23 November 1962, Volume 138, Number 3543 SCIENCE

Primary Quantum Conversion in Photosynthesis

Low-temperature photoparamagnetism bespeaks electron transfer and migration as the earliest event.

Melvin Calvin and G. M. Androes

One of the outstanding features, possibly a unique feature, of the process of photosynthesis as it occurs in nature today is the ability of the organism, either green plant or bacterium, to utilize a quantum of energy of the order of 38,000 calories for green plants and 40,000 for the bacteria to accomplish an ordered chemical transformation at room temperature with a relatively high degree of efficiency. The apparatus which accomplishes this, we must remember, is of labile organic construction, and the thermal reactions which can be performed by such a system rarely, if ever, involve energy changes higher than 10,000 or 15,000 calories; thus, manipulation of a package of energy two or three times that size without damage to the apparatus and in a highly directed and specific way is an impressive accomplishment indeed.

The ultimate products of this energy transformation have long been known to us, in the form primarily of carbohydrate and oxygen but of course including all of the plant substances. In fact, it is currently possible to describe some more immediate products of this energy conversion process in terms of more transient, specific energy-storing materials. We have every reason to believe that two such energy-storing intermediates which can be used to produce the final, or more long-term, storage materials are reduced pyridine nucleotide and adenosine triphosphate. It may turn out that other transient energy-bearing chemical intermediates may be still closer to the energy transformation step itself.

At this point it is perhaps worth while to define, as nearly as we can, the properties of the energy-bearing intermediate or intermediates which we consider to be the earliest form of chemical energy into which the electromagnetic quantum may be converted. Such a material would be the first chemically definable compound in thermal equilibrium with its environment, but, quite clearly, not in chemical equilibrium with it since, under such a definition, oxygen itself could not be evolved.

We will consider the primary quantum conversion act, then, as that act, or sequence of events, that follows the absorption of the electromagnetic quantum and terminates with the appearance of the thermally relaxed, chemically defined individual which may then proceed, by direct thermal work-performing reactions, to produce the next transient and, finally, the ultimate products of photosynthesis.

Under such a definition, an electronically excited state of a molecule, or array of molecules, such as might result from the primary absorption of a quantum of light would not be considered a chemical entity distinct from the parent material before light absorption. Only after the energy stored in this electronically excited state had been transformed into new chemical species which could then proceed to react, or interact, with their environment in accordance with thermodynamic principles would we consider the quantum conversion process accomplished. All succeeding reactions from these initial chemical species would, of course, be dark reactions.

Very early in the consideration of theories of photosynthesis it was recognized from the nature of the ultimate reaction that an oxidation and a reduction must be involved. The earlier proposals involved a direct transformation of the electronic excitation into the energy of atomic rearrangement, resulting in the transfer of hydrogen from water to carbon dioxide. There have been many variations of this proposal. However, it remained for van Niel, in a brilliant analysis on the comparative biochemistry of the photosynthetic process throughout the scale of living organisms, to simplify the primary quantum conversion act into the production of a primary transient oxidant and a primary transient reductant (*1*). These could then go their separate ways, the reductant ultimately converting the carbon dioxide to the level of carbohydrate and the oxidant converting some suitable substrate, in the case of the bacteria, to an oxidized form, or ultimately being eliminated as molecular oxygen in the higher green plants.

This separation of oxidant and reductant was formulated by van Niel in terms of [OH] and [H], as representative symbols of the oxidant and reductant, respectively. In green plant photosynthesis, these two fragments

Dr. Calvin is professor of chemistry at the University of California, Berkeley, and a member of the staff of the Lawrence Radiation Laboratory. Dr. Androes, until recently affiliated with the University of California, Berkeley, is now professor of physics at the American University, Beirut, Lebanon. This is the text of a lecture delivered at a conference on photosynthesis held in Gif-sur-Yvette, France, in July 1962.

would ultimately be derived from water. However, the essential feature is the primary production of oxidant and reductant, and in physical terms this means the production of a molecule, or species, avid for electrons, frequently represented by + or "hole," and a species generous with its electrons—that is, with a relatively high electron pressure—most readily represented by e^-, encircled (sometimes the e is omitted).

How these two particles, or species, which would be produced as a result of the conversion of 30 to 40 kilocalories of energy might be separated from each other so as not to back-react is one of the problems. Any mode of reaction, such as molecular rearrangement or dissociation, which might be used to store the 30 or 40 kilocalories must of necessity be so arranged that the product does not immediately revert to its initial state with the evolution of the stored energy in the form of electromagnetic radiation or heat. This requires one of two assumptions: either that a suitable energy barrier is interposed between the primary products and the initial state or that the primary products are effectively separated from each other physically so that the recombination is statistically improbable.

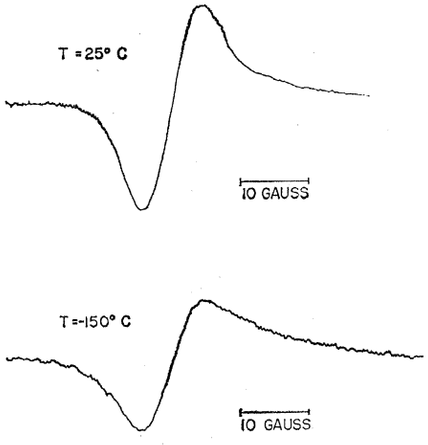


Fig. 1. Light signals from whole-spinach chloroplasts.

