

## Photooxidation of Water by Ferric Hexathiocyanate

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**Abstract:** Ferric hexathiocyanate ion is found to oxidize water on irradiation with visible and near U.V. light (quantum yield  $\sim 0.2\%$ ). Reaction rates are measured and a simple theory is presented to explain the results.

### 1. Introduction

In recent years the studies on photodissociation of water has received great deal of attention.<sup>1,8</sup> The methods proposed for the achievement of these oxidation reduction processes fall into three main categories - photoelectrochemical cells<sup>2,3</sup> semiconductor powder suspensions<sup>7,10</sup> and redox systems with stable sensitizers.<sup>4,8</sup> Regenerative systems of the third type with stable inorganic sensitizers seems to be one of the most promising methods for conversion and storage of solar energy.<sup>8</sup> In this work we report our observations on oxidation of water by visible and near U.V. light ( $\lambda < 360$  nm) in presence of the ferric hexathiocyanate (FH) ion.

### 2. Experimental

Ferric chloride solution ( $\sim 0.01$  mol dm<sup>-3</sup>) is centrifuged to remove the ferric hydroxide suspension and the Fe<sup>3+</sup> concentration is determined. Aqueous KCNS is mixed with the above until the resulting solution is  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> in Fe<sup>3+</sup> and  $0.01$  mol dm<sup>-3</sup> in KCNS. The pH is adjusted by addition of HCl maintaining these concentrations. Photolysis is carried out in a rectangular glass cell (7.5 cm x 6 cm x 3 cm) using a medium pressure mercury lamp (100W). Experiments are also carried out in direct sunlight. In all cases U.V light is  $\lambda \lesssim 360$  nm filtered off with pyrex glass sheets and the intensity is estimated using a calibrated thermopile. The time variation of the concentration of FH under constant irradiation is determined by colorimetry. To remove photogenerated O<sub>2</sub>, the solution is kept purged with oxygen free N<sub>2</sub>. The oxygen entry from the atmosphere is completely prevented. Absorption spectra and molar extinction coefficients are measured using the Unicamp Sp 500 Series II spectrophotometer.

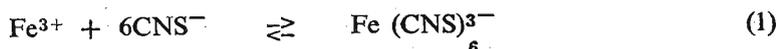
### 3. Results

A plot of  $C/C_0$  ( $C_0$ ,  $C$  = concentrations of FH at time  $t = 0, t$ ) is indicated in Figure 1. There is no evidence for an equilibrium, the reaction proceeds in the forward direction until all ferric ions are reduced. Again it is found that the plots of

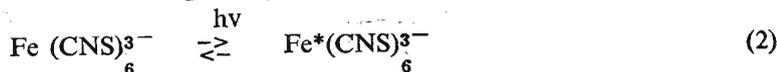
$\ln (C/C_0)$  vs  $t$  are linear (Figure 2) with slopes independent of temperature and the concentration of KCNS but directly proportional to  $[\text{OH}^-]$  and the irradiation intensity. The reaction occurs when  $\lambda \lesssim 550$  nm, this corresponds to absorption region of the FH ion (Figure 3). At a given intensity of illumination ( $\lambda$ , 360 - 550 nm) there is a tendency for the slopes to decrease with the increase of wave length. Unfortunately we did not have facilities to investigate the wave length dependence of the reaction rate.

