

# THE PHOTOCHEMICAL ORIGINS OF LIFE AND PHOTOREACTION OF FERROUS ION IN THE ARCHAEOAN OCEANS

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**Abstract.** A general argument is made for the photochemical origins of life. A constant flux of free energy is required to maintain the organized state of matter called life. Solar photons are the unique source of the large amounts of energy probably required to initiate this organization and certainly required for the evolution of life to occur. The completion of this argument will require the experimental determination of suitable photochemical reactions. Our work shows that biogenetic porphyrins readily photooxidize substrates and emit hydrogen in the presence of a catalyst. These results are consistent with the Granick hypothesis, which relates a biosynthetic pathway to its evolutionary origin. We have shown that photoexcitation of ferrous ion at neutral pH with near ultraviolet light produces hydrogen with high quantum yield. This same simple system may reduce carbon dioxide to formaldehyde and further products. These reactions offer a solution to the dilemma confronting the Oparin-Urey-Miller model of the chemical origin of life. If carbon dioxide is the main form of carbon on the primitive earth, the ferrous photoreaction may provide the reduced carbon necessary for the formation of amino acids and other biogenic molecules. These results suggest that this progenitor of modern photosynthesis may have contributed to the chemical origins of life.

## 1. Introduction

The study of the chemical origins of life has progressed to the point where quantitative measures of the probability of a particular hypothesis are possible. Miller and Orgel (1974) have stressed that such quantitative measures as rates and yields of reactions are necessary to select among the myriad possibilities. Bioenergetics is a particularly appropriate sub-field for these measures and Broda (1975) has given it careful attention. Our aim is to apply these methods to the problem of the energy flux requirements for the evolution and possibly for the very origins of life.

The organized state of matter called life exists in a state far from the equilibrium of its chemical components. Thus a continued flux of free energy is required to maintain this organized state. One cannot yet quantify the minimal flux necessary to originate a living cell, but the energy required to maintain even a simple modern cell is large. The original self-duplicating system is unlikely to have been as bioenergetically efficient as the modern cell, but the system may have been simpler. Thus the energy requirement of a modern cell can be assumed to be a not unreasonable estimate of that required for the original system. Since the biosphere is much thinner than its lateral dimensions, the use of two-dimensional flux of energy is appropriate. This energy flux must be multiplied by a molecular yield per unit energy factor to obtain an estimate of the useful available flux. A zero approximation is to compare the energy flux required by a modern cell:  $10^{-2}$  W cm<sup>-2</sup> for a rapidly respiring bacterium (min per cell division) to  $10^{-5}$  W cm<sup>-2</sup> for a slow growing plant cell (days

per cell division) (Broda, 1975a). The required flux is large, but could be (and is) supplied by solar photosynthesis with an effective energy flux of roughly  $10^{-2}$  W  $\text{cm}^{-2}$ . In contrast, the next largest source of energy on earth, electrical discharge (Miller and Orgel, 1974a; Miller *et al.*, 1976) has an energy flux of  $10^{-8}$  W  $\text{cm}^{-2}$ . The energy yield for electrical discharge, defined as moles of a product per joule of energy, analogous to a photochemical quantum yield, is about 1 nmole  $\text{J}^{-1}$  (Stribling and Miller, 1987). The energy yield for photochemical reactions is, for near UV to red quanta, 3 – 6 nmole  $\text{J}^{-1}$  times the quantum yield. Because of the vastly higher flux of solar photons,  $10^{-1}$  W  $\text{cm}^{-2}$ , a quantum yield of  $10^{-7}$  could produce a greater flux of product molecules than electrical discharges. Note that this level of the argument is product dependent. Solar photons may easily form vast amounts of formaldehyde, but not of hydrogen cyanide, which is only formed by far UV, and thus rare, photons. Boston and Stoker (1990) have made a more quantitative assessment of the adequacy of electrical discharge as a source of energy for primordial cells. They used atmospheres of various compositions and a shock heating model to calculate the formation of carbon compounds. Even assuming 100% utilization of the compounds formed, a highly reduced atmosphere, a small maintenance energy requirement, and a very small cell size (0.2  $\mu$ ) a steady state of only 10–100 organisms per  $\text{cm}^3$  can be maintained. They conclude that only an early invention of autotrophic metabolism can allow a globally viable biosphere. This point of view has also been taken by Krasnovsky (1974) and by Shidlowksi *et al.* (1975). It is accepted that biological evolution required the massive energy input of efficient photosynthesis. It is the photochemical origin of life that is problematical.