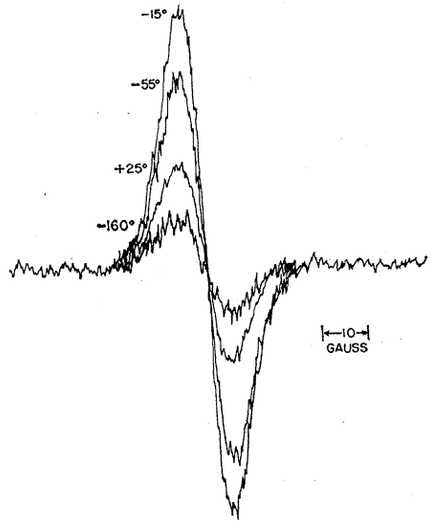


Fig. 2. Electron-paramagnetic-resonance signals from *Rhodospirillum rubrum* (5 minutes continuous illumination).

To overcome a barrier of any appreciable size would require such a large fraction of the initially absorbed energy quantum that the total energy stored in the process would be a relatively small fraction of the quantum absorbed. The relatively high efficiency of the overall process is at variance with this deduction, and so we turn to the other alternative—namely, effective separation of the reaction products. This can be most easily accomplished if the reaction products are not massive atoms but only electrons. We are thus led to the obvious suggestion that the primary quantum conversion act involves a separation of electrons from the "holes," or positive charges, which they leave behind in the molecules from which they come, a theoretical suggestion made very early by Katz (*2*). It has been elaborated independently in our laboratory from similar theoretical reasoning (*3*), and based upon model experiments (*4*) and direct biological observation in recent years. A good deal of supportive evidence has been accumulating in the last half dozen years (*5–7*).

With the discovery, by Davenport and Hill (*8*), of cytochrome *f* in the green tissues of plants, Hill was even able to suggest that the separation took place in two distinct quantum steps (*9*)—that the first one led to the reduction of the cytochrome associated with the production of a high-level oxidant and the second, ultimately to the oxidation of cytochrome with the concomitant production of a strong reducing agent.

Experimental evidence for such a process has since been accumulating. That the illumination of the photosynthetic apparatus of either green plant or bacterium would result ultimately in an electron transfer reaction was first seen in the results of Lundegardh (*10*) and Duysens (*11*). They demonstrated by differential spectrophotometry that the illuminated plant, or particle, carried more oxidized cytochrome than did the corresponding plant or particle kept in the dark. Since then, this type of experiment has been broadly expanded in many laboratories.

However, it remained for another type of observation to show unequivocally that the absorption of light by the apparatus of any photosynthetic organism resulted in the transport of an electron from a paired condition at one site to an unpaired condition at another. Such an observation would distinguish the transport of one electron from the transport of a pair. The unpaired electron should make itself apparent by virtue of its paramagnetism, and with the appearance of high-sensitivity microwave techniques for the observation of electron paramagnetic resonance, it was possible to demonstrate just such a process (*12, 13*).

We are concerned in this article (*14*) with the information that can be obtained by such measurements in conjunction with other physical and

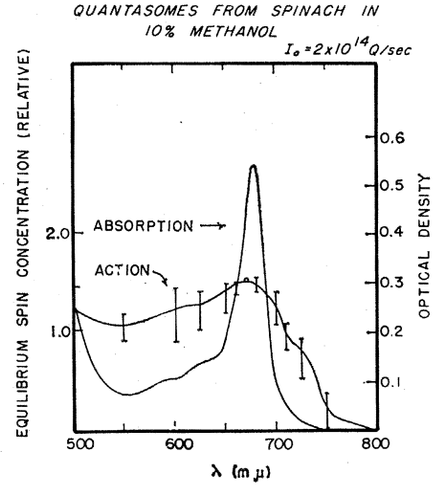


Fig. 3. Absorption and action spectra of quantasomes from spinach chloroplasts.

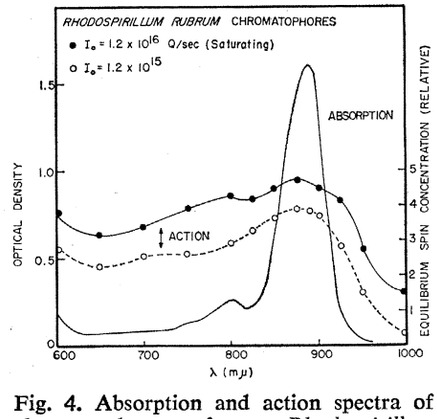


Fig. 4. Absorption and action spectra of chromatophores from *Rhodospirillum rubrum*.

chemical parameters that can be varied, as well as with the relationship of these magnetic changes to the optical changes upon illumination, which are many and varied.

Experimental Results

Electron spin resonance experiments (*15*). When photosynthetic tissue, suitably prepared, is illuminated in a cavity of an electron paramagnetic resonance (EPR) spectrometer, it is possible to see the electron paramagnetic resonance of the unpaired electrons that are produced. Such signals are produced in whole-spinach chloroplasts, both at 25° and at −150°C, at a rapid rate. The rise time is less than the response time of the instrument in both cases. The signals so produced are shown in Fig. 1 for whole-spinach chloroplasts (*13*). Signals produced in the whole organism of *Rhodospirillum rubrum* maintained at various temperatures and illuminated with white light are shown in Fig. 2. The signals produced in the isolated chromatophores from these organisms are identical in shape and form and other physical properties, insofar as we have been able to determine.

