

THE CATALYSIS OF WATER PHOTO-OXIDATION BY HEAVY METAL HEXACYANIDES

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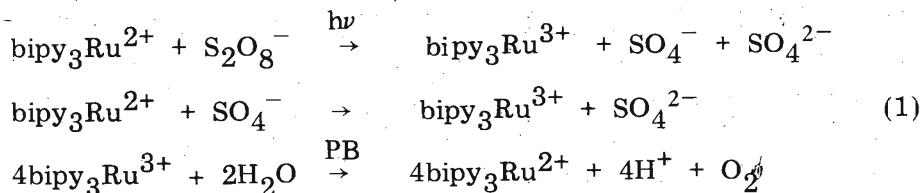
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Abstract : A number of heavy metal hexacyanides are tested for their ability to catalyse photo-oxidation of water with $\text{bipy}_3\text{Ru}^{2+}$ as the sensitizer and $\text{K}_2\text{S}_2\text{O}_8$ as the sacrificial agent. Strongest catalytic activity is seen in $\text{Zn}_3(\text{Fe}(\text{CN})_6)_2$, $\text{Cd}(\text{Fe}(\text{CN})_6)_2$ and $\text{Fe}_3(\text{Fe}(\text{CN})_6)_3$. Semiconducting properties of heavy metal hexacyanides and their relevance to catalytic activity are discussed.

1. Introduction

Photo-oxidation of water in the presence of sacrificial agents has attracted much attention as models of photosystem II in natural photosynthesis.^{1,2,3,4,5,6} Heterogeneous sensitizers (semiconductors) generally photo-oxidise water under sacrificial conditions even in the absence of other catalysts.^{2,3,6} However, in the case of homogeneous sensitizers the presence of catalysts become essential for oxygen generation.^{1,3,4,8} It is known that one electron oxidant tris (2,2' - bipyridyl ruthenium (III) ($\text{bipy}_3\text{Ru}^{3+}$) could bring 4 - electron transfer leading to photo-oxidation of water in the presence of catalysts such as RuO_2 , IrO_2 and MnO_2 .⁹⁻¹¹ Recently it has also been noted that prussian blue (PB) could also catalyse the same reaction with persulphate as the electron acceptor.¹² A suspension of PB in a solution containing $\text{bipy}_3\text{Ru}^{2+}$ and $\text{K}_2\text{S}_2\text{O}_8$ photogenerate O_2 via following reaction scheme.¹²



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We have tested a number of other water insoluble heavy metal ferro- and ferri- cyanides (PB type structure) for the above catalytic activity and found that $\text{Zn}_3(\text{Fe}(\text{CN})_6)_2$, $\text{Cd}_3(\text{Fe}(\text{CN})_6)_2$ and $\text{Fe}_3(\text{Fe}(\text{CN})_6)_3$ are superior to PB. It was also noted that $\text{Cu}_4(\text{Fe}(\text{CN})_6)_2$ behave differently, this material does not catalyse water oxidation reaction with persulphate in the presence of $\text{bipy}_3\text{Ru}^{2+}$. However, in the absence of $\text{bipy}_3\text{Ru}^{2+}$, $\text{Cu}_4(\text{Fe}(\text{CN})_6)_2$ catalyses photo-oxidation of water with sacrifice of persulphate. Again $\text{Cu}_4(\text{Fe}(\text{CN})_6)_2$ is found to catalyse sacrificial photoreduction of water. These observations can be attributed to semiconducting properties of $\text{Cu}_4(\text{Fe}(\text{CN})_6)_2$.

2. Experimental

Ferro- and ferri- cyanides of several heavy metals (Zn, Cd, Cu, Fe, Mn, Cr) were prepared by double decomposition of the solutions of their salts (Chloride or Sulphate, Analar) with a solution of $\text{K}_4\text{Fe}(\text{CN})_6$ or $\text{K}_3\text{Fe}(\text{CN})_6$. The metal salt was kept in large excess to prevent the formation of double salts containing K.¹³ Precipitates were washed and dried at 90°C . The photochemical reactions were carried out in a thermostated (26°C) quartz cell (35 ml) equipped with a polarographic detector (Applied Photophysics). The solution contained $9.2 \times 10^{-3} \text{ mol dm}^{-3}$ of $\text{K}_2\text{S}_2\text{O}_8$ and various concentration of different catalysts. All solutions were purged with argon and the cell was sealed before irradiation. The light source used was a 90 W medium pressure mercury lamp (UV and IR filtered off). Light intensities were measured with an International Light IL 700 Radiometer.