The standard view of the chemical origins of life attempts to bypass this argument of assuming that low flux sources such as lightning, a UV solar light, volcanism, etc. formed large pools of molecular precursors for the first self-duplicating system. The size of these pools would be strictly limited by the inevitable chemical reactions other than those required for progress along the chemical origin of life. Applying the Malthusian argument, such pools would be exhausted in a ‘nanosecond’ of geological time by a successful self-duplicating system. It would then have to survive, if at all, at the very low duplication pace set by the low flux energy source. Thus we could have the view of Pirie (1957) where there may have been many ‘origins’ but only one succeeded. Our claim is that the survivor was connected to photochemistry. We tentatively conclude that only solar energy has a sufficient energy flux to safely allow for the inefficiencies inevitable in organizing the first self-duplicating structures. It is clear that for evolution to occur on the scale now known to be so, the coupling of self-suplication and the energy flux of solar energy becomes a necessity.

In the next sections we will review experimental results which support a view of the early evolution of photosynthesis and open a possible photochemical origin of the reduced carbon necessary for the chemical origins of life.

## Theory

For many years we have been using the accumulated knowledge of the photochemistry of porphyrins to obtain experimental evidence for the Granick hypothesis (1965, 1967). The Granick hypothesis states that a biosynthetic pathway recapitulates its evolution. It was his answer to the problem of how a complex biosynthetic pathway could have ever arisen by random mutations. The pathway is built forwards, beginning with simple precursors such as glycine and succinate or glutamate. Each molecule fulfills a function in its time. Random mutations lead to other molecules which are selected by evolution because of their increased usefulness or efficiency. The Horowitz hypothesis (1945) is that the pathways were built backwards. Random mutations made connections to simpler molecules as the presumed stockpiles of useful molecules were exhausted. Aside from the Malthusian difficulty, any chemist would claim this hypothesis is extremely unlikely for complex molecules.

The biosynthetic pathway of porphyrins is shown in Figure 1. It is one of the constants of biology. Porphyrins are made in the same way, down to details of the enzymes involved, by all living organisms from archaebacteria through plants to animals (Beale and Weinstein, 1990). There are only two paths to the initial intermediate,  $\delta$ -aminolevulinate. The glutamate pathway is thought to be more primitive than the glycine-succinate path since it occurs in cyanobacteria (Reibel and Beale, 1988) and an archaebacterium (Friedman and Tower, 1986). The simplicity of the pathway may be one of the reasons it is so highly conserved: it may well be the chemically minimal pathway to these pigments. A second reason for its being conserved is that it plays so crucial a role in supplying energy to all living matter. The metalloporphyrins are involved in electron transport at all levels of biological organization. The pathway is a prime example of the Oparin-Haldane hypothesis (Bernal, 1967): that life began in the ocean and developed within aggregates. One begins with ionic, water soluble compounds. The ionic charges are methodically stripped away forming porphyrins that self-aggregate and bind to proteins and lipid bilayers. One ends with completely hydrophobic pigments which are confined to the organized structures of lipids and hydrophobic proteins.

Application of the Granick hypothesis to the origins of life implies that porphyrins can be made abiotically. In fact the early steps in the biosynthetic pathway can almost all be carried out *in vitro* under gentle conditions, may in near quantitative yield. The  $\delta$ -aminolevulinate can be formed in quantitative yield from glycine and dioxoallevinate (Beale *et al.*, 1979). Porphyrins in general can be formed in high yield under very gentle conditions from substitute benzaldehydes and pyrroles (Lindsey *et al.*, 1987). The yield of porphyrins from  $\beta, \beta'$  substituted pyrrole (as occurs in the biosynthesis) or from porphobilinogen itself can be nearly quantitative (Mauzerall, 1960a). Moreover, the natural isomer (III) is the most random sequence and thus is formed in highest yield. The actual product of these reactions is the hexahydroporphyrin, or porphyrinogen (Mauzerall, 1960b). These can be photooxidized to porphyrins by far UV light (Mercer-Smith *et al.*, 1985). The Achilles heel

