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An Investigation of the Behaviour  
of the Maleonitriledithiolate Dianion of Platinum  
in Heterogeneous and Homogeneous Systems  
Under Visible Irradiation

André Richard Joseph Domingue

A Thesis  
in  
The Department  
of  
Chemistry

Presented in Partial Fulfillment of the Requirements  
for the Degree of Master of Science at  
Concordia University  
Montréal, Québec, Canada

June, 1988



André Richard Joseph Domingue, 1988

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ABSTRACT  
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An Investigation of the Behaviour  
of the Maleonitriledithiolate Dianion of Platinum  
in Heterogeneous and Homogeneous Systems  
Under Visible Irradiation

André Richard Joseph Domingue

The dianionic maleonitriledithiolate complex of platinum is shown to display behaviour indicative of a photocatalytic redox reaction. In heterogeneous and homogeneous systems, there are indications of the existence of a rather complex photoprocess not occurring with the similar but unreactive nickel complex. During irradiation with visible light, a homogeneous solution containing the dianionic platinum complex and a suitable electron donor species undergoes a sustained, photocatalytic redox process. Several mild reductants (thiosulfate, bisulfate), can be used to maintain this oxidative reaction indefinitely. The reaction starts with a reduction of

oxygen by the photoexcited complex producing a bound (or unbound) peroxide species. Rapid disappearance of the dianionic form of the complex is accompanied by the appearance of a new, photoactive and previously unreported intermediate species. The significant concentration of peroxide generated during irradiation rapidly consumes all reductant species in the solution and even the photocatalyst itself is eventually degraded. The photocatalytic species may be an adduct of dioxygen related to a similar complex formed by the cobalt dithiolene complex. The processes that had been observed occurring in the system are attributed to strictly oxygen-dependent photoprocesses.

- v -

DEDICATION  
-----

To the eternal spirit  
who resides among us all ...

8  
I would like to dedicate this work to my dear wife  
who provided the love, optimism and understanding required  
and, especially, to our families who provided support and  
love. Also, to all the wonderful people with whom I shared  
all the times, hopes and enthusiasm.

---

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## CHAPTER 1

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### INTRODUCTION

#### 1.1 General Introduction

One of the most interesting strategies for harnessing solar energy has involved the use of a photocatalytic system which selectively promotes a specific reaction. This may produce a high energy product. The photocatalytic system promotes the occurrence of photochemical steps, overcoming severe kinetic limitations, and catalyzes the subsequent dark reaction steps. This has become of great importance to the increasingly important efforts devoted to energy conversion, waste processing and chemical synthesis (5,6).

Over the last several decades, there have been a number of photocatalytic systems investigated (7,8). Although the most significant activity has centered around heterogeneous systems (9,10), important contributions to the development of photocatalytic systems have also occurred using homogeneous systems and a large number of simple

homogeneous photoredox systems are currently known (11,12,13). The development of photocatalytic systems has generally followed a multicomponent design with each component contributing to a distinct process. Sensitizers, electron relay species, catalysts and donor species have been combined to produce rather complex systems (14). Many photoredox systems use acridine dyes or the metal-organic complex sensitizers eg.  $\text{Ru}(\text{bpy})^{+2}_2$ , the porphyrin derivatives (15). Some of these systems have achieved limited success but they have not usually attained sufficient stability against decomposition for a practical process (14). Generally, the sensitizer or catalytic component is decomposed or poisoned. Since chemical and photochemical stability is an important problem, an efficient photochemical and photocatalytic system requires relatively stable, selective components. The general instability of metal complex catalysts in homogeneous photosystems (16) has necessitated further research into system component stability.

The most important photochemical and photocatalytic systems have usually been transition-metal-centered (17,18). Suitable candidates for a photoredox system possess several characteristics. They have strong absorption in the visible, a rich electronic spectrum essential for electron-transfer reactivity, an ability to exist in more than one oxidation state and appropriate

redox potentials. They should also possess a catalytic ability to overcome significant kinetic barriers present in the reaction pathway as well as a reasonable efficiency and minimal chemical and photochemical side-reactions which could lead to system instability.

The search for photocatalysts eventually led to those compounds possessing metal-sulfur bonds. Among the numerous transition metal-sulfur chelates, the sulfur-donor-ligand-containing metal dithiolene systems have been shown to possess many properties of interest to photocatalysis. The dithiolene ligand (figure 1.1) stabilizes a wide variety of transition metal ions in complexes exhibiting a variety of structural forms eg. the Ni, Co, Cu, Pd and Pt metal

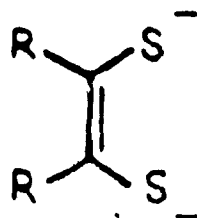
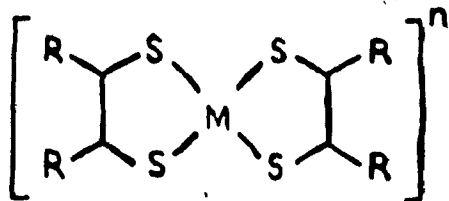


Fig. 1.1 The 1,2-Dithiolate Dianion

ions are stabilized in the square-planar geometry (figure 1.2) (19), the Zn complex is tetrahedral and tris complexes may be octahedral or trigonal prismatic (20,21). These weakly semiconducting dithiolene complexes (22) have the ability to exist in several distinct oxidation states (net



M = metal ion

n = 0 , -1 , -2 , -3

Fig. 1.2 The Square-Planar Metal  
Bis-1,2-Dithiolenes

charge varies from 0 to -3) (figure A-2) and the electron transfer process readily occurs with little or no structural reorganization. Their structural analogy to important biosynthetic redox systems (23), their favourable excited-state redox potentials (as calculated from ground-state values and excited-state energies) as well as their often strong electronic absorptions in the visible are very promising characteristics. Since their discovery in 1962 (24,25), there have been many novel dithiolene redox systems and a diversity of applications. Useful as important reagents, additives and developpers, along with other uses (21), they are also used as catalysts for oxidations and polymerizations. Although it had been known for some time that metal dithiolenes could be catalytically

active, photocatalytic activity had been relatively unexplored.

Metal dithiolenes have the best known catalytic properties and exhibit the best potential photocatalytic behaviour among metal-sulfur compounds (figure A-1). Some of the most interesting prospects are the maleonitriledithiolate or mnt dithiolenes complexes (figure 1.3) (8). In addition to electron-transfer capabilities,

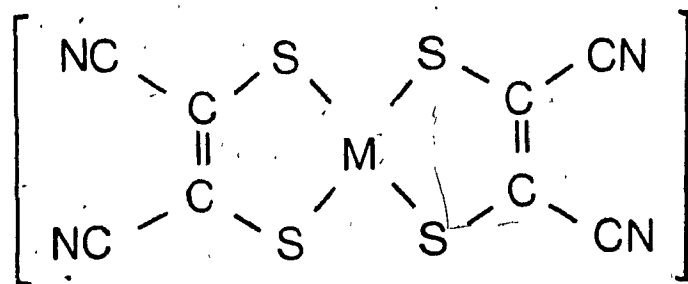


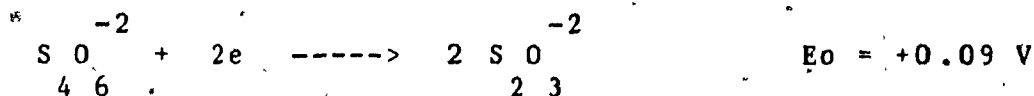
Fig. 1.3 \* The Metal Maleonitriledithiolate  
Complex

they possess strong absorption bands in the visible. Under visible irradiation, the dianionic mnt complexes of Pt and Ni will undergo a photo-induced electron transfer to transparent electrodes producing measurable photocurrents (1,2). The metal-to-ligand charge transfer ( $M \rightarrow L^*$ ) is

responsible in both cases (table A-3) but the platinum species possesses a much longer-lived excited-state (10-40 nsec vs 4-7 nsec) (1). In addition, the photo-reactivity of the  $\text{Pt}(\text{mnt})^{2-}$  species shows unusual characteristics. Its induced photocurrent undergoes an unusual quenching behaviour and quenching of the excited-state is observed (figure A-9) which may represent an electron transfer step associated with an oxidation (1,4). Electrochemical studies have also shown that the irradiated species, unlike its non-irradiated counterpart, induces an anodic shift in the normal solvent reduction wave (1). In view of this intriguing behaviour, the nature of these processes must be determined and evaluated.

The reductant species, thiosulphate ( $\text{S O}_3^{2-}$ ) and sulfur dioxide ( $\text{SO}_2$ ), were used in these investigations. A review of their oxidation and photo-oxidation reactions follows.

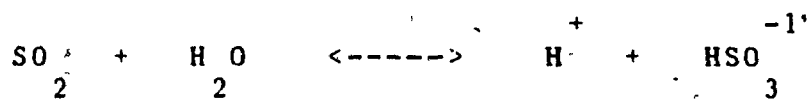
Thiosulphate oxidation produces the tetrathionate species :



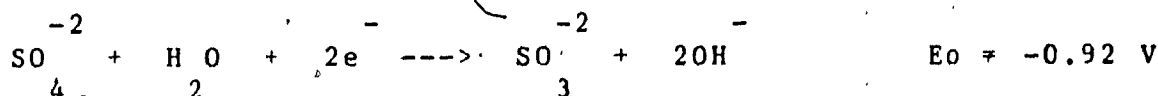
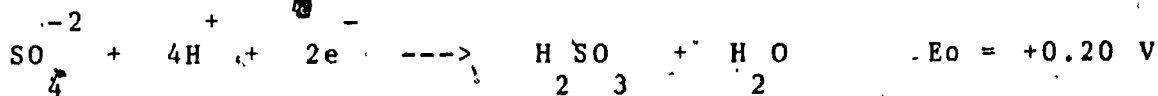
This reaction is extremely sensitive to impurity catalysis (esp. cupric ion). The oxidations generally proceed via metal-thiosulphato intermediate complexes or via simple electron transfer (26). Thiosulphate is easily oxidized by

Cu (II), its complexes and comparable redox species (27). Oxygen accelerates the oxidation. Copper-oxygen complex intermediates activate an oxygen molecule and subsequently transfer it to the coordinated thiosulphate ion (27). Copper-molecular-oxygen complexes have been postulated in several oxidation reactions and a transfer of oxygen to oxidizable substrates at a metal-ion site via an ionic mechanism is possible (27). The oxidation of thiosulphate in aqueous solution by molecular oxygen under ambient conditions is, otherwise, extremely slow (28). The photo-oxidation of thiosulphate proceeds only at short wavelengths.

Sulfur dioxide undergoes photo-oxidation producing sulfur trioxide or sulfuric acid if water is present. A photon must have sufficient energy, however, to break the OS-O bond in the molecule (29). The thermally-initiated oxidation occurs at room temperature in the presence of a suitable metal catalysts, otherwise, it only occurs at temperatures above 900 degrees C. Similar mechanisms may operate for both the thermal and photochemical oxidations the details of which remain unclear (29). Sulphur dioxide reacts with water to form a complicated "sulphurous acid" system (29) containing sulfite species in the following equilibrium :



It gives rise to two series of salts, the normal or neutral sulphites and the acid or hydrogen sulfites (or bisulfites), both of which are well characterized. In aqueous solutions at pH 4 - 8, the bisulfite ion is the predominant sulfite species (29). In their general reactions, these mild reductants yield either dithionate or sulphate. This reducing behaviour occurs under all pH conditions (29) :



Oxidation of sulfites by oxygen is also controlled by catalysis. They can be oxidized by oxygen in air in a reaction strongly dependent on pH. This is catalysed by manganese dioxide, Fe (II) and arsenite. The reaction does proceed in water at room temperature but does so extremely slowly unless a catalyst is present.



## 1.2 Statement of the Problem

The existence of a photocatalytic system was first suggested when the complex,  $(Et N)_4 Pt(mnt)_2$ , upon irradiation in flash photolysis experiments, underwent quenching or depopulation of the excited states in the absence of reducible components eg. oxygen (4). The photocurrents were also quenched (1). Further observations included a photoinduced electrocatalytic-like behaviour in aqueous acetonitrile whereupon the solvent reduction wave, subsequent to irradiation, undergoes a strong, distinct anodic shift (1,3). In the following investigation, the photoredox reactions occurring with the dianionic species of the nickel and platinum maleonitriledithiolate complexes are now identified and characterized.

The objectives for this project included the synthesis and examination of the square-planar, dianionic tetraethylammonium maleonitriledithiolate or mnt complexes of nickel and platinum. An analysis and measurements of the photoredox behaviour occurring in systems containing these complexes and their apparent behaviour in heterogeneous (or slurry) and homogeneous (or solution) environments is reported. As well, an examination, of previous reports on the behaviour of aqueous systems containing the dianionic platinum maleonitriledithiolate complex is presented. A

photocatalytic cycle in which this compound participates efficiently has been developed. Several interesting conclusions can now be derived about this particular photoredox compound.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

Table 2.1 Species of Chemicals Used

| <u>compound</u>   | <u>supplier</u> | <u>grade</u> |
|---|-----------------|--------------|
| NiCl <sub>2</sub> · 6H <sub>2</sub> O                             | May and Baker   | analytical   |
| K <sub>2</sub> PtCl <sub>4</sub> · 6H <sub>2</sub> O (46.7%Pt)    | Alfa            | reagent      |
| CS <sub>2</sub>   | J.T. Baker      | technical    |
| NaCN  | Fisher          | technical    |
| Et <sub>4</sub> NBr   | Aldrich         | reagent      |
| I <sub>2</sub>  | J.T. Baker      | USP grade    |
| KI  | Fisher          | lab grade    |
| Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O | Anachemia       | reagent      |

| <u>compound</u>                        | <u>supplier</u> | <u>grade</u>                |
|--|-----------------|-----------------------------|
| $\text{NaHCO}_3$                       | A&C Chemicals   | reagent                     |
| $\text{As}_2\text{O}_3$                | Fisher          | reagent                     |
| Starch (soluble)                       | Anachemia       | reagent                     |
| $\text{HgI}_2$                         | Anachemia       | reagent                     |
| $\text{H}_2\text{SO}_4$ (6% aq. sol'n) | Anachemia       | reagent                     |
| $\text{CH}_3\text{CN}$                 | Fisher          | reagent                     |
| $\text{MeOH}$                          | Fisher          | reagent                     |
| $\text{EtOH}$                          | Anachemia       | reagent                     |
| Acetone                                | Aldrich         | reagent                     |
| $\text{N}_2$                           | Linde           | prepurified                 |
| $\text{O}_2$                           | Linde           | regular                     |
| $\text{H}_2\text{O}$ , 30%             | Anachemia       | reagent                     |
| DMF                                    | Baker           | reagent                     |
| $\text{CHCl}_3$                        | Anachemia       | reagent                     |
| m-Chlorobenzoic acid                   | Anachemia       | reagent                     |
| $\text{Na}_2\text{CO}_3$ , anhydrous   | Anachemia       | reagent                     |
| Sodium citrate                         | Mallinckrodt    | reagent                     |
| Tetrasodium EDTA                       | Fisher          | recrystallized<br>(reagent) |
| Potassium oxalate                      | Baker           | reagent                     |

| <u>compound</u>                      | <u>supplier</u> | <u>grade</u>   |
|--------------------------------------|-----------------|----------------|
| Standard Buffers                     | Anachemia       | standard       |
| Potassium hydrogen<br>phthalate      | Anachemia       | reagent        |
| Potassium dihydrogen<br>phosphate    | Anachemia       | reagent        |
| NaOH pellets                         | A&C Chemicals   | reagent        |
| HCl                                  | Anachemia       | reagent        |
| CH <sub>2</sub> Cl <sub>2</sub>      | Anachemia       | reagent        |
| Isopropanol                          | Anachemia       | reagent        |
| 1,10 Phenanthroline<br>monohydrate   | Fisher          | reagent        |
| K <sub>2</sub> PtCl <sub>6</sub>     | Aldrich         | reagent        |
| Sodium acetate                       | Anachemia       | reagent        |
| Sodium perchlorate                   | Fisher          | purified       |
| Dimethyl sulfoxide                   | Baker           | reagent        |
| Isobutanol                           | Anachemia       | reagent        |
| Phenolphthalein                      | Anachemia       | reagent        |
| Zn (powder)                          | Anachemia       | reagent        |
| CuSO <sub>4</sub> · H <sub>2</sub> O | Fisher          | reagent        |
| Methylviologen                       | commercial      | recrystallized |

The water utilized during the entire investigation was deionized and distilled in glass. In all synthetic and physical procedures, only the purest grade of solvents was also utilized. All products produced using the synthetic procedures described were vacuum dried at 60° C unless specified. The purity of the products was usually established by comparison of the U.V./ visible spectrum with the published spectrum and by the use of thin layer chromatography (TLC). In the literature surveyed, the composition of the metal complexes synthesized according to the procedures followed has been confirmed by elemental analyses, conductivities and magnetic moments (1,30) as well as by x-ray crystallographic studies of a number of structures (31,32,33,34).

## 2.2 Synthesis

-2  
The maleonitriledithiolate ligand, <sup>-2</sup>mnt (or mnt), necessary to produce the desired dianionic mnt complexes, has been synthesized according to a variety of procedures since the first synthesis by Bahr and Schleitzer (35).

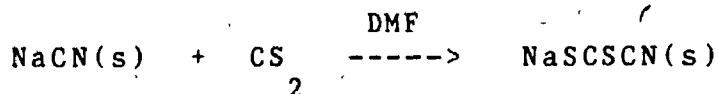
### 2.2.1 The Preparation of Sodium

Maleonitriledithiolate Ligand (Na mnt)

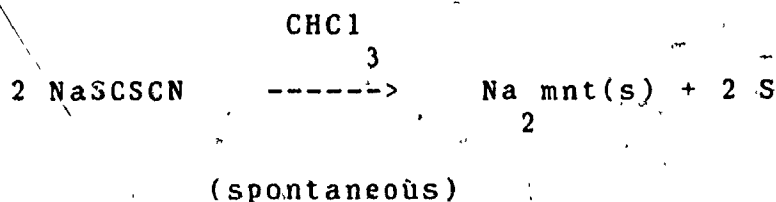
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The original procedure (35) was modified and improved

by Simmons et al. (36). The sodium salt of the dianionic ligand may be obtained in good yield and purity using a new modification of the procedure (37). Into a solution of sodium cyanide (NaCN; 30 g) dissolved in dimethylformamide (DMF; 150 ml), carbon disulfide (CS<sub>2</sub>; 45 g / 35.7 ml) is

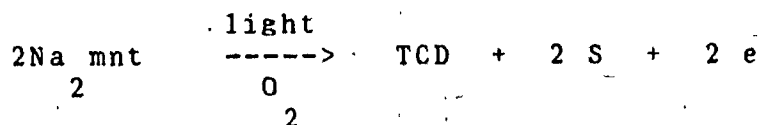


added resulting in the appearance of a dark brown precipitate. After cooling the slurry and filtering it under vacuum with air-drying, the precipitate is recovered. Recrystallization can be carried out using isobutanol. The hot super-saturated solution is hot-filtered, cooled, filtered under vacuum and air-dried. The wet sodium dithioformamide crystals (120-140 g) can then be dissolved in approximately 900 ml of chloroform and tightly stoppered

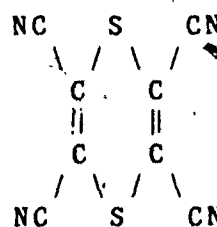


and kept in the dark for two days. In these conditions, a spontaneous desulfurization occurs producing the sodium salt of the maleonitriledithiolate (35,38). Insufficient amounts of either chloroform or the dithioformate results

in an accelerated oxidation of the components in the solution thereby reducing the yield of the Na<sub>2</sub>mnt product. The impure yellow product can be filtered and air-dried. The sulfur present with the product is easily removed by dissolving with a minimal amount of methanol and filtering. The product, after concentrating the filtrate to approximately 200 ml, can be precipitated by the addition of excess chloroform (approximately 350-400 ml). The purified product, Na<sub>2</sub>mnt, is filtered and air-dried. The yield for this procedure is approximately 89% (or 49 g). The compound is subject to oxidation in certain conditions involving light and oxygen. This oxidation involves the condensation



where TCD =



of two molecules of the disodium maleonitriledithiolate to form tetracyanodithiadiene (TCD) (24,36). To avoid or minimize this reaction, the mnt ligand can be stored for an extended period in a dessicator over calcium chloride (39).

A wide variety of metal ions can form complexes with



the maleonitriledithiolate ligand including Cu(II), Co(II), Ni(II), Pd(II), Pt(II) and Au(III) (20) and in each case, the synthesis basically follows the same procedure (39).

### 2.2.2 The Preparation of Dianionic Tetraethylammonium Metal Bis Maleonitriledithiolate Complex

filtered. The solubility of this complex can then be significantly reduced by adding a concentrated methanolic solution of tetraethylammonium bromide ( $\text{Et}_4\text{NBr}$  or  $\text{TEABr}$ ) to form the relatively insoluble dianionic tetraethylammonium salt of a metal mnt complex. Removal of the methanol from the solution by reduced pressure / evaporation results in the crystallization of a dark red solid. The solution is cooled, filtered under vacuum and the product air-dried. It can then be recrystallized from acetone-ethanol (1:1). Removal of the acetone results in crystallization. The air-dried crystals are dried in vacuo at  $60^\circ\text{C}$  (40,41). The dianionic complexes are sensitive to light when in solution and undergo oxidation so they must be kept in the

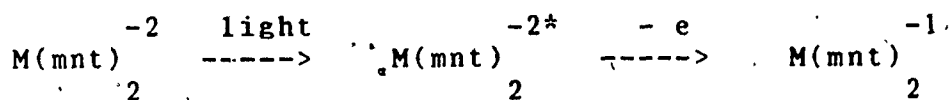


Fig. 2.2 Photoexcitation and Oxidation of  
the mnt Complex

dark. To ensure a pure dianionic product, purification and crystallization steps can be supplemented by the addition of a slight amount of sodium thiosulphate which reduces any of the monoanionic species present without hindering the crystallization and purification steps. Thiosulphate can also be used to recover and reduce a significant amount of the complex which is oxidized during irradiations. The

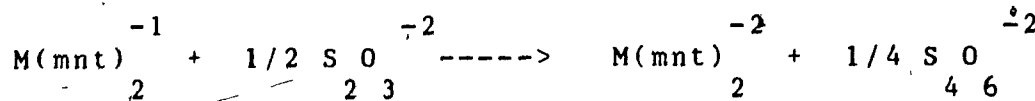


Fig. 2.3 Reduction of the Monoanion by Thiosulphate

yields obtained for the metal complexes in all cases are greater than 75%.

### 2.3 Experimental Apparatus

#### 2.3.1 The Simple Open Set-Up

In the preliminary investigation of heterogeneous systems to determine heterogeneous photoreactivity eg. the dechlorination of chlorobenzoic acid, the oxidation of alcohols, a very simple system was used including an erlynmeyer flask, stirring bar and a tungsten-halogen 300 W white light source (no filters or temperature control). The flask contained a slurry of the complex tested (0.1 or 0.5% ground metal complex) suspended in water by magnetic stirring of the slurry. A known concentration of a test compound (generally 100 ppm) was introduced and direct irradiation of the slurry with the light source was sufficient for preliminary work with non-volatile components.

### 2.3.2 The Closed Set-Up

A closed system was used in the heterogeneous system for the detection of any hydrogen produced and for some of the early studies in the homogeneous system. It was also found useful for work with volatile components. More parameters are controlled. It includes a ground glass water-jacketed irradiation cell and the system is closed using a rubber septum or ground-glass stopper. This special cell has a smaller volume than the simple system (20 ml) using the erlenmeyer flask but it can be closed to prevent loss of volatiles. There is some temperature control as well as improved system stability. There is, thus, an improvement in the accuracy of measurements.