That these unpaired spins are produced by light absorbed by the corresponding chlorophylls is shown in the action spectra for green plant quantasomes, reproduced in Fig. 3 (*16*), and for *R. rubrum* chromatophores as shown in Fig. 4 (*16*). It is interesting to note the possibility that an inflection point exists on the long-wave side of the absorption spectra of the quantasomes, corresponding to what may possibly be a difference in the action of light at wavelengths somewhat longer than 700 millimicrons.

It has been possible to separate the green-particle EPR signal into two components, as shown in Fig. 5*a*. In the whole chloroplasts, two distinct signals can be seen. One of them is a sharp signal with a very rapid growth and decay time at room temperature; the other is a much broader signal with a slow growth and decay time at room temperature. It has been possible, by suitably fracturing the chloroplasts, not only to separate them into a soluble component and a green particle containing all, or almost all, of the chlorophyll (the quantasome) (*17*) but also to show that the sharp signal remains associated with the quantasome particle while the broad one is washed out with the soluble component and can be observed separately, as shown in Fig. 5*c*.

Temperature effects. Very early in the work on the observation of the production of unpaired spins in photosynthetic tissue it was recognized that temperature was one physical variable which would help to distinguish between the production of ordinary chemical radicals involving the separation of atoms, or at least the diffusion of molecular particles, and unpaired electrons produced by simple electron transfer and more or less delocalized orbitals in molecular arrays. Quite clearly, the ability of such signals to appear at very low temperatures, at least as low as liquid nitrogen temperature and perhaps lower, would imply the physical nature of the mechanism that was forming them.

Therefore, the appearance of these signals was examined as a function of temperature, almost down to liquid nitrogen temperatures. Thus, in Fig. 6 we see that the rise time of the spin produced in whole-spinach chloroplasts is still less than the instrument response time, even at the low temperatures. It is important to note, however, that in this material the signal, once it is produced at low temperatures, does not decay until the material is warmed.

When the temperature is lowered on the chromatophores from *Rhodospirillum rubrum*, the rise time is again unchanged within the limitations of the instrument (Fig. 7). However, there is an important difference in the signals in this organism and in the green plant material—namely, in *R. rubrum*, while the decay of the signal is complex (that is, shows a number of different decay constants) at room temperatures, by the time the temperature reaches −112°C, all of the slow decays have been frozen out, and they remain so down to −150°C; all that remains is a decay time more rapid than the instrument can follow. In other words, there exists in the chromatorphores a system for the production of unpaired spins at low temperature which appears to be kinetically temperature-independent for both its formation and its decay (*16*).

Optical density changes. An examination of the kinetics of the color changes in both of these materials (chromatophores and quantasomes) has been under way in several laboratories, particularly those of Duysens, of Witt, of Chance, and more recently, of Kok. It was observed by Chance and Nishimura that the color changes in the region 550, 523, and 430 mμ induced by illumination could be achieved at liquid nitrogen temperature quite as rapidly as at room temperature (*18*). However, these changes did not decay at liquid nitrogen temperature. Similar changes at around 550, 430, and 405 mμ induced by illumination of chloroplast material have also been induced at liquid nitrogen temperature, but they do not recover—that is, the optical-density

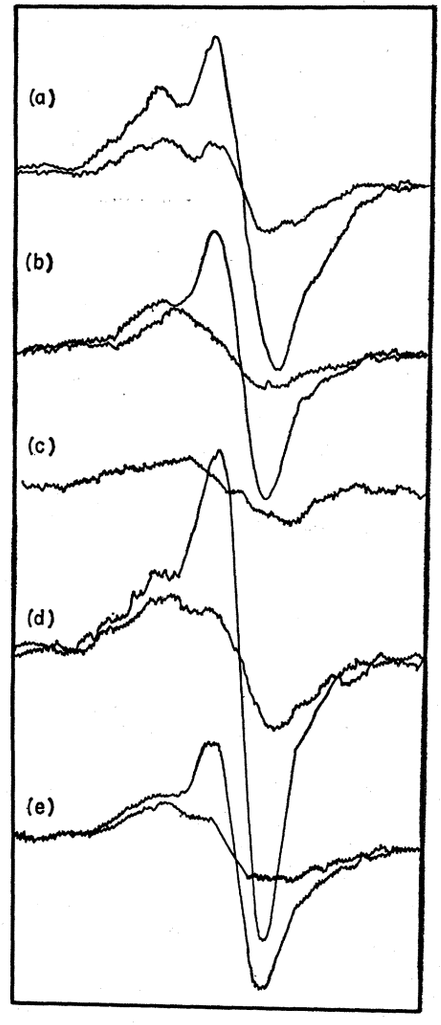


Fig. 5. Electron-paramagnetic-resonance signals (dark signal and light signal, if any) in several green-particle fractions. (*a*) Whole chloroplasts; (*b*) quantasomes plus soluble protein; (*c*) colorless soluble protein bleached from whole chloroplasts; (*d*) washed quantasomes; (*e*) quantasomes plus soluble protein. In each case the trace containing the larger signal is the one produced in the light. The magnetic field increases to the right. If a basic chlorophyll concentration C_o is defined as 15 milligrams of chlorophyll per milliliter of sample, the chlorophyll concentrations in the samples containing pigmented particles are as follows: (*a*) $\sim 3\,C_o$; (*b*) $\sim C_o$; (*d*) $\sim 2\,C_o$; (*e*) $\sim C_o$.

changes are "frozen in" (*19*). These changes have been called cytochrome oxidations in both cases. It is therefore clear that, at least in the case of the purple bacteria (*Chromatium, Rhodospirillum rubrum, Rhodopseudomonas spheroides*) (*20*), the unpaired spin signal which is reversible at low temperature does not reside in the cytochrome (*20*).

