Title

Photosynthesis

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Photosynthesis is the synthesis of organic compounds such as starch and sugar from inorganic substances including water and carbon dioxide by living plant cells using the energy of light absorbed by the plant pigments. Photosynthesis in all land plants and in most aquatic plants forms oxygen gas in addition to organic material. This type of photosynthesis is quantitatively by far the most important. However, some microorganisms perform other types of photosynthesis which do not produce oxygen.

The major photosynthetic reaction, which produces oxygen, is expressed in words by the equation:

WATER + INORGANIC COMPOUNDS + LIGHT → ORGANIC COMPOUNDS + OXYGEN.

Organic compounds are compounds of the element carbon excluding its oxides and nitrides. The organic compounds made by photosynthesis in the greatest quantity are carbohydrates (including sugars and starch), amino acids (from which proteins are made), and fatty acids and glycerol phosphate (from which fats are made). The inorganic compounds required for every product of photosynthesis are water (H_2O) and carbon dioxide (CO_2). For the synthesis of amino acids, the elements nitrogen and sulfur are also needed. These elements may be absorbed by the plant in the form of their oxides, nitrate (NO_3^-) and sulfate ($SO_4^=$), or in other, more reduced forms such as ammonia (NH_3) and hydrogen sulfide (H_2S). Other elements built into organic compounds by photosynthesis include phosphorus (which the plant absorbs as phosphate), and the metal ions of iron and magnesium. Manganese and several other elements are essential for photosynthesis, but are needed in only trace amounts.

In land plants, all of these inorganic compounds, except CO_2, normally are absorbed through the roots. CO_2 is absorbed by land plants from the atmosphere where it occurs at an average concentration of 0.03%. The CO_2 enters the leaves and O_2 escapes from the leaves via small openings in the epidermis called stomata. The opening and closing of the stomata are controlled by special cells, called guard cells, which are also green cells, capable of performing photosynthesis. When the light falls on these cells, they photosynthesize and the products of photosynthesis cause the cells to expand away from the opening making it larger and permitting more CO_2 to flow into the leaf. Thus the stomata need only be open during active photosynthesis. The loss of water by evaporation from the leaf, called transpiration, is controlled by the stomata, since most water vapor escaping from the leaf passes out through these openings.

Aquatic plants absorb all nutrients from the water in which they live. Carbon dioxide and bicarbonate ion (HCO_3^-) both are present in lakes and seas and are directly absorbed by algae and other water plants.

Light is a reactant in photosynthesis, not merely a catalyst.

Much of the light energy used by plants to drive the photosynthetic reaction is stored as chemical potential energy in the products of the reaction. For oxygen-evolving photosynthesis, all visible light from violet (wavelength 4000 Å) to medium red (7000 Å) is effective to some extent. For certain types of bacterial photosynthesis in which oxygen is not evolved additional longer wavelengths out to the far red (9000 Å) are effective.

Historical. The discovery of the nature of photosynthesis goes back to the beginnings of modern chemistry. In 1772, Joseph Priestly found that several days after he placed a sprig of mint in a closed jar, where previously candles had burned until they went out, the air was "restored", and the candles would burn again. Jan Ingen-Housz (1780) found that light was necessary for this restoration of the air, and Jean Senebier (1782) showed that "fixed air" was transformed by photosynthesis into "pure air". With the discovery of oxygen by Lavoisier (1775) and his discovery that "fixed air" is a compound of carbon and oxygen (1781), it was clear from these early findings that plants convert carbon dioxide to oxygen in the light. The role of water remained to be established by Nicolas de Saussure in 1808. By careful experiments, he determined the increase in dry weight of a plant growing in a pot of earth. He also measured the volume of carbon dioxide taken up by the plant and the volume of oxygen evolved. He confirmed the fact that all of the carbon made by the plant into organic materials comes from carbon dioxide. At the same time, he showed that the increase in dry weight of the plant was greater than the difference in weight between the carbon dioxide taken up and the oxygen evolved. However, the weight of the soil in the pot did not change significantly. The only other source of weight increase was water; thus water is a reactant in photosynthesis.

The importance of photosynthesis as an energy converting reaction had to await the development of the concept of chemical energy. In 1845 Robert Mayer recognized that the energy of sunlight was converted by photosynthesis to the stored chemical potantial of the products.