To measure the electrical conductivity of $\text{Cu}_4(\text{Fe}(\text{CN})_6)_2$, the material in the powder form was compacted between stainless steel electrodes to a pressure $\sim 80 \text{ K bar}$, in a glass tube (diameter $\sim 0.6 \text{ cm}$, pellet length $\sim 0.4 \text{ cm}$), the ends of the tube were sealed with epoxy resin and the resistance at different temperature was measured with an ohm-meter. The diffuse reflectance spectra of the catalyst in the dry powder form or the absorption spectra of the suspensions were determined using an Unicamp SP 500 Series II spectrophotometer.

3. Results and Discussion

As the catalyst and $\text{bipy}_3\text{Ru}^{2+}$ absorb light in the same spectral region, the reaction rates vary with the concentration of the catalyst and in each case an optimum concentration is found to exist.¹² Figure 1 indicates the variation of the initial reaction rate with the concentration of $\text{Zn}_3(\text{Fe}(\text{CN})_6)_2$. Figure 2 shows O_2 photogeneration with different catalysts at their optimum concentrations (pH 7, as in PB¹² the reaction rates are

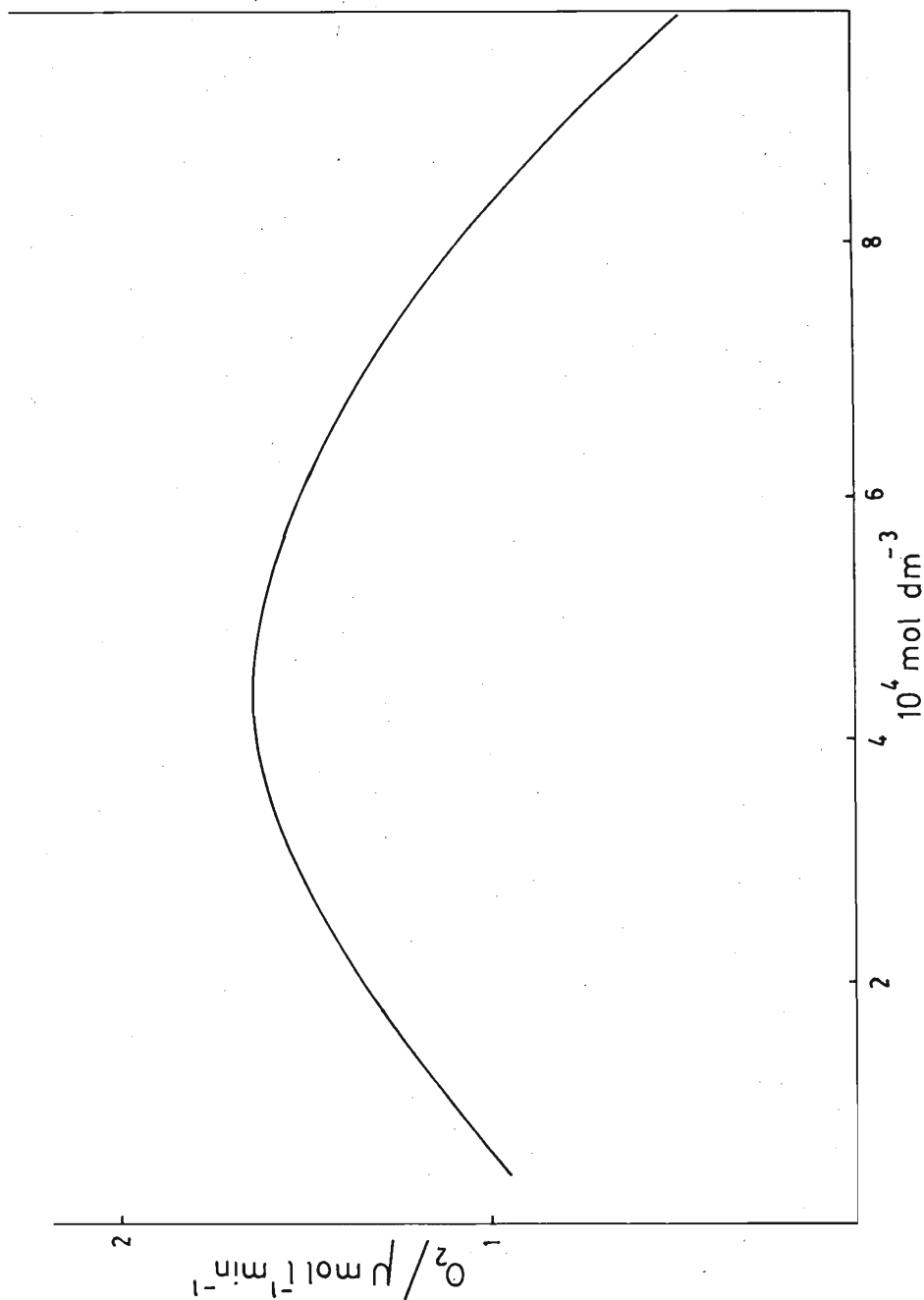


Figure 1. Variation of the initial reaction rate with concentration of $Zn_3(Fe(CN)_6)_2$.
 Reaction conditions ($bipy_3Ru^{2+}$) = $9.2 \times 10^{-3} \text{ mol dm}^{-3}$ ($K_2S_2O_8$) = 0.03 mol dm^{-3} . Illumination = $400W/m^2$ at the window of the reaction cell.