#### 4. Theory and Discussion

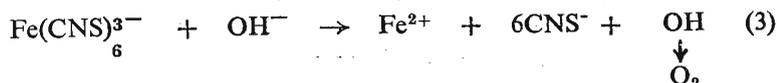
Experimental results indicate that the reaction obeys simple apparently unimolecular kinetics. It is possible to give a simple theory to explain these observations. The photoactive species in the solution is FH ion generated via,



We assume that the primary photochemical act is the formation of excited ions



and these participate in the oxidation process



The step (3) can be written in other equivalent ways ( $\text{CNS}^-$  does not complex with  $\text{Fe}^{2+}$ ). Since the rate of (3) is proportional to  $(\text{FH}^*)(\text{OH}^-)$  and  $(\text{FH}^*)$  in turn is proportional  $[\text{FH}]$  via (2) have,

$$dC/dt = -kcC \quad (4)$$

$$\text{ie } C = C_0 e^{-t/\tau},$$

where  $c = [\text{OH}^-]$ , which remains nearly constant and  $\tau = (ke)^{-1}$ . The rate constant  $k$  is proportional to the number of photons absorbed per ion and if the reaction is carried out in a cell of volume  $V$ , cross sectional area  $A$  and length  $l$

$$k = \frac{IA\eta}{CV} \quad (5)$$

where  $I$  = einsteins absorbed per sec from light passing through unit area of the cell and  $\eta$  = a constant which is a measure of the quantum yield (quantum yield per unit concentration of  $\text{OH}^-$ ). From Beer-Lambert law,