The Role of Photosynthesis. The net result of the chemical processes of photosynthesis can be expressed by specific chemical equations for each photosynthetic product. The formation of a simple sugar, glucose is represented by the equation:

$$\text{light} + 6\ CO_2 + 6\ H_2O \xrightarrow{\text{green plant}} 6\ O_2 + C_6H_{12}O_6$$

which says that a green plant converts the energy of light plus six molecules of water and six molecules of carbon dioxide into a molequle of glucose and six molecules of oxygen. Glucose is but one of many carbohydrates formed in plants. A general equation for the photosynthesis of a carbohydrate with $\underline{n}$ carbon atoms is:

$$\text{light} + \underline{n}\ CO_2 + \underline{n}\ H_2O \xrightarrow{\text{green plant}} \underline{n}\ O_2 + (CH_2O)\underline{n}$$

Equations for the formation of other types of organic compounds are not as simple, and when an amino acid is formed, additional inorganic reactants are required, as in the formation of cysteine:

$$\text{light} + 3\ CO_2 + \overset{2}{/}H_2O + SO_4^{=} + NO_3^{-} + 3\ H^{+} \xrightarrow[\text{plant}]{\text{green}} C_3H_7O_2NS + 6\ 1/2\ O_2.$$

The fact that light is a reactant in photosynthesis is more easily understood by considering another chemical reaction - combustion. Glucose is a subunit of cellulose, a major constituent of wood. The equation for the combustion of glucose is:

$$C_6H_{12}O_6 + O_6 \xrightarrow[\text{combustion or respiration}]{} 6\ CO_2 + 6\ H_2O + \text{heat, etc.}$$

This is the reverse of the equation for the photosynthesis of glucose, except that heat and other forms of energy are produced more than light. By the principle of conservation of energy, if the combustion reaction liberates energy, the reverse , photosynthetic reaction must absorb energy.

The biological combustion reaction is called respiration and is represented by the same equation as for non-biological combustion. All living cells except green plants in the light must rely upon biochemical reactions as a source of energy.

Respiration is the principal energy-producing biochemical reaction.

All life processes require a continuous supply of energy, and light energy converted by photosynthesis to chemical potential energy of organic matter and oxygen is the only significant primary source of energy for life. Living cells then respire ("burn") these organic compounds with oxygen, harnessing part of the energy released by the reuniting of oxygen with the elements of carbon, hydrogen, nitrogen and sulfur for use in various life processes such as movement and growth. As oxygen combines with these elements, it forms their oxides which are carbon dioxide, water, nitrate and sulfate, and the cycle is complete. According to E.I. Rabinowitch, all organic matter now present on earth will be oxidized by combustion and respiration within ten to twenty years. If this matter were not replenished by photosynthesis during that time, all life would stop.

The chemical basis for energy storage by photosynthesis and energy release by respiration is in large part the reactivity of oxygen. The cloud of electrons surrounding the nucleus of a neutral oxygen atom contains two electrons less than the number needed to satisfy the most stable electronic arrangement for this element. For this reason, oxygen atoms have a very strong tendency to acquire the presence of two additional electrons by forming two partnerships, called bonds, with other atoms. An oxygen atom can form bonds with two different atoms or it can form both bonds with one atom. In each of its bonds the oxygen atom contributes one electron and the other atom contributes one electron. Thus, in water, H_2O, each of the two hydrogen atoms contributes its single electron to a bond with the oxygen atom, thereby fulfilling the tendency of oxygen to acquire two additional electrons. In CO_2, two atoms of oxygen each form two bonds with the single carbon atom which has four bonding electrons. Thus in H_2O and in CO_2 the oxygen atoms satisfy their requirements for electrons for stable arrangements. However, when two oxygen atoms bond with each other the positions of the electron orbitals about the nuclei are such that only one bond is formed between the atoms. This means that they only half fulfill their requirement for electrons. Therefore, the O_2 molecule is relatively less stable than CO_2 and H_2O. The organic products of photosynthesis such as carbohydrate, $(CH_2O)_n$ are quite stable, since C, H and O all have requirements of electrons for stability satisfied. The photosynthetic reaction making carbohydrate thus converts two very stable substances, CO_2 and H_2O, to one stable substance, $(CH_2O)_n$, and one less stable substance, O_2. In doing this, the plants store chemical potential energy, obtained by transforming absorbed light energy. In a similar way, energy is stored in the photosynthesis of fats or proteins.

