THE GREENING OF PHYSICAL CHEMISTRY

Learning how chlorophyll moves electrons to turn light into chemical energy will increase biological understanding and could someday lead to new technology

BY DIETRICK E. THOMSEN

"Have you thanked a green plant today?" exhorts the familiar bumper sticker. Everyone knows that without green plants animal life would be impossible. Green plants are the first link in the food chain. As we all know, they make food out of inorganic materials by photosynthesis. They are also responsible for nearly all the energy we consume from firewood to oil and natural gas.

The overall chemistry of photosynthesis, the input of water and carbon dioxide plus certain minerals, the output of sugars and starches and the role of chlorophyll as the energy-supplying catalyst are quite well known. Lately the emphasis of study has shifted to the physical and chemical details of the process: how the energy conversion is managed and the sequence of chemical changes that take place at the picosecond (one trillionth of a second) level. Such studies can provide a more thorough understanding of the basic process that has made the earth what it is today. But participants in the research also stress that another result might be artificial photosynthesis, an ability to mimic the way plants turn solar energy into chemical energy.

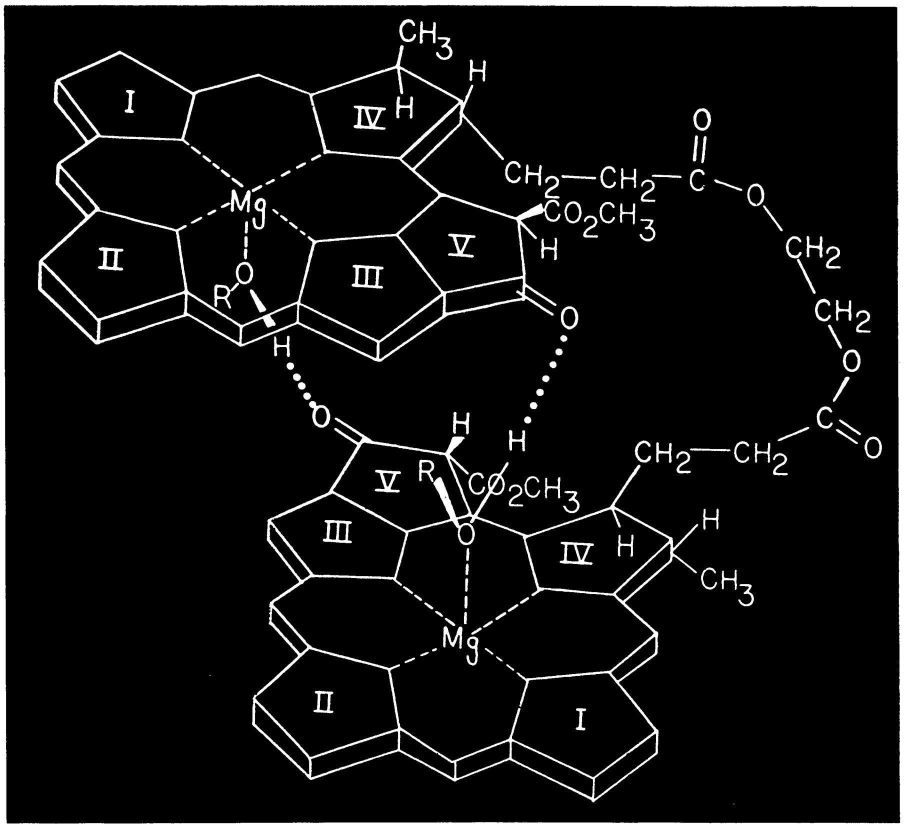
The approach of these studies is not that of plant physiologists, but that of physical scientists, says Joseph J. Katz of Argonne National Laboratory. Such interest led to a symposium at the recent meeting of the American Physical Society in Chicago. They want to learn, he says, "how chlorophyll functions from a physicist's point of view." These procedures start with nothing so complicated as a whole leaf. They begin with chlorophyll molecules and try to set up *in vitro* the immediate physical and chemical surroundings in which the chlorophyll acts in a leaf or in photosynthetic bacteria. These organisms are simpler and therefore especially useful for some of these studies.

