

EFFICIENT NEAR ULTRAVIOLET LIGHT INDUCED FORMATION OF HYDROGEN BY FERROUS HYDROXIDE

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Abstract. The formation of hydrogen on irradiating ferrous ion in aqueous solution or suspension was studied over a wide range of pH. In addition to the known reaction in acid solution which decreases in yield with increasing pH and required far UV light, there is an efficient reaction occurring between pH 6 and 9 which utilizes near UV light. The latter reaction is an approximately linear function of both the concentration of ferrous ion and the light intensity. The quantum yield of hydrogen from the suspension of $\text{Fe}(\text{OH})_2$ at pH 7.2 is very high: ≥ 0.3 . The quantum yield decreases by a factor of five at 1 mole percent of ferric ions. To explain these observations it is proposed that an intermediate formed on excitation of the $\text{Fe}(\text{OH})_2$ polymer is further reduced by a neighboring Fe^{+2} to form H_2 . These results support the work of Braterman *et al.* (1983) which claimed that the near UV driven photooxidation of ferrous ions could be responsible for formation of the Banded Iron Formations on the early earth. The efficient photoreaction observed in the present work could also serve as a source of active reducing equivalents to reduce CO_2 and thus provide a solution to a dilemma in the arguments on the role of reduced carbon in the origin of life.

1. Introduction

Braterman *et al.* (1983, 1984) have found that irradiation of ferrous ion at pH 7 with near ultraviolet (UV) light leads to the formation of ferric ions and acidification of the solution. They suggest that near UV light, prevalent in the anoxic primitive earth could have led to precipitation of ferric oxides. Calculation by Francois (1986) supports this route of formation of the Banded Iron Formations. This photoreaction of ferrous ions is in strong contrast to the well studied (Weiss, 1935; Hayon, Weiss 1960) system of ferrous ion in acidic solution, where photooxidation of ferrous ion decreases with increasing pH and requires short wavelength (UV \sim 240 nm). The reaction studied by Braterman *et al.* is constant between pH 5 and 6 and can be carried out with long wavelength UV (to 420 nm). They measured proton release and ferric ion formation.

Chang and coworkers (pers. comm.) have made similar observations. It was of interest to directly measure the hydrogen formed in this novel reaction. We were particularly interested in the relevance of this reaction to our hypothesis that early photosynthesis could involve the formation of hydrogen (Mercer-Smith and Mauzerall, 1984). This source of hydrogen may also contribute to the solution of an increasingly vexing problem concerning the origin of essential constituents for the origin of life. The comprehensive data of Scribbling and Miller (1985) clearly show that at least an intermediate level (about that of formaldehyde) of reduced carbon is needed to form amino acids in substantial amounts. However, geochemical

observations increasingly favor the emission of carbon dioxide, not methane, from degassing of the early earth (Walker, 1977; Holland, 1984; Mattioli and Wood, 1986). A continuous and large scale production of reducing equivalents is thus needed to rescue the standard model of the origin of life. It is possible that hydrogen formation from irradiated ferrous ion at neutral pH or more likely the highly reactive intermediate reducing equivalents, will serve to reduce the emitted carbon dioxide to useful redox level (Joe *et al.*, 1986).