When an element loses electrons, or has bonded hydrogen atoms removed, as oxygen of water does during photosynthesis, it is said to be oxidized. When an element gains electrons, or gains bonds to hydrogen, as carbon does during photosynthesis, it is said to be reduced. Photosynthesis is therefore an oxidation of water coupled with reduction of carbon dioxide and other inorganic oxides.

Mechanism of photosynthesis: Photo and synthesis stages. Although the net result of photosynthesis is the transfer of hydrogen atoms from oxygen to carbon (as well as to nitrogen and sulfur) by means of light energy, this fact does not describe the mechanism of photosynthesis. For many years scientists were misled by the seemingly simple but untrue theory that O_2 was somehow formed from CO_2, leaving carbon (C) to react with H_2O to form carbohydrate $(CH_2O)_n$. Then photosynthesis by certain sulfur bacteria which do not form O_2 led C.B. van Niel to realize that the oxygen formed by photosynthesis in oxygen-evolving plants comes from water. These sulfur bacteria carry out a reaction which can be written:

$$\text{light} + CO_2 + 2\,H_2S \longrightarrow (CH_2O) + 2\,S + H_2O.$$

Instead of O_2, these organisms make sulfur. Van Niel reasoned that all types of photosynthesis could be represented by the equation:

$$\text{light} + CO_2 + 2\ H_2X \longrightarrow (CH_2O) + 2\ X + H_2O$$

where X is oxygen in oxygen-evolving photosynthesis, but is sulfur in the photosynthesis of sulfur bacteria. He also proposed that this reaction occurs in two stages:

$$\text{light} + 2\ H_2X + 2\ A \longrightarrow 2\ AH_2 + 2\ X \quad \text{(photo-stage)}$$

and $2\ H_2A + CO_2 \longrightarrow (CH_2O) + 2\ A$ (synthesis stage)

A is some compound that carries hydrogen atoms from water to CO_2. Support for this theory came from the discovery of Robert Hill that broken up or partly inactivated green cells could be made to carry out a reaction in the light in which oxygen is evolved but no CO_2 is reduced. In order for this reaction, called the Hill reaction, to work, some chemical must be added to accept the hydrogen atoms or the electrons split from the water molecule. This chemical is called an oxidizing agent because it takes electrons or hydrogen atoms from oxygen in water. One Hill oxidizing agent is quinone, which accepts two hydrogen atoms and becomes dihydroquinone. Other Hill oxidizing agents often contain iron which has lost three electrons and carries a +3 charge (ferric ion, Fe^{3+}). As the green material is illuminated, electrons are transferred from water, O_2 is evolved, and each plus 3 iron ion gains an electron and becomes +2 iron (ferrous ion, Fe^{2+}). In this case, only electrons are transported from the oxygen of water to the oxidizing agent. As they are removed from the water, hydrogen nuclei come off into solution as hydrogen ions (H^+). It is now thought that during photosynthesis itself, some steps in the movement of hydrogen atoms from oxygen to carbon take place as the independent movement of electrons and hydrogen ions. It is the movement of electrons from one atom to another that is important, for hydrogen ions can be released to the aqueous solution or absorbed from it as needed. The Hill reaction, in which light energy is used to bring about the movement of electrons from oxygen to an oxidizing agent probably is similar to the photo- stage of photosynthesis.

The theory that O_2 comes instantaneously from water during photosynthesis was further substantiated by Samuel Ruben and his colleagues who let plants photosynthesize in water enriched with the heavy oxygen isotope, ^{18}O, in place of ordinary oxygen (^{16}O). Plants cannot distinguish isotopes of the same element when they are chemically identical, and so the plants use $H_2{}^{16}O$ just the same way they normally use $H_2{}^{16}O$. The evolved oxygen gas was found to contain ^{18}O. In another experiment just the opposite kinds of water and CO_2 were used. When the plants photosynthesized with $H_2{}^{16}O$ and $C^{18}O_2$ the evolved oxygen contained no ^{18}O at the start of the experiment.