$$I = I_0 (1 - e^{-x}) \approx I_0 x, \quad x = \epsilon cl \quad (6)$$

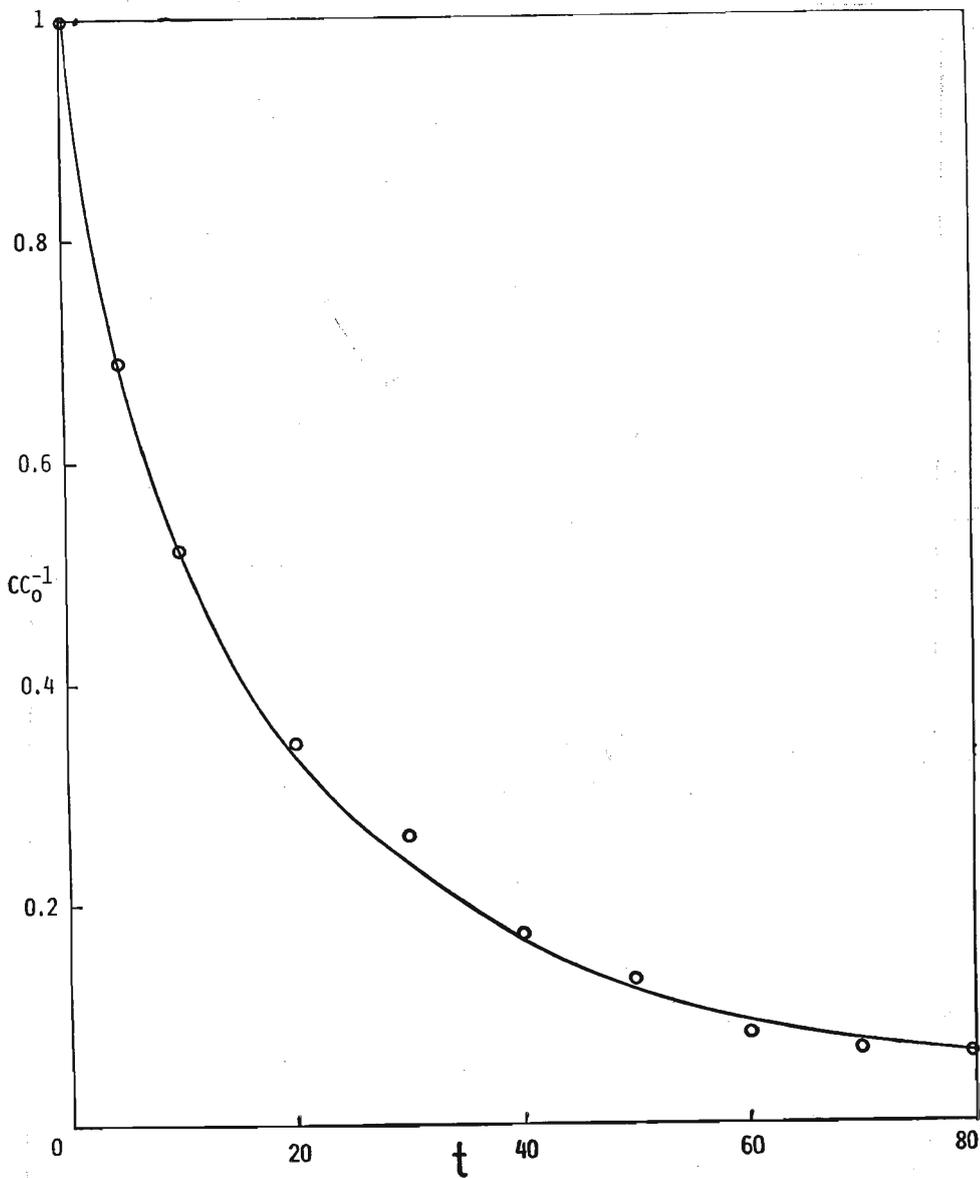


FIGURE 1 — Plot of  $C/C_0$  vs  $t$  (pH = 1.2, irradiation intensity =  $1.5 \times 10^{-7}$  einsteins  $\text{cm}^{-2}\text{sec}^{-1}$  from a 100 W mercury lamp,  $\lambda < 360$  nm filtered off)

