THE HILL REACTION DEMONSTRATED BY THE ACTION OF ELECTRIC CURRENT INSTEAD OF LIGHT AND CHLOROPLASTS

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Without depending upon both light energy and isolated chloroplasts, the Hill reaction [1,2] can be demonstrated by the expenditure of electrical energy. When an electric current (direct current) passes through a *dilute* aqueous salt solution containing an oxidizing agent as a hydrogen acceptor (we used either 0.005% NaCl, plus 0.01% indigocarmine solution, or 0.002% 2,6-dichlorophenol-indophenol) phenomena occur similar to the Hill reaction, *i. e.*, we are able to observe dye reduction and oxygen evolution. The following are the electrode reactions:

The cathode reaction is

$$2e^- + 2H_2O \longrightarrow 2H + 2OH^- \tag{1}$$

$$2H + \text{Indigocarmine} \longrightarrow \underset{\text{(Indigowhite)}}{\text{Indigocarmine-2H}} \tag{2}$$

Two electrons from the cathode (we used a lead electrode) react with two molecules of water to produce two hydroxide ions and two hydrogen atoms. The hydroxide ions produced near the electrode can be proved by means of indicators. The hydrogen atoms never form molecular hydrogen (because a high over voltage is required to form molecular hydrogen when a *pure* lead electrode is used), but reduce indigocarmine to form indigowhite. The solution near the cathode, therefore, graduallv becomes colorless. The lead electrode must be purified before use by an electrolytic method (using the lead electrode as the anode, another supplemental lead electrode as the cathode, and 20% sulfuric acid as an electrolyte). By this purification, the lead electrode, which is coated with a dark brown layer of lead dioxide, is ready for use.

The anode reaction is

$$2H_2O \longrightarrow O_2\uparrow + 4H^+ + 4e^- \tag{3}$$

The anode (we used platinum) obtains four electrons from two water molecules which decompose to form four hydrogen ions and one oxygen molecule. The production of hydrogen ions near the anode can be proved by means of indicators. Oxygen can be proved by indigowhite. The diaphragm was not used in order to observe the instantaneous result of electrolysis.

The over-all reaction is obtained by multiplying Equation (1) and (2) by two and adding Equation (3). It is

$$6H_2O + 2\ \text{Indigocarmine} \longrightarrow \underbrace{2\ \text{Indigocarmine-2H} + 4OH^-}_{\text{cathode}} + O_2\uparrow + \underbrace{4H^+}_{\text{anode}} \tag{4}$$

The hydrogen ions and hydroxide ions produced slowly diffuse together and combine to form water molecules. When 2,6-dichlorophenol-indophenol is used as an oxidant, the production and neutralization of these ions can be clearly demonstrated during electrolysis. The over-all electrolysis reaction, therefore, is

$$2H_2O+2\ \text{Indigocarmine} \xrightarrow[\text{electrolysis}]{} 2\ \text{Indigocarmine-}2H+O_2\uparrow \qquad (5)$$

This last summary equation is the same as the Hill reaction, except electric energy is used instead of light energy and isolated chloroplasts.

The result of the present experiment leads us to a suggestion that the photolysis of water by green plants in the first step of photosynthesis is presumably the process of electrolysis of water as described above. In the chlorphyllous cell, the chlorophyll molecule can be considered as a minute photovoltaic cell, generating electric current for electrolysis of water under the action of light.

LITERATURE CITED

(1) HILL, R. Oxygen evolved by isolated chloroplasts. Nature 139: 881-882. 1937.

(2) HILL, R., and SCARISBRICK, R. Production of oxygen by illuminated chloroplasts. Nature 146: 61-62. 1940.