### 2.3.3 The Expanded Set-Up (Closed)

To control more parameters in the homogeneous system, a better-controlled closed system was required. This was achieved by using ground-glass components as well as a constant-temperature, flow-through water bath with a thermostated circulator with the irradiation cell. Also, a 5 cm water-containing glass cell I.R. heat filter was included along with U.V. cut-off filters (340, 400, 420 nm) and a focusing lens which focuses light on the optical window of the irradiation cell. The system could be closed

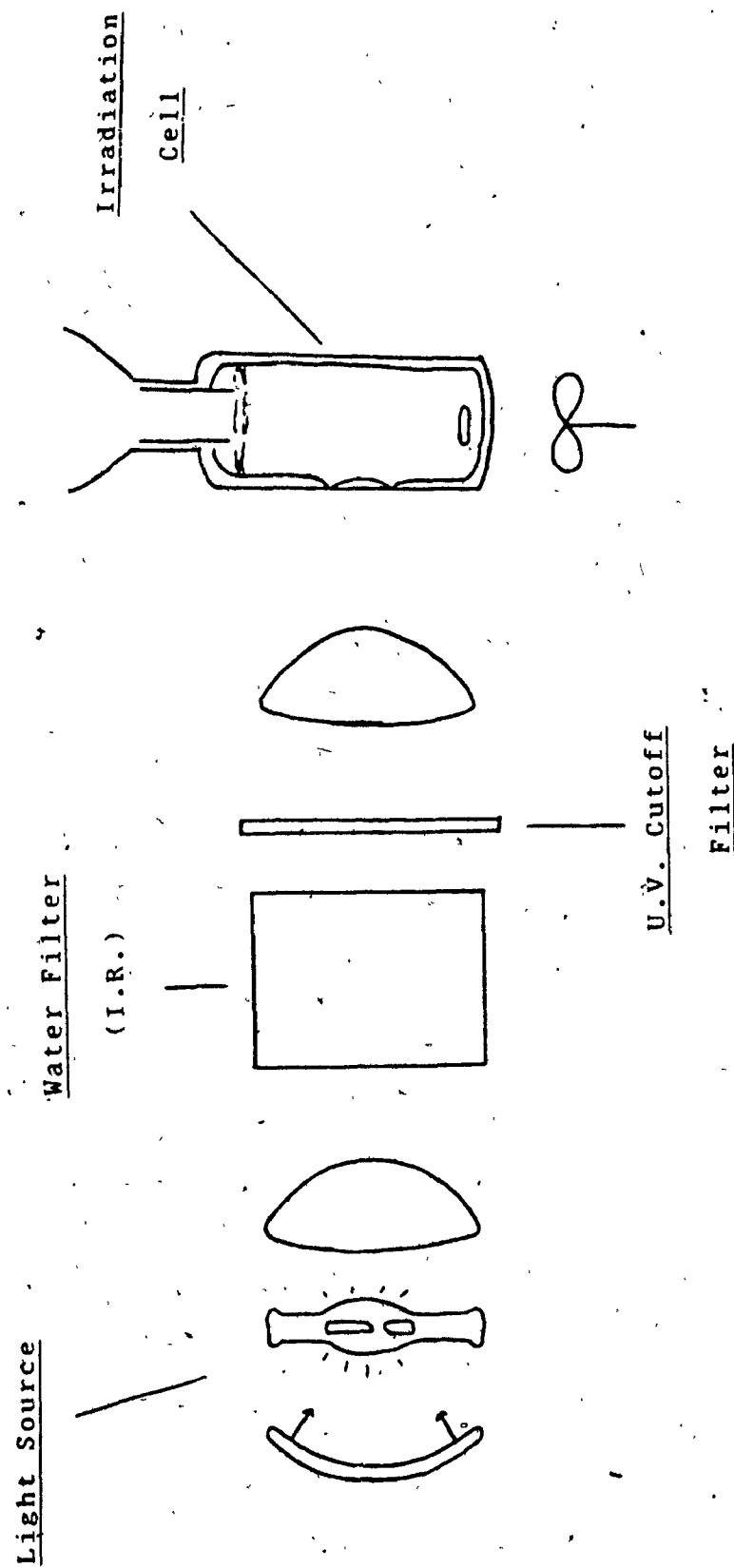


Fig. 2.4 The General Setup for Irradiation

using either a rubber septum, a ground-glass stopper or a stoppered separatory funnel (250 ml) for increased dead-air volume. The system can readily be degassed with prepurified  $N_2$  or oxygenated with pure  $O_2$ .

This final setup was used successfully for the homogeneous systems to determine photoreactivity and its dependence on temperature, pH, and various components. A general schema of the set-up utilized is shown in figure 2.4.

#### 2.3.4 The Irradiation Cell

A special cell was used extensively with the irradiations involving the homogeneous solutions and was necessary to control conditions. It consisted of a 20 ml water-jacketed, foil-covered, ground-glass irradiation cell with an optical window. It is capable of accomodating a micro-magnetic stirring bar. Constant-temperature water is circulated through the cell constantly throughout the period of irradiation.

#### 2.3.5 Gas Chromatography

Analyses depended on gas chromatography. The determination of a chlorinated hydrocarbon such as m-chlorobenzoic acid requires an electron capture detector (ECD). Samples are taken by extracting with a solvent such

as dichloromethane. Aliphatics such as alcohols can be determined with a flame ionization detector (FID) on samples taken directly from solution. Diatomic gases such as hydrogen, however, required a thermal conductivity detector (TCD). Dry gas samples were taken over the solution.

#### 2.3.6 Ultraviolet-visible Spectroscopy

The instrument utilized was the Perkin-Elmer 552 UV/vis spectrophotometer with the Watanabe SR6254 servo-recorder. Most spectra involving the metal complexes were recorded in acetonitrile or aqueous acetonitrile solutions.

#### 2.3.7 Infrared Spectroscopy

Infrared spectra utilized the Perkin-Elmer 599B IR spectrophotometer. The use of KBr pellets was in all cases quite satisfactory for our purposes.

#### 2.3.8 Cyclic Voltammetry

Cyclic voltammetry was carried out using the PAR 363 potentiostat with a triangular pulse generator, a standard electrochemical cell and the silver ion reference electrode. This reference electrode was used during both the scans of dry and aqueous acetonitrile without any

problems. The silver ion electrode, in a 0.010M  $\text{AgNO}_3$  / 0.100M tetraethylammonium perchlorate (TEAP) solution contained in a fritted tube, is separated from the electrochemical solution by a strictly 0.100M TEAP solution. The literature redox potential for such an electrode is +0.532V versus the normal hydrogen value (NHE) in a dry system (50). The addition of some water does not drastically alter this value but will induce a rapid loss of  $\text{Ag}^+$  from the reference electrode into the aqueous system if disturbed. Stirring before or during scans is not desirable since a significant leakage of the reference solution and a significant distortion of voltammograms occurs. Solutions are therefore very sensitive and must be treated carefully in order to obtain satisfactory scans.

## 2.4 Techniques

### 2.4.1 Buffer Solutions

Irradiation solutions necessitated the presence of buffer solutions with some redox stability in a photoreactive environment. Satisfactory buffers were prepared and were found to be relatively inert and quite satisfactory for our purposes. Buffers of various pH values were produced (6). A solution of 50.0 ml of 0.100 M potassium dihydrogen phosphate along with 5.60 and 29.1 ml of 0.100 M NaOH diluted 100 ml produces buffers with pH



values of 6.00 and 7.00 respectively. A buffer of pH 5.00 requires 50.0 ml of potassium hydrogen phthalate along with 22.6 ml of 0.100 M NaOH diluted to 100 ml.

#### 2.4.2 Solutions of the Complex

The metal-mnt complexes can be dissolved in several solvents. Acetonitrile and methanol were used. The volatilities of these solvents or the resulting loss of solvent is not as significant as would be the case with other good solvents eg. acetone so concentrations remain relatively constant during use. The solution concentrations of complex used vary between 0.100 and 10.0 mM eg. 10.0 ml of a 1.00 mM solution can be readily used to make 20.0 ml of a 0.500 mM irradiation solution.

#### 2.4.3 Donor Compounds in Solution

##### a. Preparation of Thiosulphate Solution

To prepare a 0.100 M thiosulphate solution, water (1200 ml) is boiled for 5-10 min. and cooled to room temperature. All glassware is cleaned with dichromate solution and rinsed with regular water, then boiled distilled water. Approximately 12.5 g of thiosulfate and .0500 g of sodium carbonate is weighed out, dissolved in the boiled water and diluted to 500 ml (titer of the solution degrades gradually due to oxygen but this reaction

is very slow; the solution, however, should be refrigerated) (42). This solution can be used directly or diluted as desired.

#### b. Preparation of Bisulfite Solution

A concentrated solution of dissolved sulfur dioxide or sulfurous acid (6% aqueous solution) is easily obtained and can be used to make a solution of a reductant comparable to thiosulfate. The concentrated solution (0.576 M) can be adjusted by dilution. It is diluted 5x using water (20.0 ml to 100 ml) and diluted another 5x using a desirable buffer solution (5.00 ml of diluted acid to 25.0 ml pH 6.0 buffer). The acidic solution is hence buffered to a desired pH and concentration (approx. 25 mM), and the species exists in solution primarily as the bisulfite species.. The final concentration after combining with complex solution to make the 1:1 aqueous irradiation solution further dilutes the solution. The actual final concentration to be irradiated is measured to be 15.9 mM in the solution.

#### 2.4.4 The Irradiation Solutions.

A convenient solution of complex and components is obtained using the following general recipe:

- a 10.0 ml aliquot of MeCN or MeOH is added to the cell; this solution may or may not contain

one of the complexes

- a 6.0 ml aliquot of buffer solution or water is added
- a 4.0 ml aliquot of donor solution or water is added

The total amount of solution obtained for the irradiation cell is 20.0 ml which is almost exactly the volume of the cell when closed with a ground-glass stopper. This solution is continually stirred so as to maintain a homogeneous system.

#### 2.4.5 Iodimetry and Reductant Concentrations

The use of iodine as a titrant requires a neutral or mildly alkaline (pH 8) to weakly acidic solution (necessitating a buffer eg.  $\text{NaHCO}_3$ ) otherwise disproportionation (alkaline) or oxidation (acidic) of the iodine occurs. The acidic solution may also hydrolyse or decompose the starch indicator during titrations affecting the titration end-point. A neutral solution will maintain the maximum reducing power of the reductant being titrated, thus producing the most accurate results. The solution must, therefore, be buffered at a relatively constant neutral pH for effective measurements using titrations.

##### a. Preparation of Iodine Solution for Titrations

A 0.005M (0.01 N) solution of iodine is needed to produce the titration solution and can be prepared by

weighing 0.650 g of I<sub>2</sub> and 2 g of KI. The iodine crystals can then be ground in a mortar with repeated additions of KI and water until all the iodine is dissolved. Dilute to 500 ml and mix. Let stand overnight (42). Titrating or titrant solution concentrations of approximately 0.00025M or 0.0005M (approximately 250 or 500 uM) are required to titrate the solutions obtained. They are prepared by diluting the iodine solution approximately 10 or 20 times (25.0 ml is diluted to 250 or 500 ml). This solution can be standardized using dried primary standard arsenic trioxide (As<sub>2</sub>O<sub>3</sub>) as explained in standard procedures (42).

2 3

#### b. Preparation of the Buffered Titration Solution

In order to improve the efficiency of titration, a buffered titration solution was prepared which could be poured directly into a titration flask along with a sample and rapidly titrated. This solution contains all the ingredients required that are usually added individually before the titration. This solution is prepared by dissolving approximately 120 g of bicarbonate in water, approximately 60 ml of the starch solution is added and the solution is diluted to 2000 ml. This solution can be diluted 10 times in usage since the concentrations titrated are very low. Approximately 50 ml of the diluted titration solution is used and is sufficient for each titration.

### c. Standardization of the Iodine Solution

The iodine titrating solution (especially the diluted version) will rapidly degrade upon exposure to air and its titer must be verified frequently during titrations. This would be a tedious endeavour if not for the observation that a neutralized solution of arsenic trioxide is quite stable for long periods of time. A standardized solution of arsenic can be maintained which can be used to standardize the iodine solution during titration runs thereby saving time. Weigh accurately 0.01978 g of arsenic trioxide, dissolve in approximately 5 ml of warm 1N NaOH, cool and neutralize with 1N HCl. Dilute to 100 ml with water (or weigh 0.04946 g and dilute to 250 ml). This 0.00100M solution of arsenic can be used to determine the titer of the iodine titration solution. Add 5.00 ml of this solution to 50 ml of the buffered titration solution, titrate with the iodine titrating solution and a simple calculation gives the titer.

#### 2.4.6 Sampling

Sampling has been done using disposable plastic syringes which are quite stable to the solvents utilized. Some deterioration does eventually occur but not before several weeks of extensive use. Both the 1 and 3 ml syringes have been used in sampling from the irradiation cell setup but the 1 ml syringe is preferred and used due to

its much greater precision and accuracy ( $\pm 0.005$  ml vs  $\pm 0.02$  ml) (42). Samples are taken for analysis at regular time intervals during the irradiations (0.5, 1.0, 1.5 and/or 2.0 hour intervals).

#### 2.4.7 Titrations

A 50.00 ml  $\pm 0.05$  ml TD glass titration burette is used to contain the iodine titration solution. Approximately 50 ml of titration buffer solution is added to an erlenmeyer flask with stirring. It is then titrated to the end-point (slight blueish tinge) prior to sample addition. A sample (0.500 or 1.00 ml) is taken from the irradiation cell and is added to the continually-mixed titration buffer and the sample is titrated to the end-point (identified as a (i) a loss of complex colour (if complex present), (ii) a small colourless gap and, finally, (iii) a slight blueish tinge). The quantity of iodine titrant required to reach the end-point, by using the titer of the titrant determined during each titration, can be used to calculate the amount of donor species present in the irradiation solution.

#### 2.4.8 Detection of Strong Oxidants in Solution:

##### Reduced Phenolphthalein Indicator

Phenolphthalein can be dissolved in an alkaline

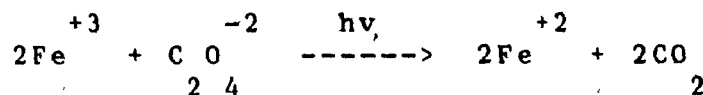
solution (2 g in 50% sodium hydroxide (20 ml)) and the resulting intensely red solution can be decolourized by refluxing for 2 hours with zinc dust (5 g). The resulting reduced phenolphthalein solution, after filtering and dilution to 50 ml with water, will turn red upon exposure to a strong oxidizing agent. The solution eventually does turn red upon standing in air but simple decolourization with zinc dust regenerates the solution. Hydrogen peroxide by itself reacts quite slowly but the addition of some copper salt greatly accelerates the process resulting in a sensitive test for peroxides in the absence of other strong oxidizing agents (43). The reduced phenolphthalein is transparent in the visible region but, upon oxidation, absorbs strongly at 550 nm which can be readily used for analysis of an oxidant concentration. Further dilution of the solution reduces the chances of obtaining a white precipitate produced upon oxidation of the concentrated solution which strongly interferes with spectrophotometric determinations.

#### 2.4.9 Actinometry

The actinometer used is the commonly used potassium ferrioxalate system (44) since it is probably the best solution-phase chemical actinometer for photochemical research available and it has a good sensitivity for the wavelengths from 254-480 nm, especially the wavelengths

above 350 nm in which we are interested.

The net photochemical reaction occurring is:



the resulting ferrous ion can be determined spectrophotometrically at 510 nm. The quantum yields, accurately known in the blue region of the visible spectrum, allow a simple and rapid actinometric measurement of light intensity during irradiations. The technique used is practically identical to Hatchard and Parker (44) except that the sampling was done with a syringe from a small, continuously mixed volume at specific intervals of time determined so that photolysis of the actinometer solution is not extensive (to avoid secondary photolysis). It was determined that, since the quantum yields for the actinometer are lowest at the longer wavelength region utilized in the system, a more concentrated actinometer solution was required (a 0.150 M solution is used versus the 0.00600 or 0.0200 M solutions suggested). The conditions employed were identical to a sample irradiation. The number of ferrous ions formed during irradiation and therefore the light intensity can be calculated using the formula:



$$n_{\text{Fe}^{+2}} = \frac{6.023 \times 10^{23} \cdot V_1 \cdot V_3 \cdot \log(I_0/I)}{V_2 \cdot l \cdot e}$$

where  $V_1$  = volume of irradiated solution (20 ml)  
 $V_2$  = volume of aliquot (ml)  
 $V_3$  = volume of dilution of aliquot (ml)  
 $\log(I_0/I)$  = measured absorbance at 510 nm  
 $l$  = optical path (1 cm)  
 $e$  = experimental molar extinction coefficient = slope of calibration plot (approx.  $1.11 \times 10^4$  L/mole-cm)

#### 2.4.10 Air Volumes and Oxygen

It is necessary to control the dead air space above the irradiated solution and, to do this, the system was closed eg. using a ground-glass stopper (a rubber septum is insufficient since it is penetrable to gases and volatile solvents). This closed system could be deaerated with a chosen gas without evaporating the solvent by the use of a solvent-saturated gas (gas is bubbled through solvent first) and maintained closed by using a paraffin bubbler at the gas outlet. Increasing the dead air volume was achieved using several methods such as inverted test tubes or containers. The most convenient container proved to be the

separatory funnel (250 ml) which could close the system quite securely while allowing the access to air (ambient) or oxygen (0 ).

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#### 2.4.11 Thin Layer Chromatography (TLC)

A convenient method to determine the purity of the complexes is thin layer chromatography which can be readily used to identify and isolate the metal mnts and their analogs, derivatives and components. Suitable TLC material can be obtained from commercially available plates (silica) which are easily cut into convenient strips upon which samples can be applied with capillary applicators. The commonly used solvents for the mnts, when mixed with a suitable counter-solvent eg. ethyl acetate, allows a partition of the solution components.

## CHAPTER 3

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### RESULTS

#### 3.1 Relevant Preliminary Observations

The strongly stabilized, square-planar,  $d^8$  system maleonitriledithiolate complexes have well-known chemical properties (20) and represent unusually stable complexes resistant to substitution by most common ligands (22). The weakly semiconducting dianionic forms of these complexes are air-stable, high melting point solids which possess characteristic solubilities (the tetraethylammonium salt is soluble in acetone, acetonitrile, partially soluble in alcohols, insoluble in dichloromethane and completely insoluble in water) and exist in solution as 1:2 electrolytes. They undergo redox reactions in characteristic potential regions (table A-4) linking several available oxidation states (figure A-2) (20). The complexes all absorb visible light in approximately the same spectral region (465-475 nm) (table A-3) and produce dark red solutions and crystals. The nickel and platinum

complexes both have very similar photochemical characteristics and generate photocurrents in the visible region which are, at least partially, quenched by oxygen (1). They are also potentially good reductants upon excitation (excited-state potentials are  $-0.5V$  for the Ni and  $-0.7V$  for the Pt complex) (1). In fact, results and properties for the Ni and Pt complexes parallel except for a relatively longer excited-state lifetime in the Pt species. Upon irradiation, however, aqueous acetonitrile solutions of the Pt complex undergo changes not seen with the Ni complex such as the changes in absorption spectrum (figure A-10) and cyclic voltammogram (figure A-11).

Previous electrochemical results have underlined this particular behavior by the irradiated solutions with the observation of a significant shift of the solvent reduction wave in the anodic direction (figure A-11b). In addition, the solutions were observed to undergo sedimentation and the appearance of particulates. Their participation in the activity is underlined by voltammograms which indicate a distinct loss of activity when the solution is allowed to settle (figure A-12a). The activity can be renewed upon agitation or mixing (figure A-12b). The fine insoluble precipitate displays a characteristic solution absorbance spectrum (figure A-13). Since suspension of the particulates in the solution (via stirring) during progressive irradiation is required in order to obtain

cyclic voltammograms exhibiting characteristic electrocatalytic behaviour, the particulates clearly show indications of being involved in the photocatalytic activity. An obviously heterogeneous system would suggest the existence of semiconductor processes and a heterogeneous photocatalytic system.

### 3.2 Heterogeneous Systems

In order to investigate the system for photocatalytic behaviour, a strictly particulate or heterogeneous form of the system is needed to allow the complex to behave as semiconducting particulates. Such a system was easily prepared with a 0.1% or 0.5% aqueous slurry of the complexes. Initial experiments always provided comparisons between a blank, a dark and an irradiated test solution.

The first test compound chosen was m-chlorobenzoic acid which can undergo dechlorination or hydroxylation via radical processes (45,46). When a significant concentration of this chlorinated compound, (100 ppm) was irradiated using a 300 W tungsten-halogen projector lamp in the presence of a slurry of either nickel or platinum complex in an open cell setup, no degradation or modification of the compound could be detected according to the electron-capture detection (ECD) G.C. analyses after 20 hrs of irradiation.

When alcohols (100 ppm of ethanol, methanol, isopropanol) were utilized to search for photooxidative capability, no modification of the alcohols was observed as determined by examining samples with flame-ionization-detection gas chromatography (FID) with the same times of irradiation. The use of a known charge mediator or electron relay species ( $\text{CuCl}_2$ ) (47) for the photooxidation of alcohols by oxygen (2:1 mediator:complex) resulted in the rapid oxidation of the complex but no oxidation of the alcohols was detected. In comparison, platinized titanium dioxide produced and used according to literature methods (48,49) showed a significant degradation of the alcohols (>10%) under the same conditions, underlining the lack of activity of the mnt complexes in these heterogeneous conditions.

Gas samples obtained over the irradiated solutions were analysed using thermal-conductivity-detection gas chromatography (TCD). Under a variety of conditions including long irradiation times, high concentrations of complex, addition of charge mediators and improvements in cell design as well as use of the highest sensitivity of the detector (capable of detecting 0.01% hydrogen), no hydrogen was found.

### 3.3 Homogeneous Systems

The slurries are not strictly heterogeneous systems because the complexes are found to be slightly soluble in the aqueous systems. The complete precipitation of the complex requires excess common ion species eg. tetraethylammonium bromide (TEABr). The slurries have also proven to be difficult systems for monitoring since there is always some complex present in the samples injected into the G.C.s. As well, the particulates tend to render the sampling unreliable. Homogeneous systems were, therefore, produced using acetonitrile (MeCN) solvent in the solutions. A 1:1 MeCN / H<sub>2</sub>O mixture was found to possess the desirable characteristics.

#### 3.3.1 The Persisting Absence of All Activity

In an extreme experiment, a degassed, 20% aqueous solution of acetonitrile containing a high concentration of the Pt complex (20.0 mM) was irradiated with the unfiltered light from the projector lamp for a significant amount of time. Upon sampling the gas volume above the solution, no hydrogen was detected. An observable qualitative change in the solution irradiated had, however, occurred eg. colour is measurably altered.

### 3.3.2 Turnover and Catalysis

When a solution of unbuffered 50% aqueous acetonitrile solution with dianionic Pt mnt (0.870 mM) and a known concentration of thiosulfate in an approximately 1:2 ratio (2.5x) was irradiated in a simple, closed flask (rubber septum,  $T = 15^{\circ}\text{C}$ , no buffer, no filters), a measurable change was detected. A significant reduction in the concentration of the thiosulphate had occurred (a 30% or 0.653 mM reduction with apparent rate =  $-0.340 \text{ h}^{-1}$ ) (figure

3.1). The turnover (substrate consumed vs. complex) obtained was, however, less than 1 (approx. 0.8) and the reaction was short-lived (does not continue beyond 4 hours). The solution was also observed to undergo a colour change (solution darkens with irradiation). Degassing was attempted but solvent volatility is significant.

A higher thiosulphate concentration (initial concentration = 3.45 mM or 6.9x complex) produced a greater change in concentration with irradiation ( $-0.880 \text{ mM}$ ) (apparent rate =  $-1.76 \text{ h}^{-1}$ ) (figure 3.2). A turnover or catalytic consumption of the substrate had clearly occurred in this system after 2 hours of irradiation (1.8x) (a turnover of substrate vs. complex greater than 1 is catalytic). The reaction was again short-lived and eventually halted. The addition of a small amount of buffer solution (pH 7) allowed the photoreaction to resume and a



total thiosulfate decrease of  $-1.28 \text{ mM}$  ( $2.6x$ ) was measured. This indicates a pH dependence in the process. In comparison, dark and irradiated blank solutions were made.

### 3.3.3 Buffering

The irradiation solutions were subsequently buffered to pH 6.0 to permit the reaction to continue. A ground-glass stopper (replaces the septum to reduce MeCN leakage) and water-jacketed flasks (to eliminate any undesirable thermal fluctuations) were also added. Irradiation of a buffered solution (thiosulfate =  $4.00 \text{ mM}$ , complex =  $0.200 \text{ mM}$ ,  $15^\circ \text{C}$ ) for almost 8 hours produced a continuous and significant reduction in concentration ( $-2.00 \text{ mM}$ ) ( $-2.50 \text{ mM}$ ) and the resulting time-concentration plots indicated a relatively linear relationship in the system (figure 3.3). At least 10 turnovers are achieved. Blank and dark conditions for the system show no changes in reductant concentrations.

In order to remove any possible ultraviolet component present in the irradiating light, a  $340 \text{ nm}$  ultraviolet cutoff filter was introduced to the system. It was then observed that, during irradiations, filtered light results in a darkened irradiation solution (complex is oxidized; monoanion appears) versus the bleached solution obtained in the absence of filters (solution is lighter coloured: yellowish). The irradiation of a  $24 \text{ mM}$  thiosulfate solution

(with 0.500 mM Pt complex) with filtered light, nonetheless, results in a nearly complete reaction ( $-22.0$  mM) ( $-2.00$  h<sup>-1</sup>) (figure 3.4a). At least 44 turnovers of catalyst are achieved. The addition of more thiosulphate resumes the reaction until, again, no more thiosulphate remains. A total of over 50 turnovers are achieved by the system with no definite limits to the reaction. A linear relationship continues to be indicated. The process does not proceed in the dark and halts when irradiation is discontinued. The extensive irradiation of comparable solutions of thiosulphate containing dianionic Ni mnt and no complex (blank) produce no detectable decreases in concentrations (figure 3.4b and 3.5 respectively).