However, some color change which is reversible even down to 1°K, can be induced by illumination in purple bacteria. Arnold and Clayton observed an optical-density increase at approximately 420 mμ in chromatophores from *Rhodopseudomonas spheroides* which was reversible down to 1°K (*7*). Further studies by Clayton on purple bacteria have demonstrated reversible changes at around 430 mμ without concomitant cytochrome changes (*21*). It therefore appears certain that at least some of the optical-density change observed in the 420-mμ region is due not to cytochrome change but to some other change resembling a simple physical electron transfer reaction.

While the electron spin resonance experiments have not yet been carried to this lower temperature, the fact that no change at all in either the signal or its kinetics has been observed on passing from −112° to −150°C suggests that the situation will remain unchanged at lower temperatures. We are therefore inclined to associate the unpaired spin which we have observed with the light-induced reversible optical-density change at 420 mμ seen by Arnold and Clayton.

Redox reactions. In an attempt to place the redox level of some of the constituents in the electron transport chain which seem to be involved here, the assumption has been made that an external redox couple could control the oxidation level of a component in the electron transport chain at the corresponding redox level. Various such couples have been used, ranging in potential from those having a high electron pressure, approaching that of pyridine nucleotide −0.3 volt, to those having a high electron affinity, such as ferricyanide with a potential of about +0.45 volt.

When bacterial chromatophores were treated with a variety of such redox systems, it was found that ferricyanide would induce optical changes in the chromatophores which resembled very closely the changes produced by illumination. A comparison of these optical-

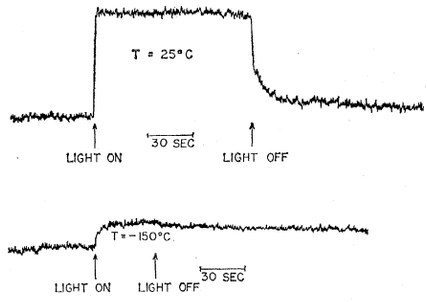


Fig. 6. Growth and decay curves from whole-spinach chloroplasts.

density changes induced in the chromatophores of a carotenoidless mutant of *Rhodopseudomonas spheroides* is shown in Fig. 8, taken from the work of Clayton (*21*). It seems quite clear that the major optical-density decreases at 870 to 890 mμ are indeed associated with the oxidation of chlorophyll.

A similar relationship between the light-induced optical changes and changes induced by ferricyanide on the green particles (chloroplasts or quantasomes) has been observed by Kok and Hoch (*22*) and by Witt (*19*). Here the change is a decrease in optical density at 705 mμ as well as a decrease at 430 mμ. The fact that the light-induced optical-density changes are reversible at low temperatures in the chromatophores and not reversible at low temperatures in the quantasomes, corresponding in behavior to the unpaired spins in both cases, is added evidence that the changes are indeed due to the same, or to closely related, species in the two cases—namely, to the chlorophyll.

Finally, it has been found that the electron spin signal can also be induced in these two particles by oxida-

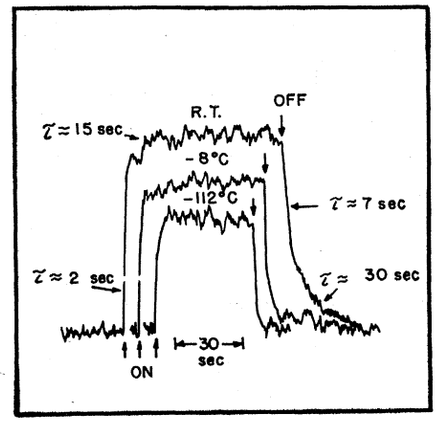


Fig. 7. Rise and decay of the electron paramagnetic resonance in the chromatophores of *Rhodospirillum rubrum.*

tion with ferricyanide. This is probably the same process as that reported for particles from a red alga by Kok (*23*). Since the oxidation of the chlorophyll (Chl) could produce a Chl^+ radical or "hole" in an ordered array, it would appear that the optical signal and the spin signal might, to a first approximation, be due to the formation of Chl^+. Further evidence can be found in the fact that when the Chl^+ is produced chemically by ferricyanide, as evidenced either by the optical-density change or by the electron spin resonance signal in the dark, the magnitude of the light-induced optical changes and the light-induced EPR signals is diminished.

In fact, when a quantitative estimate is made of the amount of oxidation-produced EPR signal as a function of the ferro- ferricyanide ratio (and thus of the electrochemical potential) in the medium and when this amount is compared with the amount of additional unpaired spin that can be induced by the light on the same system, a complementarity between the two is exhibited, as shown in Fig. 9 (*24*). The point for production of the dark signal up to half its maximum value corresponds approximately to the point for reduction of the light-induced signal to half its maximum value, both points lie at an apparent oxidation-reduction potential of about ±0.46 volt. A similar value was obtained in particles from red algae by Beinert, Kok, and Hoch (*23*).