2. Experimental Methods

The stock solution of aqueous 0.2 M FeSO_4 (containing less than 0.02% Fe^{3+}) was prepared using deionized and subsequently double distilled water. The three ml samples (total volume) that formed a 3 mm deep layer in the photolysis cell were prepared by syringing aliquots of 0.2 M FeSO_4 and of water into the cell continually deaerated by a flow of the helium carrier gas at a constant rate of 10 ml min^{-1} . The helium gas used in these experiments contained 4 ppm O_2 . The pH's of samples were adjusted by the addition of helium purged aliquots of 1 M H_2SO_4 or 1 M NaOH. Samples were magnetically stirred under the flow of helium gas during the entire experiment as the O_2 level was monitored. Samples were irradiated by a xenon arc lamp (150 W) or by a mercury arc lamp (200 W). A 50 mm path length quartz cell of distilled water was interposed between the lamp and the photolysis cell. The distance between the lamp and the cell was 12 cm. The light intensity was changed by using screen filters. Monochromatic illumination (band pass 20 nm) was obtained by using a high intensity monochromator (Bausch and Lomb). Absolute light intensities for the quantum yield of molecular hydrogen production were measured by ferrioxalate actinometry (Hatchard and Parker, 1956). The amount of molecular hydrogen produced during the irradiation was measured with a zirconium oxide electrode (Amtek Thermox). This is a high temperature (800°C) Nerstian O_2 electrode that we have adapted to measure H_2 by combustion with the trace O_2 present in the carrier gas (Mercer-Smith and Mauzerall, 1984). By this method quantities of $0.3 \text{ nmoles of H}_2 \text{ sec}^{-1}$ can be detected. The sensitivity of the instrument is calibrated in situ by electrolyzing water and capturing H_2 (or O_2) in the carrier gas. The formation of H_2 in the dark was negligible over most of the pH range used here (Shrauzer and Guth, 1976).

It was necessary to prove that the signal observed was indeed H_2 and not an uptake of the small amount (4 ppm) of O_2 in the system. The latter is highly unlikely because of kinetic limitations at this low O_2 concentration. The absence of negative O_2 signal and the presence of a positive H_2 signal was shown in two ways. In the simpler method, the cell was not stirred during illumination with 300 nm light at pH 7.2. After several minutes of darkness the cell was stirred. A burst of H_2 was seen with the characteristic gaseous equilibration time of 30 sec. The signal was far greater (28 nmoles) than the O_2 present in the cell which could have been consumed (0.002 nmoles). For the O_2 to have been removed from the gas on stirring would

require highly reactive photoformed intermediates with lifetimes of 100–1000 sec. The second method was the use of a catalyst Chemalog R3-11 (CuCrO), which in the oxidized form at 200 ° removes H_2 from the stream but has no effect on O_2 . This was proven by the electrolysis of water and observing the H_2 so formed to be removed. Illumination of the ferrous ion solution also produced no signal with this catalyst in the flow system. Thus the signal is caused by positive H_2 , not negative O_2 .

3. Results and Conclusions

We were able to observe hydrogen formation on illumination of ferrous hydroxide both at acid and neutral pH. However we discovered a strong dependence on the details of the illumination. Use of a 150 W xenon arc and a quartz cell produced hydrogen at a rate that decreased between pH 1 and 4, with a constant residual rate to pH 8 (Figure 1). But a 200 watt mercury arc produced hydrogen at a rate that decreased only by 60% between pH 1 and 4, and then rose sharply to the original level between pH 6 and 9 (Figure 1). Substitution of a pyrex cell (cut off 305 nm) with the mercury arc showed formation of hydrogen only between pH 6 and 8. Wavelengths greater than 410 nm did not produce detectable H_2 . Thus there are (at least) two different sources of hydrogen: the classical ferrous ion reaction in acid requiring short wavelength UV, and one (or more) reactions at neutral pH which can use near UV light. The differing output of the xenon arc (broad continuum) and the mercury arc (pressure broadened lines near 400, 363, 300, and 240 nm an order of magnitude more intense than the continuum) and the cutoffs of the cells then explain the data of Figure 1. The use of a monochromator to obtain specified bands of light and irradiation of the FeSO_4 at two different pH's gave similar results (Table I). The rate of H_2 formation is an approximately linear function of both FeSO_4 concentration (Figure 2) and light intensity (Figure 3) over the range studied. Thus the conditions are simple enough to define a quantum yield.

The quantum yield measurements were carried out with ferric oxalate actinometry. Since this reaction is also insensitive to wavelengths longer than 450 nm, small amounts of stray visible light from the monochromator were innocuous. The results are shown in Table 1. The quantum yield (Table II) of H_2 formation at 300 to 370 nm is surprisingly high: 0.3 if it is assumed that all the light is absorbed. Correction for the measured absorbance of the 30 mm layer of suspension could increase the quantum yield to 0.5. Since it is hardly likely that all of the species absorbing in the near UV are photoactive, the absolute quantum yield may be even higher. The addition of 0.56 M NaCl changed the quantum yield by less than 10%.