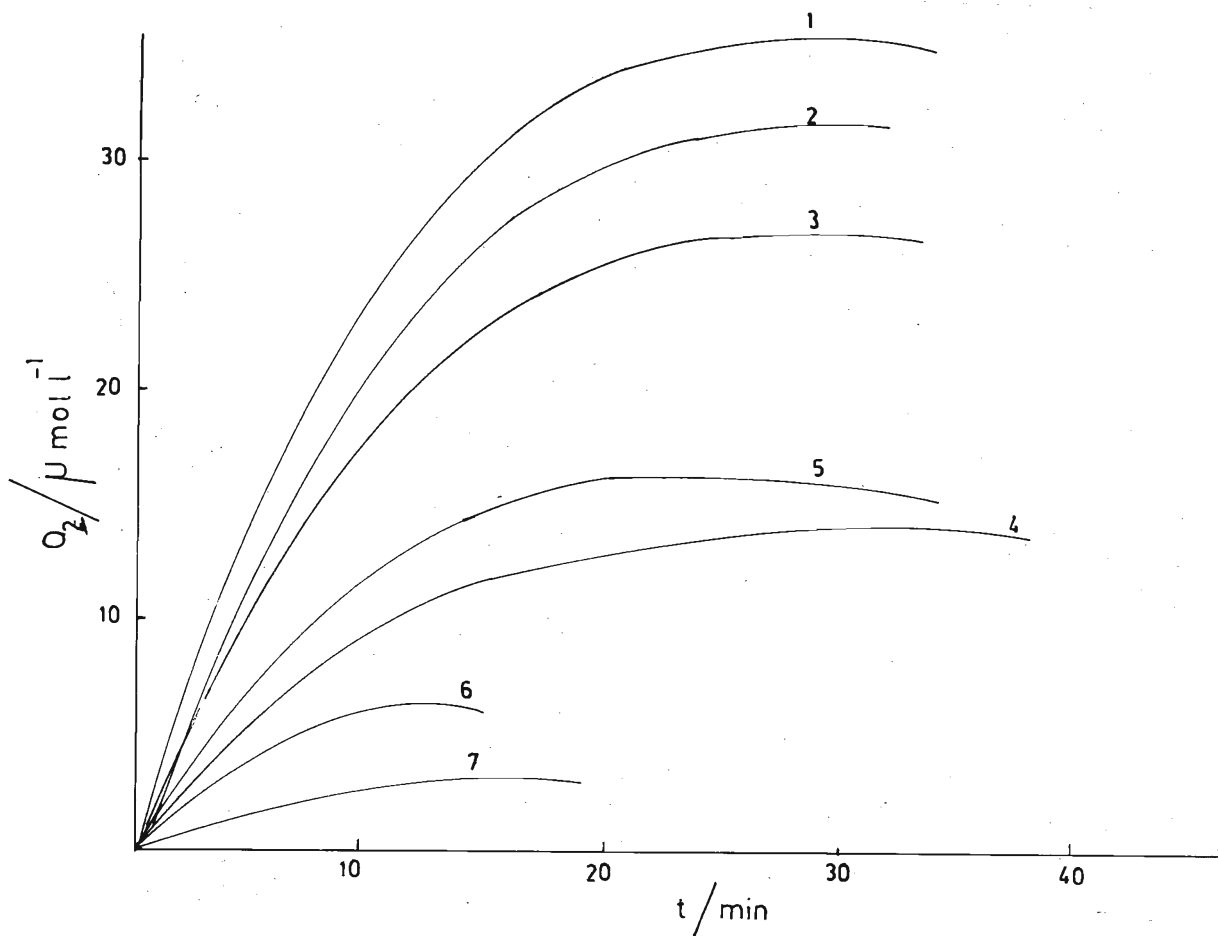


Figure 2. Photogeneration of O_2 from different catalysts at their optimum concentrations (other conditions as in Figure 1).

1. $Zn_3(Fe(CN)_6)_2$ (4.3)
2. $Cd_3(Fe(CN)_6)_2$ (3.8)
3. $Fe_3(Fe(CN)_6)_3$ (4.0)
4. PB (3.6)
5. $Cu_3(Fe(CN)_6)_3$ (4.8)
6. $Cr_4(Fe(CN)_6)_3$ (3.9)
7. $Mn_4(Fe(CN)_6)_2$ (3.0)

Numbers given inside the brackets are catalyst concentrations in 10^4 mol dm^{-3} .

maximum when the pH is ~ 7), the other conditions kept constant. The highest initial reaction rate and the highest final O_2 concentration are obtained with $Zn_3(Fe(CN)_6)_2$, $Cd_3(Fe(CN)_6)_2$ and $Fe_3(Fe(CN)_6)_3$ (Berlin Green) which are superior to PB. $Zn_3(Fe(CN)_6)_2$ absorbs more in the absorption region of $bipy_3Ru^{2+}$ than PB (Figure 3). Again as the particle sizes (estimated from the sedimentation ratio) of all the compounds are found to be nearly same, the observed difference in catalytic activity could not arise as a result of any difference in the degree of dispersion.

Cupric ferrocyanide behave differently from other compounds. Here in the presence of $bipy_3Ru^{2+}$ with $K_2S_2O_8$ as the sacrificial agent, O_2 is not photogenerated. But in the absence of $bipy_3Ru^{2+}$ (ie, only $K_2S_2O_8$), O_2 is generated with visible light (Figure 4). All the other hexacyanides we have examined