A corresponding complementarity would be expected to exist with respect to production of the spectral change induced by oxidation and production of the same change introduced by illumination. Experimentally it is found that the magnitude of the change in optical density at 700 and 420 mμ produced by illumination of the quantasomes decreases with increasing degree of oxidation as determined by the ferro- ferricyanide ratio in the medium (*25*).

A complementarity in electron spin signal has also been observed in chromatophores; the data are shown in Fig. 10. A complementarity in the light-induced optical-density changes also exists (*25*).

An additional feature appears in the chromatophores under reducing conditions. Under these conditions the light-induced spin signal is suppressed (Fig. 10). Similarly, the light-induced increase in optical density of the chromatophores at 430 mμ is suppressed

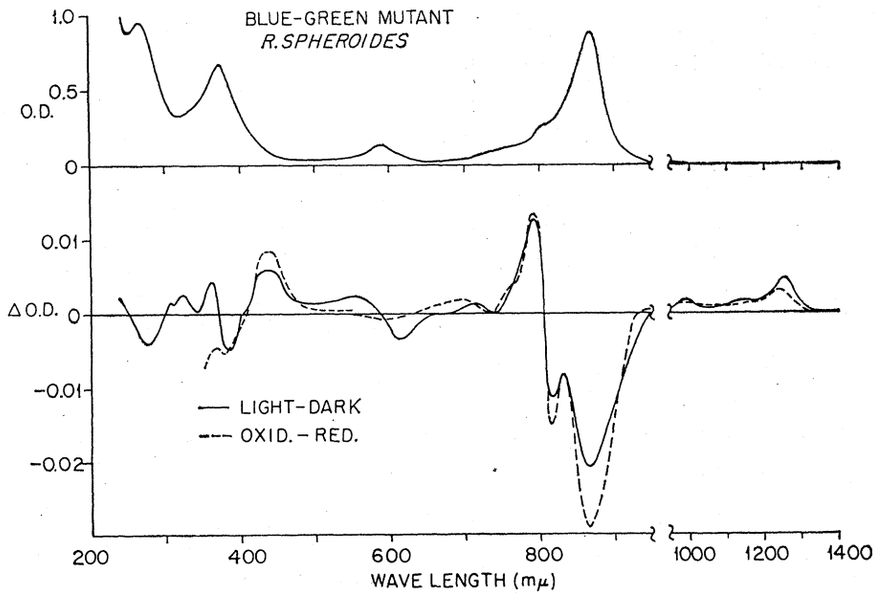


Fig. 8. Optical-density changes induced by ferricyanide in chromatophores of a carotenoidless mutant of *Rhodopseudomonas spheroides* (*21*).

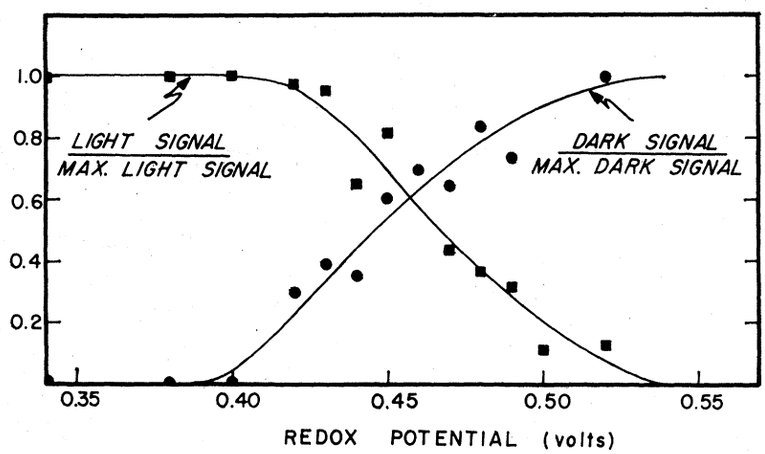
by this reducing medium (*25*). No quantitative correlation between the two has as yet been made.

For the moment, then, we will assume that the oxidation-induced EPR signal and optical-density changes are due to the removal of an electron from chlorophyll, or bacteriochlorophyll (BChl), as the case may be, a Chl^+ radical ion being left behind, situated among neutral chlorophyll molecules. It may thus be called a positive "hole." Since the light is not sharply monochromatic and since the two assumed absorption wavelengths in green material are not widely separated, it is possible that at least part of the light-induced EPR signals here may be due to a second primary species—for example, Chl^-—not to mention the secondary possibilities. The EPR signal would be expected to be very similar to that of $BChl^+$ (*26*).

Discussion

The fact that the light-induced spin signal, as well as the light-induced optical-density changes in the chromatophores, seems to be reversible down to the very lowest temperatures (the optical-density change down to 1°K, the electron spin signal down to 77°K) requires, first, that the electron transfer reactions which produce these species be simple physical transfer reactions not involving the migration of molecular species and, second, that the return to the original condition, with respect to both optical density and spin signal, proceed by a path that is a reversal of the path of formation. Thus, we require that the energy level for the electron acceptor, in the case of the formation of the chlorophyll positive ion radical, or hole, be separated from the level for the hole by very nearly the full value of the quantum of energy which is accomplishing the electron transfer. We are thus constrained to place the potential of the electron acceptor at a very negative value, perhaps even as low as −1 volt or lower (Fig. 11). Direct evidence for a similar wide separation between donor and acceptor in a second quantum act, which would be involved in the neutralization of the hole, is not yet available.