In the 1950s Daniel Arnon and other scientists learned how to prepare plant cell fragments which can perform the entire photo- stage of photosynthesis. Under illumination, these preparations transfer electrons from water to the photosynthetic oxidizing agent which then becomes the reducing agent for the reduction of carbon dioxide in the synthesis stage. This carrier of electrons is a compound called triphosphopyridine nucleotide. In its oxidized form it is denoted as TPN^+, while after it accepts two electrons and a hydrogen ion, it is denoted by TPNH. TPN^+ contains a pentavalent nitrogen atom (it has four bonds and a + charge) while in TPNH this nitrogen atom is trivalent (three bonds and neutral). These forms correspond to van Niel's A and AH_2. TPN^+ (reduced form TPNH) is a type of compound called a coenzyme. Coenzymes work with enzymes to bring about chemical reactions in living systems. Enzymes are biological catalysts - they cause a chemical reaction to proceed at an accelerated rate, but are not charged themselves in the process. Most of the converted light energy that is stored in the photo- stage is stored by the movement of electrons from water to TPN^+. This storage of energy has a mechanical analogy in the pumping of water from a low lake to a pond high on a hill above the lake. The energy used to make the pump run is stored in part in the potential energy of the water in the pond on the hill. If the water is allowed to flow back down the mountain, the energy liberated by its fall may be used to perform useful work.

In an analogous way, energy is stored when electrons are taken from water at a lower chemical potential and transferred to TPN^+, which holds them less tightly than did the oxygen in water. When TPNH releases these electrons, useful chemical work can be performed. An important additional amount of energy is stored another way. Accompanying the transport of electrons another coenzyme which is really an acid anhydride is formed by the elimination of water from inorganic phosphate ion ($HPO_4^=$) and an organic phosphate, adenosine diphosphate or ADP. This reaction can be represented by the equation:

$$\underset{\text{ADP}}{\text{AMP-0-PO}_2^-\text{OH}} + \underset{\text{phosphate}}{\text{HOPO}_2\text{OH}^=} \longrightarrow \underset{\text{ATP}}{\text{AMP-0-PO}_2^-\text{-0-PO}_2\text{OH}^-} + \underset{\text{water}}{\text{HOH}}$$

This is another example of a chemical reaction which goes in the direction written only if energy is supplied from some other source. The reverse reaction, in which the anhydride reacts with water to make ADP and phosphate, liberates energy. The formation of ATP is found in all biochemical systems, and is a universal mechanism for storing and transporting chemical energy. The ATP often gives up its energy to other chemical substances by reactions which replace hydrogen with phosphate. Thus a sugar, which can be represented by R-OH can be converted to a sugar phosphate by the reaction:

$$\underset{\text{ATP}}{\mathrm{AMP{-}O{-}PO_2^-{-}O{-}PO_2OH^-}} \rightarrow \underset{\text{sugar}}{\mathrm{ROH}} \rightarrow \mathrm{AMP{-}O{-}PO_2^-OH} + \mathrm{ROPO_2OH^-}$$

The sugar phosphate has more energy stored in its bonds than does sugar, hence it is more reactive. The formation of ATP during photosynthesis is called photosynthetic phosphorylation or photophosphorylation. Both ATP and TPNH, formed concurrently with O_2 by the photo- stage of photosynthesis, are used in the synthesis stage during which carbon dioxide is reduced to carbohydrate and other organic compounds.

Transformation of light energy. The first step in the transformation of light energy is its absorption by plant pigments. All photosynthetic plants contain some form(s) of the green pigment, chlorophyll, and probably all contain carotenoids, which are generally yellow. Higher plants contain chlorophyll a ($C_{55}H_{72}O_5N_4Mg$) and chlorophyll b ($C_{55}H_{70}O_6N_4Mg$) and four major carotenoids, β-carotene ($C_{40}H_{56}$), luteine ($C_{40}H_{56}O_2$), violaxanthin and neoxanthin. Some algae contain essentially the same pigments, but many algae have other pigments which differ from these in chemical details. These pigments, as well as the entire photosynthetic apparatus, are contained within a membrane-enclosed unit called the chloroplast which is inside the green cell. The green color of plant cells is due entirely to these chloroplasts, since the remaining part of the cell has no green pigments. A typical chloroplast is shaped roughly like a bent cucumber and is about one micron (one thousandth of a millemeter) across and four microns long. This shape and size varies considerably. Large green plant cells, such as occur in the leaves of many land plants, contain many chloroplasts. Small unicellular algae, for example Chlorella pyrenoidosa contain only a single chloroplast, which occupies the greater part of the cell.