evolve O_2 only if $bipy_3Ru^{2+}$ is present in addition to $K_2S_2O_8$. Again with sacrificial electron donors, eg, acetic acid, $Cu_4(Fe(CN)_6)_2$ is found to catalyse photoreduction of water (Figure 5).

Hexacyanides exhibit semiconduction which is often enhanced by adsorbed water.^{13,14,15} Although there are exceptions, the general trend is, ferrocyanides are n-type and ferricyanides are p-type.¹⁵ PB is known to have p-type behaviour.^{16,17} Thermoelectric and Hall tests indicate that $Zn_3(Fe(CN)_6)_2$, $Cd_3(Fe(CN)_6)_2$ and $Fe_3(Fe(CN)_6)_3$ are p-type, whereas $Cu_4(Fe(CN)_6)_2$ is n-type!⁵ It is likely that higher hole mobility favours catalytic activity towards photo-oxidation of H_2O as holes can get more easily accumulated in a p-type material.

The temperature variation of the electrical conductivity of $Cu_4(Fe(CN)_6)_2$ is presented in Figure 6(a), the thermal activation energy is found to be 0.57 eV and the diffuse reflectance spectrum (Figure 6 b) suggests band gap ~ 2.0 eV. The catalysis of sacrificial photo-oxidation and reduction (visible light) by this material can be understood as in other semiconductors and band positions should be favourably located. When $bipy_3Ru^{2+}$ is present O_2 generation is inhibited possibly because $Cu_4(Fe(CN)_6)_2$ effectively catalyse O_2 - depleting reverse reaction.