4. Mechanism

The mechanism of the formation of the H_2 from Fe^{+2} at neutral pH is of interest because of the high quantum yield of the reaction with near UV light. These

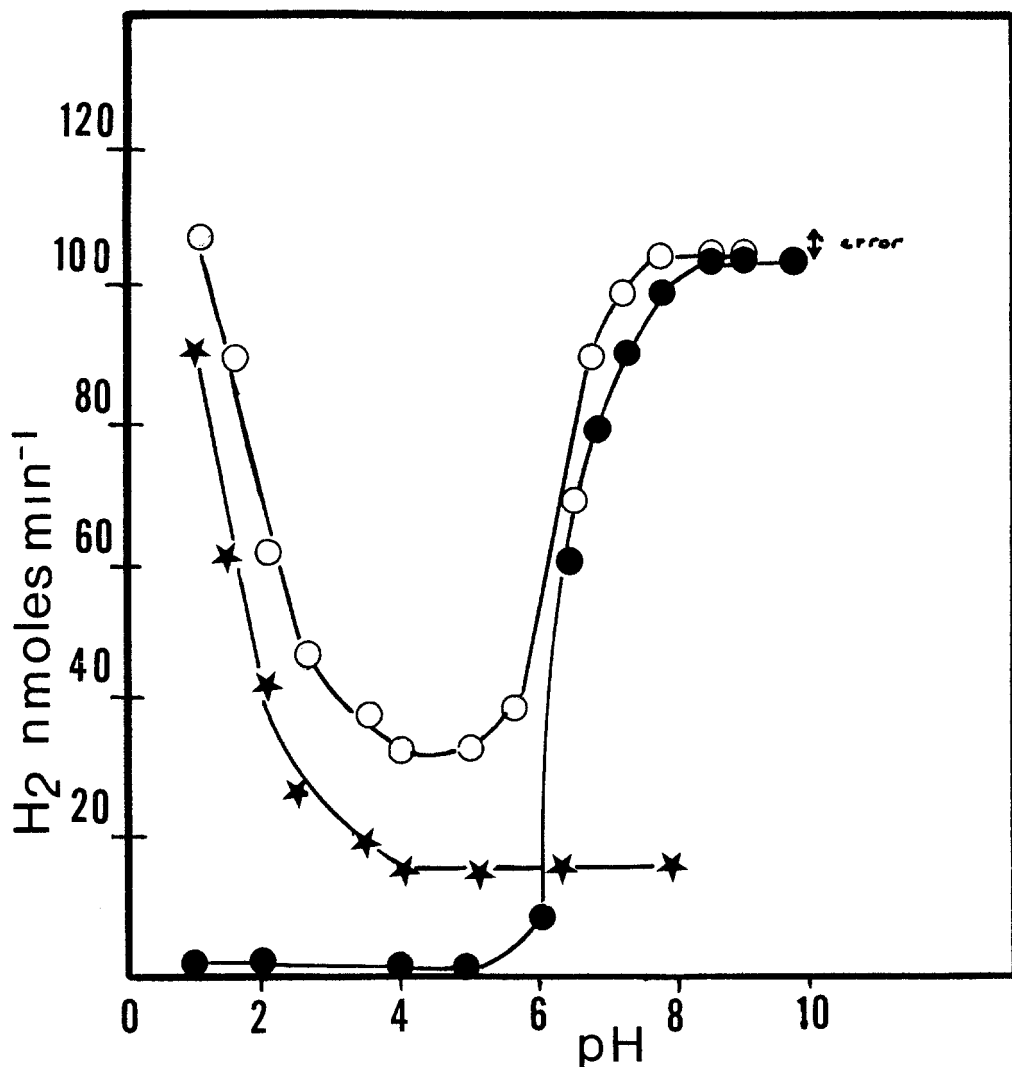


Fig. 1. Rate of H₂ formation on irradiation of 0.1 M FeSO₄ as a function of pH and range of UV sources. 150 W xenon arc lamp and quartz cell: (★), 200 watt mercury arc lamp and quartz cell: (○) or pyrex cell (●).