A chloroplast is a highly complex structure. This structure can be seen with the electron microscope which permits viewing much smaller structures than can be seen with a light microscope. The smallest particle which can be distinguished (resolved) with the light microscope is about 0.5 micron. By 1961, electron microscopes could resolve particles one thousandth that size (0.5 millemicrons = 5 Å), under the best conditions. The electron microscope has revealed very thin sheets or layers of different kinds of material which sometimes extend the length and breadth of the chloroplast. The repeating interval (thickness of a set of layers) is about 160 Å - 220 Å. A set of layers appears to consist of a sandwich made up of a layer of lipid (fat and similar substances) and protein globules between two smooth layers of lipid and perhaps structural protein. The globules are about 100 - 150 Å thick. The smooth layers are closed at the ends, making a unit like a very thin envelope. In some chloroplasts, particularly those of leaf cells, these layers, called lamellae, are thicker and stacked more closely in some regions of the chloroplast. These regions, called grana, are often circular. In some pictures made with the electron microscope these grana appear like stacks of very thin hotcakes. The regions of the chloroplasts in which the lamellae are thinner and less abundant are often referred to as the stroma. Regardless of the presence or absence of grana, the site of the photo- stage of photosynthesis is considered to be in the lamellae, which contain the pigments. It is suspected that the stroma is the site of the synthesis stage: that is the reduction of CO_2 to organic compounds. The role of grana in higher plants is not yet clearly understood. Perhaps they represent an evolutionary step towards a more efficient flow of energy and materials through the complex but microscopic living factory we know the chloroplast to be.

Scientists have broken up cells and isolated whole chloroplasts by grinding up spinach leaves, separating out the large pieces, and then spinning down the chloroplasts out of the cytoplasmic fluid in a centrifuge. Properly prepared, these chloroplasts can carry out photosynthesis, though the rate of carbon reduction is slower than in the whole plant. Chloroplasts have been broken up into smaller and smaller fragments by means of high frequency sound waves and in other ways. Particles of different sizes are separated from the mixture by centrifuging at several speeds. In this way, particles containing only one to six of the protein and lipid globules plus some of the smooth layer have been obtained. These particles still contain chlorophyll and other key compounds. When illuminated they absorb light and perform the Hill reaction, described earlier, in which they transfer electrons from water to a suitable electron acceptor. Under some conditions, these particles, like larger chloroplast fragments, can use light energy to make ATP from ADP and inorganic phosphates. The smallest particle which can use light energy to transfer electrons from water to TPN is defined as a quantasome. It appears that the quantasome may be identical with the protein-lipid globule.

Under suitable conditions, another kind of material, soluble in water and colorless can be obtained from the chloroplasts. This material is left after all the green, particulate matter is spun out by centrifugation. It contains the protein molecules that serve as enzymes, or biological catalysts for the reduction of carbon dioxide to organic compounds. However, this soluble fraction cannot reduce carbon dioxide unless it is supplied with ATP and TPNH. When this soluble material, itself unable to make ATP and TPNH, is mixed with a preparation of small lamellar fragments, the mixture absorbs light and reduces CO_2. The lamellar fragments plus the soluble proteins and other substances in the soluble fraction are therefore carrying out photosynthesis, after recombination of the two preparations. The lamellar fragments perform the photo- stage while the soluble fraction performs the synthesis- stage of photosynthesis.

Two very important questions about the mechanism of photosynthesis are: how do the quantasomes use the light energy absorbed by the pigments to cause the transfer of electrons from water to TPN^+; and, how do they use some of the light energy to make ATP? These questions are still not completely answered. It now appears that electrons are taken from water and transferred step by step to TPN^+, which then becomes TPNH. Some of these steps are "downhill". That is, they occur spontaneously and give up energy to the surrounding environment or to other chemical reactions. Two of the steps are thought to be "uphill". These steps require an input of energy from the light. The evidence indicates that the light energy used in each of these two steps may come from a specific pigment system.