The first thing that becomes apparent is that the overwhelming majority of the chlorophyll molecules play the role of antennas, absorbing photons from sunlight and transmitting the energy to a special pair of chlorophyll molecules that serves to convert light energy to chemical energy.

In a sample of 300 chlorophyll molecules, 298 can function as antennas and one pair functions as the photoreaction energy-conversion center. The antenna chlorophyll is bound together in giant polymeric groups—the binding is a reaction involving the central magnesium atom of one chlorophyll molecule and an oxygen atom (the one called the ketone atom) in the next. Polymers using this connection have been built in the laboratory, and they seem to show properties similar to those of chlorophyll aggregates in plants.

The focus of physical chemical interest is the dimer, the two-molecule unit that does the energy conversion. It seems to require a special chemical connection and geometric orientation for its function. James R. Norris of Argonne showed that it took two chlorophylls working together to use the absorbed light to eject an electron. This electron ejection is the beginning of the chemical process.

Chlorophyll molecules are flat structures composed of a number of pentagons and hexagons. The proposed structure for the energy-converting pair has them oriented parallel to each other by the influence of water molecules or by chemical groupings found in the proteins that are always present in chloroplasts. In the laboratory, Michael R. Wasilewski of Argonne has managed to join two chlorophylls by means of a complicated carbohydrate bond. Introduction of water or alcohol then causes the two bound chlorophylls to fold over into the configuration that the experimenters have deduced exists in living chloroplasts. Katz credits Thomas R. Janson of Argonne with having made a system using these



The synthetic reaction pair of chlorophyll molecules used in chemical studies.

Katz

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chemically synthesized special pairs to make a device that uses light energy to make chemical reactions, a so-called synthetic leaf.

What they can mimic well so far is the reduction part of the process. They can show that chlorophyll mediates electron transfer from a donor to an acceptor when energized by light. In the laboratory case a metal disk is coated with chlorophyll. On one side is an electron donor, ascorbic acid, on the other side, in contact with the chlorophyll, is an electron acceptor. When light shines on this device, electrons flow from the donor through the chlorophyll into the acceptor.

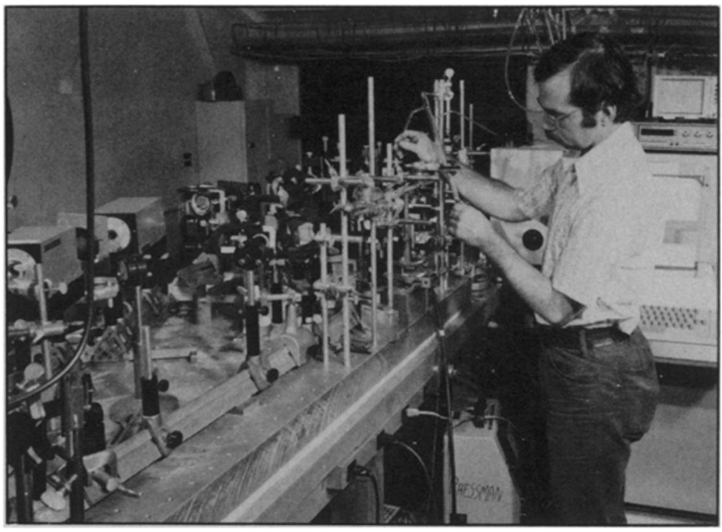
But that is not exactly the way plants do it. In a plant, the electron donor has to be a water molecule, and it is a difficult thing to detach an electron from a water molecule. It takes as much energy to pull one electron out of water as it takes to eject four from the paired chlorophyll molecules. "Nature has some way of summing it up," Katz says. "We must understand how electrons come out of water to get biomimetic technology." The researchers have "a pretty good idea" about the reducing part of the chemistry; the oxidation remains to be learned.

As yet, the reaction centers have not been isolated from living plants, but Katz expects that it will be possible soon. Photosynthetic bacteria are simpler than leafy plants, and at the moment more can be done with them *in vivo.* "Katz and his co-workers began with monomer chlorophyll and built up from there," says Kenneth J. Kaufmann of the University of Illinois at Urbana-Champaign. Kaufmann and his collaborators, P. Leslie Dutton (now at the University of Pittsburgh) and Peter M. Rentzepis, have started with photosynthetic bacteria and attempted to isolate the parts that perform different functions.