characteristics differentiate this reaction from the classical hydrated ferrous ion photoreaction (Weiss, 1936) which may involve solvated electrons and hydrogen atoms. The reaction mixture in the present case is heterogeneous and thus may also be different from that observed by Braterman *et al.* (1983). The latter authors suggested Fe(OH)⁺ as the reactive species. A future aim of this work is to overlap the low concentration of the earlier work. The conditions of the present measurements are closer to those of Schrauzer and Guth (1976) who claimed (following earlier work) that precipitated Fe(OH)₂ produced H₂ in the dark at pH

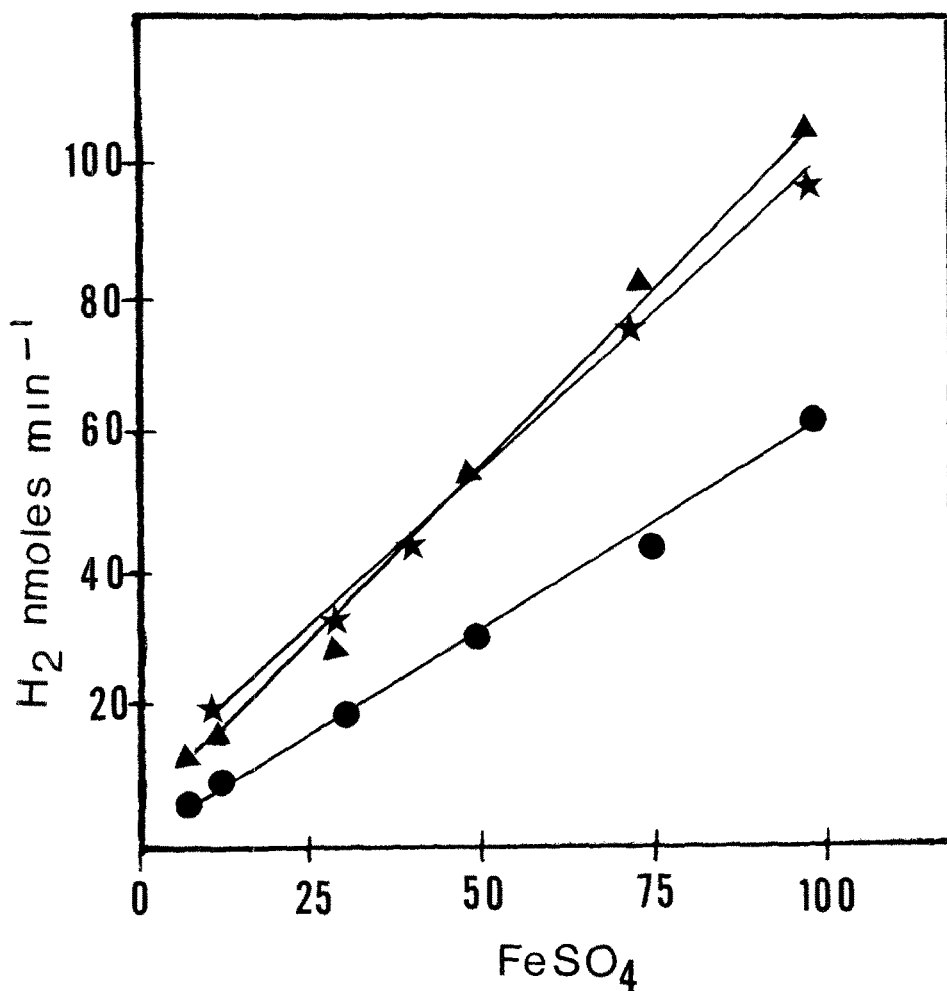


Fig. 2. Rate of H₂ formation as a function of FeSO₄ concentration. 150 watt xenon arc lamp and quartz cell, pH 1.0: (★), 200 W mercury arc lamp and quartz cell, pH 1.6 (●) or pH 7.2 (▲).