The electrons carried from the oxygen atom of water to TPN^+ must be carried each step by a different chemical compound. Not all of these electron carriers have been identified. Several of the electron carriers contain oxidized iron which lacks two or three electrons compared with metallic iron. These forms of iron are ferrous iron, abbreviated Fe^{2+}, and ferric ion abbreviated Fe^{3+}. When Fe^{3+} accepts an electron it becomes Fe^{2+}. The electron, which has one minus charge, neutralizes one of the iron's positive charges while it is being held by the iron. The Fe^{3+} and Fe^{2+} carriers are not free ions, for they are held by special organic compounds. One effect of these compounds is to make the iron hold electrons more or less tightly during electron transport. Thus the transfer of an electron from one bound iron atom to another iron atom held by a different organic compound may release energy (downhill step) if the acceptor iron holds more tightly to the electron than the giver, or donor, iron. Other steps in the electron transfer may be performed by other metal atoms, particularly magnesium (Mg) and manganese (Mn), and by other types of electron carriers, such as plastoquinone.

The absorption of light by a pigment molecule results in an increase of energy of the molecule. The molecule is then in an excited state. In this excited state, some of the electrons of the molecule have been shifted from their normal orbitals about the nucleus to other orbitals in which the molecule has a greater total energy. If the electrons return to their normal orbitals, the molecule returns to its ground state and gives off energy, as emitted light, as heat, or by some chemical reaction. In photosynthesis, the return of the excited pigment molecules to their ground state is accompanied by the transfer of electrons in one of the "uphill" steps between water and TPN^+.

One or more of the "downhill" steps of this electron transport gives its energy to a reaction which makes ATP from ADP and inorganic phosphate. Thus photophosphorylation is accomplished.

Synthesis: The reduction of CO_2. The synthesis of organic compounds by the reduction of CO_2 (and of nitrate and sulfate) also takes place in the chloroplast. The steps in this synthesis are mediated by enzymes and coenzymes. The coenzymes ATP and TPNH come from the photo- reaction in the lamella and supply the energy and electrons necessary for the synthetic reactions.

The reduction of CO_2 consists of the transfer of electrons to CO_2. As a result, some of the C-O bonds are replaced by C-H, C-C and O-H bonds. This reduction of CO_2 takes place in a number of steps of which some 15 or more are part of a cyclic sequence of reactions discovered in 1953 by Melvin Calvin and his coworkers. This group used radioactive carbon, ^{14}C, as a tracer element in place of ordinary carbon, ^{12}C, to follow the path of carbon from CO_2 through these reactions. In 1961 Calvin was awarded the Nobel Prize in chemistry for this work.

The important compounds in the cyclic pathway have from three to seven carbon atoms linked together in a chain so that each carbon atom has one or two bonds to another carbon atom, one or two bonds to oxygen, and one or two bonds to hydrogen. The total number of bonds per carbon atom is always four. All but one of the compounds in the cycle are sugar phosphates. That is, they are sugars to which one or two phosphate groups ($-OPO_3H^-$) have replaced OH groups. The other compound is a sugar acid phosphate called 3-phosphoglyceric acid and abbreviated PGA. It is similar to a sugar phosphate with three carbon atoms but differs in that one of the carbon atoms has three bonds to oxygen.

One of the sugar phosphates which has five carbon atoms is called ribulose monophosphate. ATP from the photo- stage reacts with ribulose monophosphate to add a second phosphate group and make ribulose diphosphate. The addition of this extra phosphate group gives the compound more energy because it now contains some of the energy that had been stored in the ATP molecule. Consequently, the ribulose diphosphate has a stronger tendency to react with other substances and to form new bonds.

An enzyme of the chloroplast binds CO_2 and holds it and a Mg^{2+} ion in a tight complex. This CO_2-enzyme complex reacts with the reactive ribulose diphosphate to form a new C-C bond between carbon dioxide and one of the carbon atoms of the sugar phosphate. The result of this reaction is the formation of a compound with six carbon atoms. This six carbon compound is so delicate that it can be broken by water into two fragments, each of which is PGA. In the intact cell where this unstable six-carbon compound is protected by subcellular structure a different reaction may conceivably occur, though there is as yet no definite proof. This hypothetical reaction would result from the addition of two electrons to the unstable six-carbon compound, causing it to be reduced and split to one molecule of PGA and one molecule of three carbon sugar phosphate. This reduction reaction would use up a molecule of TPNH, converting it to TPN^+.