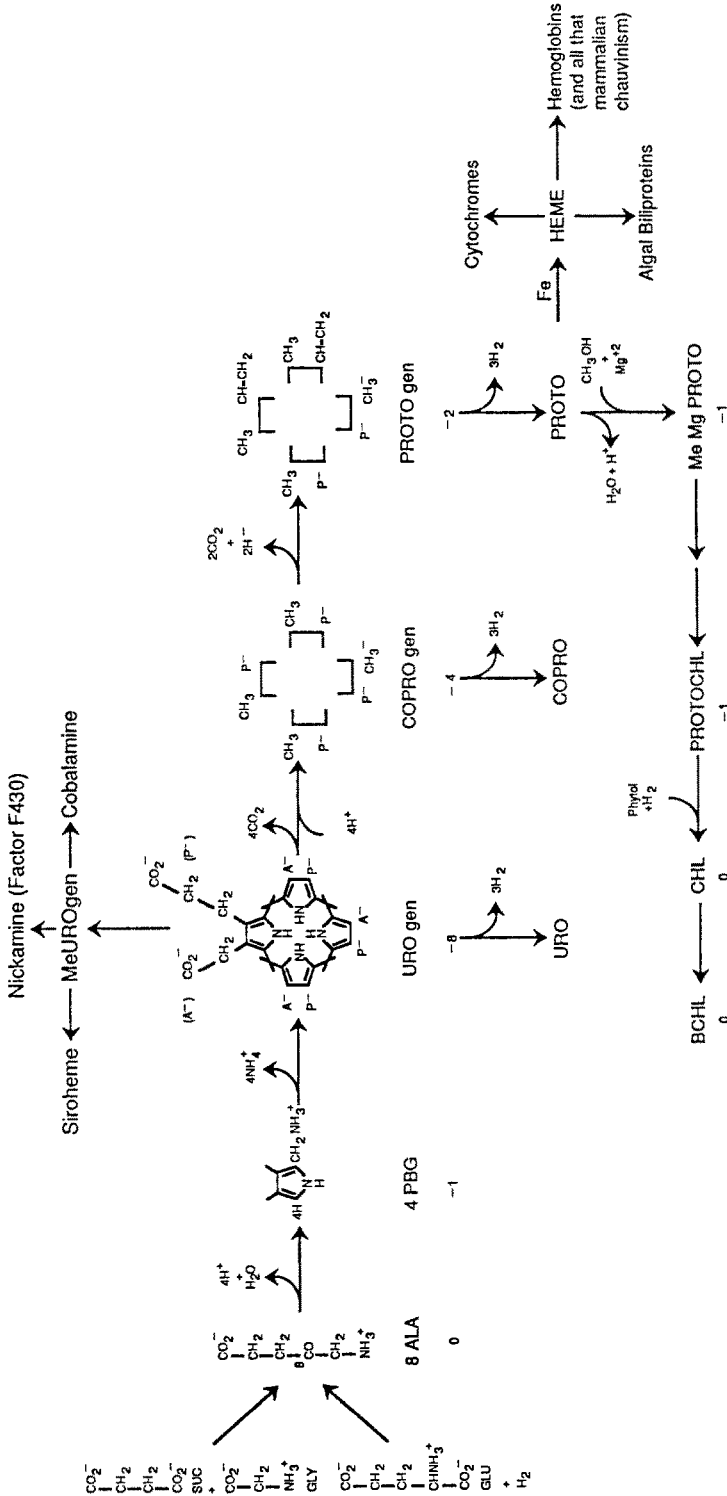


Fig. 1. Schematic of the biosynthetic pathway of porphyrins. The numbers below the abbreviations are the ionic charges per molecule in neutral solution. Abbreviations: SUC: succinate, GLY: glycine, ALA: 5-amino-levalinate, PBG: porphobilinogen; URO: uroporphyrin; COPRO: coproporphyrin; PROTO: protoporphyrin; ---gen: porphyrinogen, hexahydroporphyrin; MeMgPROTO: magnesium protoporphyrin monomethyl ester; PROTOCHL: protochlorophyllide; CHL: chlorophyll.

of this argument is in the formation of the pyrrole. The chemical reaction of  $\delta$ -aminolevulinate forms porphobilinogen only in low yield if at all. Whether this is a flaw in the argument or only a lack of good chemistry, requires investigation. This problem can be by-passed, by a small modification of the pathway. For example the condensation of  $\delta$ -aminolevulinate with activated carbonyl compounds (the Knorr condensation) proceeds with ease. In fact the condensation with  $\beta$ -dicarbonyl compounds was developed into a useful, quantitative assay for  $\delta$ -aminolevulinate (Mauzerall and Granick, 1956).