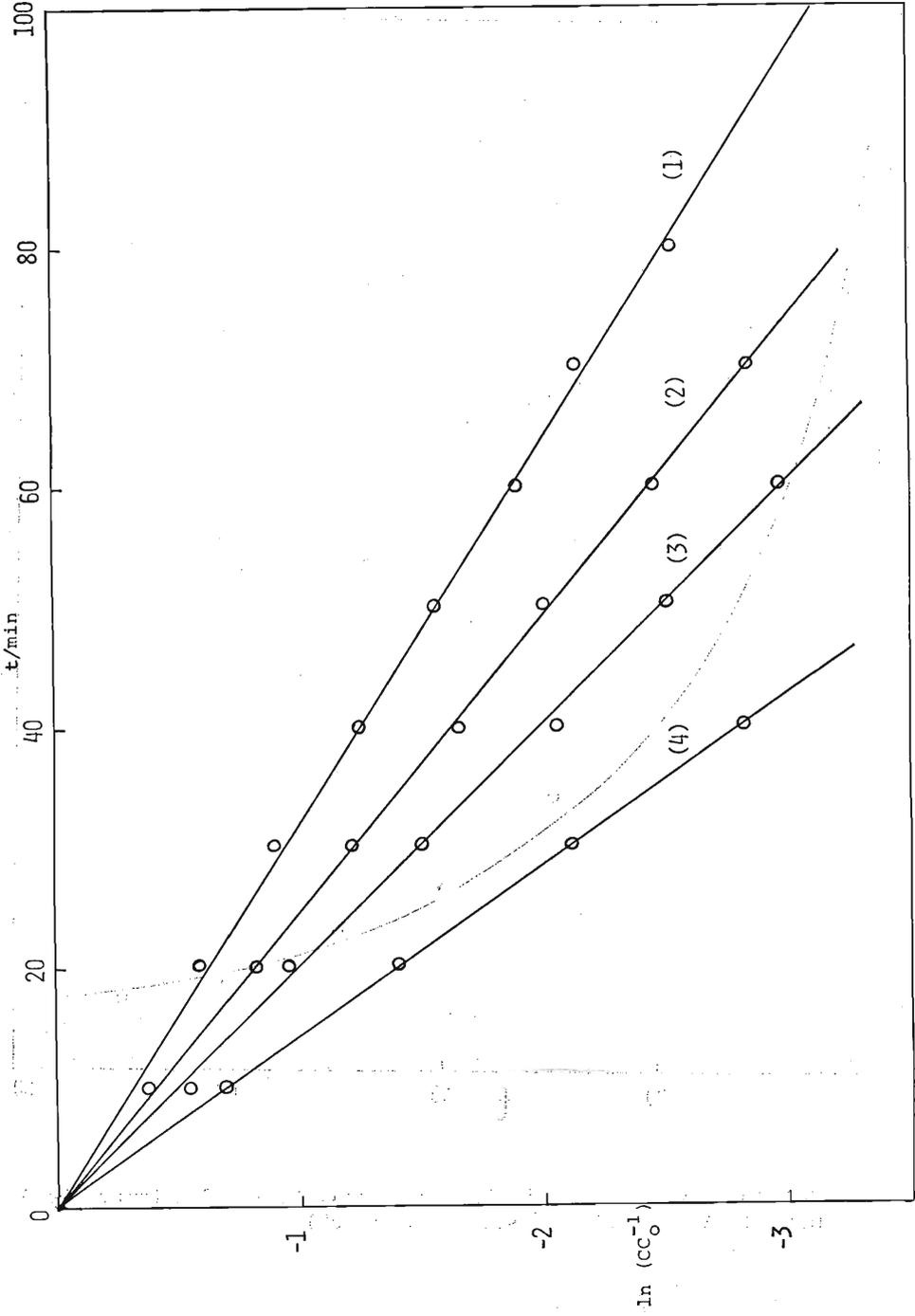


FIGURE 2 — Plot of  $\ln(Cc^{-1})$  vs  $t$  at different p Hs (1) 0.6 (2) 1.2 (3) 2.5 (4) 3.8 corresponding value  $\tau$  are 32, 25, 20 and 14 mins respectively.