The one or two molecules of PGA formed by the carboxylation reaction are then reduced by one molecule of TPNH each to make three carbon sugar phosphate (triose phosphate). This reduction amounts to the transfer of two electrons to that carbon atom of PGA which has three bonds to oxygen. Such a group of atoms consisting of a carbon atom linked by one bond to one oxygen and by two bonds to another oxygen atom is called a carboxylate group ($O=\overset{|}{C}-O^-$). It is responsible for the acid properties of PGA. In this group, the oxygen atom with only one bond to carbon has a negative charge due to an electron excess of one over that required for neutrality. Actually, this electron is shared equally by the two oxygen atoms of the carboxyl group, so that each of the oxygens has an average negative charge of 1/2 and an average 1 1/2 bonds to the carbon atom. This kind of arrangement makes this group rather stable, hence somewhat unreceptive towards additional electrons. Once again, therefore, ATP is called on to prime the molecule by putting more chemical energy into it and making it more reactive. The enzyme system accomplishes this priming by transferring the end phosphate group of ATP onto one of the oxygen atoms of the carboxyl group, thereby making the two oxygen atoms dissimilar and spoiling their equal sharing of electrons and bonds to carbon. The oxygen atom linked to phosphorus now has only one bond to carbon ($O{=}\overset{|}{C}{-}OPO_3H^-$).

When TPNH transfers a hydrogen atom plus an electron (equivalent to two electrons plus a hydrogen ion, H^+) to the carboxyl carbon, the single C-O bond is broken, and the oxygen linked to phosphorus comes off in inorganic phosphate, HPO_4^{2-}. The carbon atom now has two bonds to a single oxygen atom, one bond to hydrogen and one bond to the next carbon atom in the chain ($O{=}\overset{|}{C}{-}H$). This new group is called an aldehyde group, and is one of the functional groups of one kind of sugar. Thus the sugar acid phosphate (PGA) has been reduced to a sugar phosphate (triose phosphate).

The biochemical steps just described can be denoted by chemical equations in words and symbols as follows:

1) Ribulose monophosphate + ATP → ribulose diphosphate + ADP

2) Ribulose diphosphate + CO_2 → unstable C_6 compound

3a) Unstable C_6 compound + H_2O → 2 PGA

or

3b) Unstable C_6 compound + (+ ATP?) + TPNH ——

→ triose phosphate (C_3) + PGA

4) PGA + ATP + TPNH → ADP + $H_2PO_4^-$ + triose phosphate (C_3)

Reaction 3a) represents the split of the unstable C_6 compound by water to two molecules of PGA, while 3b) is the split by reduction, discussed earlier. Either way, the end result of reactions 1) through 4) is the conversion of ribulose monophosphate (C_5) and CO_2 to two molecules of triose phosphate (C_3) with the expenditure of two TPNH molecules (four electrons) and of two or three ATP molecules. This series of reactions represents the entire input of electrons and energy from the light reaction to the basic carbon reduction cycle. Of course additional expenditures of cofactors from the light reaction are required from the reduction of nitrate and sulfate, and for the conversion of compounds such as triose phosphate and PGA from the cycle into organic materials such as carbohydrates, proteins and fats.

Once triose phosphate is formed, five molecules of this

C_3 (that is, three carbon) compound are converted to three molecules of the C_5 compound, ribulose monophosphate, and the cycle is complete. This conversion takes about 11 separate biochemical steps in all. Beginning with triose phosphate (C_3) and expressed only in terms of changes in the numbers of carbon atoms linked together in sugars, this part of the cycle proceeds as follows:

$C_3 + C_3 \longrightarrow C_6$, $C_6 + C_3 \longrightarrow C_4 + C_5$, $C_4 + C_3 \longrightarrow C_7$, $C_7 + C_3 \longrightarrow C_5 + C_5$

which in sum gives $5\ C_3 \longrightarrow 3\ C_5$. The three molecules of ribulose monophosphate made from <u>five</u> molecules of triose phosphate after carboxylation and reduction give <u>six</u> molecules of triose phosphate. Thus the net result of one complete turn of the cycle is the conversion of three molecules of carbon dioxide to one extra C_3 organic compound. This gain in organic material is drained from the cycle by reactions which make sugars, fatty acids, and amino acids, from which such materials as starch, fats and proteins are built.

The fact that not only carbohydrates, but also amino acids, and presumably fatty acids, are direct products has also been established through the use of radiocarbon as a tracer. The chloroplast is not merely a particle specializing in the synthesis of starch and sugars, but rather it is a highly complex and well-organized factory capable of synthesizing virtually all of the materials from which it is built and at the same time satisfying the needs of the nonphotosynthetic parts of the cell and the plant for reduced carbon compounds.