All the above compounds remain stable in persulphate (9pH \approx 10). The strongest resistance to oxidation is seen in Berlin Green, which is unaffected even by conc. boiling HNO_3 .

We are not in a position to give a detailed explanation as to why PB type complexes catalyse photo-oxidation of water. Perhaps the combination of semiconducting and zeolitic properties play an important role.

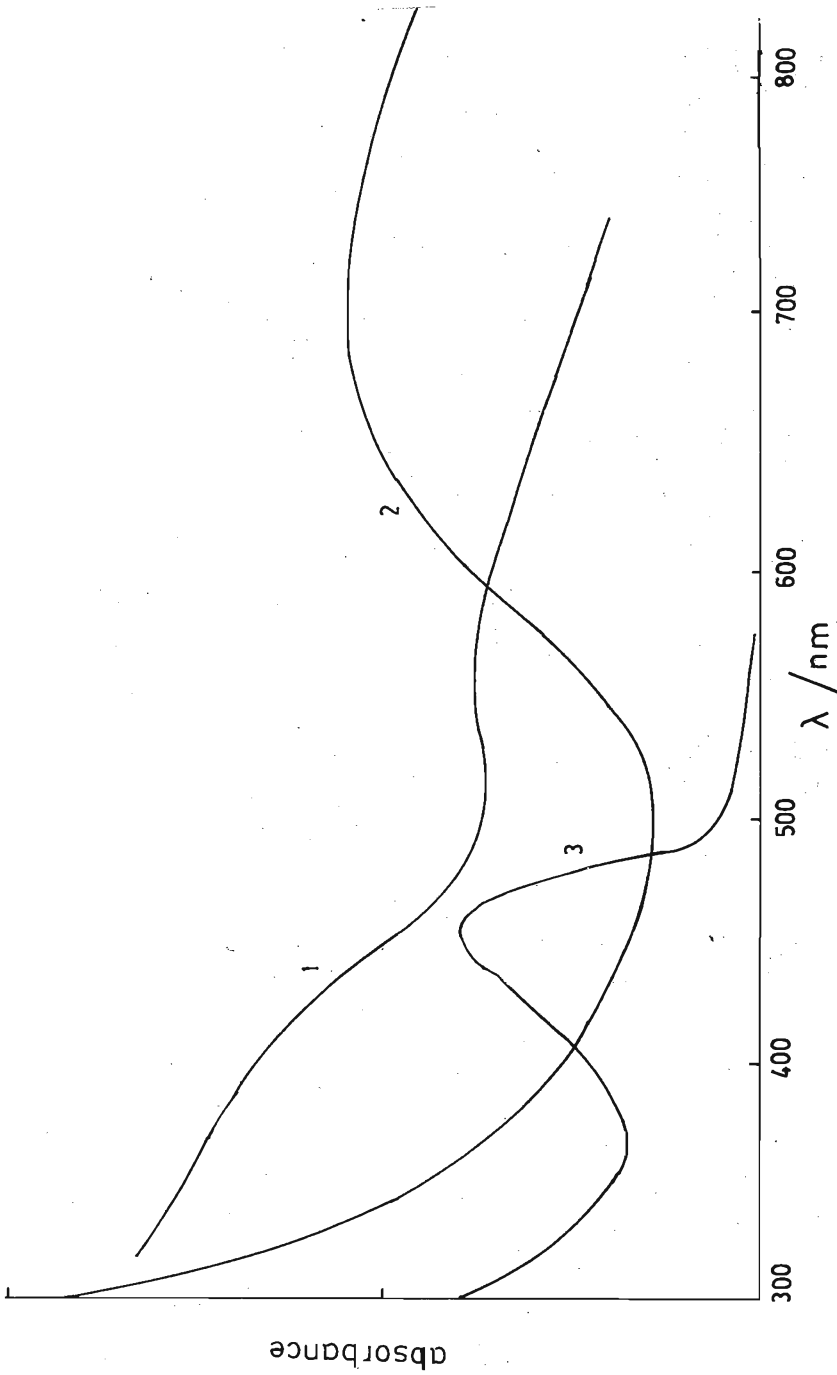


Figure 3. Absorption spectra of aqueous suspensions of

1. $\text{Zn}_3(\text{Fe}(\text{CN})_6)_2$ (4.3)

2. PB (3.6)

3. $\text{bipy}_3\text{Ru}^{2+}$ (9.2)

The numbers given inside the brackets are concentration in 10^4 mol dm^{-3} .