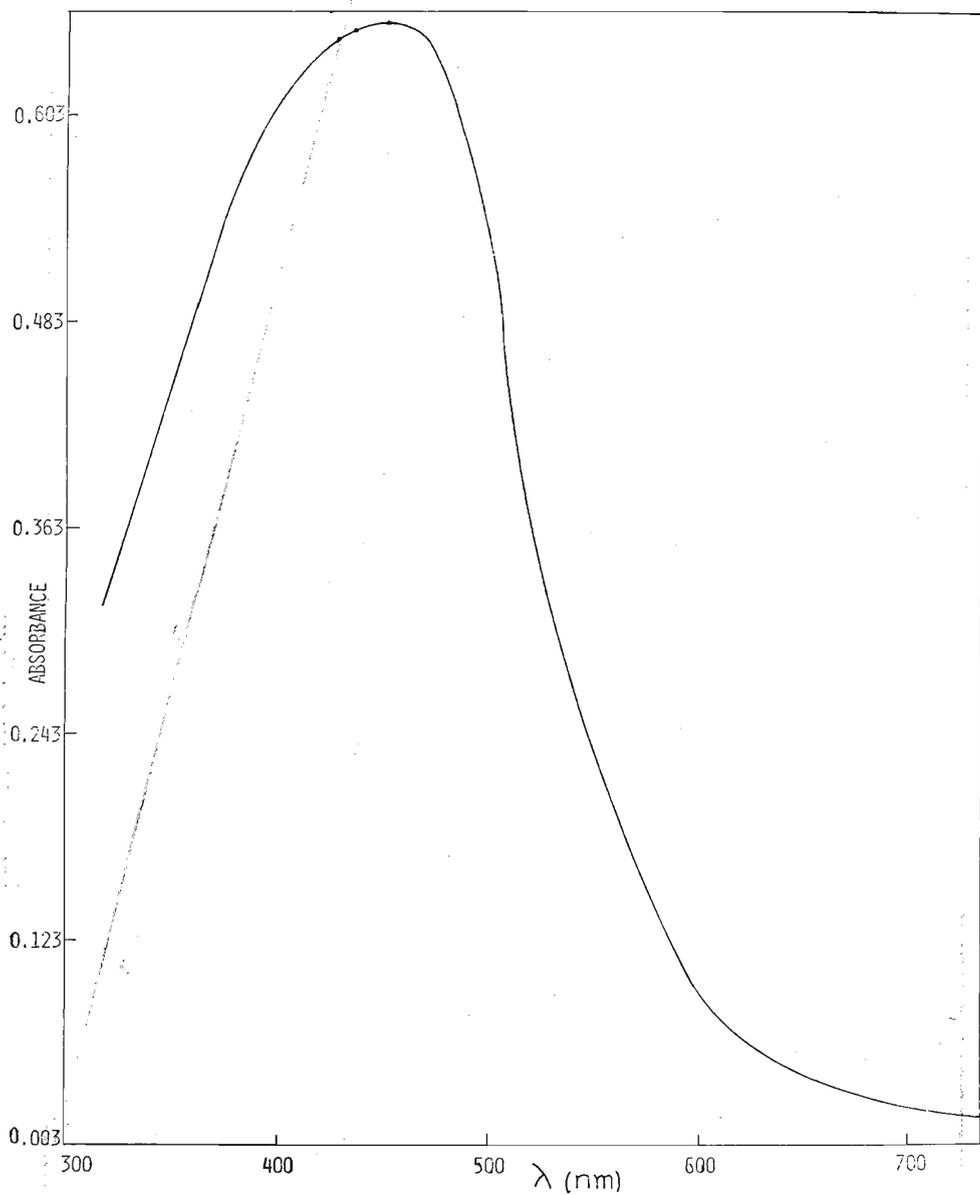


FIGURE 3 — Absorption spectrum of Ferric hexathiocyanate solution (1 cm cell, concentration  $\sim 1 \times 10^{-4}$  mol dm<sup>-3</sup>).