For the benefit of those familiar with chemistry, the path of carbon in photosynthesis is summarized in the diagram in Fig. 1. The identities of the compounds as numbered in the diagram are as follows:
(1) the unstable C_6 addition compound, (2) phosphoglyceric acid (PGA), (3) phosphoglyceraldehyde and (4) dihydroxyacetone phosphate, both triose phosphates, (5) fructose diphosphate, (6) erythrose phosphate, (7) sedoheptulose diphosphate, (8) xylulose phosphate, (9) ribose phosphate, (10) ribulose phosphate, and (11) ribulose diphosphate. A few, but by no means all of the paths leading from the cycle to synthetic products are indicated. UDPG stands for uridine diphosphoglucose, an important intermediate substance for the synthesis of polysaccharides, such as starch and cellulose, as well as sucrose which is ordinary table sugar. Serine, alanine, and aspartic acids, are amino acids, basic units for the construction of protein.

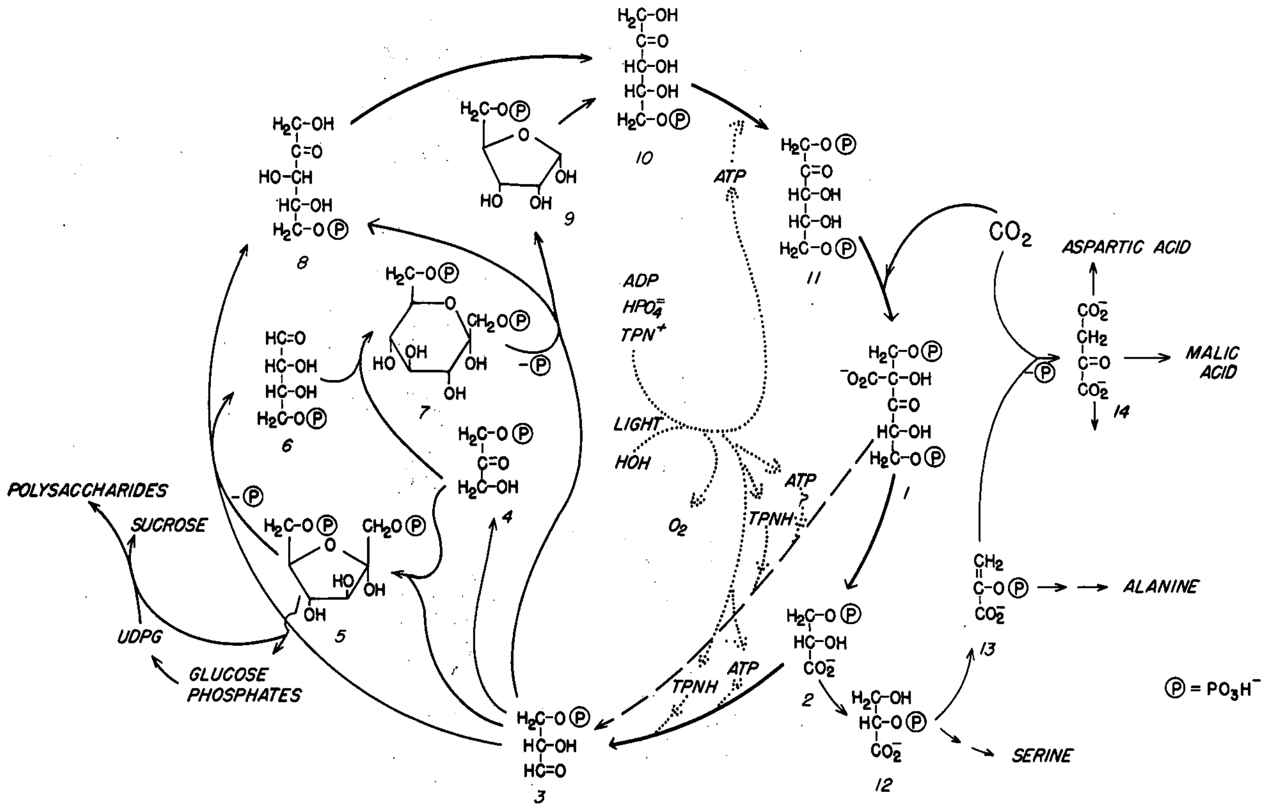

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Figure 1. The Carbon Reduction Cycle (Calvin Cycle) of Photosynthesis.