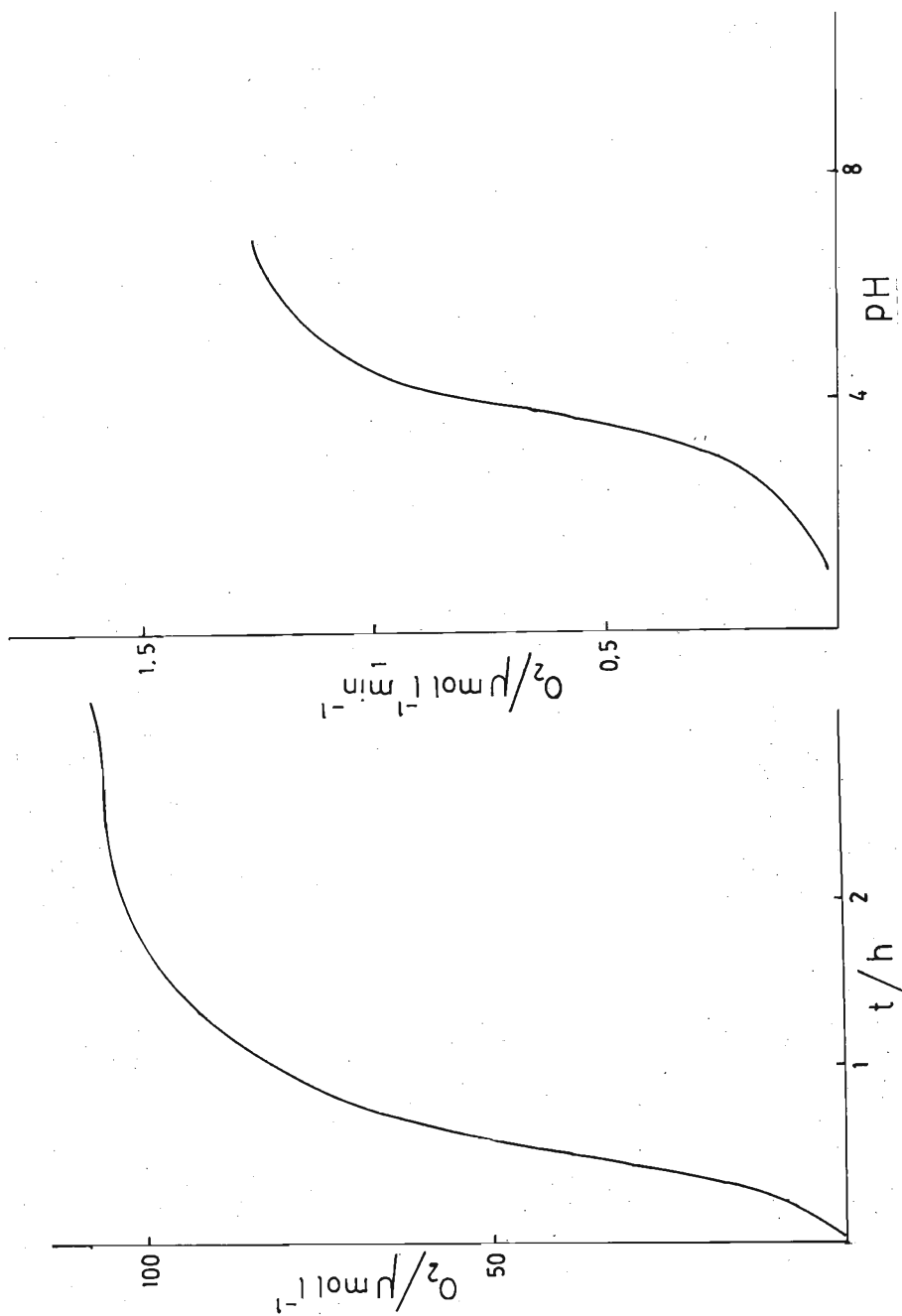


Figure 4. Photogeneration of O_2 with $Cu_4(Fe(CN)_6)_2$ (3.6) in the presence of $K_2S_2O_8$ (0.03). The numbers given inside the brackets are concentrations in 10^4 mol dm^{-3} .