The next step in the pathway, decarboxylation of uroporphyrin to coproporphyrin occurs, on heating, and thus is inevitable. It is the coproporphyrin III to protoporphyrin IX step (Figure 1) that is the break point in the biosynthetic pathway (Mauzerall, 1978a). This reaction is not simply thermal: it is an *oxidative* decarboxylation. Moreover, two *specific* propionate residues out of four are changed. The implication is that enzymatic specificity began at this step in the chemical evolution of the pathway.

Following the Granick hypothesis and based on our extensive studies of the photochemistry of porphyrins (Mauzerall, 1978b), in turn based on the work of Krasnovsky (1974), our view of these early reactions is as follows. The first formed free base porphyrins photooxidize substrates and are reduced. In the presence of a catalyst the reduced porphyrin is reoxidized and hydrogen is emitted. Free energy is stored in the products: oxidized organics, ferric ion, sulfur and hydrogen. This energy can be used by the cell and the use of hydrogen implies the utilization of protons and thus the possibility of gradients across membranes now so well employed in bioenergetics for the formation of ATP. The oxidized organics have functional groups such as a carbonyl and are useful biogenetic intermediates. These can enter the pathway to form more pigments thus providing a positive feedback. The metalloporphyrins formed later in the biosynthetic pathway preferably photoreduce substrates and form stable cationic free radicals (Fuhrhop and Mauzerall, 1969) of extraordinarily high oxidizing power: +0.8V vs NHE, sufficient for the oxidation of water. This is the modern form of photosynthesis which reduces carbon dioxide to sugars and oxidizes water to oxygen. It provides the very large free energy gap which in turn allowed the formation of the multicellular parasites which now occupy a fair fraction of the biosphere.

### Results — Porphyrins

We summarize the results of our experiments. All were carried out in dilute aqueous solution at neutral pH (Mercer-Smith and Mauzerall, 1981, 1984).

(1) Early biogenetic porphyrins in the free base form can oxidize organic compounds and emit  $H_2$  in the presence of a catalyst such as Pt.

(2) Combining the porphyrin and the catalyst on polyvinyl alcohol increase the efficiency of the reaction. This is analogous to the function of a reaction center in photosynthesis.

(3) Attempts to use an iron-sulfur cubane compound as a more biogenetic catalyst failed, but the cobalt complexes with Ru chelates as sensitizers described by Lehn and Sauvage (1977) did form  $H_2$ . We obtained a low yield using vitamin  $B_{12}$  (Borowska and Mauzerall, 1985, unpublished). This is of interest because a combination of uroporphyrin, sirohemes, nickel 'tetrapyrroles F430', found in the archaebacteria and cobalamins could function as an early reaction center for photosynthesis. The branch point to these compounds occurs at the very beginning of the biosynthetic pathway (Figure 1) and by the Granick hypothesis at the beginning of their functional evolution.