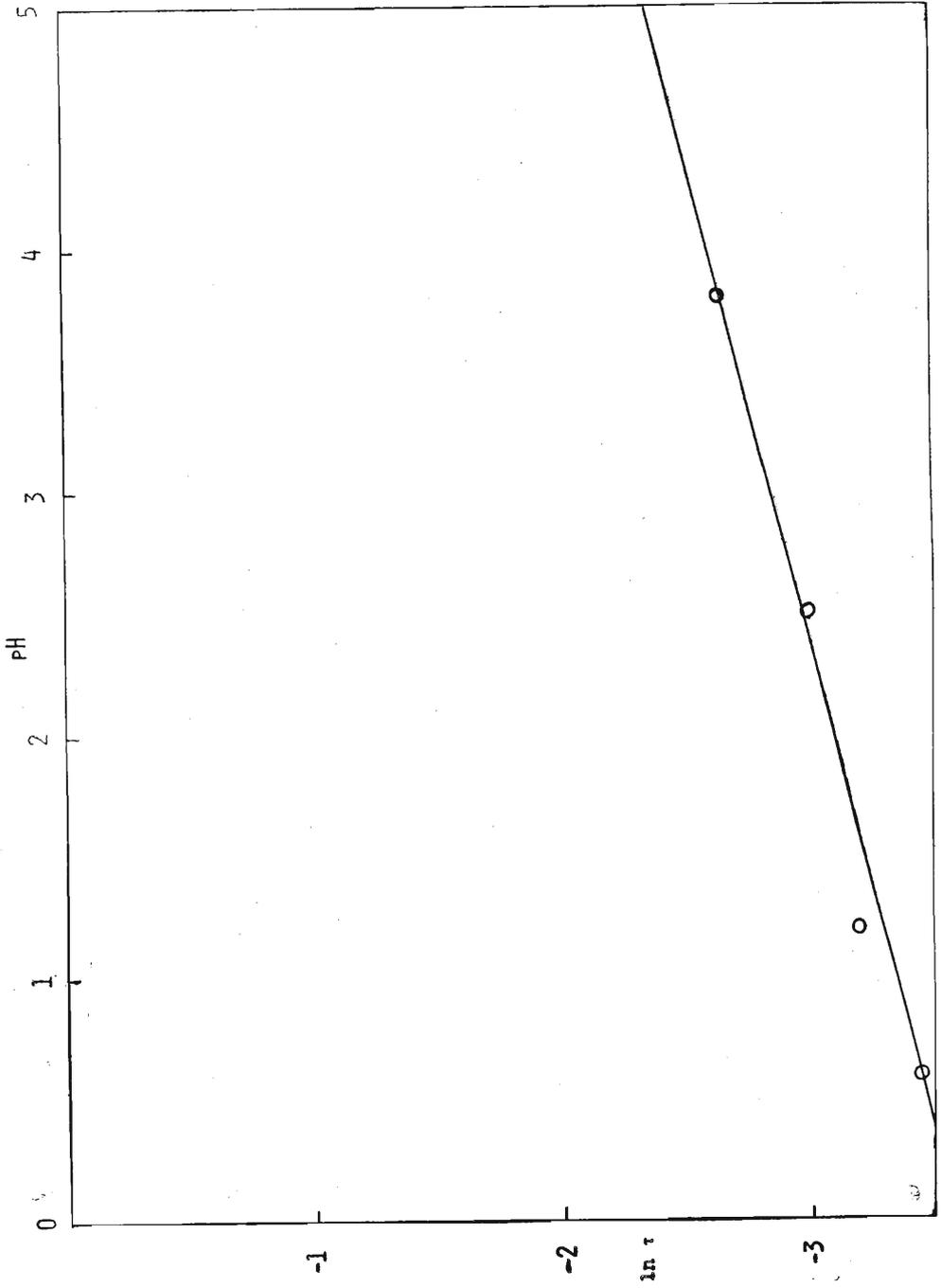


FIGURE 4 -- Plot of  $\tau$  vs pH.

where  $\epsilon$  = extinction coefficient,  $I_0$  = einsteins incident on front face of the cell per sec per unit area. From (5) and (6) we get

$$k = 2.303 I_0 \epsilon \eta \quad (7)$$

The plot of  $\ln \tau$  vs pH (Figure 4) is linear in agreement with the theory, the slope this plot gives  $\eta = 2.1 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3$  for  $I_0 \simeq 1.5 \times 10^{-7} \text{ einsteins cm}^{-2} \text{ sec}^{-1}$ . Thus  $\tau_1[\text{OH}^-]$  (pH = 3)  $\simeq 0.23\%$  which is the maximum possible quantum yield as the pH cannot be increased further. The reason why  $\tau$  is independent of temperature can be understood. The de-excitation time of  $\text{FH}^*$  is very small compared to its thermal collision time with  $\text{OH}^-$ . Thus the rate of the reaction cannot depend on temperature.

### 5. Conclusion

The system is interesting because of the extremely simple kinetics and the adaptability to accurate measurement of the reaction rates. As the quantum yield is quite small, the  $\text{O}_2$  evolution rate cannot be directly measured. However, the analysis of outgoing gases used for purging reveals the presence of  $\text{O}_2$ . The analysis of the residual solution also proves that oxygen evolution had taken place. The molarity of KCNS remains constant while ferric is reduced to ferrous, showing that any other material had not oxidized.

$\text{Fe}^{3+}$  ions are known to oxidize water on irradiation with U.V light<sup>10</sup> ( $\lambda < 300 \text{ nm}$ ). In our process which is sensitive to higher wave lengths the active species is FH ion and there is no evidence that  $\text{Fe}^{3+}$  participate in the primary photochemical act. The shifting of the equilibrium in (1) towards left by decreasing the concentration of KCNS does not change the quantum yield of  $\text{Fe}^{2+}$ .

In principle the system is regenerative, when atmospheric oxygen is allowed to combine with the reduced product the ferric complex is regenerated with the release of energy.

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