While the action spectrum for spin production does show some inflections on the long-wave side, the spin signal itself does not vary sufficiently with wavelength for us to be able to specify the existence of two different kinds of unpaired spins produced by two different colors of light. However, the accumulating literature seems to show that a second light act is involved in the green material. This conclusion stems from the early suggestions of Hill (*9*) and from the experimental observations of Emerson (*27*) and, more recently, of Kok (*23*) and Witt (*28*) and Duysens (*29*). The evidence prompts us to assume another electron transfer act, for which the product in this case is a Chl^- radical ion, also



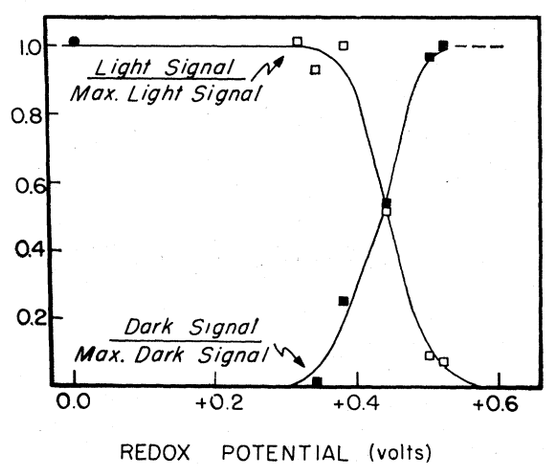


Fig. 9 (left). Redox titration of the chemically induced and photoinduced electron paramagnetic resonance in quantasomes from spinach chloroplasts. E_m (Fe^{3+}/Fe^{++} cyanide) = 0.44 volt; pH = 7.2. Fig. 10 (right). Redox titration of the chemically induced and photoinduced electron paramagnetic resonance in chromatophores from *Rhodospirillum rubrum* (—O_2; pH = 7.3). (Circle) potential measured directly: indigo tetrasulfonic acid couple present; (squares, open and solid) potential calculated: E_m (0.02 mole of Fe^{3+}/Fe^{++} cyanide) = 0.44 volt.

imbedded in a matrix of neutral chlorophyll molecules, thus corresponding to a conduction electron. Here, a quantum requirement of less than 8 (deduced from efficiency arguments) would seem to require the donor molecule for this electron transfer act to have a potential in the vicinity of +1.5 volts, to make more efficient use of the quantum by providing an additional site for adenosine trisphosphate production.

We thus arrive at a modification of the two-quantum proposal of Hill (*9*) and of Witt (*28*), of Kok (*23*), and of Duysens (*29*); in this modification the primary donors and primary acceptors at each end of the scale are further apart than has heretofore been supposed, and thus provide two more possible sites for adenosine triphosphate production than Hill's scheme provides. The first of these sites would be at energy available in the passage of the electron from the primary acceptor, at −1 volt, down to the ultimate reducing agent, such as triphosphopyridine nucleotide, at about −0.3 volt, the electron perhaps passing through either lipoic acid, PPNR (*30*) [ferredoxin (*31*)], or both, or several other cofactors on its way. The second site would be the one proposed by Hill and would lie along the route of the electron in passing from the first acceptor, at approximately 0.0 volt (cytochrome b_6, plastoquinone), to the cytochrome *f*, at approximately 0.4 volt, where it would enter the second pigment system. It is interesting to note in this connection the recently reported probable value of 2 for the number of adenosine triphosphate molecules produced by electron transfer in bacterial chromatophores (*32*). The third site for adenosine triphosphate production would be at the other end of the scale, on the route along which the electron passes from water to the primary donor, through as yet unknown cofactors, among which we may expect to find a manganese function (*33*). The ultimate result of such a scheme would be the separation of the oxidant and reductant to the levels of oxygen and pyridine nucleotide and the production of three adenosine triphosphate molecules through the action of two successive quanta, as shown in Fig. 11.

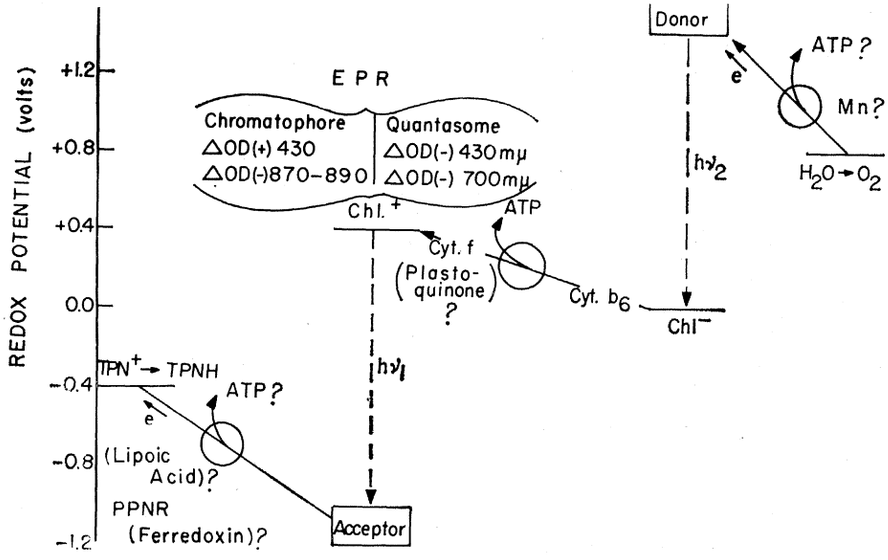


Fig. 11. Schematic diagram showing the approximate redox relationships of some species proposed as involved in the primary quantum conversion act or acts.