### Results — Ferrous ion

Cairns-Smith (1978) has suggested that the extensive Banded Iron Formations were built by the photooxidation of ferrous ion, and he and his coworkers (Braterman *et al.*, 1983) showed that ferric ion was formed by near UV light at neutral pH. Schrauzer and Guth (1976) had shown the photochemical formation of hydrogen from ferrous ion and also formation of hydrogen in the dark over the narrow pH range 8.0 to 9.5. Borowska and I found that hydrogen was efficiently formed photochemically at  $pH > 6$  by a novel mechanism (Borowska and Mauzerall, 1987). The previously studied reaction of ferrous ion to form  $H_2$  requires protons and far UV light,  $< 240$  nm (Hayon and Weiss, 1960). We observed the decrease in rate of this reaction as the pH was raised from 1, but at pH 6 the rate increases to a plateau at  $pH > 7$ . The reaction occurs in a pyrex cell which blocks light of wavelengths  $< 310$  nm. Thus the new mechanism requires only near UV light. Since the reaction is linear in light intensity and in ferrous ion concentration we can define a quantum yield. Between 300 and 370 nm it is at least 0.3  $H_2$ /photon (Borowska and Mauzerall, 1987). This is a minimal estimate since not all the light may be absorbed, and not all the species absorbing may be active. It is amusing that we used the ferric oxalate actinometer to measure the quantum flux. In this reaction the oxalate is oxidized to  $CO_2$  and the ferric reduced to ferrous, just the reverse reaction of that of ferrous hydroxide.

To account for the extremely high quantum yield and linearities, we postulate the reaction is concerted (Borowska and Mauzerall, 1987). It occurs in a Fe-O-Fe polymer (at least a dimer), and in fact works when  $Fe(OH)_2$  is precipitated. On exciting ferrous ion, an electron is transferred to a nearby bound proton to form a hydrogen atom. Another electron from a neighboring ferrous ion reduces the H atom to  $H^-$ . With a neighboring proton,  $H_2$  is formed. The concertedness of the reaction makes it efficient. The local driving force is simply the increased strength of the  $Fe^{3+}$ -OH bond over that of the  $Fe^{2+}$ -OH bond. We estimate the difference to be 15 kcal/mole/bond. The reaction is very sensitive to added  $Fe^{3+}$  ion. Some of the inhibition is caused by screening of the light by the more highly absorbing  $Fe^{3+}$  ion, but also any  $Fe^{3+}$  ion within tunneling distance (possibly 10 Å, Mauzerall, 1978b) will soak up the electron from the excited  $Fe^{2+}$  ion thus efficiently

quenching the reaction. If the polymer is three dimensional, only a few percent of  $\text{Fe}^{3+}$  ion suffices to quench the reaction. Thus this quenching is in agreement with out concerted mechanism.

The mechanism proposed by Schrauzer and Guth (1976), formation of elemental iron and reaction with protons, is highly unlikely under our conditions. Our samples are at worst light bluish i.e. lightly oxidized, not the 'green rust' of partially oxidized ferrous hydroxide, since we work at a controlled level of  $\text{O}_2$ , 5–50 pm. The ferromagnetic component found in the oxidized samples by Schrauzer and Guth could well be magnetite. We also disagree on the rate of hydrogen formation, in the dark. Our measurements indicate a rate of only 1% of that quoted by Schrauzer and Guth i.e. 50 nmoles  $\text{H}_2$   $\text{hr}^{-1}$  with 3 mL of 0.1M  $\text{Fe}(\text{OH})_2$  at 25 C versus 1000 nmoles  $\text{H}_2$   $\text{hr}^{-1}$  with 5 mL of 0.02 M  $\text{Fe}(\text{OH})_2$  at 29 C, both at pH  $\sim$  8.6. However, the rate is variable.

This photoreaction may reduce  $\text{CO}_2$ . If bicarbonate is added to the ferrous hydroxide one can detect formaldehyde on irradiation (Borowska and Mauzerall, 1988) and the yield of hydrogen decreases. The carbon dioxide is reduced only when  $\text{H}_2$  is formed i.e., at pH  $\geq$  6. The yield of formaldehyde decreases at pH  $>$  7.5 where  $\text{H}_2$  is still formed. This implies that carbonate ion is unreactive and possibly that a proton is required for efficient reduction of bicarbonate ion. Our more recent measurements have difficulties in confirming these early results. We attribute this to baseline problems which the color reaction, aggravated by the previous single wavelength measurements. Other methods such as the use of  $^{14}\text{C}$  bicarbonate will be used to substantiate these conclusions. If formaldehyde is added to the mixture, it is rapidly consumed. This is consistent with the view that more formaldehyde may be reduced than is formed in the steady state. We have not yet identified the products but reports exist for the formation of methanol and methane under somewhat similar conditions (Getoff, 1962; Ackerman *et al.*, 1980).