Kaufmann and associates have been able to break down the bacteria and isolate the photosynthetic reaction centers. They can then put these into a species that has no reaction centers, a mutant that has antenna chlorophyll but no reaction chlorophyll, and as a result they find that these things do in fact make the reaction occur. Their work with living cells essentially agrees with what Katz and his co-workers have reasoned from the behavior of chlorophyll in chemical studies.

Another important aspect of the work Kaufmann and his co-workers have concentrated on is why the reduction part of photosynthesis operates with such high efficiency. Its quantum efficiency, which is the way things are measured at this level of physics, is equal to one. For every photon (quantum of light) absorbed, an electron is knocked out of the chlorophyll.

There are a number of ways in which this energy could be wasted or degraded before the electron gets far enough away from its starting point. The key to the high efficiency, Kaufmann states, is speed. It's what he calls the principle of hedonism: "You want to get in as much fun as possible before the angel of death comes to take you away."



Kaufmann

Kaufmann adjusts apparatus that follows picosecond-long processes in the photosynthetic reactions of bacteria.

Previous studies had indicated that the electron ejected from the chlorophyll wound up in a chemical called quinone, which is present in the living organisms and plays a role in the reduction chemistry. But how the electron got as far as the quinone was still a problem. Kaufmann and his associates decided to try to find out by following the reactions, picosecond by picosecond.

A picosecond is a trillionth (10^{-12}) of a second. One of the first requirements was to be able to excite the part of the bacterium that converts light to chemical energy with pulses of this order of length so that the reaction chain started by one pulse would not overlap that of the previous pulse and confuse the issue. For this they used a neodymium-glass laser capable of producing a pulse less than 10 picoseconds long. After the excitation of the bacterium weaker pulses of light were shone upon it. The idea was to determine what chemical substances were formed and when. When each substance is formed, it absorbs a characteristic spectrum from this second irradiation, and the experimenters wanted to follow the time sequence of the formations.

As Kaufmann points out, "for such very fast events, there are very few clocks available to keep track of the time." The solution is to use the speed of light as a timing standard. Light travels a very short distance in a few picoseconds. So Kaufmann and his co-workers devised what is called an etalon, a mirror made in stepwise fashion. Such a mirror sends back a timed sequence of reflected pulses as light hits the riser of each step in turn. Comparing these reflections with the light flashes from the chemical events can time the chemical events.

With this method Kaufmann and his team discovered a couple of very quick steps between the reception of light energy by the active chlorophyll and the acceptance of the loose electron by the quinone. First the electron comes immediately loose from the chlorophyll, creating an electron-hole pair; that is, the electron leaves behind an empty space, which acts like a positive charge. This is a more efficient way of beginning than simply exciting the chlorophyll molecule as a whole. Such an excitation is easily dissipated as heat. The electron-hole pair gets away from that possibility.

But an electron-hole pair is still in a parlous position. The attraction between electron and hole is strong, and unless something further happens quickly, the electron will fall back into the hole, and the energy will reverberate away through the molecule. The second step takes the electron further from the hole to a point where it is safe from falling back and can go on about its chemical business. Crucial to this is the presence of pheophytin, a molecule similar to chlorophyll. It is the pheophytin that first receives the electron ejected from the chlorophyll. The quinone receives the electron in a later step. Pheophytin is known to be present in photosynthetic bacteria. Researchers are now searching for it in leafy plants.

Even when the reduction part of the cycle is well unraveled, the mystery of the oxidation remains. It still takes four times as much energy to pull one electron out of a water molecule as it does to get one out of chlorophyll. Somehow the system sums up that energy. Here too the photosynthetic bacteria may help. They get their oxidation electrons, not from water, but from organic debris on the bottoms of streams and marshes where they live. Comparison of the two systems may help elucidate what is going on, or it may offer an alternative to the difficulties of electrolyzing water. Eventually, when the chemical dynamics of the whole process is understood, and when the best kind of chlorophyll to use has been determined, it may be possible to work out a biomimetic technology that will convert sunlight directly to chemical energy. ☐