8–10. We have confirmed the sharp pH dependence of the dark reaction. The dark rates were negligible as compared to the light rates under most of our conditions. Schrauzer and Guth noted that the reaction was enhanced by UV light of 300–330 nm. The photoreaction may well occur in the solid state. The precipitate in our experiments had a yellowish color to pH 7 then greyish at more alkaline pH but never green. We explain the efficiency of the reaction by the reduction of an intermediate formed after excitation of the ... Fe(OH)₂ ... polymer (Figure 4) by the neighboring Fe²⁺ ions. In both steps a driving force for the reaction is the much increased bonding of OH⁻ (or O²⁻) to the Fe³⁺ ion. This mechanism accounts for the single photon formation of H₂, for the absence of measurable lag and for the

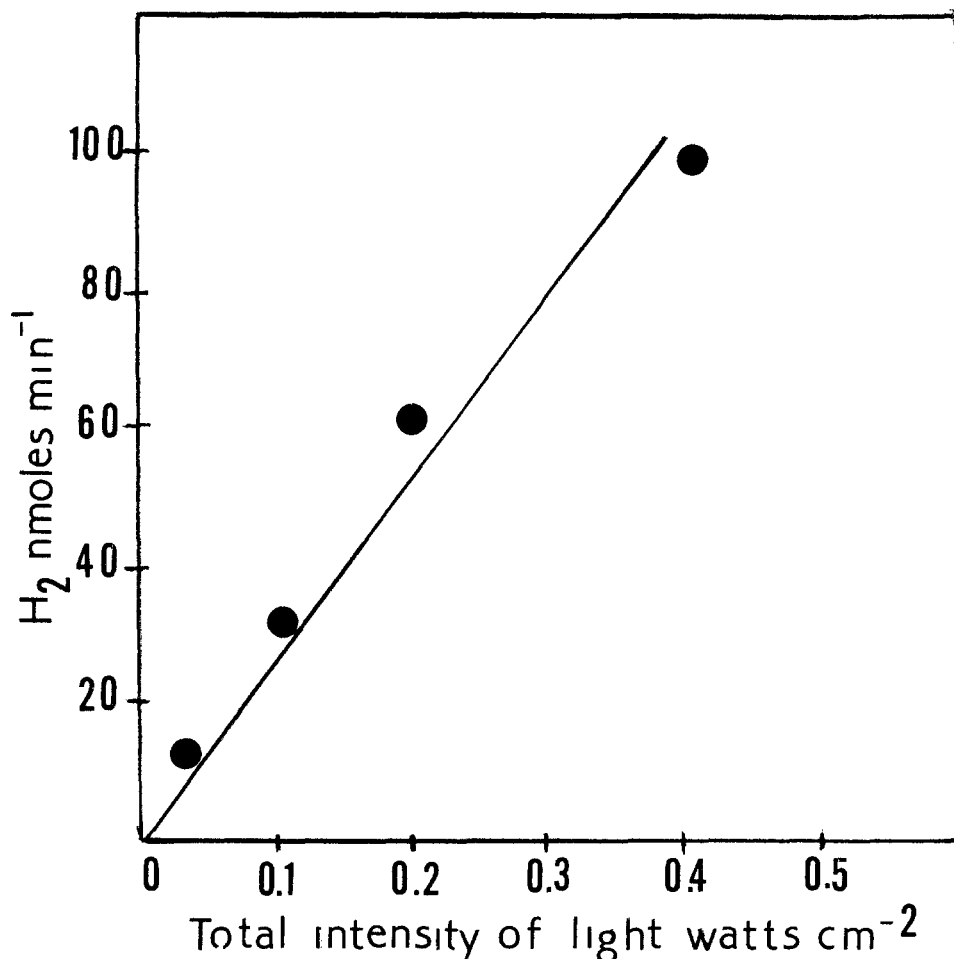


Fig. 3. Rate of H₂ formation as a function of light intensity. 200 watt mercury arc lamp and quartz cell; 0.1 M FeSO₄; pH 7.2.

linear dependence on both light fluence and concentration of ferrous ion. It also accounts for the extraordinary sensitivity of the reaction to ferric ions: the quantum yield decreases by a factor of five at 0.01 mole fraction of Fe³⁺/Fe²⁺!. This is because in the polymer any Fe³⁺ in the neighborhood of the excitation completely quenches the reaction: (Fe²⁺)^{*} + Fe³⁺ → Fe³⁺ + Fe²⁺. This short circuit may actually occur through the intermediary (H[•]), thus extending the range of quenching. The strong inhibiting effect of ferric ions suggests that the photo-oxidation of ferrous hydroxide complexes will never be complete. In fact the banded iron deposits often contain magnetite, the mixed Fe²⁺ - Fe³⁺ oxide.