Improvements and modifications to the system included the use of new filters (420 cutoff, I.R.), changes in irradiation parameters and generally improved cell setup. A solution with an increased donor concentration (40.5 mM), increasing the donor to complex ratio (91:1), was, then, irradiated and resulted in a significant decrease of the donor concentration ( $-25.0$  mM) at a significant rate ( $-3.33$  h<sup>-1</sup>) (figure 3.6).

### 3.4 Oxygen Dependence

The air layer above the solution was sampled and analysed again using TCD gas chromatography. There is no

hydrogen product detected under any circumstance. A subsequent investigation of the irradiated system after a successful degassing with nitrogen (using an acetonitrile bubbler) shows and clearly demonstrated the absence of any detectable process in this system in the absence of air or oxygen. The introduction of an electron relay species did not have any effect on the system and did not promote or facilitate any possible oxygen-free photoprocesses. The air oxidation of mnt complexes is known to occur in acidic solutions so samples of the Ni and Pt complexes were degassed with nitrogen in acidic solution to determine the effect by oxygen. Degassed samples were stable and did not undergo oxidation while the aerated samples underwent a significant amount of oxidation (to the monoanionic form).

Increasing the concentration of complex or substrate in this system does not result in any significant increase in the reaction rate and, since it can be assumed that an increase in the availability of oxygen might improve the reaction rate, a larger source of air was provided to the system. When solutions were exposed to a greater source of oxygen (via a large funnel) and irradiated using filtered (400 nm and I.R. filters), focused light, the solutions (pH 6.0, 25°C) reacted at increased rates. Concentrations of 13.4 mM (26.8x) and 71.0 mM (140x) thiosulfate gave apparent rates of -3.16 (-15.8mM or 31.6x) (figure 3.7) and -2.67 (-25.6mM or 51.2x) (figure 3.8) per hour

respectively. Despite widely varying concentrations, the rates, again, do not change significantly. Comparable solutions, but buffered to different pH values, show very little pH-dependent behaviour expected of these systems when irradiated while exposed to the air reservoir. Apparent rates did not vary significantly if at all for the buffered systems (pH 6.0 and 7.0). Meanwhile, unbuffered systems produce the same comparable rates. All irradiated thiosulphate solutions tested negative for the presence of sulfate products (using barium chloride on irradiated samples).

#### 3.4.1 Use of Pure Oxygen

The irradiation of both buffered and unbuffered thiosulphate solutions in the presence of pure oxygen (flushed separatory funnel) presented a different behaviour pattern than that observed in previous irradiations. The solution buffered at pH 6.0 (22.6mM or 45.6x, 25°C, 400 nm filter) underwent a significant change in concentration (-21.2mM or 42.4x) in less than half the time and at a significantly increased rate (-20.0 h<sup>-1</sup>) (figure 3.9). Buffering at pH 5.0 (22.9mM or 45.8x) under the same conditions resulted in a similar behaviour (-19.3mM or 38.6x, -17.4 h<sup>-1</sup>) (figure 3.10). Again, the irradiation of a similar buffer-less system (22.6mM or 45.2x) gives a similar result (-18.0mM or 36.0x, -18.4 h<sup>-1</sup>) (figure

3.11). The apparent rates obtained are at least 6 times greater than systems exposed to air. No significant changes in behaviour are observed with either pH or filter changes.

Although the experimental behaviour in this system can be represented by the generalized rate expression:

$$-d[\text{thiosulphate}]/dt = k[\text{thiosulphate}]^x [\text{O}]^y [\text{complex}]^z,$$

the reaction displays a pseudo-dependence with respect to only one component, oxygen. This behaviour can be described by the expression:  $-d[\text{thiosulphate}]/dt = k'[\text{O}]^x$ . It can also be seen that the changes in concentration which occur during irradiation are no longer strictly linear with time. Significant changes in concentration occur only after a short initial period has elapsed. This effect is not observed in thiosulphate systems not exposed to pure oxygen. This may correspond to an induction process where the complex undergoes transformation.

#### 3.4.2 An Alternative Donor : Sulfur Dioxide

A solution of sulfurous acid,  $\text{H}_2\text{SO}_3$  (sulfur dioxide in water), was diluted and buffered to pH 6.0 for use as an alternate reductant species for the system. It was found to be unstable in the aqueous acetonitrile mixture used. A solution of purely aqueous sulfur dioxide is, however, quite stable over the time scale of irradiations and a satisfactory irradiation mixture was prepared using methanol as a solvent instead. Under exactly the same conditions

used previously for acetonitrile systems (50% aqueous mixture, 400nm and I.R. cutoff, pH 6.0, 25°C, air reservoir), a methanolic solution of dianionic Pt mnt containing thiosulfate (24.2 mM or 48.4x) was irradiated. In comparison to previous irradiations, the change in concentration and apparent rate observed in the methanolic solution is considerably reduced (-2.90 mM or 5.8x) (-1.45<sup>-1</sup> h<sup>-1</sup>).

The irradiation of a solution of the buffered sulfur dioxide (400 nm and I.R. cutoff, 25°C, 16.3 mM or 32.6x<sup>-2</sup> SO<sub>3</sub>), in contrast, undergoes remarkably significant changes in donor concentration with a significantly higher apparent rate than any previously measured in air (-6.70 mM or 13.4x) (-3.82 h<sup>-1</sup>) (figure 3.12). The behaviour of the observed changes can be seen, however, to be significantly different. The reaction is greatly accelerated suggesting the existence of a facilitated process. The presence of induction behaviour, though, is similar enough to the behaviour in thiosulphate systems with pure oxygen that it may be likely that the process in each system is the same. The irradiated solutions, in this case, tested positive for sulfate products (using barium chloride).

### 3.5 Electrochemistry

#### 3.5.1 Cyclic Voltammetry of the Solutions

Voltammetric scans were obtained from the irradiation solutions (aqueous acetonitrile solutions of complex) as well as from the nonaqueous systems (acetonitrile solutions of complex) using a single common reference electrode, the  $\text{Ag}/\text{Ag}^+$ , 0.010N  $\text{NO}_3^-$ , 0.100N tetraethylammonium perchlorate or TEAP reference electrode (+0.532V versus NHE) (50).

#### 3.5.2 The Non-Aqueous System

A voltammetric scan of dianionic Pt mnt in acetonitrile indicates that the integrity of the complex is maintained during scanning only when the applied potential is kept within the range lying between -1.0 and +0.4V versus the reference. Scanning beyond this range results in a decomposition of the complex with the resulting artifacts growing with each scan. Within the recommended range, the characteristic voltammogram of this complex is readily obtained (figure 3.13).

#### 3.5.3 The Aqueous System

The voltammogram of a deaerated and relatively

concentrated solution of dianionic Pt mnt in acetonitrile  
(5 x 10<sup>-4</sup> M) in an electrochemical cell does not change significantly during extensive irradiation. The addition of a slight amount of water (5% aqueous) before irradiation also does not produce any change in the voltammogram of a deaerated sample (no significant modification of the voltammogram can be detected). As well, the irradiation of a 30% aqueous solution of dianionic Pt mnt in acetonitrile for 2 and 4 hours in a deaerated system shows no significant change in voltammogram (figure 3.14a).

When the solution is aerated, however, irradiation of the solution for 1.5 hours produces a significant change in voltammogram (figure 3.14b). The wave for the complex in the voltammogram is severely diminished. Irradiation for 3.0 hours results in further changes (figure 3.14c). Scanning at an increased sensitivity shows the changes more clearly (figure 3.15). In all cases, there was no evidence of a precipitate or any tendency for precipitation in any of the irradiated systems.

### 3.6 Spectroscopy

#### 3.6.1 UV / Visible Spectroscopy

The spectra of the maleonitriledithiolates are characteristic and have been previously assigned (table A-3) (1,2,51,52). The reduced dianionic form of Pt



maleonitriledithiolate is characterized by a strong primary absorption peak in the visible at 470 nm ( $\epsilon = 7,000$ ). The oxidized or monoanionic form, meanwhile absorbs at 450 nm ( $\epsilon = 8,800$ ), 600 nm ( $\epsilon = 1,700$ ) and 850 nm ( $\epsilon = 3,260$ ). Upon electron transfer, therefore, there is a characteristic hypsochromic shift of the main visible absorption band from 470 nm to 450 nm. In addition, there is the appearance in the oxidized spectra of the new identifying absorptions at 600 nm and at 850 nm (figure 3.16).

#### 3.6.2 Changes Upon Irradiation

Homogeneous solutions of the complexes and their mixtures display the straightforward spectra of pure, unaltered substances. The spectra taken of an irradiation solution ( $5 \times 10^{-4}$  M dianionic Pt mnt in 50% aqueous acetonitrile) show that practically no change in spectra occurs with the presence of water or any of the other components (figure 3.17). No discernible changes occur when a comparable solution of the Ni complex is irradiated but little irradiation is required to produce a substantial change in the spectrum of a solution of the platinum complex (figure 3.18). The solution undergoes a distinct bleaching process which changes the colour of the intensely red dianionic solution to a light orange and, subsequently, to the eventual pale yellow solution. All solutions of

dianionic Pt mnt undergo this bleaching effect when exposed to light, even when left exposed to standard lighting. Once the yellow colour is attained, the solution seems relatively stable to any further changes. In contrast to a solution of the oxidized complex which is reversible and easily reduced, the bleached solution resists reduction.

### 3.6.3 Spectral Changes Occuring With Time

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Spectra of the irradiated solution clearly show the shift in the main visible absorption band which has occurred from 470 nm to approximately 400 nm. During the irradiation of a buffered substrate-less irradiation solution, this shift in absorption occurs in a dramatic fashion especially within the first hour of irradiation (figure 3.19). The typical Pt mnt peak at 465 nm rapidly disappears and is replaced by a strong peak at 390 nm which subsequently decreases slowly. A careful monitoring of the peaks during the first hour of irradiation shows the change more clearly (figure 3.20). Within 20 minutes, the dianionic form of the platinum complex has reacted exhaustively and there is the appearance of a new species with  $\lambda_{max}$  at approximately 390 nm. In a solution which is buffer-less, the result is similar (figure 3.21) except that the appearance of a small concentration of oxidized complex as seen from the 750 nm absorption is more obvious.

Monitoring several important wavelengths during the

first hour of irradiation of a buffer-less and substrate-less solution can help to give a clearer outlook on the nature of the degradation process. At the 390, 465 and 750 nm wavelengths, corresponding to the new, the dianionic and the monoanionic species present in the solution, there is a relatively large increase in the concentration of the new species along with a small increase and subsequent decrease of the monoanionic species (figure 3.22). The dianionic species, used up early in the process, disappears within 20 minutes. A slow decrease of the other species also eventually occurs. This eventually results in the disappearance of all peaks and indicates that there is an ongoing decomposition of all chromophores in the solution. A change in filters (400 to 420 nm) does not result in any significant change except that generation of the new species is not as great and the decomposition-like event is slowed. If a sample of the irradiated solution is treated with a dilute solution of buffered  $\text{SO}_2$  (pH 6), spectra of the solution taken before and after show that the species in solution are reduced to the dianionic form to a limited extent by this mild reductant (figure 3.23).

#### 3.6.4 Search for an Intermediate

A comparison of the spectra of reduced, oxidized and yellowish, irradiated solutions of Pt mnt (0.10 mM) suggests the presence of an intermediate in the irradiated

solutions. The spectrum of the irradiated solution, ignoring the minute quantity of oxidized species, displays a new, distinct absorption at 390 nm. Indications are that this is a related but altogether new form of the Pt complex. In an effort to identify this intermediate, a solution of reduced alkaline phenolphthaline, a substance readily oxidized by peroxo compounds, was used. Samples of an irradiated substrate-less solution test positive for peroxide (turns light red immediately) when treated with this indicator. With a suitable absorption in a non-interfering wavelength region (550 nm), the easily measurable colour change can be used to determine concentrations in solution. After correlating the absorbance with a diluted peroxide standard, it was possible to measure the appearance of the peroxide-like intermediate in a substrate-less, buffer-less solution of complex during irradiation. After less than 5 minutes of irradiation, the concentration had increased rapidly and significantly (figure 3.24). The appearance of the peroxide species correlates directly with the time scale of the induction period observed previously.

The generated intermediate can be isolated from an irradiated (1 - 2 hours) buffer-less, substrate-less solution of the complex ( $5 \times 10^{-2}$  M) in 1:1 aqueous acetonitrile. With the addition of TEABr salt, crystals of the intermediate can be recovered by rotoevaporation and

recrystallization. The dark brown crystals are obtained and dried for several days in a vacuum oven at  $-60^{\circ}\text{C}$ . The spectra of these crystals suggest only a single component (figure 3.25). The isolated intermediate was found to be quite sensitive and unstable. It readily undergoes a spontaneous decomposition to non-chromophores when exposed to extreme conditions eg. heat.

The possibility of obtaining a dark or chemically-generated intermediate was entertained and it was decided to attempt a modification of the complex by using a powerful reductant or oxidant to actually generate the species without irradiation. Treatment of a solution of the dianionic complex with hydrogen peroxide resulted in no observable changes in the complex. Treatment with sodium borohydride also resulted in no reaction. When long term exposure to a greater concentration of these compounds was attempted, however, different results were obtained. Borohydride still had no effect but exposure to a high concentration of peroxide for half an hour resulted in a significant colour change of the solution (figure 3.26). (A colour change occurs which is qualitatively identical to irradiated solutions. Long-term exposure to a high concentration of peroxide is, therefore, necessary to generate the intermediate component (403 nm). No dianionic (465 nm) and only a small quantity of monoanionic component (450 nm) remains in the solution (figure 3.27). One possible candidate for the chromophoric intermediate, the

free maleonitriledithiolate ligand, absorbs at a significantly different wavelength region (368 nm) (figure 3.28). Crystals of the generated intermediate are readily obtained from a concentrated solution of the complex treated with peroxide.

### 3.6.5 IR Spectra of Components.

The infrared spectra of various components were taken in order to determine the characteristics relative to each spectra. Spectra were taken of the pure dianionic complex, the isolated intermediate mixture obtained from an irradiated solution and recovered crystals of the peroxide-generated intermediate (figure 3.29). There is very little difference in spectra between the dianionic complex (figure 3.29a) and the intermediate mixture from the irradiated solution (figure 3.29b). (The broad band appearing at 3400<sup>-1</sup> cm may be associated with water). There does not seem to be any significant structural changes in the complex. The spectrum of the peroxide-generated intermediate displays a significantly degraded complex (figure 3.29c). The isolation procedure (recrystallization) has produced a severe loss of the complex because it accelerates the decomposition reaction to which the intermediate is sensitive. Still, remnant peaks can be observed which show that the intermediate species is also not significantly different structurally from the original complex. Peaks

which would indicate the presence of an oxygen species in the irradiated and peroxide-treated complex ( $1145\text{ cm}^{-1}$ ,  $770\text{ cm}^{-1}$ ,  $1556\text{ cm}^{-1}$  representing superoxide, peroxide and molecular oxygen respectively) are seen here to be either absent or very weak.

### 3.7 Actinometry

Light intensity measurements done using ferrioxalate actinometry show that photon influx into the standard irradiation cell using a 420 nm filter is approximately  $9.2 \times 10^{15}$  photons per second in dim lighting,  $1.7 \times 10^{16}$  photons per second in normal laboratory fluorescent light and  $6.7 \times 10^{17}$  photons per second during irradiation using tungsten-halogen projector light. This corresponds to a ratio of intensity of approximately 1:2:73 respectively.

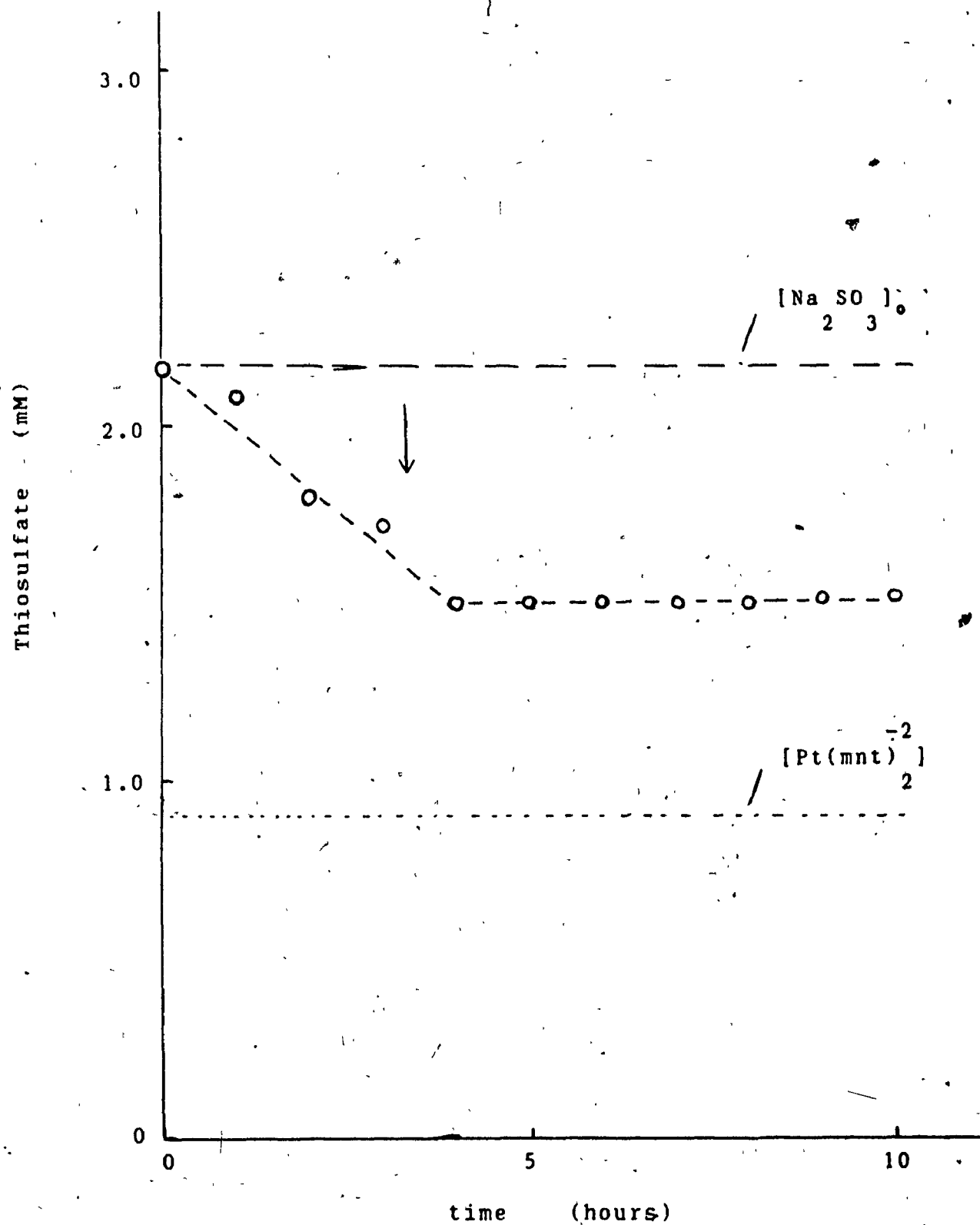


Fig. 3.1 Change in Thiosulphate Concentration During Irradiation (○) (Photoreaction Occuring)



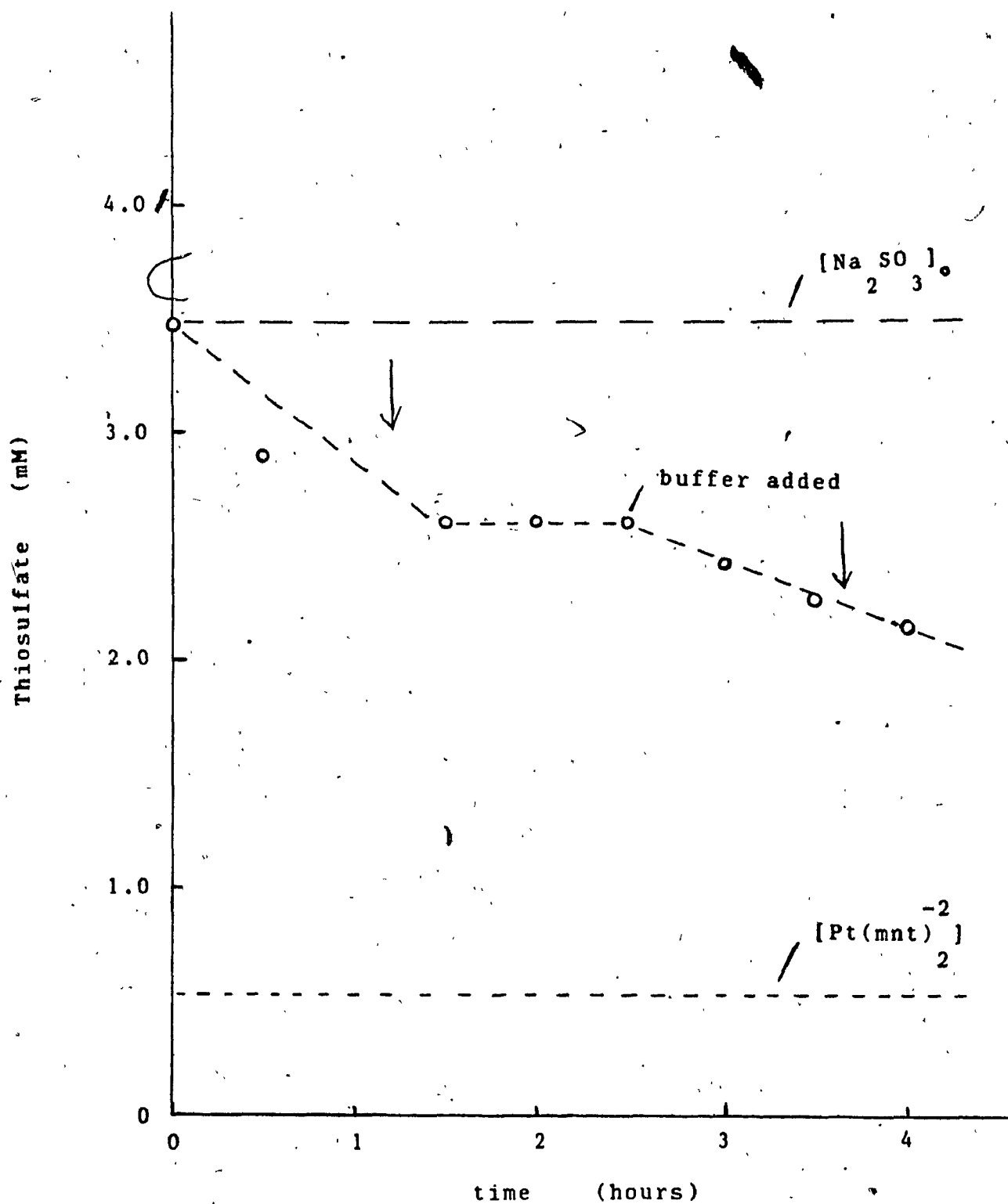


Fig. 3.2 Change in Thiosulphate Concentration Attains a Catalytic Quantity (Photocatalytic Process Observed)