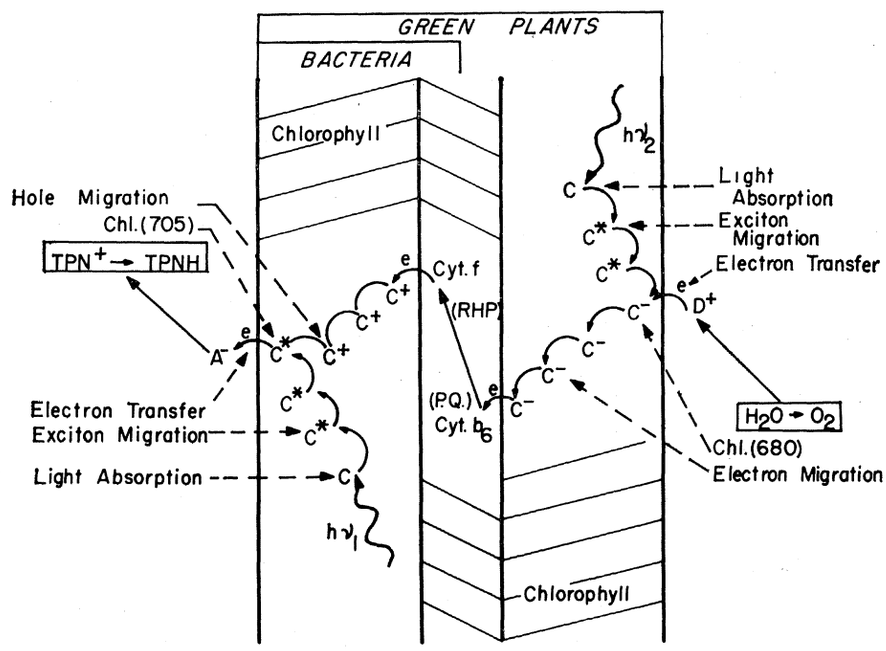


Fig. 12. Schematic diagram of the proposed mechanism for the primary quantum conversion act or acts.

A physical depiction (Fig. 12) of the entire quantum conversion process can now be formulated in terms of the absorption of light by the pigment, followed by exciton migration to the site of electron transfer (*21, 35*). In the case of the bacteria, this electron transfer would involve the production of a $BChl^+$ radical ion and a reduced acceptor at high reduction potential. The $BChl^+$ radical ion could migrate by hole migration to a site where it might recover its electron from a donor such as cytochrome c_2, which is common in the bacteria (*36*). In the green plant, a second chlorophyll system is provided which undergoes similar excitation and exciton migration to a site of electron transfer. But, in this case, the electron transfer is from the donor at some potential higher than that of molecular oxygen—that is, a potential equal to or greater than 1 volt—and the electronic conduction process carries the resulting electron in the chlorophyll

system to the site of its deposition at the connecting link between the two chlorophyll systems.

We have thus expanded a system originally proposed some years ago, at which time we could not adequately distinguish between electron migration and hole migration in the chlorophyll array (*6*). In the present proposal it now appears that in the green material, both systems are possible transport systems. The primary quantum conversion and the separation of oxidant and reductant would thus depend in both pigment arrays on semiconduction mechanisms—hole migration on one side and electron migration on the other. While the low-temperature reversibility of spin signal and optical-density changes is strong evidence for the proposed hole migration system, corresponding evidence is still lacking for the electron migration system.