It has often been commented that the reaction:

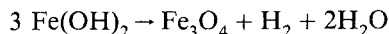


TABLE I

The wavelength dependence of H₂ formation at acid and neutral pH.

Samples of 0.1 M FeSO₄ in quartz cell were irradiated with monochromatic light obtained from a 200 W mercury arc lamp with Bausch and Lomb high intensity monochromator, 20 nm band pass.

Wavelength (nm)	Light intensity ($\mu\text{W cm}^{-2}$)	H ₂ formation (n moles min ⁻¹)	
		pH 2.1	pH 7.2
280	2.7 ^a	0.4 ^b	1.0
290	3.1	1.2	1.3
300	8.3	1.2	4.2
320	13.3	1.3	6.5
370	20.0	0	6.5
400	10.0	0	0

^a Total intensity, all contaminated with stray light, but shorter wavelengths more so.

^b Error: ± 0.4 nmoles min⁻¹.

TABLE II

Quantum yield of H₂ formation at pH 7.2

Experimental conditions were as described for Table I. Absolute intensities of light were measured by means of potassium ferrioxalate actinometry ($\phi_{\text{Fe}^{2+}} = 1.26$). The quantum yield is a minimum (ϕ_{min}) since it was assumed that all the incident light was absorbed.

Wavelength (nm)	Fe ²⁺ produced nanomoles min ⁻¹	$h\nu$ nanoeinsteins min	H ₂ formed	
			nanomoles min ⁻¹	quantum yield min
300	21.0	16.7	4.6	0.28
320	22.0	17.0	5.2	0.30
370	27.0	21.4	6.5	0.30

is thermodynamically favored (Schrauzer and Guth, 1976; Shipko and Douglas, 1956). However, this says nothing about how the free energy of the products can possibly affect the intermediates forming H₂ i.e. the mechanism of the reaction. Schrauzer and Guth have suggested that the thermal mechanism of this reaction involves the formation of elemental iron which then reacts with protons to form hydrogen. It is difficult to explain our observation with such a pathway. The photo-induced formation of H₂ without lag and in high quantum yield at pH 10 argues against a mechanism involving elemental iron and protons. The sharp pH dependence of the rate of the thermal reaction is also not explained by such a mechanism. It is however, conceivable that the reactive intermediate is a weakly bonded Fe⁰ or Fe-H. Note that such a species would involve breaking the strong