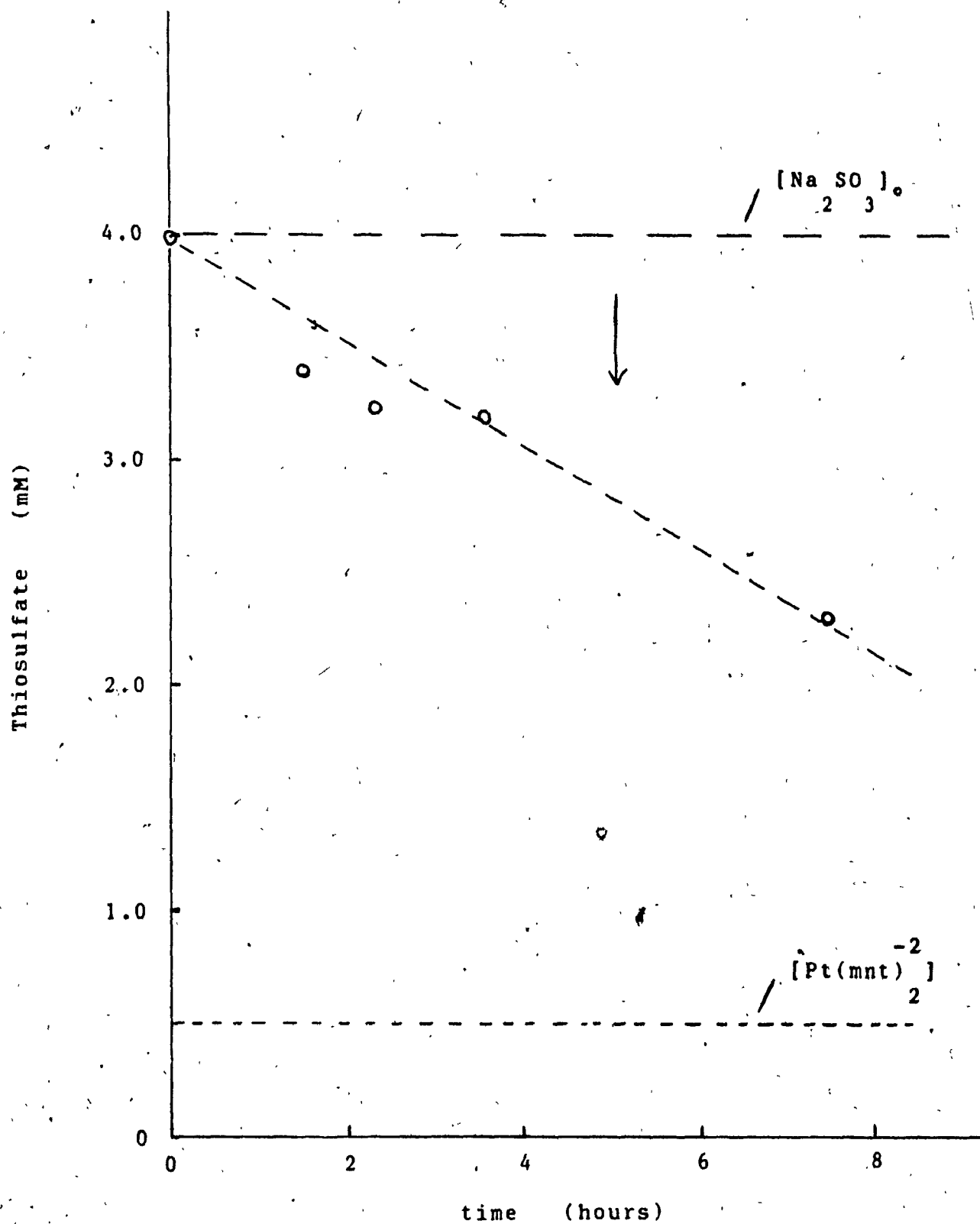


Fig. 3.3 The Photocatalytic Process Proceeding  
in the Buffered System

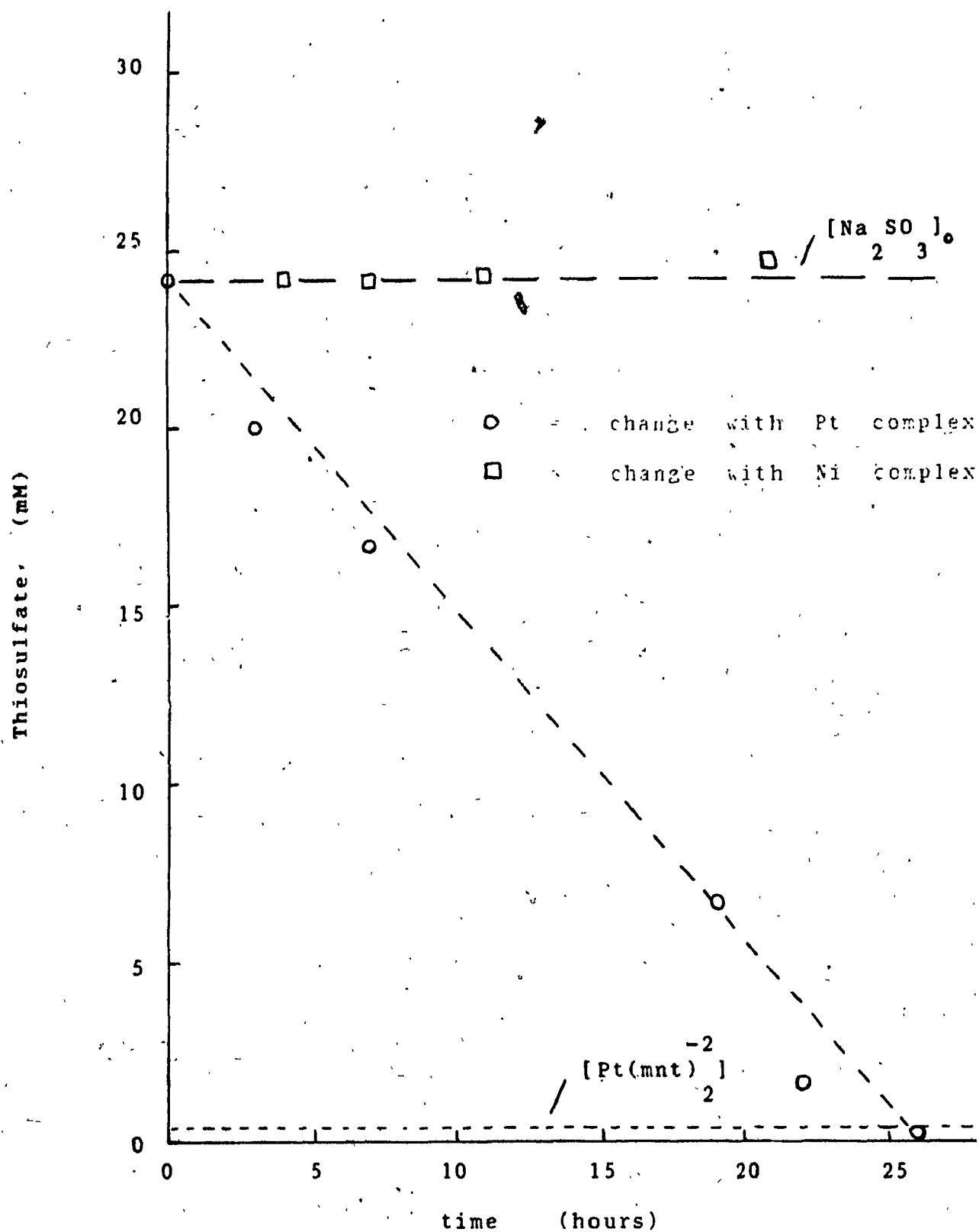


Fig. 3.4 Change in Thiosulphate Concentration During Irradiation With the Ni and Pt complex

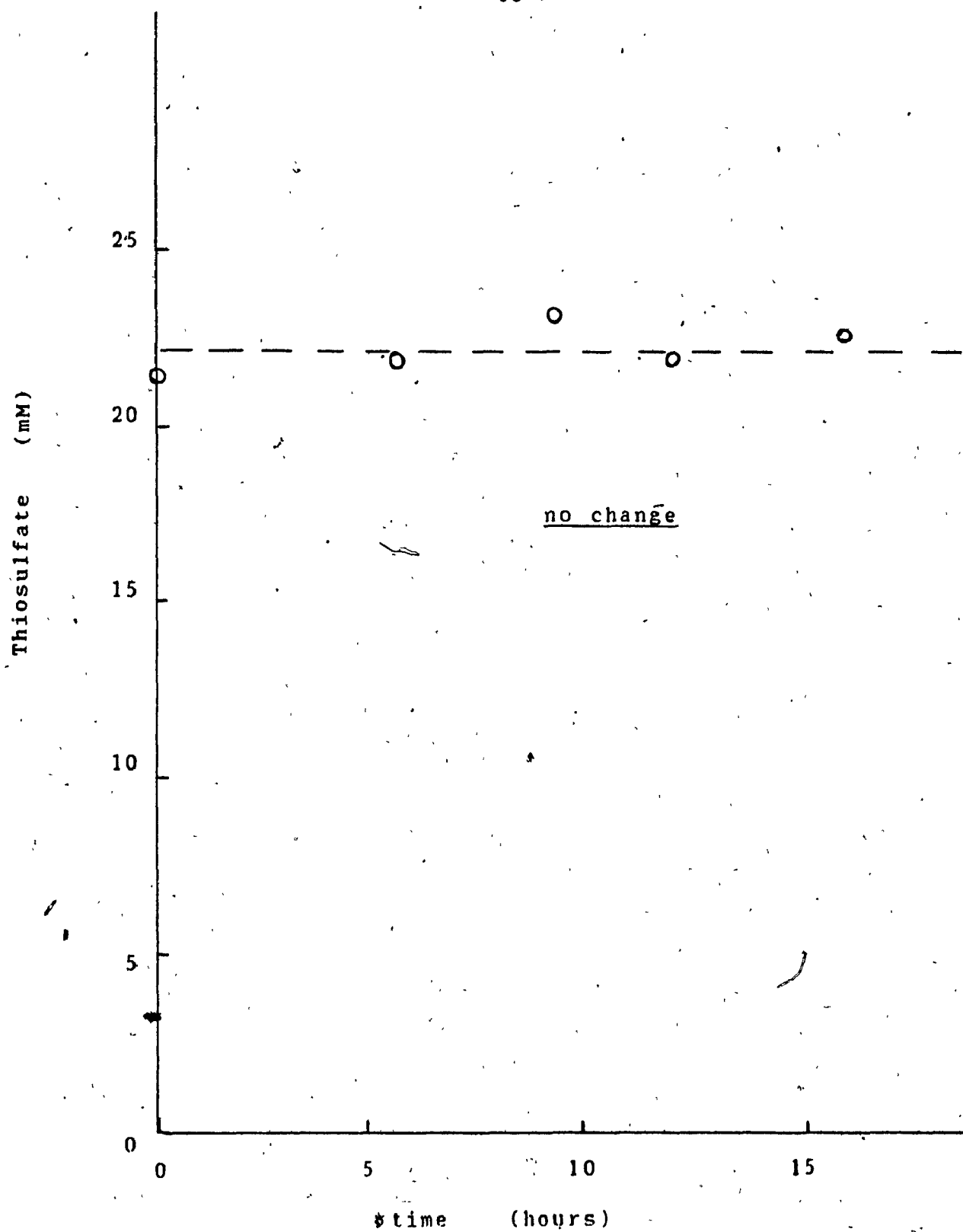


Fig. 3.5 Change in Thiosulphate Concentration During  
Irradiation Without Complex ( ) (blank)

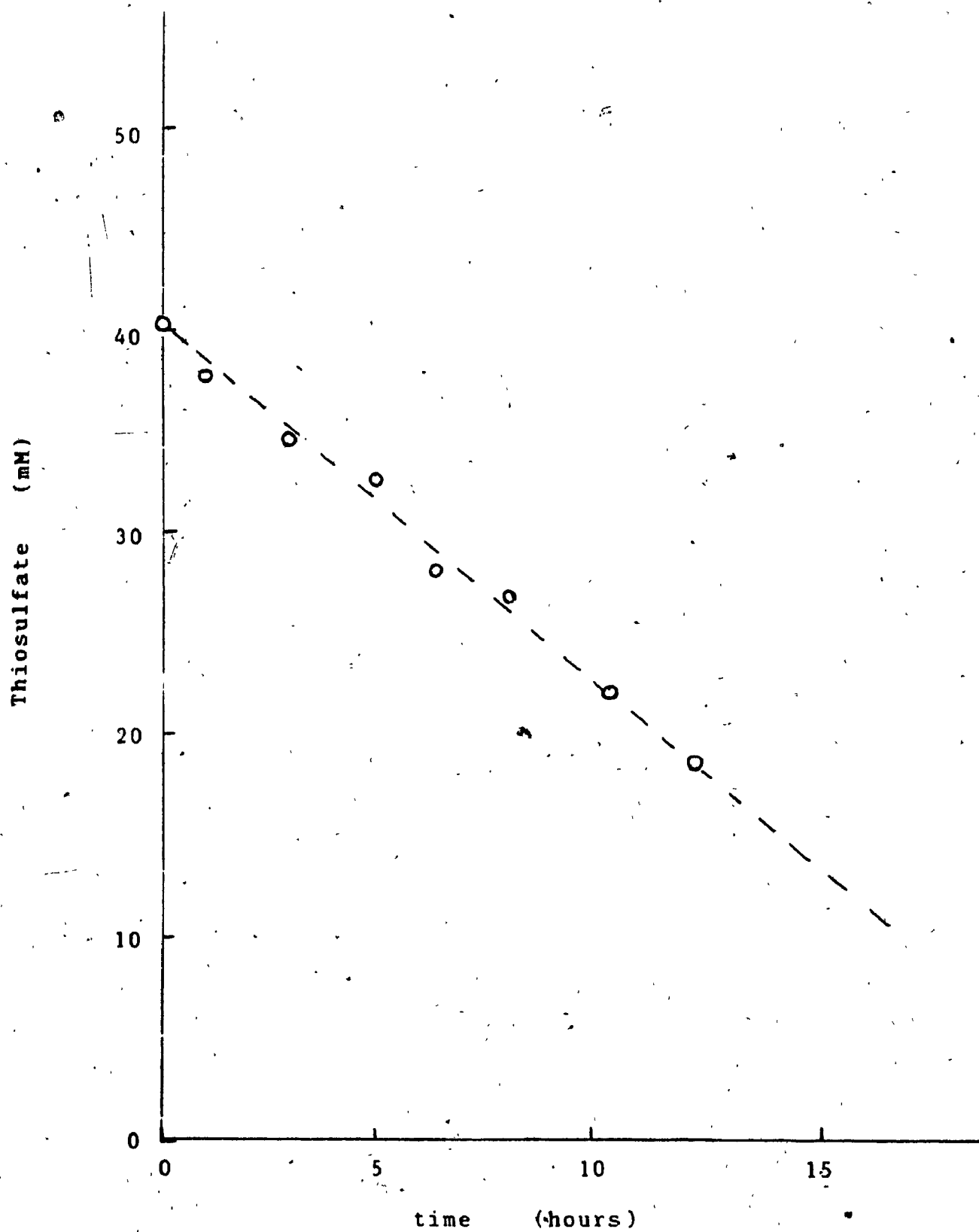


Fig. 3.6 Change in Thiosulphate Concentration During Irradiation of a 40.5 mM Solution

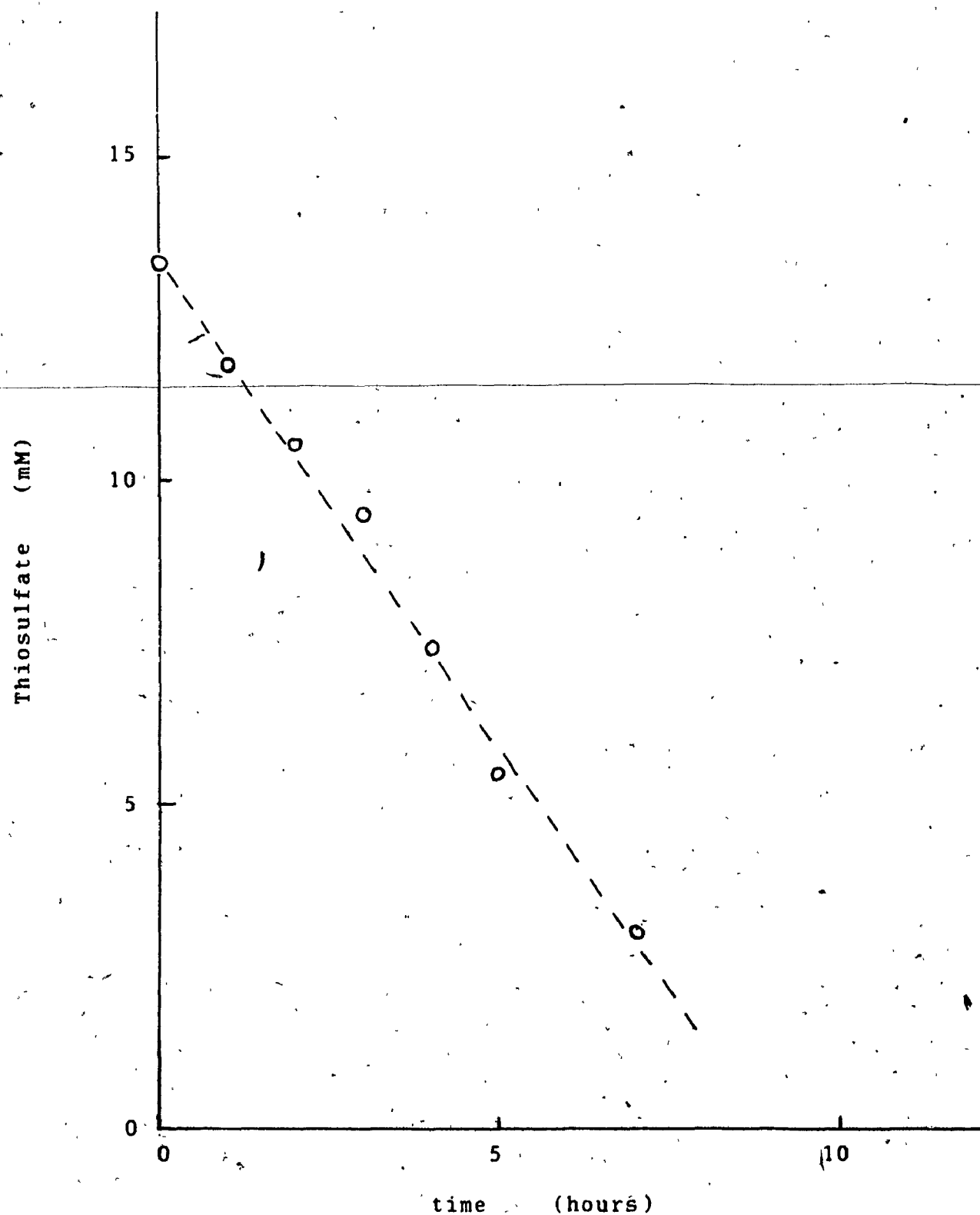


Fig. 3.7 Change in Thiosulphate Concentration During  
Irradiation of a 13.4 mM Solution (exposed to air).

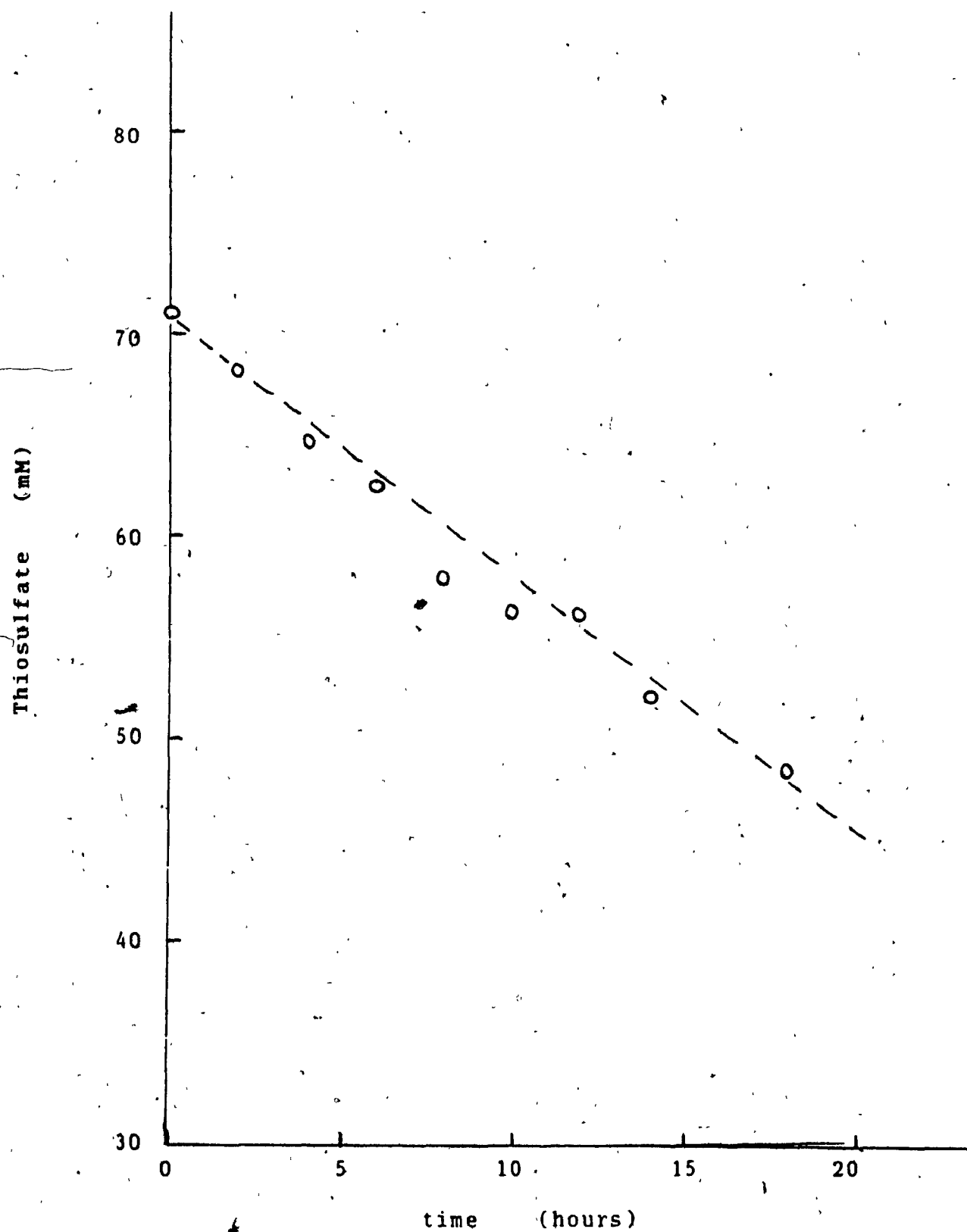


Fig. 3.8 Change in Thiosulphate Concentration During Irradiation of a 71.0 mM Solution (exposed to air)

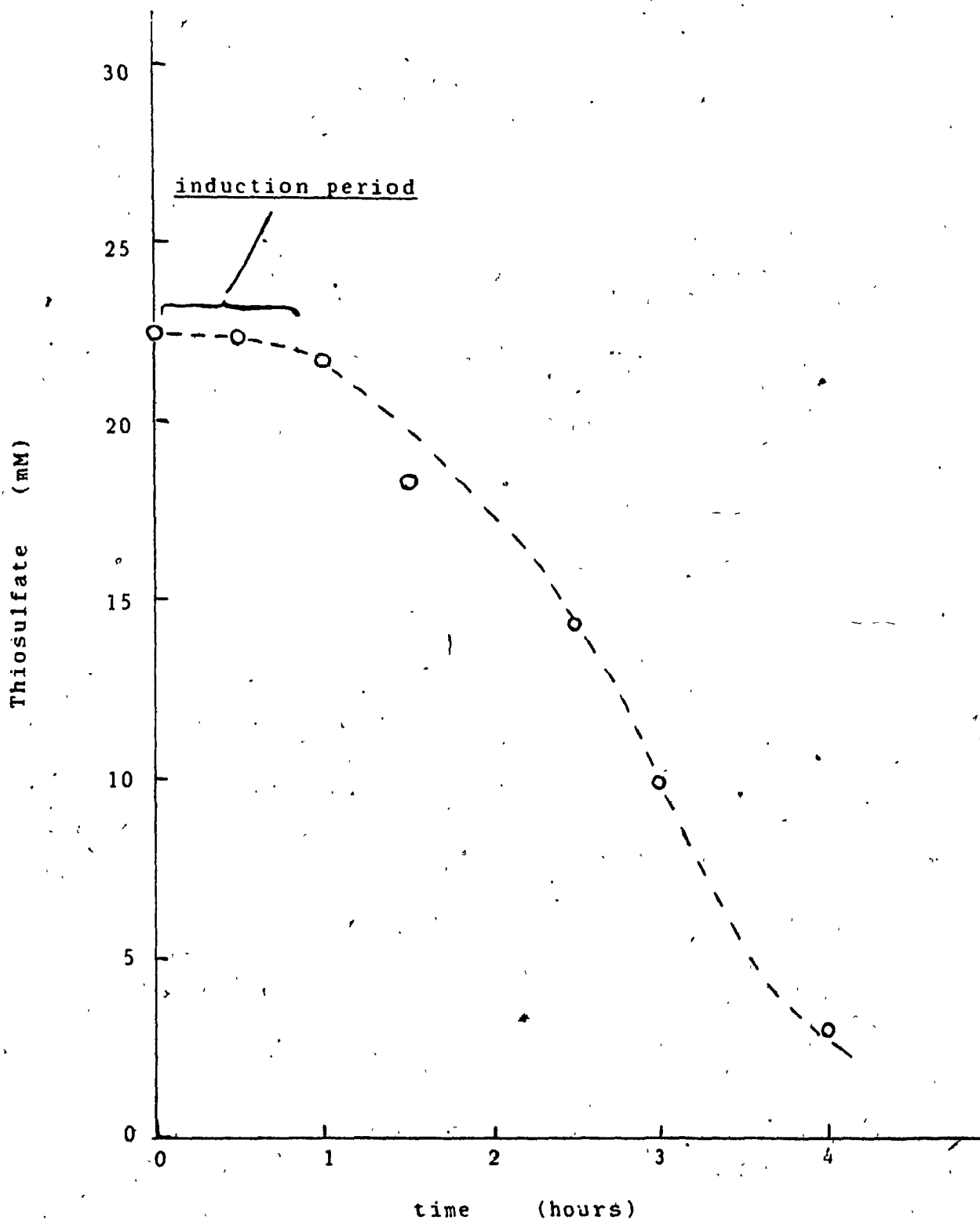


Fig. 3.9 Change in Thiosulphate Concentration During Irradiation of a 22.6 mM Solution (pH 6) (with pure oxygen).