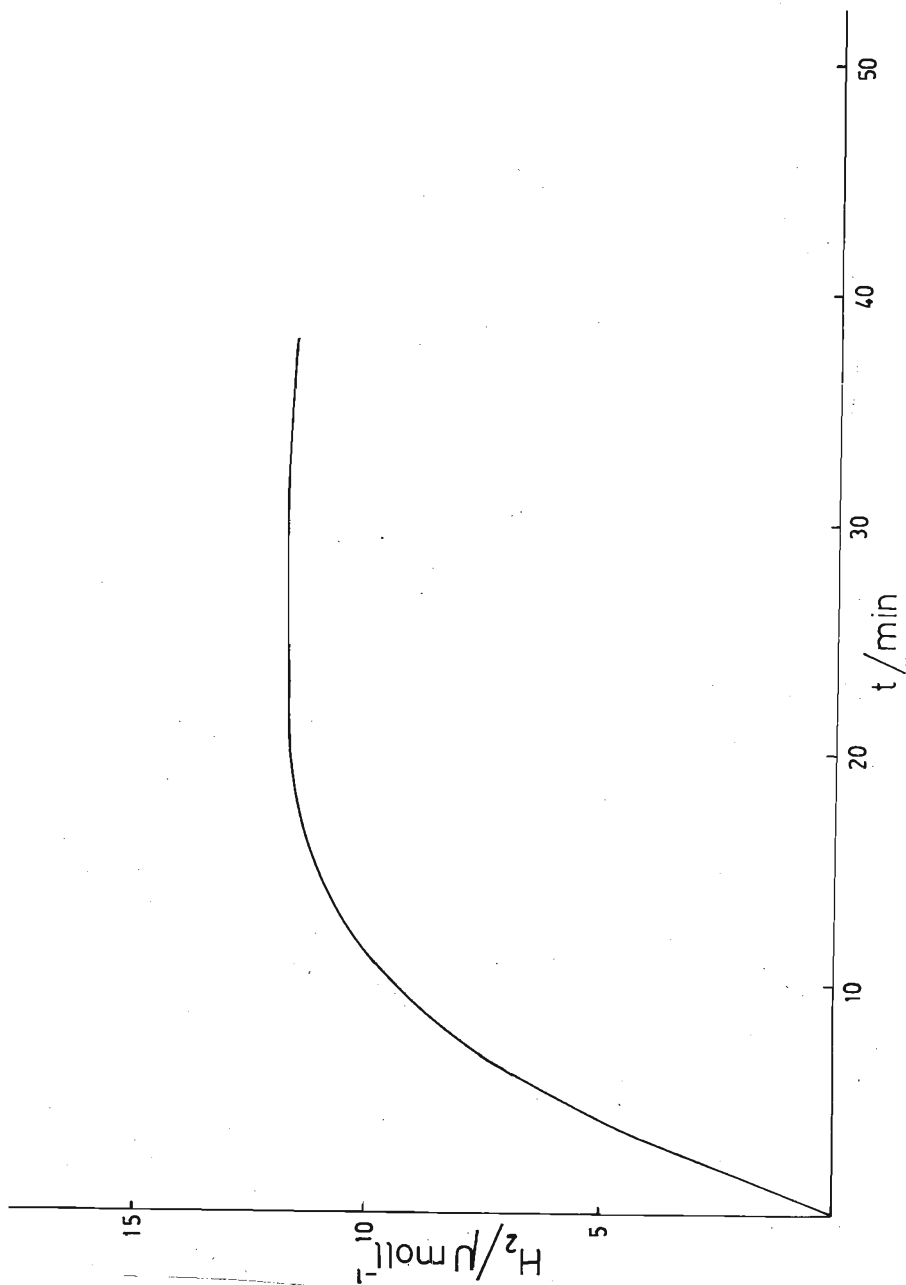


Figure 5. Photoreduction of H_2O with $Cu_4(Fe(CN)_6)_2$ (3.6) in the presence of acetic acid (0.05), concentrations in 10^4 mol dm^{-3} are given inside the brackets.