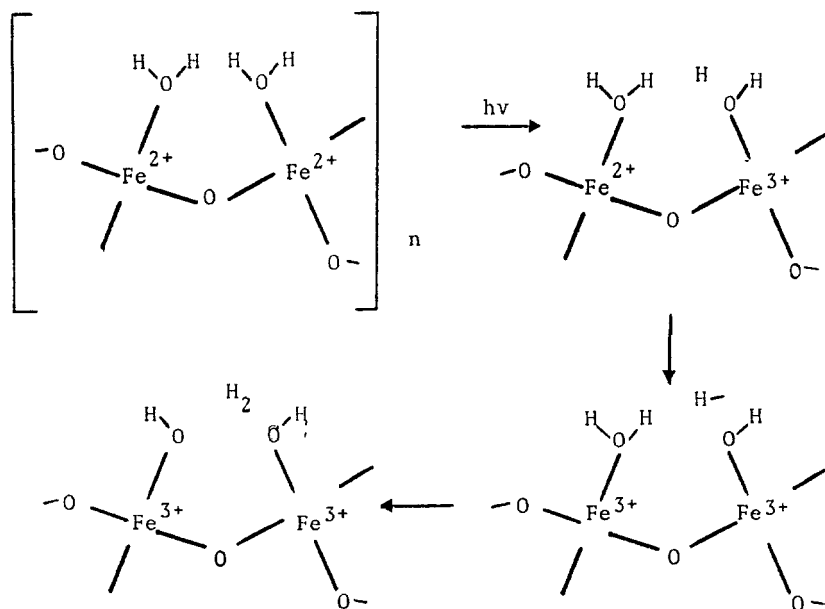


Fig. 4. Mechanism of H₂ formation from ferrous hydroxide polymer.

Fe—O bond(s). An intriguing suggestion of Bohnsack (1974) is to consider the reaction as a stepwise organic structural rearrangement. The linear ferrous hydroxide- μ oxo polymer forms Fe-oxo rings, which on oxidation and elimination of H₂ wrap themselves up in 3-dimensions into the magnetite structure! Such a concept, together with the H₂ forming mechanism suggested in Figure 4 may lead to an understanding of this unique reaction.

5. Relevance to Origin of Life

The early suggestion of Cairns-Smith (1978) and the provocative work of Braterman, Cairns-Smith and Sloper (1983) have given substance to the view that near ultraviolet light on the anoxic earth caused photo-oxidation of ferrous ion and contributed to the formation of the Banded Iron Formations. Our observation of the high efficiency of this reaction to form hydrogen, suggests that it is a prime source of highly reactive reducing equivalents on the early earth. Such active reducing equivalents have become more essential to the standard model of the origin of life as the arguments for the emission on the early earth of carbon dioxide instead of methane have grown stronger. These arguments then conflict with the necessity of reduced carbon species to form useful amounts of amino acids, purines and pyrimidines, etc. We estimate that possibly 1–10% of the total carbon could be reduced by the flux of solar near UV photons, given a sufficient flux of ferrous ions. If this reaction can be sensitized

to visible light by pigments such as porphyrins, the total carbon pool could be reduced. This photo reaction may have not only contributed the necessary reducing equivalents but may have served as an organizing center or source of negentropy for the required chemical reactions.

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References

- Bohnsack, G.: 1974, *Liebigs Ann. Chem.*, 1035.
- Braterman, P. S., Cairns-Smith, A. G., and Sloper, R. W.: 1983, *Nature* **303**, 163.
- Braterman, P. S., Cairns-Smith, A. G., Sloper, R. W., Truscott, T. G., and Craw, M.: 1984, *J. Chem. Soc. Dalton Trans.* 1441.
- Cairns-Smith, A. G.: 1978, *Nature* **276**, 807.
- Francois, L. M.: 1986, *Nature* **320**, 352.
- Hatchard, C. G. and Parker, C. A.: 1956, *Proc. R. Soc. London Ser A* **235**, 518.
- Hayon, E. and Weiss, J.: 1960, *J. Chem. Soc.* p. 3866.
- Holland, H. D.: 1984, *The Chemical Evolution of Atmosphere and Oceans*, Princeton University Press, p. 396.
- Joe, H., Kuma, K., Paplawsky, W., Rea, B., and Arrhenius, G.: 1986, *Fifth Meeting of the International Society for the Study of the Origin of Life*, Berkeley, Calif., July 21-25, Abstracts p. 191.
- Mattioli, G. S. and Wood, B. J.: 1986, *Nature* **322**, 626.
- Mercer-Smith, J. and Mauzerall, D.: 1984, *Photochem. Photobiol.* **39**, 397.
- Schrauzer, G. N. and Guth, T. D.: 1976, *J. Am. Chem. Soc.* **98**, 3508.
- Scribbling, A. and Miller, S. L.: *2nd NASA Symp.* (Moffett Field, July 1985), Abstracts p. 37.
- Shipko, F. J. and Douglas, D. L.: 1956, *J. Phys. Chem.* **60**, 1519.
- Walker, J. C.: 1977, *Evolution of the Atmosphere*, Macmillan Publ. Co., New York.
- Weiss, J.: 1935, *Nature* **136**, p. 794.