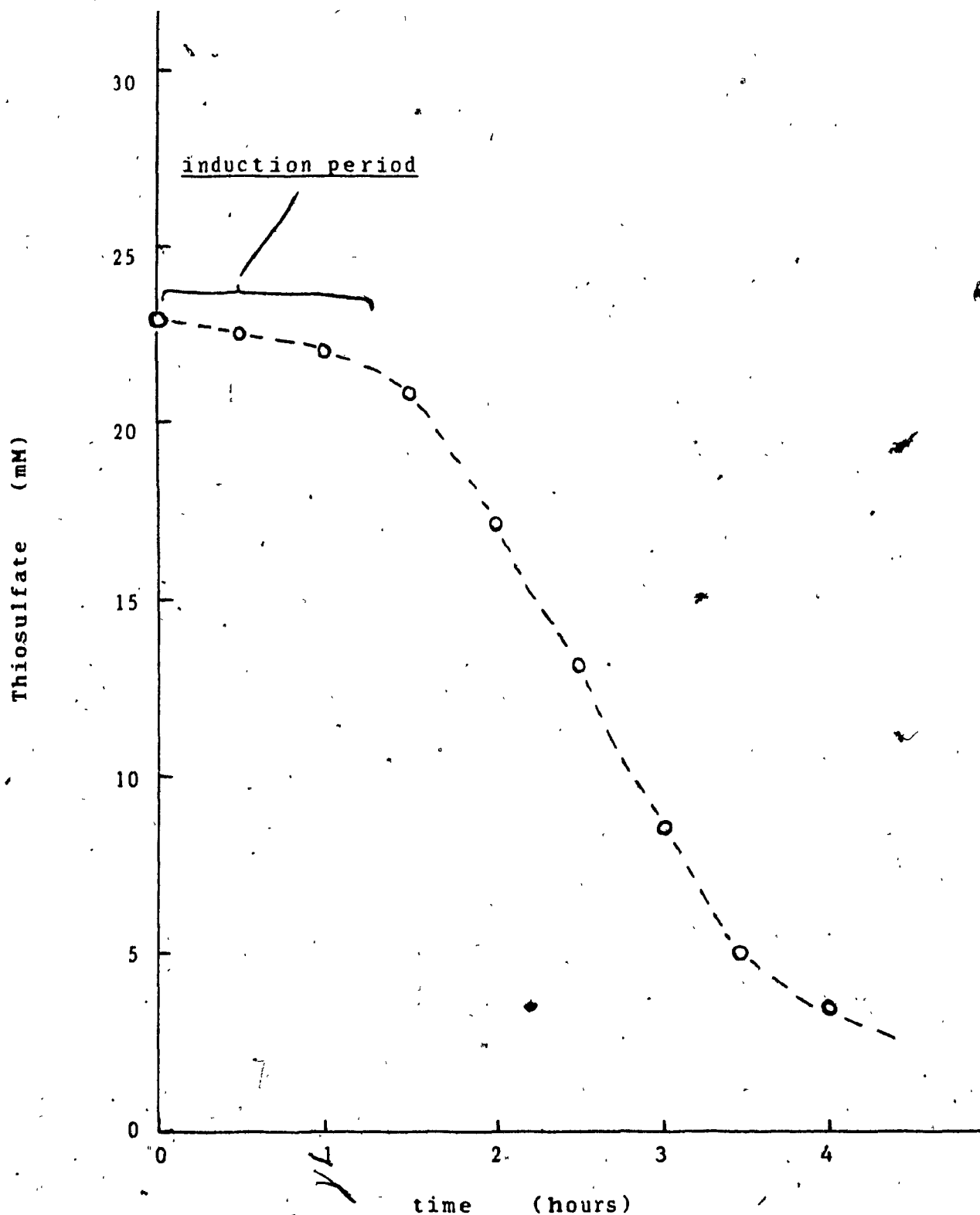


Fig. 3.10 Change in Thiosulphate Concentration During  
Irradiation of a 22.9 mM Solution (pH 5) (with pure oxygen)

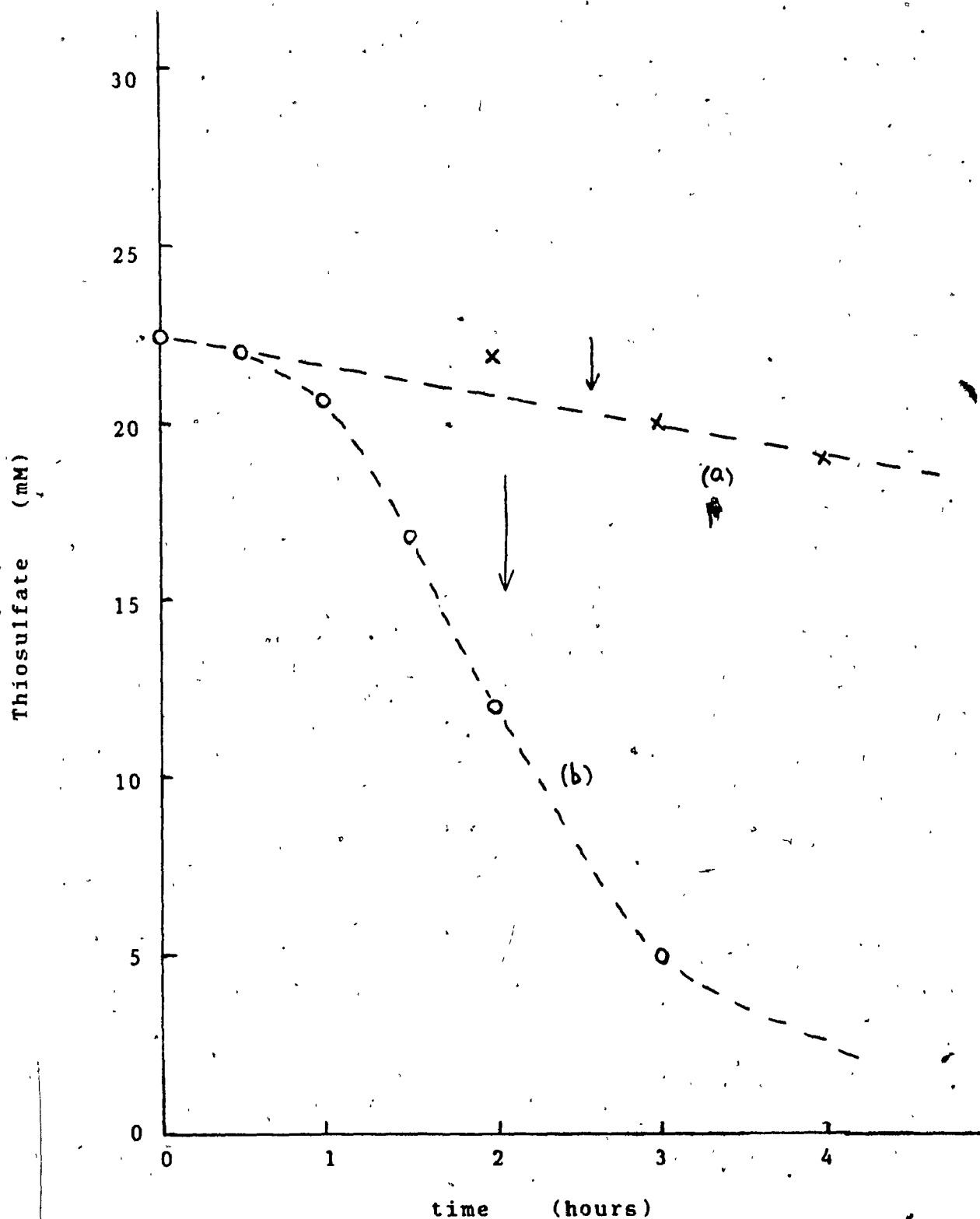


Fig. 3.11 Comparison of Changes in Concentration During  
Irradiation (a) air (b) pure oxygen (buffer-less)

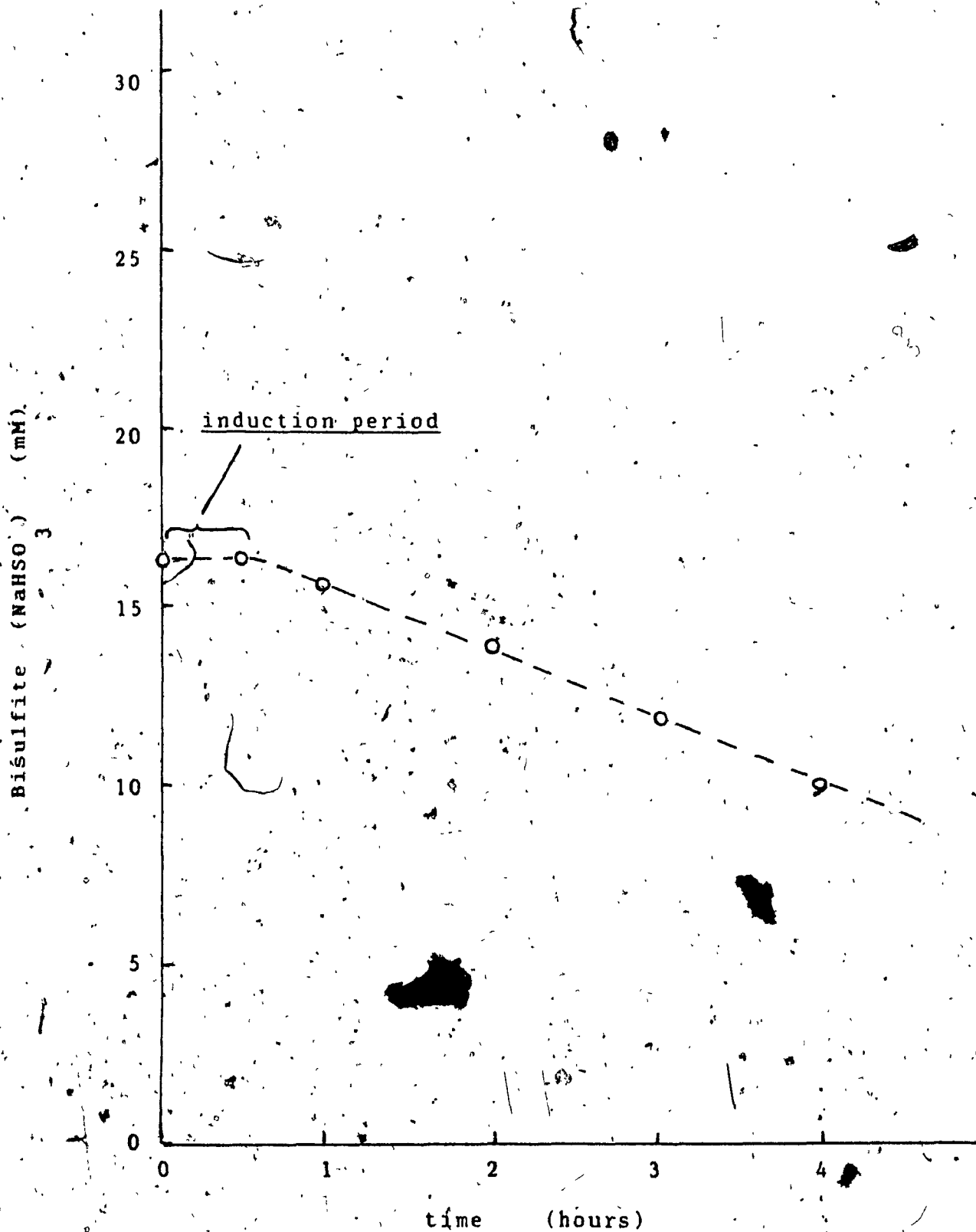
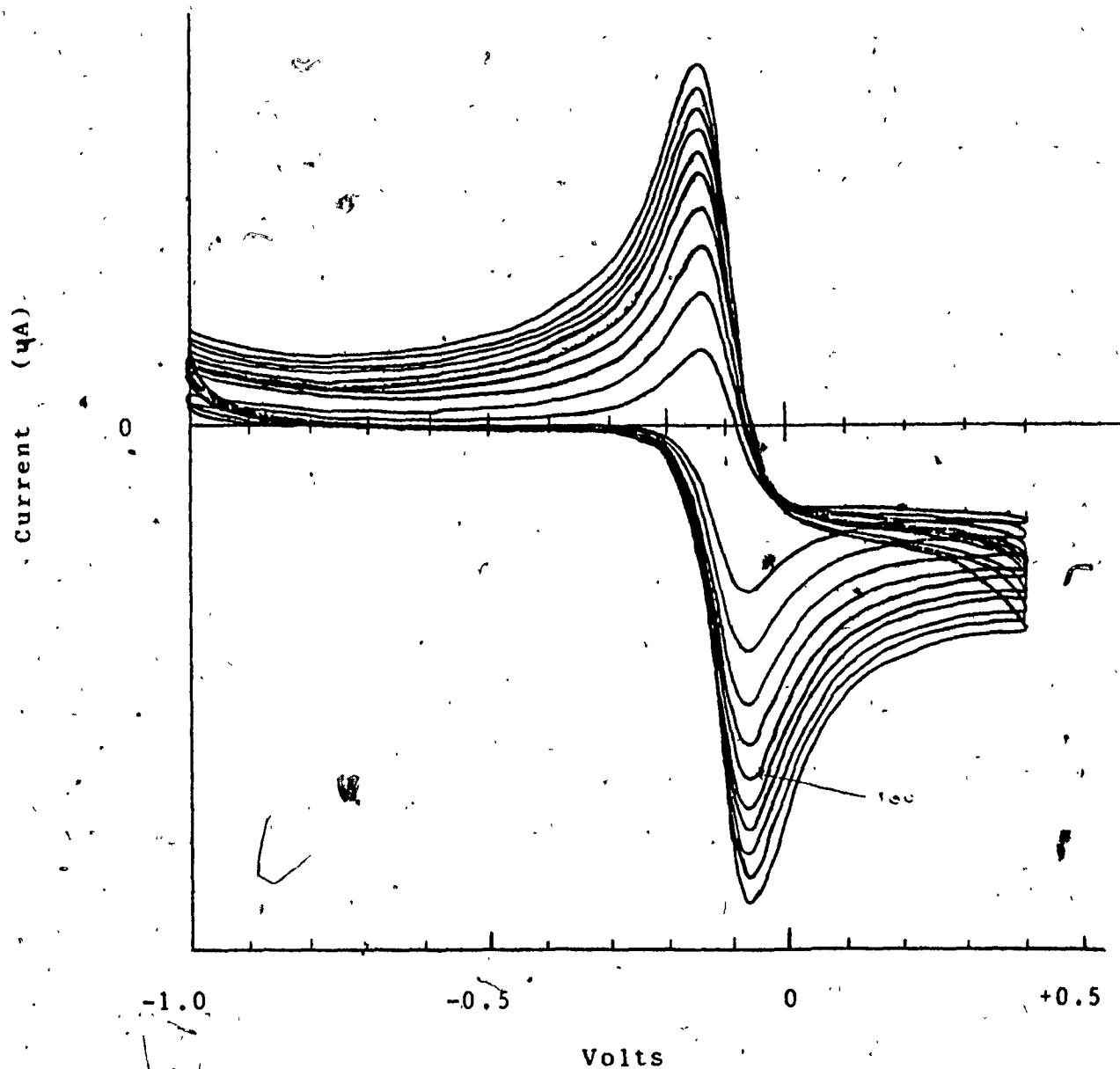
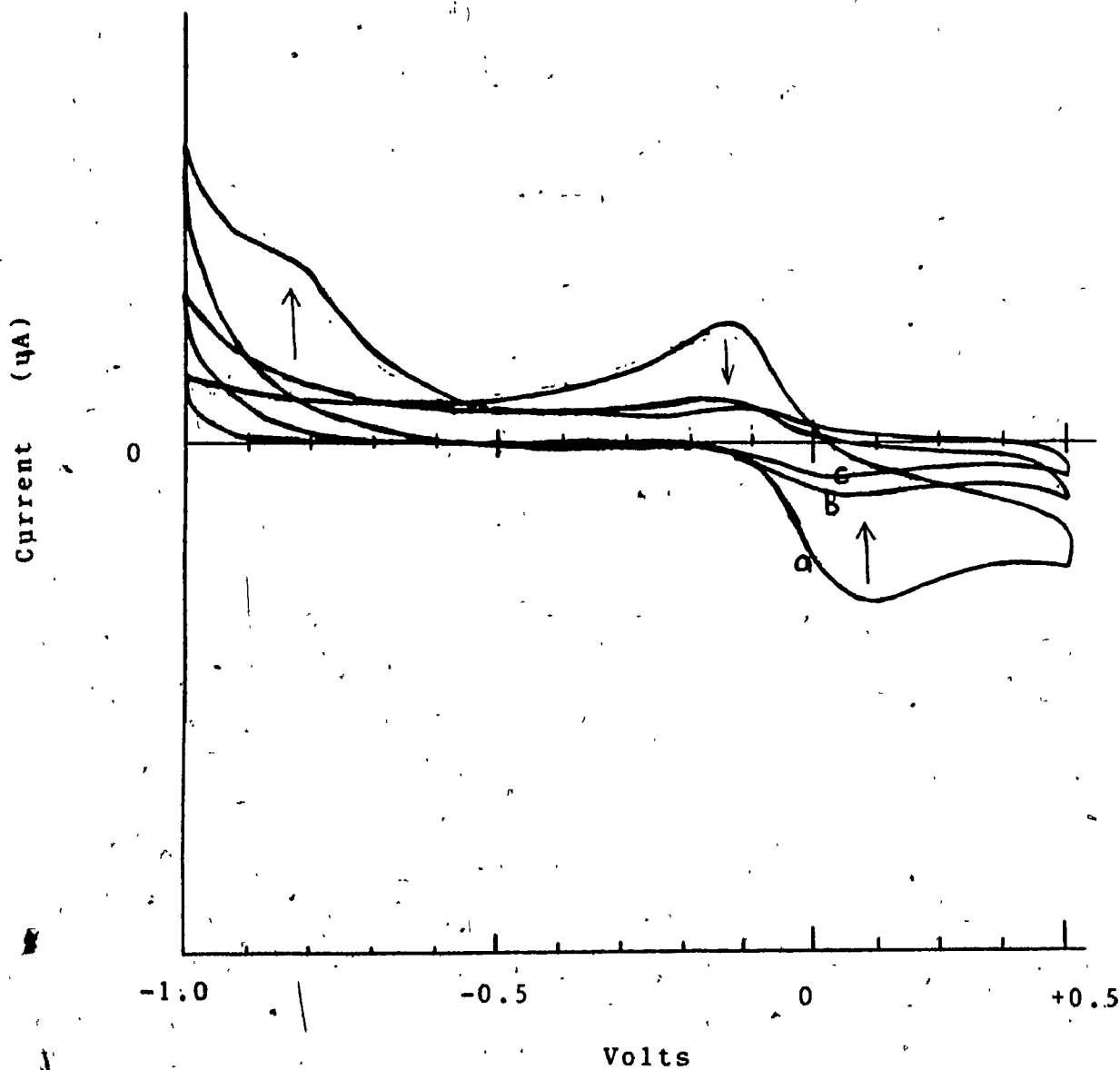


Fig. 3.12 Changes in Bisulfite Concentration (Buffered  $\text{SO}_2$ ) During Irradiation (exposed to air)



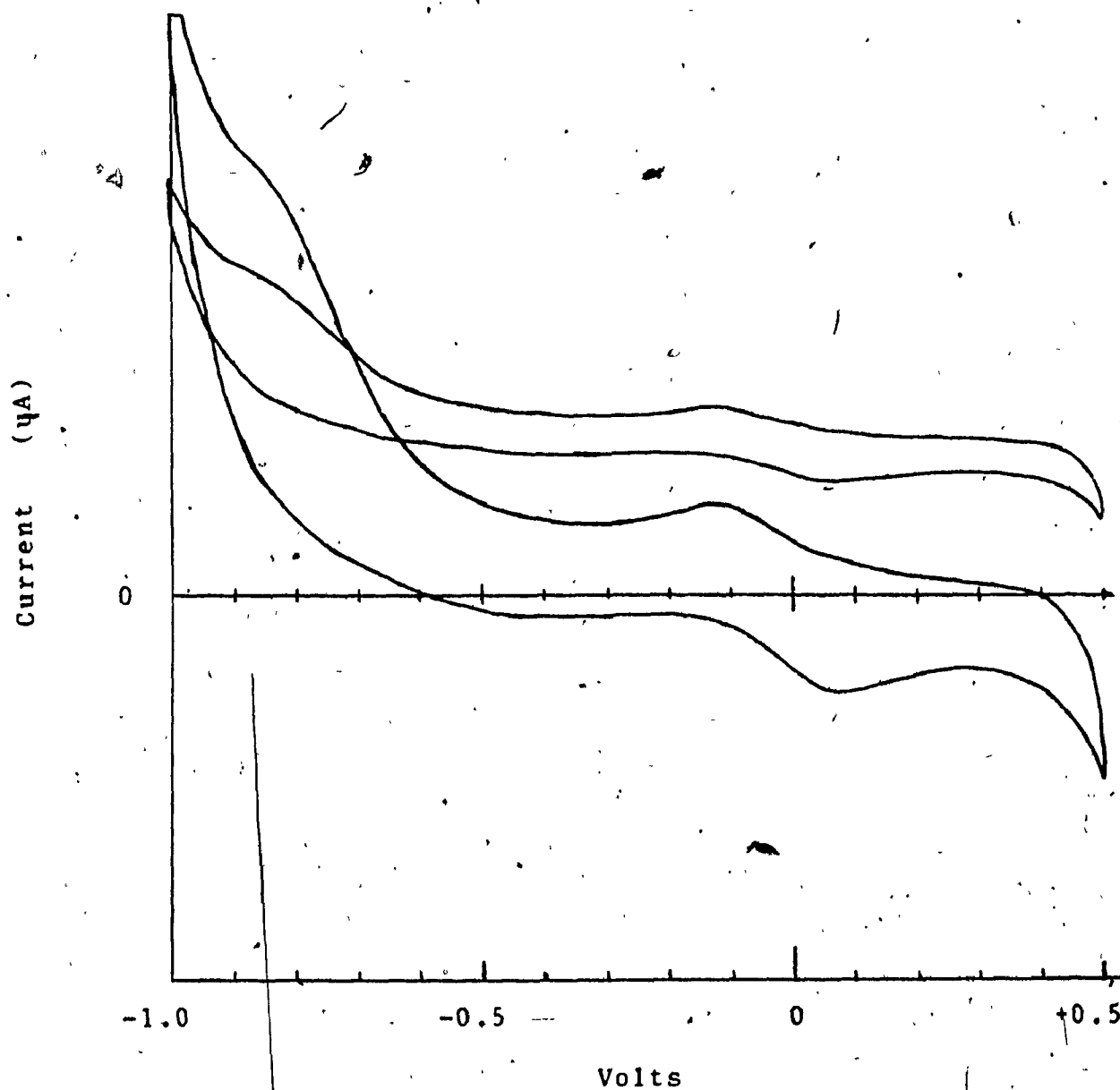
(vs. Ag/Ag<sup>+</sup>, 0.01N NO<sub>3</sub><sup>-</sup>, 0.1N TEAP)

Fig. 3.13 Voltammograms of Pt mnt in Acetonitrile  
With Variations in Scan Rate (20 to  
200 mV s<sup>-1</sup>) (5 mV)



(vs.  $\text{Ag}/\text{Ag}^+$ ,  $0.01\text{N NO}_3^-$ ,  $0.1\text{N TEAP}$ )

Fig. 3.14 Change in Voltammogram Upon Irradiation  
of Pt mnt. Solution in Oxygenated Solution  
(Aqueous and Non-Aqueous) (5 mV)



(vs.  $\text{Ag}/\text{Ag}^+$ , 0.01N  $\text{NO}_3^-$ , 0.1N TEAP)

Fig. 3.15 Change in Voltammogram Upon Irradiation  
of Pt. mnt Solution in Oxygenated Solution  
(increased sensitivity) (2 mV)

