic reactions which can be reversed in the dark at a rate which is not so fast as to be completed during exposure to the sun nor so slow as to be impractical. The reaction should take place with a quantum efficiency not appreciably less than one molecule of product per photon of absorbed light, and it should absorb most of the visible half of the solar spectrum. Many promising reactions respond only to the higher energies of ultraviolet light, but sunlight contains less than 2½% ultraviolet light.

In order to work with reasonably small equipment, photochemical reactions in liquids and solids are more hopeful than reactions in gases, and the energy storage should be of the order of 50–100 cal/g. Obviously, the materials should be inexpensive even though they are recycled an indefinite number of times. If oxygen or water is a photoproduct, it is not necessary to provide storage for it. The reverse exothermic reaction should be easily initiated by simple mixing, by raising the temperature, or by adding a catalyst.

The theoretical photochemical possibilities of sunlight are extraordinary. Assuming an acre of sunlight with energy of 500 cal/cm^2 per day, a quantum yield of 1, a photochemically active absorption of $\frac{1}{10}$ of the sunlight, and a photochemical product with a molecular weight of 100, it can be calculated (reference 3, p. 305) that over 3 tons of material can be produced by the sun *per day*. Agricultural yields are of the order of 3 tons/acre per yr. No reaction has so far even remotely approached such a high efficiency, and yet the assumptions seem reasonable. A few solar photochemical reactions have been tried (4). The photodecomposition of nitrosyl chloride, NOCl (5, 6), appeared hopeful at first. It absorbs nearly the whole of the visible solar spectrum, as does chlorophyll, and when dissolved in carbon tetrachloride, it dissociates with a quantum yield of unity and the production of nitric oxide, which escapes as an insoluble gas, and chlorine, which remains in solution. Thus the two products are automatically separated and cannot reverse the reaction. The nitric oxide is stored and later bubbled through the solution of chlorine in carbon tetrachloride to give back the original nitrosyl chloride with the evolution of heat. The difficulty with this reaction, however, is that chlorine atoms are produced by the photochemical decomposition, and they immediately recombine irreversibly to give Cl_2 molecules with the permanent loss of much of the effective heat of the reaction.

Chlorophyll is an abundant material and when appropriate water "extracts" of chlorophyll-containing plants are exposed to light, it can effect a reduction of oxidizing molecules as in the case of the Hill reaction. There should be possibilities here.

A large industrial laboratory considered seriously using sunlight in Illinois to produce an intermediate, needed in large quantities for the manufacture of a standard plastic material of high value. Before testing on a semiproduction scale, however, the costs of the conventional thermal process for synthesis were lowered so much that the new photochemical process was given up.

There is an opportunity for changing the absorption of organic molecules by changing the structure and thus extending the absorption of sunlight to longer wavelengths. Also, photosensitizers can be added to a chemical system to absorb the sunlight and transfer the energy of excitation to molecules which will then react even though they are transparent to the light passing through the system, as for example in the case of the photodecomposition of oxalic acid in water decomposed by blue light in the presence of uranyl ion.

It is possible, too, to bring about photochemical reactions with light which contains less energy per photon than is required for the chemical activation, as in the classic example of photosynthesis with chlorophyll. The photosensitizer produces intermediate products with lower energy requirements, and two or more of these products can participate in stepwise reactions which eventually give enough energy to bring about the overall reaction. Possibly, other reactions of this type can be found. Nitrogen dioxide is an inexpensive material which absorbs most of the visible sunlight and decomposes only in the violet and ultraviolet. Perhaps molecules excited with the longer waves of sunlight might be effective photocatalysts for some type of photochemical reaction.

A survey has been made of possibly suitable inorganic colored ions (7). Photochemical reactions, in solution, with sunlight can be readily studied in solar furnaces (6). A 5 ft parabolic focusing collector (reference 3, pp. 93–100, plates 3–5) can be made inexpensively for laboratory use which will deliver about a kilowatt of solar radiation into a liter flask.

Although infrared radiation does not contain enough energy per photon to bring about most endothermic reactions, exploratory efforts might well be directed toward finding a reversible, low energy photochemical reaction, such as the dehydration of hydrated crystals, which might proceed directly without first converting the radiation into kinetic energy and raising the temperature.

One of the most promising areas for exploring the direct use of sunlight is that of photogalvanic cells, in which Eugene Rabinowitch has been an outstanding pioneer. In ordinary chemical reactions, the energy of the reaction is given off as heat in the form of increased kinetic energy of the molecules, but in electrochemical reactions electrodes are inserted into the reacting mixture in such a way that electrons are drawn off at one electrode and fed along a conducting wire outside the cell to the other electrode. The flow of electrons produces an electric current at high efficiency for doing useful work. The same technique can be obtained in photochemical reactions producing useful electrical work at high efficiency. In one approach, electrons are removed from molecules or ions by absorption of light. The light energy is sometimes large enough for complete ionization, but the electrons must be close enough to the electrodes so that they reach them before positive and negative ions in the body of the solution can recombine with each other. The direct illumination of the submerged electrode surface has been tried.

In another approach, the photochemical reaction brings about a photoreduction or photooxidation which produces a reducing environment around one electrode and an oxidizing environment around the other, thus setting up a "redox" potential and a flow of current. The photochemical oxidation of many colored organic or inorganic materials with oxygen is easily accomplished. In still another type of photogalvanic cell, the light brings about reduction or oxidation of a polyvalent ion such as ferrous ion, Fe^{++}, and the ions of different valence at the two electrodes give an effective photogalvanic concentration cell. Rabinowitch (8–10) has demonstrated these reactions fully and discussed their possibilities. He stressed particularly the reversible redox system consisting of an aqueous solution of the purple thiazine dye, thionine, and a ferrous salt,

$$\text{Thionine} + 2\ \text{Fe}^{++} \underset{}{\overset{h\nu}{\rightleftharpoons}} \text{Leucothionine} + 2\ \text{Fe}^{+++}.$$

He obtained potentials up to 0.4 v with wattage equivalent to a few tenths of 1% of the absorbed light energy. The efficiency of the electrochemical energy produced depends on the ratio between the homogeneous reaction and the heterogeneous back reaction. Very little further research has been devoted to photogalvanic cells with sunlight. They deserve more attention.

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