Getoff (1962) observed the reduction of  $\text{CO}_2$  to formaldehyde with intense UV light in the presence of ferrous ion at neutral pH. The yield decreased tenfold on increasing the pH from 3 to 6.5 suggesting a large contribution from the acid-short wavelength UV ferrous reaction. This suggestion is supported by the independence of the rate on ferrous concentration implying total absorption of the far UV and by the weak effect of a near UV filter. Getoff was mainly concerned with the photolysis of water and interpreted his data in terms of the Hayon and Weiss (1960) mechanism. The incompleteness of his data and changes of more than one variable at a time prevent drawing conclusions from this work. Ackerman *et al.* (1980) observed formation of formate and formaldehyde in up to 0.5% yield on bubbling  $\text{CO}_2$  through a solution of ferrous ion and intense irradiation at 254 nm. This is thus the acid or Hayon-Weiss reaction.

### Conclusions

Our work has shown that photochemical reactions of early biosynthetic porphyrins

are consistent with the Granick hypothesis. It suggests a scheme for the early evolution of photosynthesis. The newly discovered efficient mechanism for the photoformation of hydrogen from ferrous ion at neutral pH offers a solution to a dilemma confronting the Oparin-Urey-Miller model of the chemical origin of life. The work of Schlesinger and Miller (1983a, b) has convincingly shown that the formation of formaldehyde and amino acids via electric discharge requires a reducing atmosphere. Even if  $\text{CO}_2$  is the predominant form of carbon on the primitive earth, the ferrous photoreaction may provide the reduced carbon necessary to form amino acids and other biogenic molecules.

The subject of iron photoprecipitation on the early earth has been very well discussed by Braterman and Cairns-Smith (1987a). They review the data on solar output and absorption by atmospheric gases and ions in the Pre-Cambrian oceans. They conclude that the amount of ferric ion in the Banded Iron Formations could be deposited by photooxidation using the present solar near UV output. Their use of a lower quantum yield for the photooxidation (0.02) than ours ( $\geq 0.6$  for  $\text{Fe}^{+3}$ ) is over-compensated by their use of a much larger extinction coefficient for the active species ( $10^3 \text{ M}^{-1} \text{ cm}^{-1}$  versus our  $3 \text{ M}^{-1} \text{ cm}^{-1}$  at 350 nm). The smaller extinction still gives a lifetime of less than a week even with the present flux of near UV light. Thus we agree that the hydrogen or reducing equivalents will be limited by the supply of ferrous ion. The smaller extinction also allows an optical depth of 100 m (absorbancy = 1) at a ferrous concentration of  $5 \times 10^{-5} \text{ M}$ . Ferric ion absorbs much more strongly but the very small solubility product of ferric hydroxide guarantees its aggregation and precipitation. The excess ferrous ion would favor the formation of magnetic as is observed. The amount of reducing power available is vast. In the Hamersley basin alone, about  $10^{12}$  moles of electrons per year are available (Trendall, 1972). Present photosynthesis amounts to  $\sim 4 \times 10^{16}$  moles of electrons  $\text{yr}^{-1}$  but the area of the Hamersley is about  $10^{-4}$  of that of the Earth. The Hamersley basin itself is too young,  $2.5 \times 10^9$  yr, to be part of the primordial scene, but it appears to be representative of the early banded iron formations (Walker *et al.*, 1983). Thus the Banded Iron Formations could have reduced a large part of the available carbon in archaean times.

Our estimate of the lifetime for the dark reaction of ferrous hydroxide to form  $\text{H}_2$  at pH 8.6 and 25 C is 20 weeks, whereas that of Schrauzer and Guth (1976) is about 2 days at 29 C. Thus by our measures the reaction would be predominantly photochemical.

Of further interest is the distinct possibility that the ferrous hydroxide reactions with carbon dioxide could also lead to multicarbon molecules. The dimerization of the one electron reduction product of  $\text{CO}_2$  yields oxalate. This two carbon species was observed by Getoff (1963) in a ferrous- $\text{CO}_2$  reaction of pH 3. The polymerization of formaldehyde to sugars is known. Nitrogen may well be reduced to ammonia by this reaction. Schrauzer and Guth (1976) claim that ferrous hydroxide reduces nitrogen at pH 8.6. If so, amino acids could be formed. It will be interesting to search for these products.



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