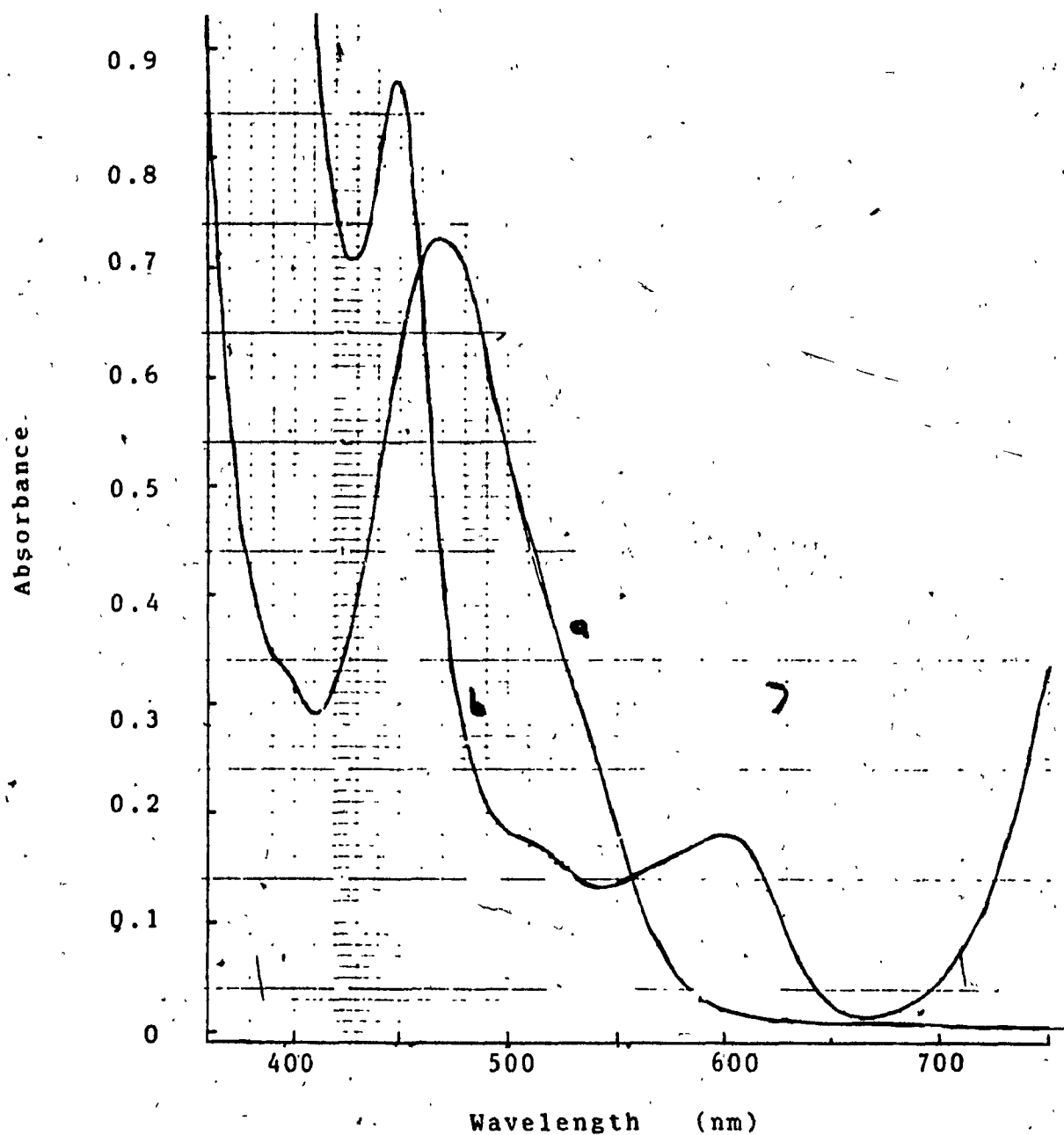


Fig. 3.16 Absorption Spectra of the Pt Complex in Acetonitrile : a) -2 or dianionic form and b) -1 or monoanionic form

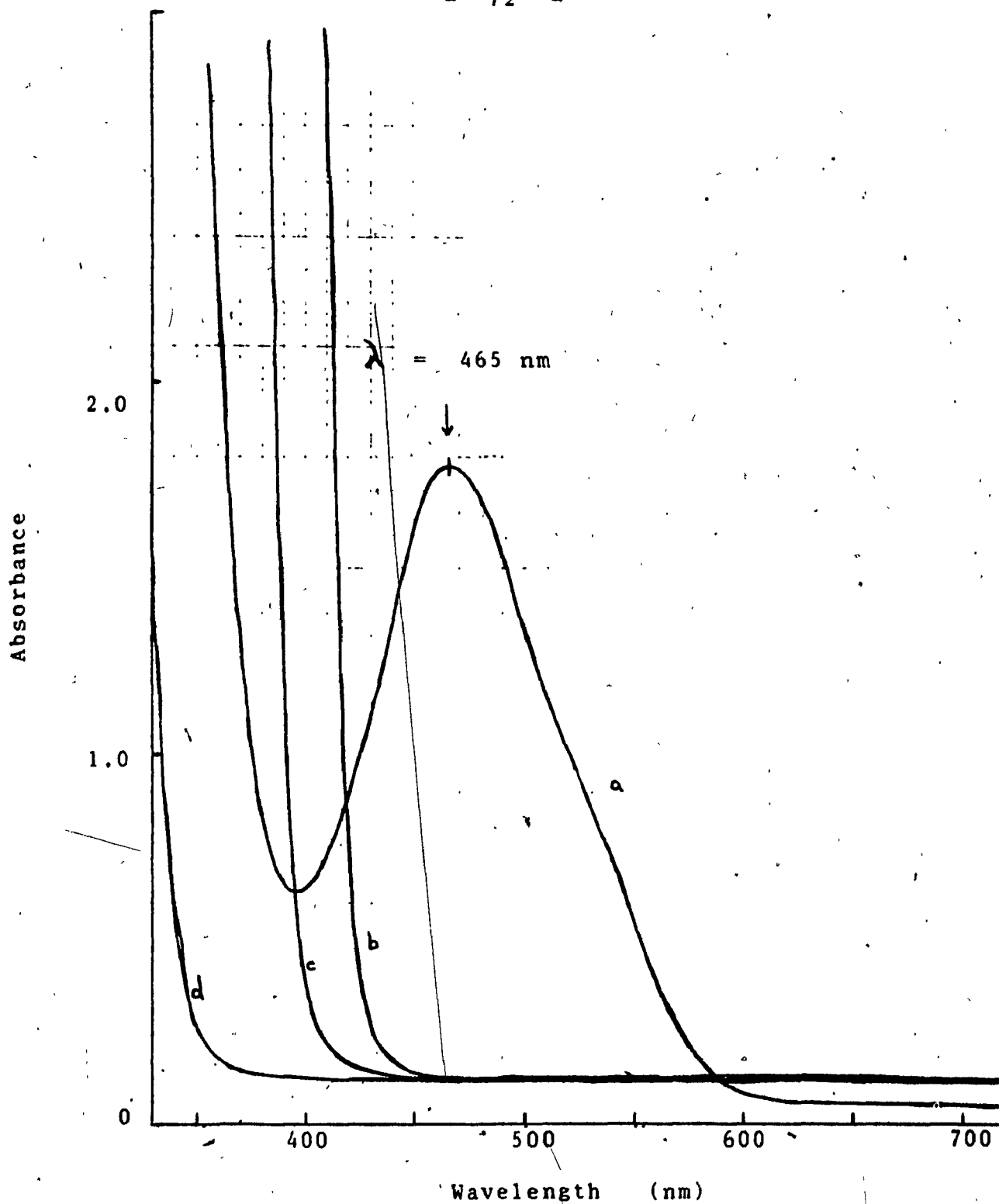


Fig. 3.17 The Absorption Spectra of a) the Dianionic Pt mnt Irradiation Solution and Several Filters :  
b) 420 nm c) 400 nm and d) 340 nm



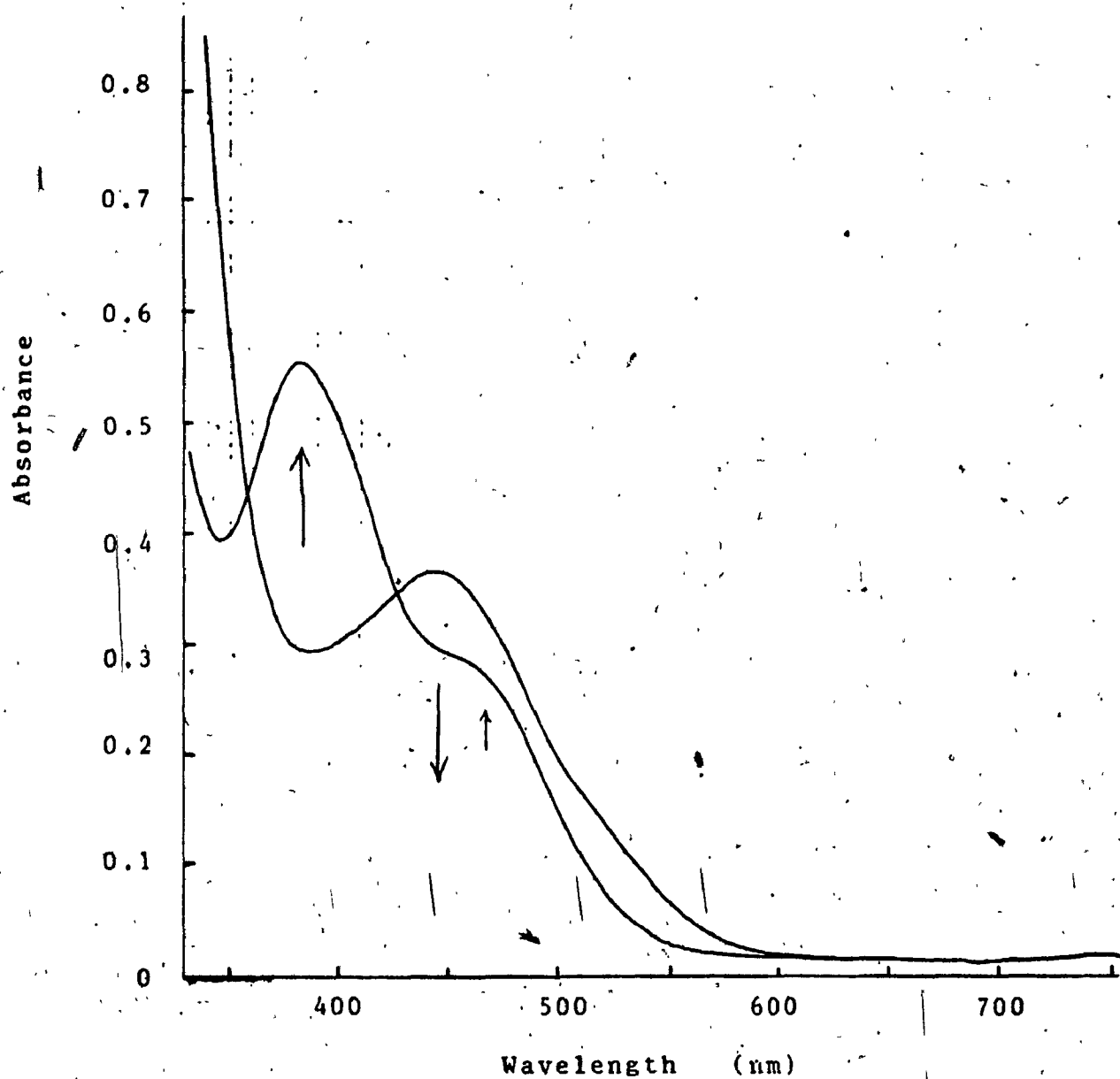


Fig. 3.18 Change in Spectral Absorption Occuring  
With the Irradiation of Pt mnt  
Solutions

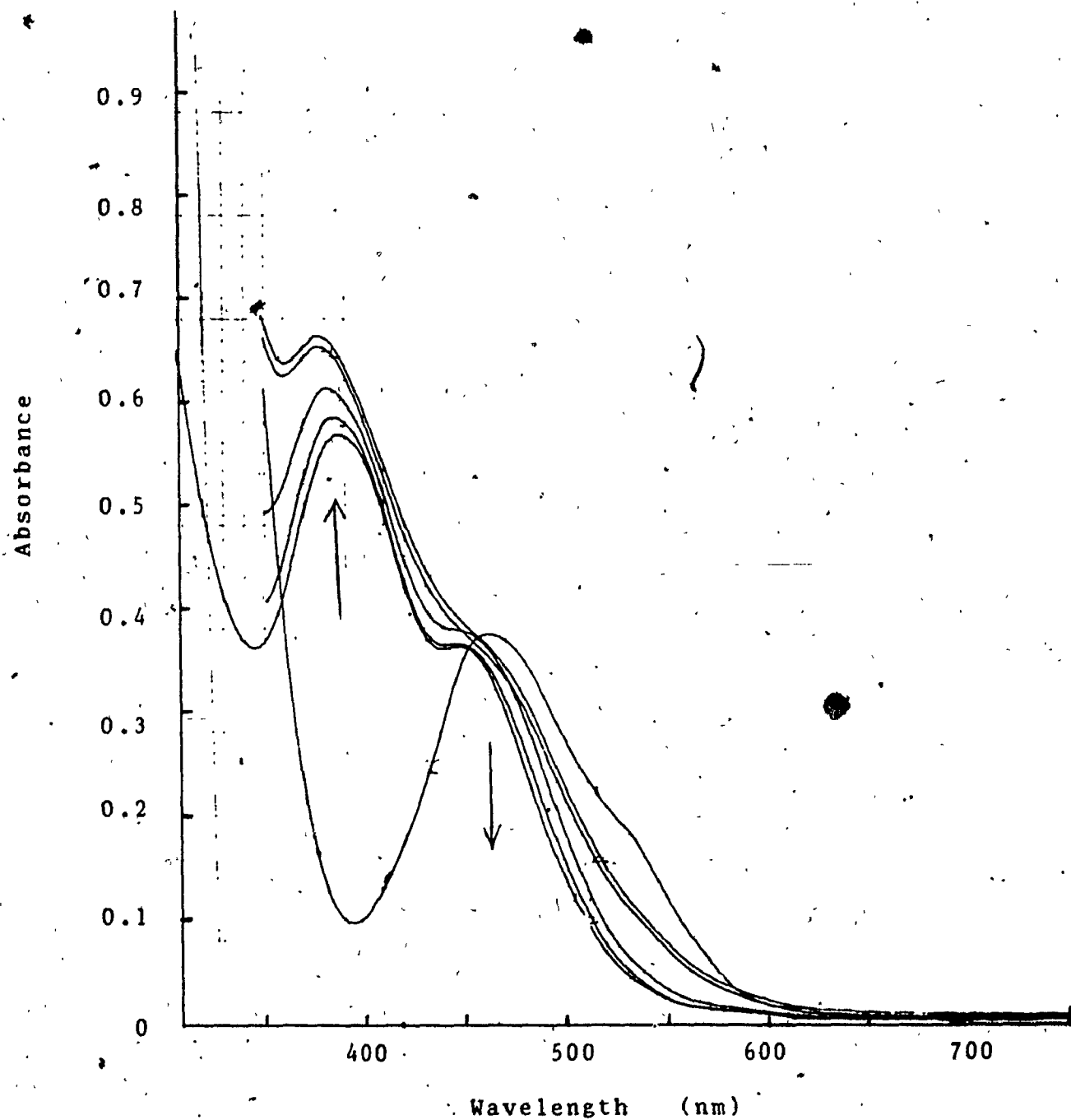


Fig. 3.19 Changes in Spectra in a Substrate-less  
Solution During Irradiation (Taken Every Hour  
During a 4 hour irradiation)

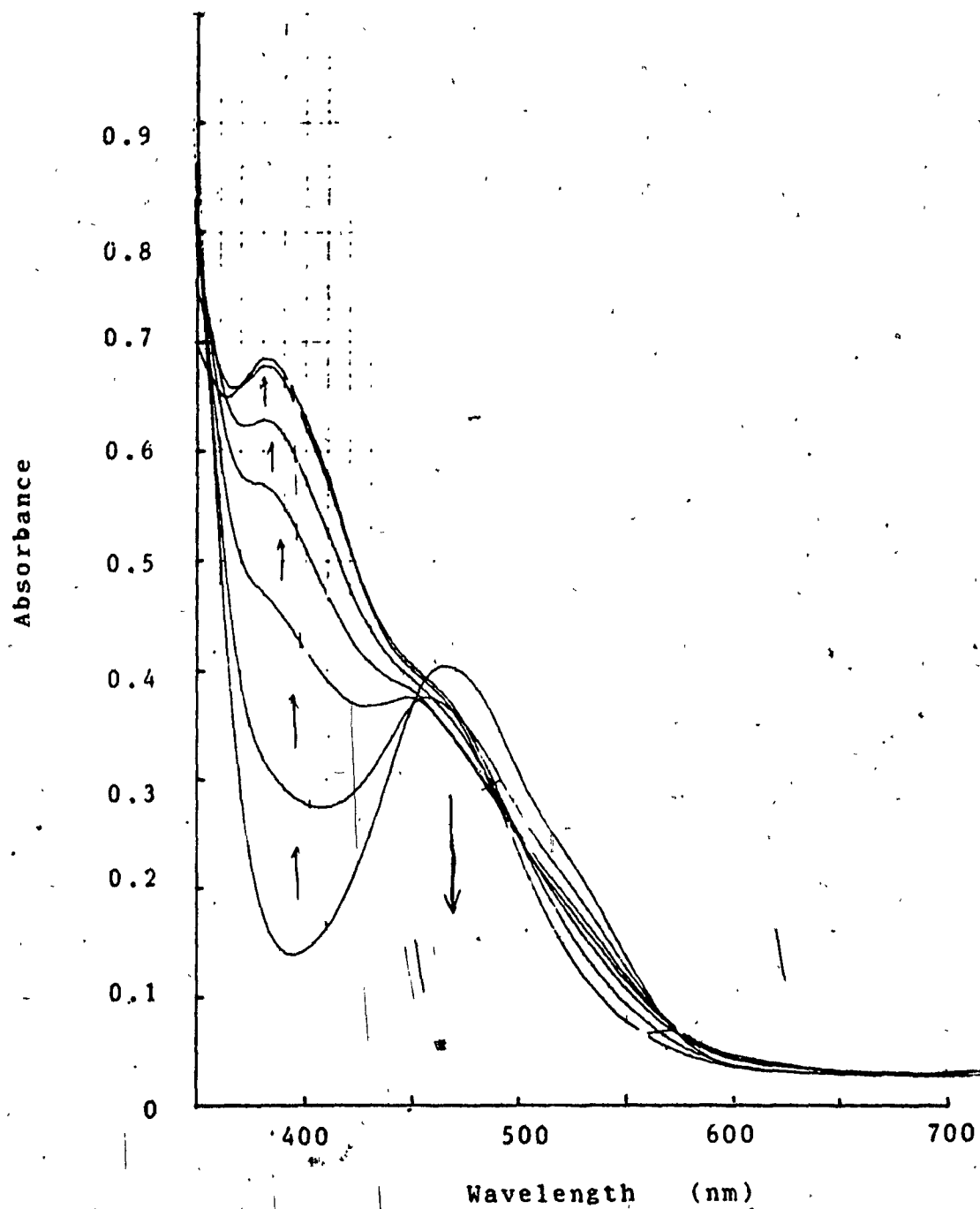


Fig. 3.20 Changes in Spectra in a Substrate-less Solution During Irradiation (Taken Every 10 Minutes During the First Hour of Irradiation)

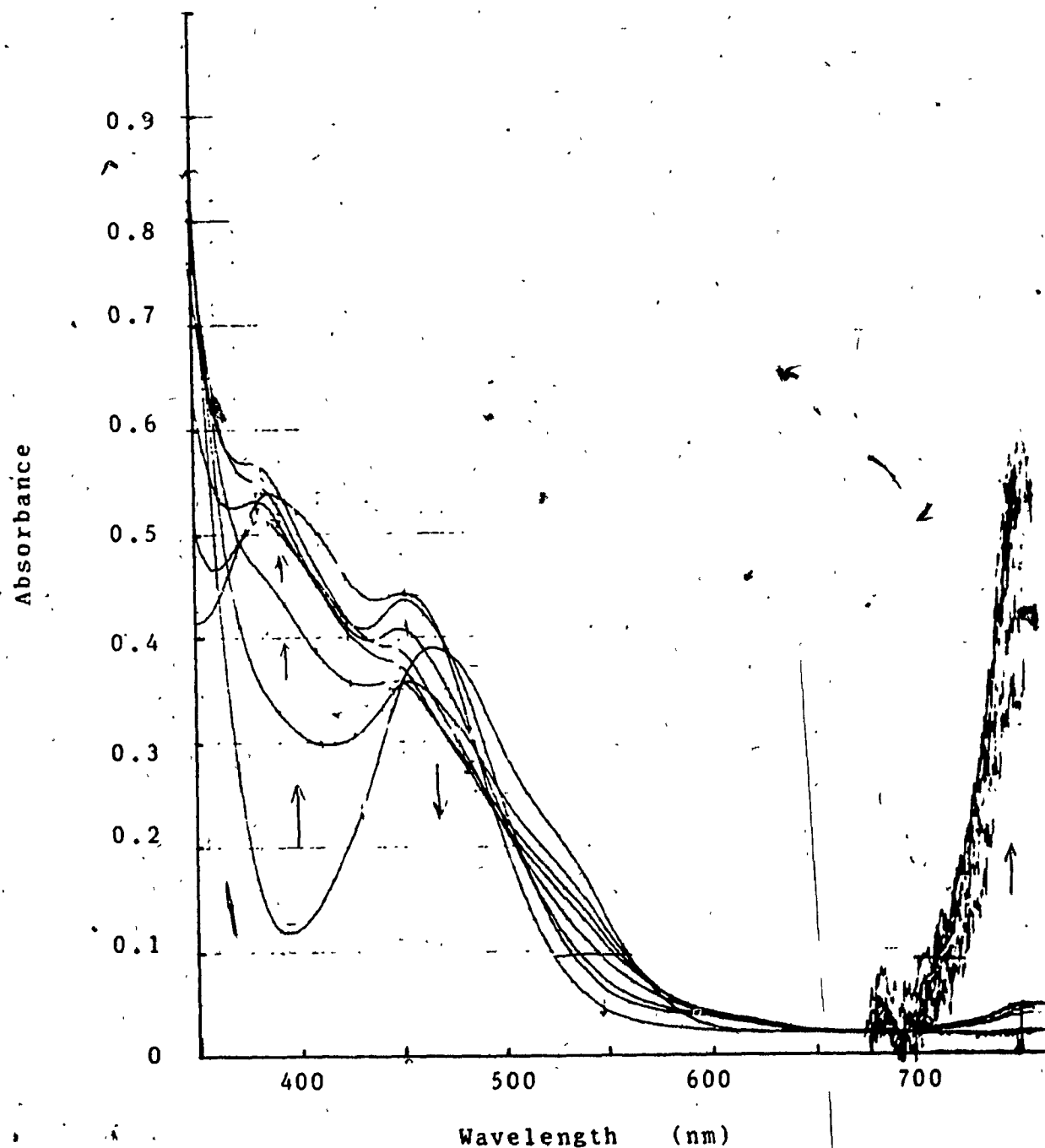


Fig. 3.21 Changes in Spectra During Irradiation of Bufferless and Substrate-less Solution During Irradiation (Taken Every 10 Minutes During the First Hour of Irradiation)

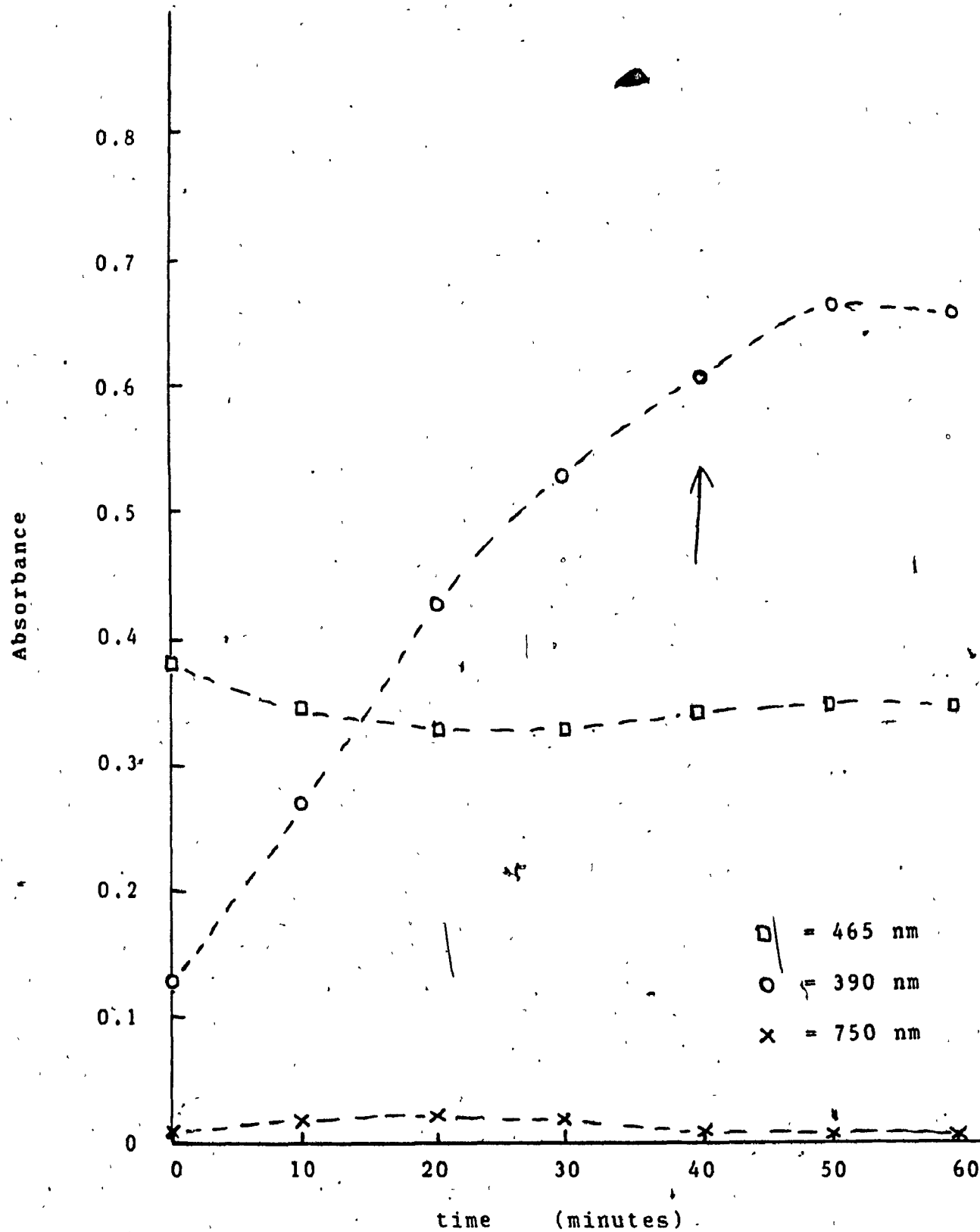


Fig. 3.22 Monitoring the Changes in Absorption at the Wavelengths of Interest During Irradiation