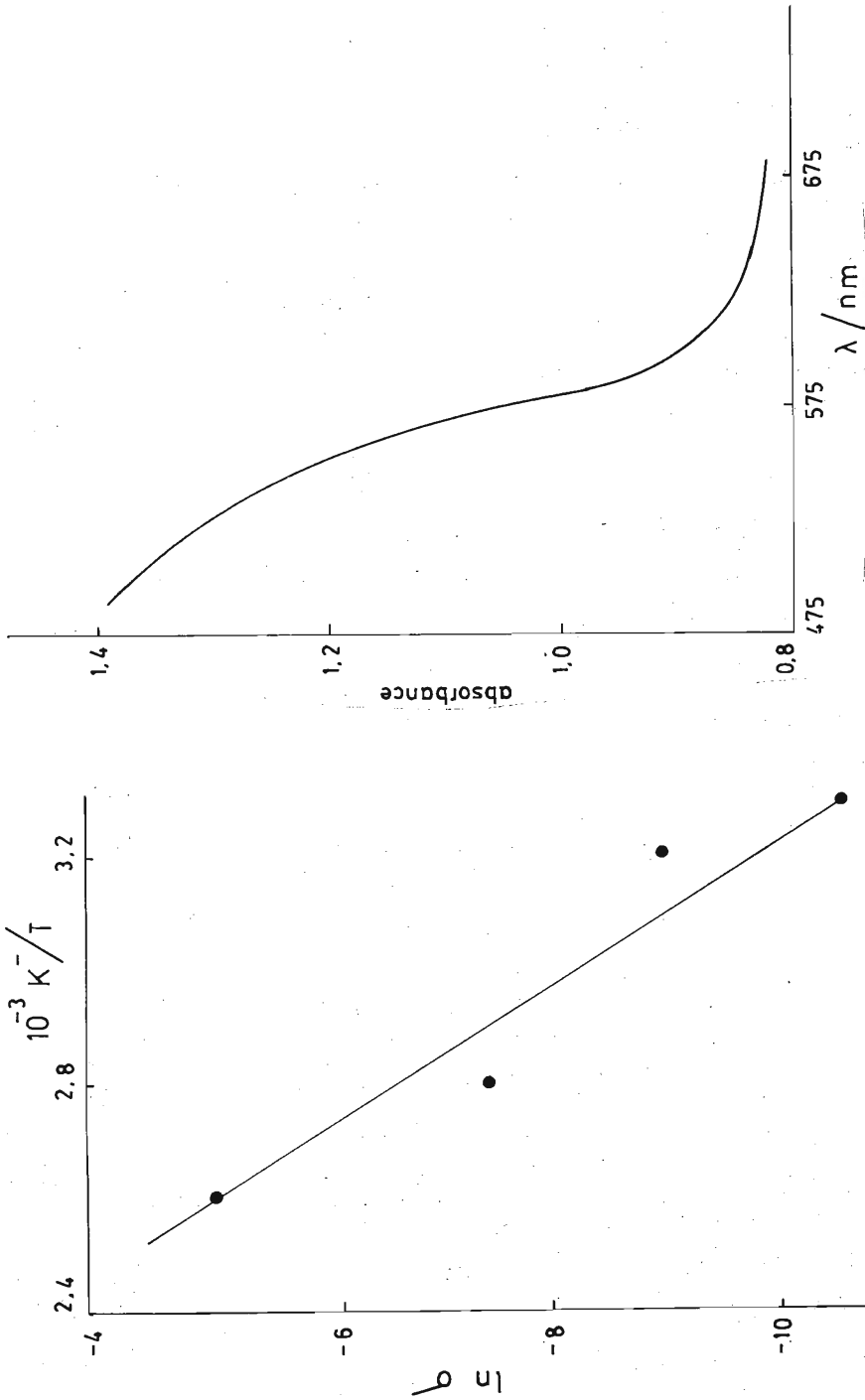


Figure 6. (a) Plot of $\log \sigma$ (σ in $\Omega^{-1} \text{ m}^{-1}$) vs T^{-1} for $\text{Cu}_4(\text{Fe}(\text{CN})_6)_2$.
 (b) Diffuse reflectance spectrum of $\text{Cu}_4(\text{Fe}(\text{CN})_6)_2$.

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