References and Notes

1. C. B. van Niel, *Advan. Enzymol.* **1**, 263 (1941).
2. E. Katz, in *Photosynthesis in Plants*, W. E. Loomis and J. Franck, Eds. (Iowa State College Press, Ames, 1949), chap. 15, p. 291.
3. D. F. Bradley and M. Calvin, *Proc. Natl. Acad. Sci. U.S.* **41**, 563 (1955); M. Calvin, *Brookhaven Symp. Biol.* **11**, 160 (1958); ———, *Rev. Mod. Phys.* **31**, 147, 157 (1959).
4. D. R. Kearns and M. Calvin, *J. Am. Chem. Soc.* **83**, 2110 (1961); J. W. Eastman, G. M. Androes, M. Calvin, *J. Chem. Phys.* **36**, 1197 (1962); A. N. Terenin and E. K. Putseiko, "Fifth International Biochemical Congress, Moscow, 1961" (Pergamon, New York, in press), symposium 6.
5. M. Calvin and P. B. Sogo, *Science* **125**, 499 (1957); M. Calvin, in *Light and Life*, W. D. McElroy and B. Glass, Eds. (Johns Hopkins Press, Baltimore, Md., 1961), pp. 317–355.
6. M. Calvin, *J. Theoret. Biol.* **1**, 258 (1961).
7. W. Arnold and R. K. Clayton, *Proc. Natl. Acad. Sci. U.S.* **46**, 769 (1960).
8. H. E. Davenport and R. Hill, *Proc. Roy. Soc. London* **B139**, 327 (1951).
9. R. Hill and C. P. Whittingham, *Photosynthesis* (Methuen, London, 1955), p. 145; R. Hill and F. Bendall, *Nature* **186**, 136 (1960).
10. H. Lundegardh, *Physiol. Plantarum* **7**, 375 (1954).
11. L. M. N. Duysens, "Transfer of excitation energy in photosynthesis," thesis, University of Utrecht (1952); *Nature* **173**, 692 (1954).
12. B. Commoner, J. J. Heise, J. Townsend, *Proc. Natl. Acad. Sci. U.S.* **42**, 710 (1956).
13. P. B. Sogo, N. G. Pon, M. Calvin, *ibid.* **43**, 387 (1957).
14. The work described in this article was sponsored by the U.S. Atomic Energy Commission. Summaries of discussions with Kenneth Sauer, I. D. Kuntz, Jr., and P. A. Loach are incorporated in the text.
15. G. M. Androes and M. Calvin, *Biophys. J.* **2**, pt. 2, 217 (1962).
16. G. M. Androes, M. F. Singleton, M. Calvin, *Proc. Natl. Acad. Sci. U.S.* **48**, 1022 (1962).
17. R. B. Park and N. G. Pon, *J. Mol. Biol.* **3**, 1 (1961).
18. B. Chance and M. Nishimura, *Proc. Natl. Acad. Sci. U.S.* **46**, 19 (1960).
19. H. T. Witt, A. Muller, B. Rumberg, *Nature* **192**, 967 (1961).
20. P. B. Sogo, M. Yost, M. Calvin, *Radiation Res. suppl.* 1, 511 (1958).
21. R. K. Clayton, *Photochem. and Photobiol.*, in press.
22. B. Kok and G. Hoch, in *Light and Life*, W. D. McElroy and B. Glass, Eds. (Johns Hopkins Press, Baltimore, 1961), p. 397.
23. H. Beinert, B. Kok, G. Hoch, *Biochem. Biophys. Res. Commun.* **7**, 209 (1962).
24. We wish to thank Dr. P. A. Loach for collaborating with us in the establishment and measurement of the potentials in these experiments.
25. I. D. Kuntz, Jr., and P. A. Loach, unpublished observations.
26. M. S. Blois, H. W. Brown, J. E. Maling, in *Free Radicals in Biological Systems*, M. S. Blois *et al.*, Eds. (Academic Press, New York, 1961), p. 117.
27. R. Emerson, R. Chalmers, C. Cederstand, *Proc. Natl. Acad. Sci. U.S.* **43**, 135 (1957).
28. B. Rumberg, A. Muller, H. T. Witt, *Nature* **194**, 854 (1962).
29. L. M. N. Duysens, J. Amesz, B. M. Kamp, *ibid.* **190**, 510 (1961).
30. A. San Pietro, in *Light and Life*, W. D. McElroy and B. Glass, Eds. (Johns Hopkins Press, Baltimore, 1961), p. 681; T. Horio and T. Yamashita, *Biochem. Biophys. Res. Commun.* **9**, 142 (1962).
31. L. E. Mortenson, R. C. Valentine, J. E. Carnahan, *Biochem. Biophys. Res. Commun.* **7**, 448 (1962); R. C. Valentine, R. V. Jackson, R. Wolfe, *ibid.* **7**, 453 (1962); K. Tagawa and D. I. Arnon, *Nature* **195**, 537 (1962).
32. M. Nishimura, *Biochim. Biophys. Acta* **59**, 183 (1962).
33. M. Calvin, P. A. Loach, A. Yamamoto, Proceedings, Conference on Theory and Structure of Complex Structures, Wroclaw, Poland, June 1962.
34. B. Chance, *Nature* **189**, 719 (1961).
35. K. Sauer and M. Calvin, *J. Mol. Biol.* **4**, 451 (1962); W. M. Butler, *Arch. Biochem. Biophys.* **93**, 413 (1961).
36. T. Horio and M. D. Kamen, *Biochemistry* **1**, 144 (1962).

The Man-Computer Relationship

The potential contributions of computers crucially depend upon their use by very human human beings.

David L. Johnson and Arthur L. Kobler

Recently Norbert Wiener, 13 years after publication of his *Cybernetics*, took stock of the man-computer relationship (*1*). He concluded, with genuine concern, that computers may be getting out of hand. In emphasizing the significance of the position of the computer in our world, Wiener comments on the crucial use of computers by the military: "it is more than likely that the machine may produce a policy which would win a nominal victory on points at the cost of every interest we have at heart, even that of national survival."

Computers are used by man; man must be considered a part of any system in which they are used. Increasingly in our business, scientific, and international life the results of data processing and computer application are, necessarily and properly, touching the individuals of our society significantly. Increasing application of computers is inevitable and requisite for the growth and progress of our society. The purpose of this article (*2*) is to point out certain cautions which must be observed and certain paths which must be emphasized if the man-computer relationship is to develop to its full positive potential and if Wiener's prediction is to be proved false.

In this article on the problem of decision making we set forth several concepts. We have chosen decision making as a suitable area of investigation because we see both man and machine, in all their behavior actions, constantly making decisions. We see the process of decision making as being always the same: within the limits of the field, possibilities exist from which choices are made. Moreover, there are many decisions of great significance being made in which machines are already playing an active part. For example, a military leader recently remarked, "At the heart of every defense system you will find a computer." In a recent speech the president of the National Machine Accountants Association stated that 80 to 90 percent of the executive decisions in U.S. industry would soon be made by machines. Such statements indicate

Dr. Johnson is professor of electrical engineering, University of Washington, Seattle. Dr. Kobler, a practicing clinical-social psychologist in Seattle, has an appointment as research associate professor in electrical engineering at the University of Washington.