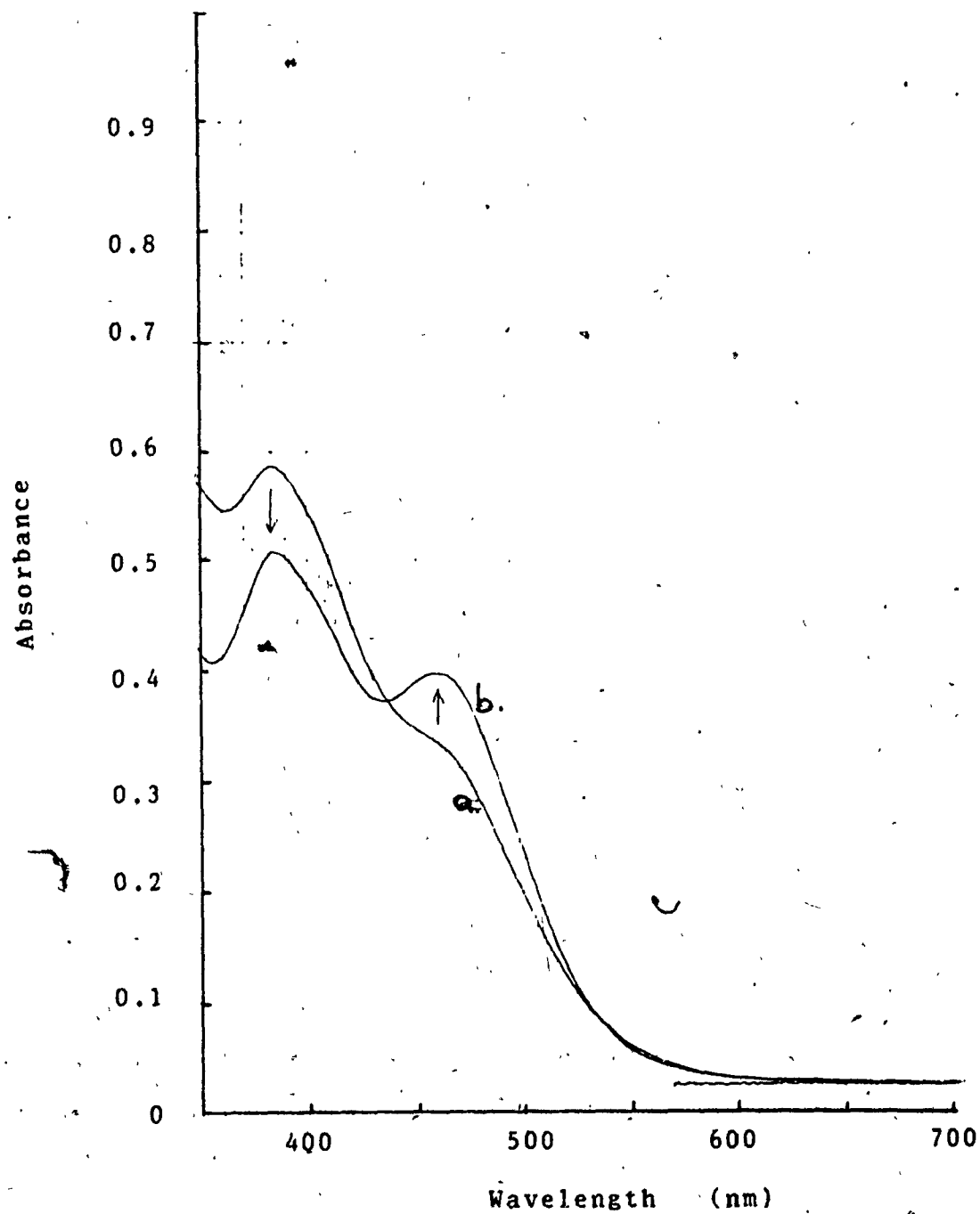


Fig. 3.23 Change in Spectra of a) Irradiated Solution  
b) After Treatment With Buffered  
Sulfur Dioxide Solution

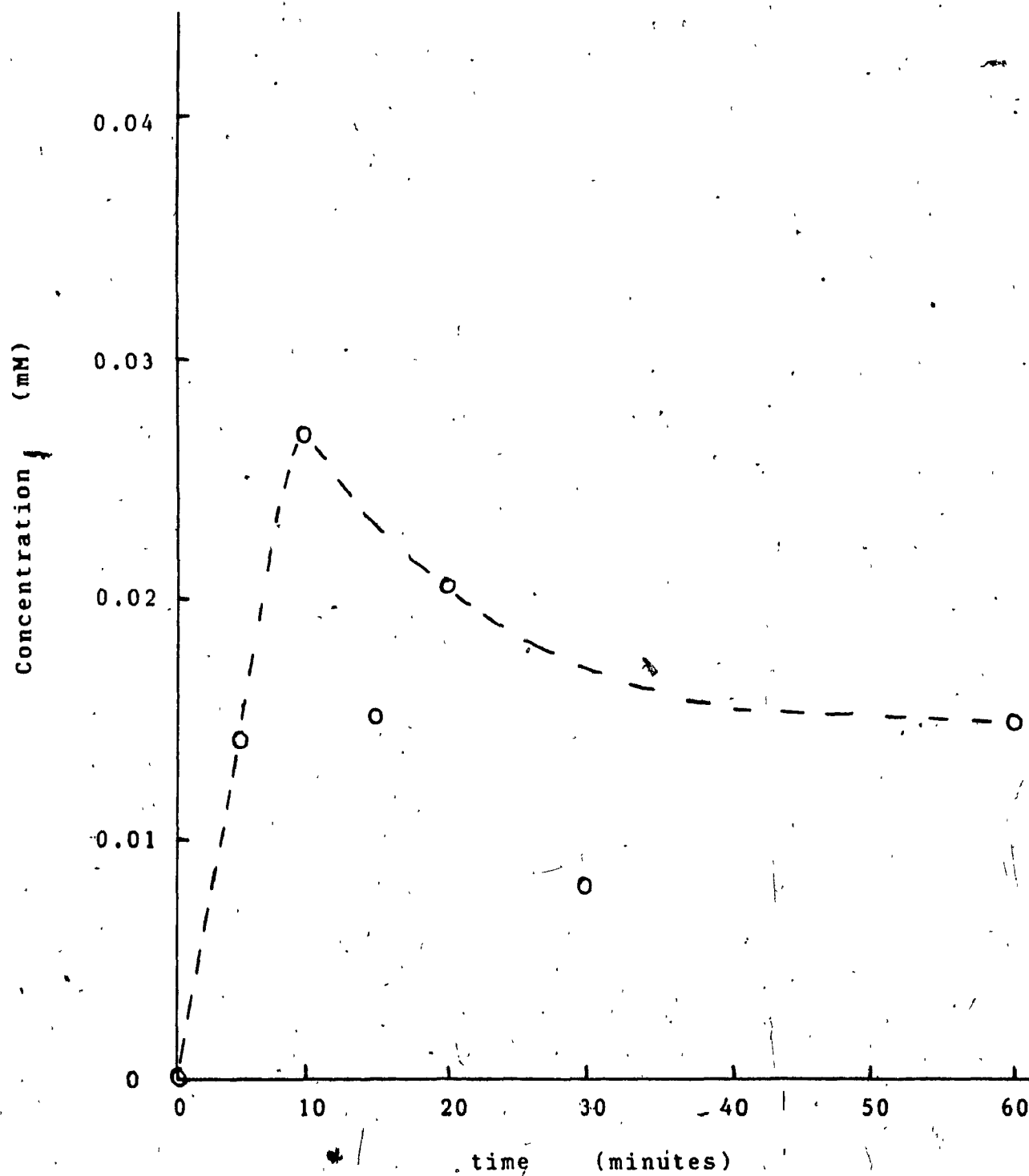


Fig. 3.24 Peroxide Generation Monitored During the  
Irradiation of a Solution of Dianionic Pt mnt

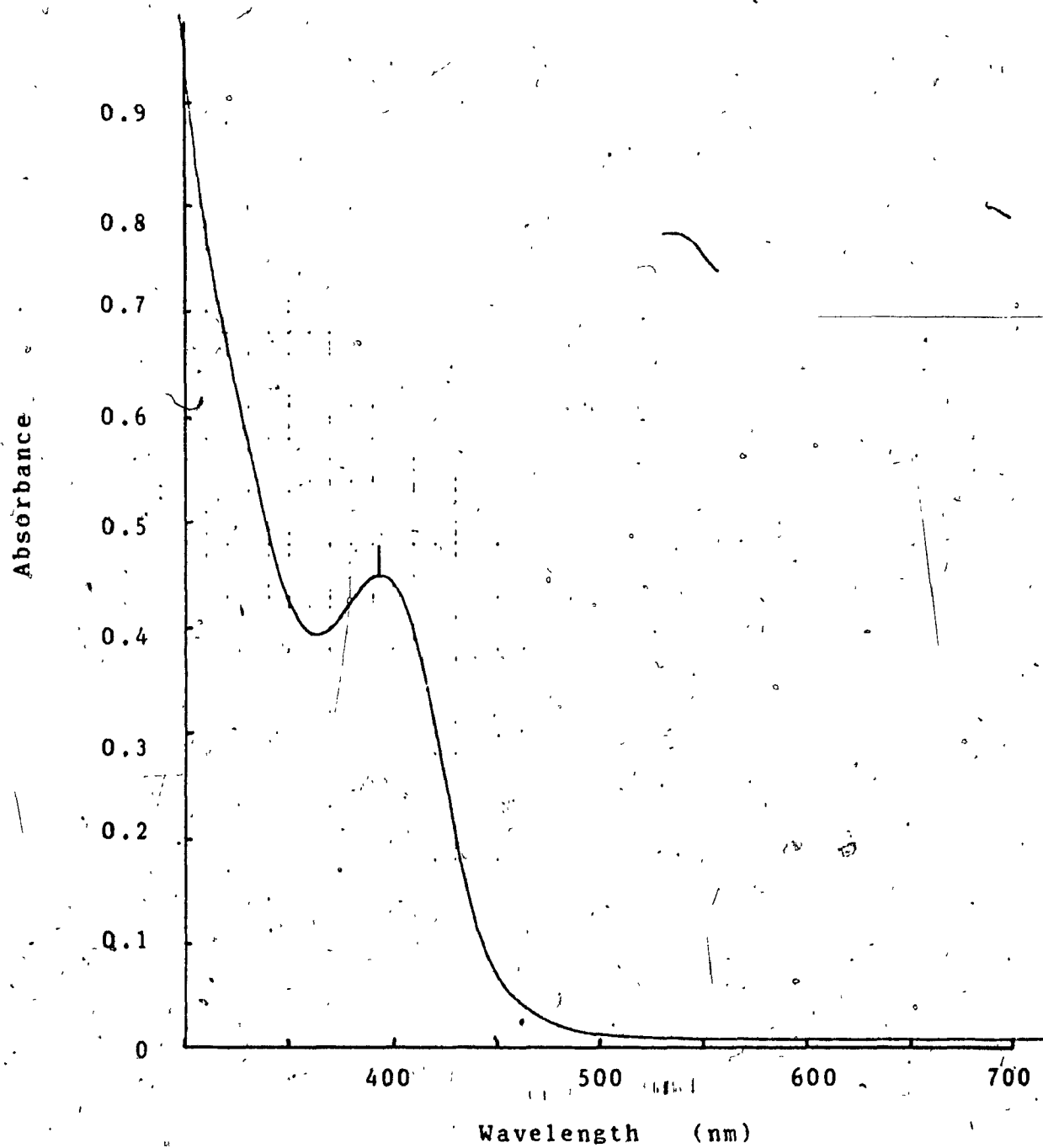


Fig. 3.25 Spectra of Intermediate Crystallites Recovered from Irradiated Solution (in Acetonitrile)



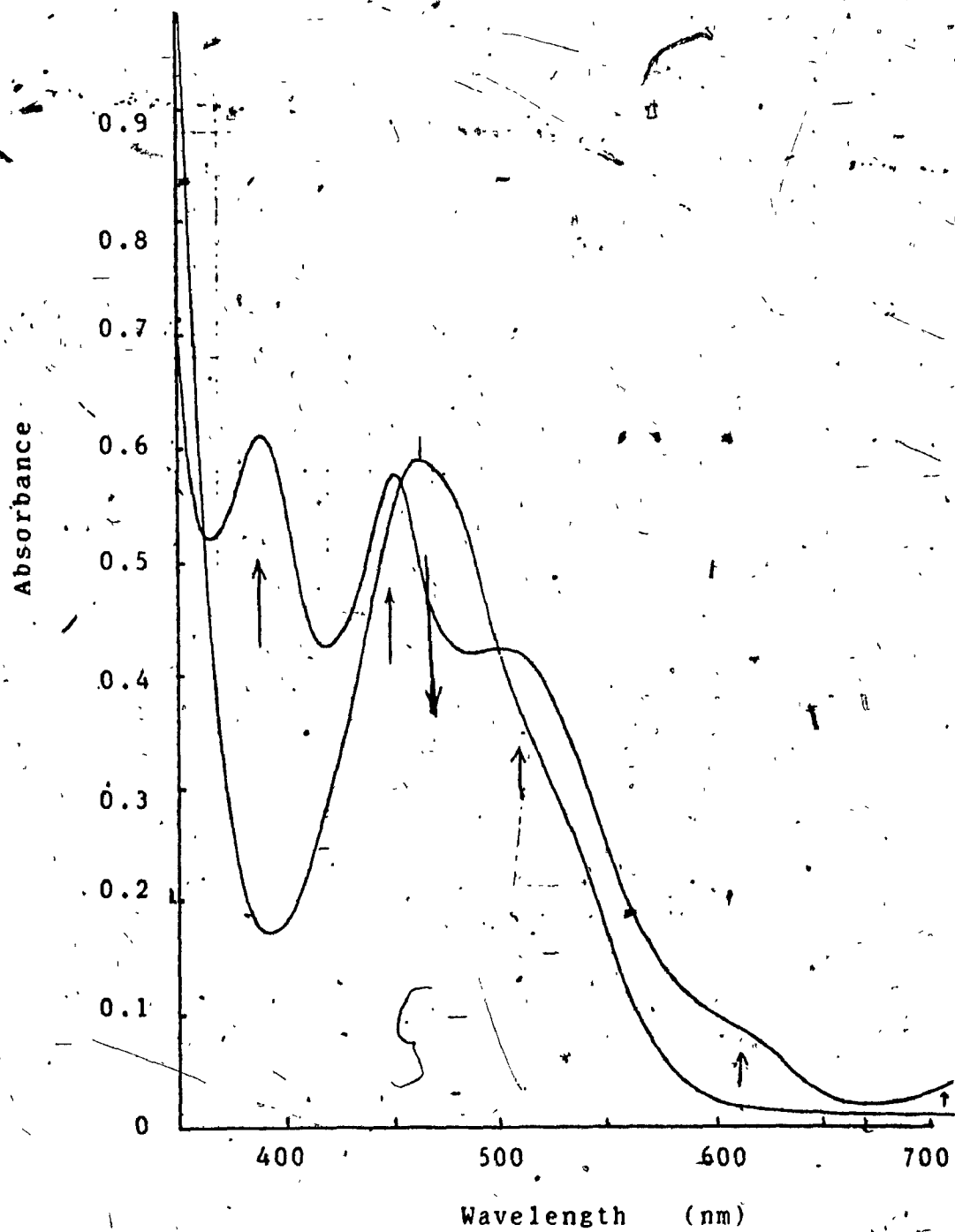


Fig. 3.26 Solution Spectra of Dianionic Pt mnt Before and After Addition of Hydrogen Peroxide

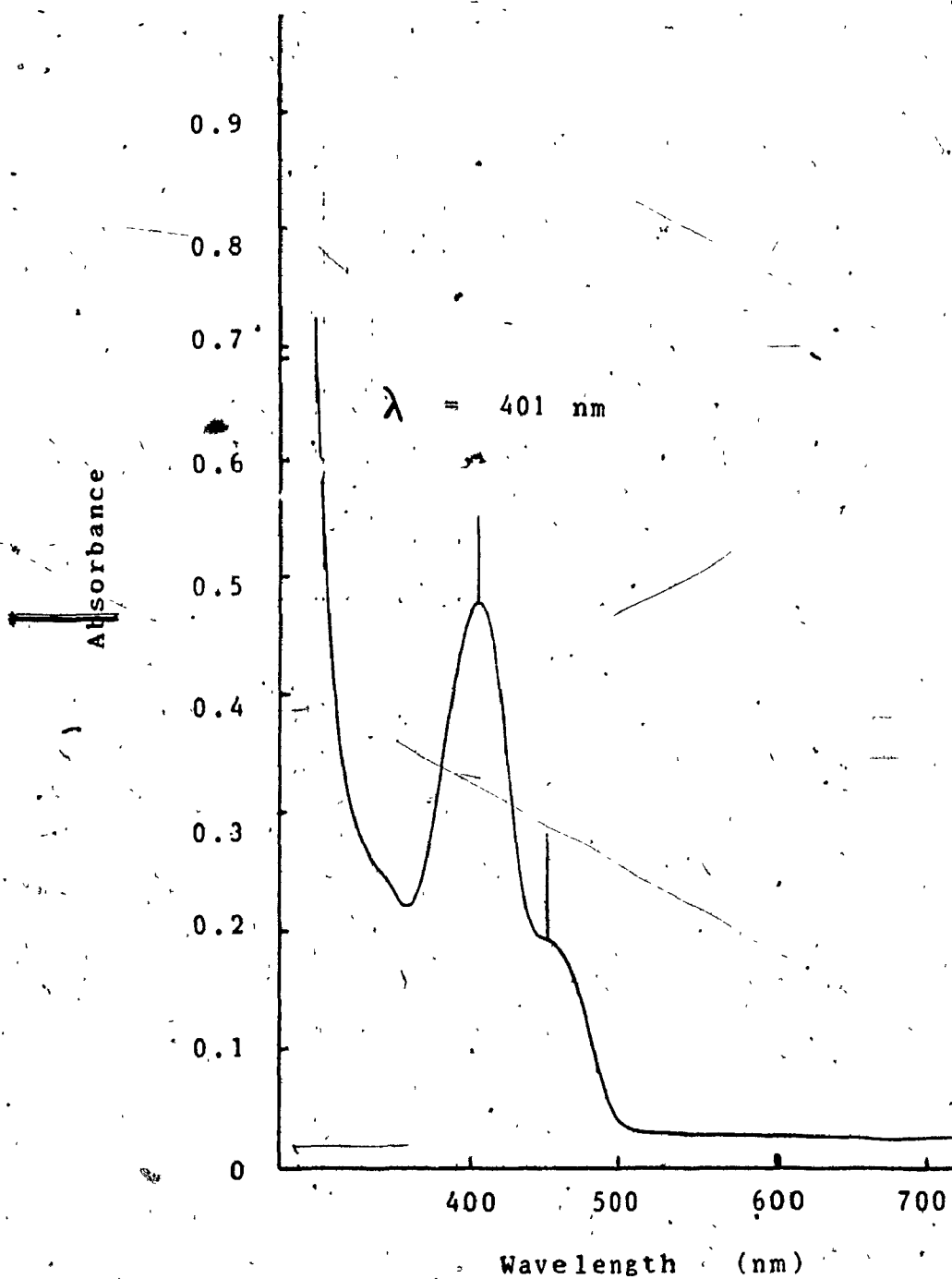


Fig. 3.27 Spectra of Recovered Crystals of the Peroxide-generated Species (in Acetonitrile)

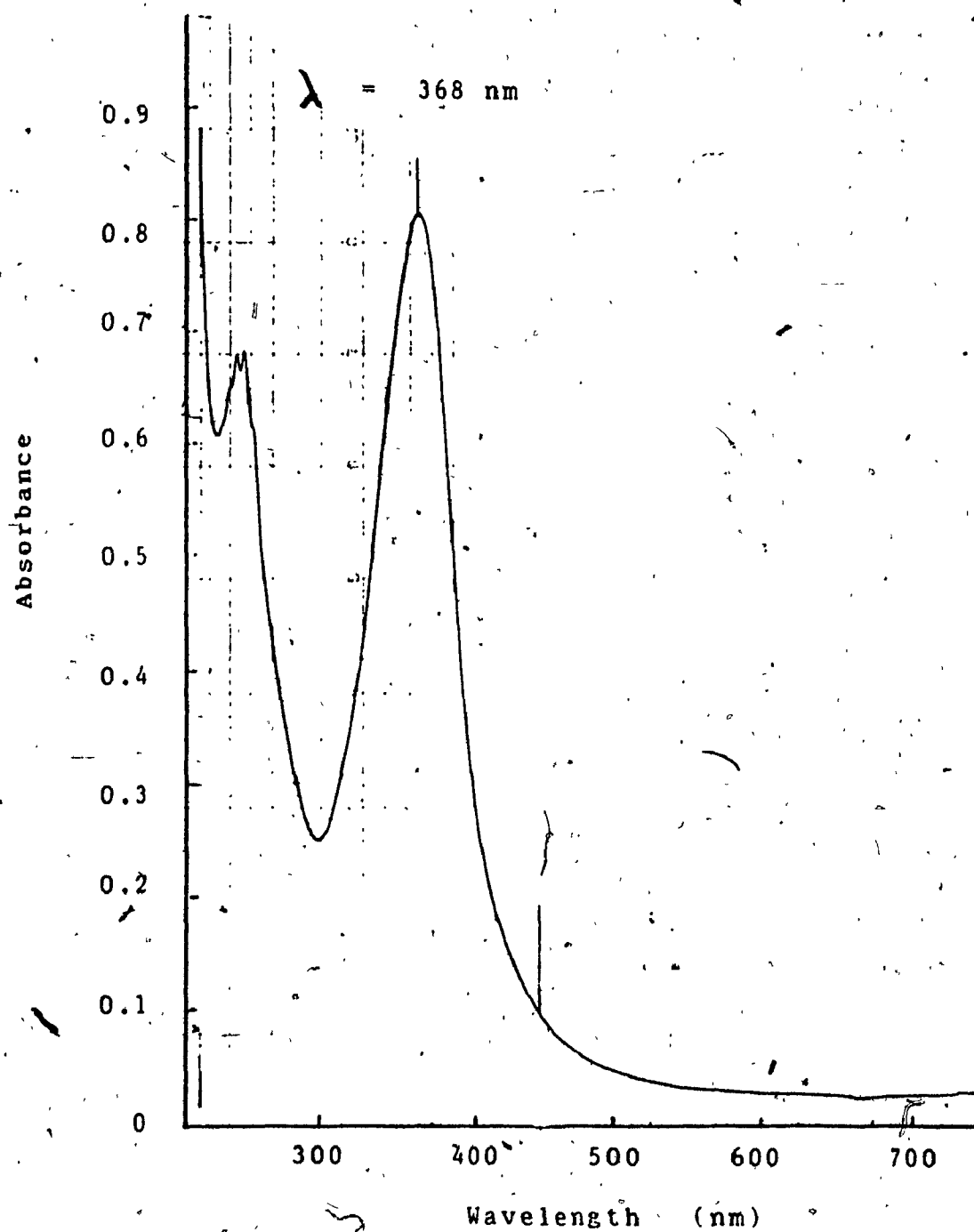


Fig. 3.28. Spectra of Na mnt (in Acetonitrile)

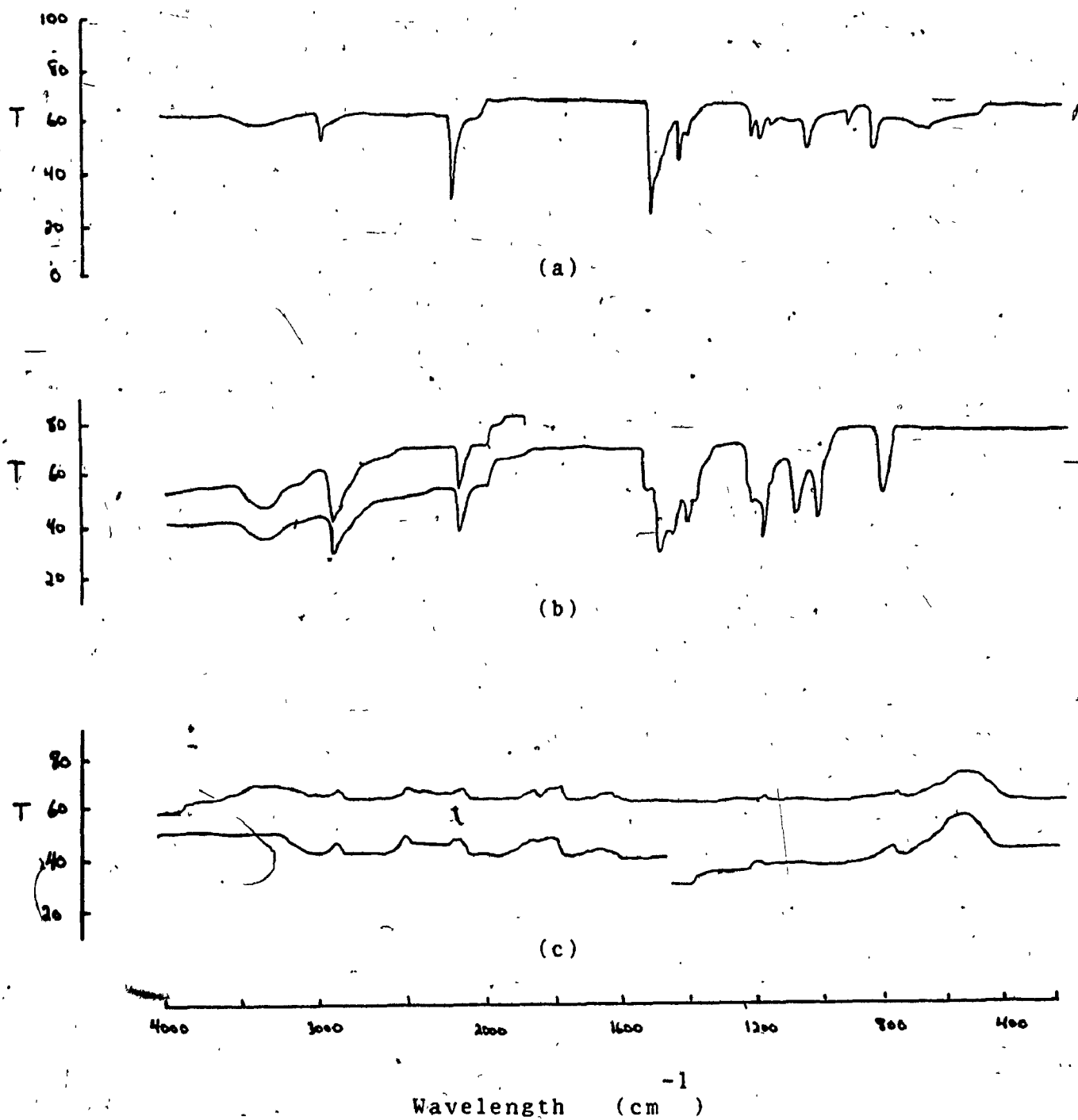


Fig. 3.29 Infrared Spectra of a) pure b) irradiated  
and c) peroxide-treated  $\text{Pt (mnt)}^{2-}$  crystals

CHAPTER 4  
-----DISCUSSION4.1 Prelude

The special properties of the metal dithiolates have generated much interest regarding photocatalytic processes. Their peculiar electrical properties, highly efficient redox reactions and the fairly stable, structurally similar ionic forms for each complex (ionic charge,  $n = 0$  to  $-3$ ) (figure A-2) make these compounds quite remarkable. Along with the capacity for electron-transfer over a wide range of potential values and strong charge-transfer bands in the visible region of the spectrum, these compounds are strong potential candidates for photocatalysis.

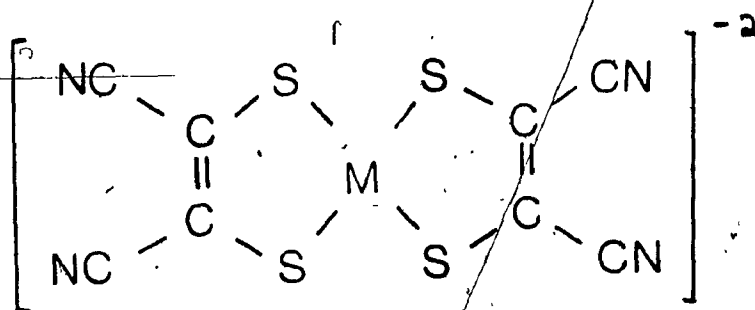
The chemical stability of these compounds can be easily underestimated. The usually reactive electrophillic sulfur groups present on the structure are strongly stabilized by resonance and this makes the complexes, as a result, unusually stable chemically, easily isolated and characterized (8,18,53). The slow interligand exchange

reactions common among dithiolates are not important in the complexes studied (Cu, Ni, Pd, Pt and Au complex exchange reactions are especially slow) (18). Solutions of the metal dithiolenes are not known to undergo any significant reactions when continuously irradiated with visible light (360-900 nm) regardless of the dithiolene concentration or the solvent utilized (54). Nonetheless, their ability to undergo a photoinduced electron transfer is of considerable interest. The absence of significant undesirable non-photochemical pathways which could severely interfere with any photochemistry permits the relatively straightforward examination of the rather simple photochemical systems.

The nitrile-substituted maleonitriledithiolate or mnt ligand, the most well-known and studied dithiolate ligand, forms very stable square-planar structures with several transition metal ions eg. Cu, Ni, Pd, Pt (figure 1.2) (20,31,32,39,41,42). The mono and dianionic forms, especially, have been studied extensively (Cu, Co, Ni, Pd, Pt, Rh, Re and Au) (25,30,51,55,56,57,58,59). Despite a relatively weak field character (similar to iodide), the ligand displays strong pi forces which contribute to extremely stable four-coordinate complexes eg. forms high melting point solids, are inert to substitution by most common ligands (CN<sup>-</sup>) and are resistant to the axial perturbations caused by solvent molecules (19,22,39). The structures exhibit no chemically significant distortion from planarity through several oxidation states. This

minimal structural change between different redox states is one reason for the rapid, reversible electron-transfers observed (20). The greater accomodation of electrons permitted by the strongly electron-withdrawing nitrile substituent also allows redox potentials to occupy the interesting range of values between +1.0 and -3.0V (vs. Ag/Ag+) (19).

The nickel, palladium and platinum dianionic ( $n = -2$ ) complexes are dark red, high melting, air-stable crystalline salts. These semiconducting and piezoresistant solids have characteristic solubilities dependent on the



M = Ni, Pd, Pt

Fig. 4.1 The Transition Metal mnts  
of Interest

counterion utilized (in this case tetraalkylammonium) (21). The monoanionic species ( $n = -1$ ), obtained via the one-

electron oxidation of the dianion, is slightly less water-soluble than the dianion (the dianionic species is only slightly soluble in water) but is also stable. Conversion of the dianion to the monoanion occurring at a very slow rate in neutral solution increases with acidity.

The reactivity of the excited states in these strongly absorbing compounds, as determined by photoactivity in the visible, shows that only the dianionic species of the Ni and Pt complexes are photoactive (metal to ligand transitions in the Ni and Pt complexes are photoactive; ligand to metal transitions in the Pd complex are inactive) (1). The photocurrents measured in homogeneous and heterogeneous systems are produced by lowest excited-states with relatively long excited-state life-times (4-7 nsec for Ni and 10-43 nsec for Pt) (1,2,3). The excitation energy of 1.45 eV for the Ni complex and 2.3 eV for the Pt complex for the first excited state and a  $-2/-3$  redox couple of -1.9 for Ni and -3.0 for Pt make both species potentially good reductants (excited state redox reaction energy is approximately -0.45V for Ni and -0.7V for Pt) (2). A longer-lived triplet, a greater redox reaction energy, and / or more suitable complex orbital energies have resulted in a markedly different behaviour for the Pt complex than for its Ni analog. This, as previously noted, has included indications of excited-state energy quenching (figure A-9) as well as evidence of electrocatalysis by the photoproduct (figures A-11 and A-



12) (1).

The processes which are seen to occur during the irradiation of the dianionic Pt complex require definition. It must be determined whether the complex is photocatalytic in visible light. Although, the existence of a clearly photoreactive redox process, the quenching behaviour and the evidence of an electrocatalytic process may suggest a photocatalytic process occurring, the actual mechanism of this behaviour has not been established.

#### 4.2 Semiconducting Particles and the Heterogeneous System

The poor solubility of the complex in water had supposedly created insoluble aggregates in the irradiated aqueous solution. The evidence indicated that these processes were occurring, in the presence of these particulates or aggregates in aqueous Pt mnt systems during irradiation (figure A-12) (1). This indicated that the system which might be responsible for the photoprocesses is heterogeneous. The participation of semiconducting particles was suggested in a manner reminiscent to other well known heterogeneous photocatalytic systems (7). To test this hypothesis, the initial manner of investigation involved a study of heterogeneous systems of the complexes in the form of aqueous slurries. Simple, reliable

heterogeneous solutions, in the presence of test compounds, would help determine the presence of any redox processes occurring with irradiation. Irradiations were carried out using the powerful but economical tungsten-halogen lamp which emits a strong white light with little ultraviolet component. With complexes of interest absorbing strongly ( $\epsilon = 3500$ ) at approximately 470 nm (blue), the intense white light was highly suitable and convenient for irradiation purposes.

The results obtained after lengthy irradiations of aqueous slurries containing redox test compounds such as the chlorinated compound, m-chlorobenzoic acid, and alcohols (ethanol, methanol and isopropanol) produced no measureable changes in concentrations in the presence of either the nickel or platinum mnt complexes. A facilitated oxidation of the dianion to the monoanion during the irradiation was observed (with the acid). Absolutely no changes occurred with the alcohols. Oxidation via photosensitized catalysis can be achieved in some systems using a third component acting as an electron relay and this was attempted with the alcohols using one such charge mediator ( $\text{CuCl}_2$ ) used in the photoactivated oxidation of alcohols by oxygen (47). After addition to the aqueous slurry and irradiation, there was still no change in the concentrations of the alcohols. Its relatively strong oxidizing capacity simply resulted in the outright

oxidation of the complexes upon contact. In aqueous systems containing a concentrated slurry (particulates) of dianionic Pt mnt, the air above the solutions was monitored after extensive irradiation. Samples showed no detectable hydrogen under any conditions so there is clearly no hydrogen generation in such systems. In spite of the significant amount of evidence for photoactivity in these systems, this must therefore not proceed very efficiently in a heterogeneous environment.

#### 4.3 The Homogeneous System and Photoreaction

The relative absence of any evidence of reactivity by the complexes in the heterogeneous systems and the corresponding absence of further evidence for the existence of relevant processes of interest does not explain some important observations eg. evidence of electrochemical (photocurrents produced and measured in the systems and observations of electrocatalytic behaviour) (1,2,3), picosecond flash photolysis (1,4) and quenching (photocurrent and excited-state quenching) (1,4). The existence of a photoinduced electron-transfer is clearly reflected in these processes which also suggest a possible reaction of the photoactivated species in solution. The absence of photoreactions associated with dechlorination, alcohol oxidation or water reduction in the heterogeneous.

systems underlines the need for a significant modification of the system.

The difficulty encountered with the precision of measurements and the substantial colour of slurries strongly suggested that the system might not be absolutely heterogeneous. Slurries filtered through a 0.1  $\mu$ m filter were found to retain a significant colour. They are, undoubtedly, slightly soluble and produce the slightly orange-red solutions observed. The presence of other ions assists solubilization. Experience with crystallization and recrystallization shows that a solution of the tetraethylammonium salt of Pt bis mnt in acetonitrile requires more than the simple addition of water to produce crystallization. In fact, an excess amount of counterion eg. tetraethylammonium is required to render the complex completely insoluble. Studies of the simple, easily isolated, well-defined and relatively heterogeneous systems demonstrated that little or no activity occurs in these systems during irradiation.

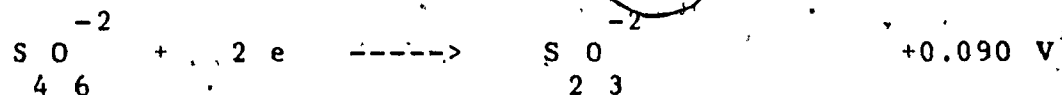
The investigation of a purely homogeneous system produced measurements which were more accurate and permitted any existing processes to proceed more rapidly and efficiently. Several solvents could be used to maintain these complexes in solution eg. acetone, methanol and acetonitrile. Of these, the preferred solvent used was acetonitrile eg. excellent solvent, resistant to oxidation and reduction, permitting reasonably high conductivities

and, of course, transparent through the entire visible spectrum and beyond (200-2000 nm) (44). Methanol was also used and found satisfactory. All components used for the irradiation solution were chosen so that only the dithiolene complex will absorb light ( $> 360$  nm).

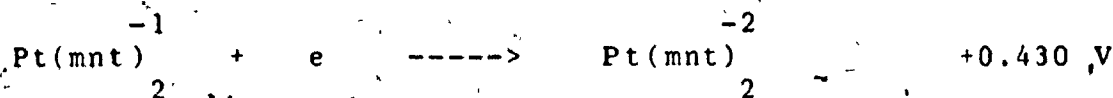
The immediate effect of irradiation on a concentrated homogeneous solution of complex (20.0 mM of each complex in 20% aqueous acetonitrile) was determined in a closed irradiation cell. No hydrogen was detected in the dead air space above the solution even at the highest sensitivity. Again, this is a suggestion of either a strong inhibiting factor in the system or that the process proceeds in manner not expected. The potential difficulties in the system may include unfavourably low catalyst concentrations, an inhibitory environment, the unfavourable solubility of a product or reactant or the low efficiencies inherent to such processes. In any event, the observed photoexcitation of the dianionic species with its subsequent oxidation does suggest activity. The actual mechanism occurring, however, is not definitely known. In order to modify the system in a possibly more favourable manner, a third component might be added. A reasonable candidate is an electron donor. The presence of a donor species favours a reduction process and increases the likelihood that the complex undergoes and maintains a reduction process eg. reduction of some component in the system. A catalytic turnover of the,

process is more likely and is highly desirable. A cyclic system would undoubtedly allow a better, more easily measured accumulation of the product.

Commonly used electron donor species, such as EDTA and triethanolamine (TEA), were found to be ineffective in the system. Presumably, this is because of their inability to reduce the oxidized monoanion to the dianion. The oxidized product accumulates in the system and the reaction stops. It became necessary, therefore, to employ a better reducing agent as electron donor in order to get a reaction started. A logical choice for this reductant was the thiosulphate species. Already used in the purification of synthesized mnt complexes and in the reduction of oxidized complex, this mild reducing agent (the sodium salt) can also be used to readily monitor the system using a redox method of analysis. The changes in the thiosulphate concentration as measured from samples taken periodically from the irradiation cell could now be followed accurately.



(a)



(b)

A relatively accurate knowledge of the behaviour of the true reductant concentration in the system and the actual progress of the probable redox reaction of interest in the system with time was hence obtained. The rate of oxidized complex generated during the irradiation was measured and correlated to the amount of reduction occurring in the sample irradiation cell.

To maintain a homogeneous system, the thiosulphate salt was dissolved in an aqueous acetonitrile solution. Unlike metal mnt complexes, thiosulfate is quite insoluble in acetonitrile. Its solubility in water requires a system that maintains both these electrolytes in solution and, thus, requires a mixture. It was readily determined that a 50% (V/V) aqueous acetonitrile mixture easily maintains a homogeneous solution and only a radical change in solvent percentage would affect the system (> 75% MeCN required precipitate thiosulphate). In this case, a simple system, easy to sample, was obtained.

The solutions of buffered, as well as, unbuffered, aqueous acetonitrile (1:1) containing dilute and concentrated amounts of thiosulfate readily maintain their reducing equivalents and stability over the space of several days and more (concentrations remain constant). The iodimetric analyses of relatively small precise samples of solution from irradiation solutions necessitated the use of a dilute iodine titrating solution (25.0  $\mu\text{M}$   $\text{KI}$ ). This assured the adequate titrating volume required (at least 10<sup>3</sup>

ml) for the small volumes analyzed (0.500 - 1.00 ml). During irradiations, the systems were closed in order to prevent the rapid evaporation of the acetonitrile and the resultant errors from the modified donor concentrations.

The irradiation of an unbuffered 50% aqueous solution of acetonitrile containing the complex, electron donor (thiosulfate) does produce a decrease in the thiosulfate concentration. A limited reaction occurs in the presence of light and no change in the homogeneity of the solution can be observed or detected. It is a photoreductive reaction which uses up available electrons from the thiosulphate donor species. The reaction does not, however, achieve a turnover in this system (the quantity of substrate consumed is less than the quantity of complex present).

#### 4.4 Turnover and Catalysis

Increased donor concentrations in the irradiation solution and comparison of blank, dark and irradiated solutions help verify the behaviour observed in solution during irradiation. The unfiltered irradiation of a solution with an increased concentration does produce a significant decrease in donor concentration again but, this time, a turnover is quantitatively measured (1.8 times the complex) indicating that a catalytic process may be occurring. The reaction is short-lived, however, and



eventually halts. Buffer solution resumes the reaction which suggests some dependence on solution pH.

The presence of a buffer in the irradiated solution is required for reaction. A buffering capacity in the solution may be favourable to the photoprocess by preventing a halt in the reaction due to the inhibiting basic products generated (producing an unfavourable pH gradient). The irradiation of such a buffered (pH 6.0) solution produces a clear decrease in the thiosulphate concentration with no noticeable changes in a comparable blank or dark reductant concentrations. The significant decrease in concentration and good apparent rates of reaction follow a clearly linear behaviour. A good number of photocatalytic turnovers are now achieved ( $> 10$ ) (a catalytic process is occurring):

The observation of a distinct bleaching effect occurring during irradiations of the complex in solution produced suspicions that an uncompensated high energy component from the light source might be producing undesirable effects on the complex. The introduction of a 340 nm ultraviolet cutoff filter, capable of removing any high energy light present, showed that observed processes still occur. The rate of reaction is only slightly reduced. The filter does, however, reduce bleaching of the solution. Extensive irradiation of the filtered solution will decrease the thiosulphate concentration to nearly zero and

produce significant turnover numbers. In a relatively concentrated solution of thiosulphate (24.0 mM), the turnover is at least 44 times. When exhausted, additional thiosulfate can be added to the solution continuing the process until all is consumed again. In excess of 50 turnovers has been achieved and there does not seem to be any limit to the reaction. The reaction proceeds indefinitely. The reaction does not proceed to any extent in the dark and it is stopped when the light source is removed. The irradiation of an identical solution containing the Ni mnt complex produces no decrease in thiosulfate concentration and shows no comparable photoactivity. The extensive irradiation of a blank irradiation solution (no complex), meanwhile, confirms the stability of the thiosulphate species in this solution within the time scale of these experiments. Irradiation of a deaerated system gives inconclusive results due to significant solvent volatility.

The introduction of a 420 nm cutoff filter (rejecting 98% of light from projector below 425 nm) further isolates active wavelengths for subsequent experiments. In addition, significantly more accurate calculations are now obtained from the system with the frequent monitoring of the titer of the iodine titrant solution. Increasing the donor concentration again produces a significantly greater donor to complex ratio (40.5 mM or 91x) which, upon irradiation, produces the substantial substrate decrease expected (-25.0

mm at -3.33 h<sup>-1</sup>). The high turnover (over 50x), highly indicative of the significant reaction process occurring in the system, also indicates a significant product formation. A measurable amount of product may now be present in the system. A sampling of the air layer above the solution shows that no hydrogen is present. Increasing concentrations is not found to increase the reaction rate in a manner normally associated with rate-limiting components and it has become increasingly obvious that the rate-limiting condition of the process does not involve either substrate or complex. A third component must exist in order for the process to proceed. An irradiated system is successfully degassed (using an acetonitrile bubbler) and the underlining behaviour of the process is clearly demonstrated when all activity ceases. The process requires oxygen in order to proceed. The addition of an electron relay species (methyl viologen) does not help induce any further oxygen-free process. Any possible water reducing process by the complex is definitely absent. The photoprocess which had been identified in systems containing dianionic Pt mnt is not a water reduction mechanism. It must involve, however, a photoactivated facilitated oxygen reduction mechanism.

#### 4.5 Oxygen Dependence

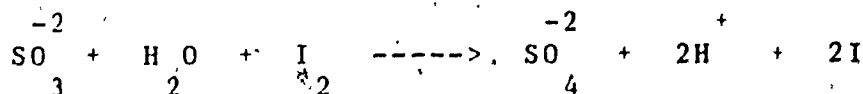
Although the importance and extent of oxygen involvement in the photoprocess occurring in these systems had been previously known and considered, it had been regarded as a slow secondary process with little or no effect on the fast primary electron-transfer processes (1). In this context, the relatively slow oxidative processes occurring in various conditions (especially acidic media) eg. dilute aqueous acid solutions were considered normal albeit intriguing. The inactivity in a deaerated system during irradiation showed beyond all doubt the exclusivity of the oxygen-dependent processes.

Exposure of an irradiation solution to a larger source of oxygen eg. a larger volume of air would, undoubtedly, have a strong influence on the behaviour of the system. A separatory funnel placed over the irradiation cell ground glass joints provided a large volume of air to the irradiation solution surface (less than 1 ml air available with stopper; over 250 ml with funnel) and allowed a continuous exposure to a larger oxygen reservoir. A filtered (400 nm and I.R. cutoff), focused (centered on cell window) light was used to irradiate several solutions with varying donor concentrations. Besides the normal high turnover rates obtained, generally higher rates of reaction

were obtained in all cases. No outstanding trends in the rates could be detected despite the widely varying concentrations. An increased supply of oxygen, therefore, increases the rate.

Irradiation of solutions buffered at different pH values while exposed to an air reservoir do not show the strong pH dependent behaviour which had been suspected. Solutions with values other than pH 6.0 do seem to undergo a slowed process rate but, generally, the actual difference is much less than would be expected from such a dependence and indicates that pH-dependance is of little actual significance in these systems. In the presence of no buffer, the reaction will still proceed when exposed to air at an uninhibited rate.

The irradiated Pt mnt system resists available electrons from other common electron donors. Therefore, a reducing species comparable to thiosulfate is necessary for the reaction to proceed. One such reducing agent is sulfur dioxide. Dissolved in water and neutralized to more moderate pH values (producing hydrogen and neutral sulfites) (29), the solution readily reduces the oxidized Pt complex. Solutions of sulfur dioxide or sulfite can also be monitored in solution using the same titrimetric procedure used for the thiosulfate via the reaction:



A neutralized (pH 6.0) solution of sulfur dioxide or hydrogen sulfite,  $\text{HSO}_3^-$  (the main species) is stable over a short period of time in an aqueous solution despite the slow, kinetically-hindered oxidation which occurs in the 4 - 8 pH range in the presence of molecular oxygen. The oxidation product is primarily sulfate with only an infinitesimal amount of dithionate. In the presence of acetonitrile, however, there is an unaccountable acceleration of this oxidation in normal ambient conditions. This unusual instability of the sulfur dioxide in acetonitrile creates the need for another solvent in the system. Methanol is a satisfactory solvent and the sulfur dioxide species are stable in this new system (a 50% aqueous solution of methanol). The addition of the thiosulphate donor does not affect the stability of this system. Irradiation (400 nm and I.R. filters, pH 6.0, 25°C, exposed to air) produces a decrease in the thiosulphate concentration but at a significantly reduced rate (approximately 1/2) versus the acetonitrile system indicating that the methanol environment has an inhibiting effect on the ongoing process. Irradiation of the methanol system with sulfur dioxide donor, however, produces an apparent reaction rate which is significantly greater than those obtained in any of the previous thiosulphate systems. The observed inhibiting effect in methanol is greatly overshadowed by this increased rate. An interesting

observation is the appearance of an "induction" period during the course of the irradiation. The lack of reaction in the initial stages of irradiation (during first 30 minutes) is followed by the accelerated decrease of donor. Previously examined systems using thiosulfate may also have this induction effect but was not observed (presumably due to the less favourable reaction conditions present).

The importance of oxygen in the photoprocess as well as the presence of an induction period during the irradiation suggested that a purely oxygen atmosphere (100% oxygen versus 20% in air) would have a significantly different effect on the process. When several buffered and unbuffered irradiation solutions were irradiated with filtered light in the presence of pure oxygen, a more clearly defined process did emerge. All solutions (pH 5, pH 6 and buffer-less) produced the same substantial decreases of the donor concentrations. The rates of the process were significantly enhanced by this increased availability of oxygen. Also, the induction period previously seen in the sulfur dioxide system is now clearly visible in the thiosulfate system. The change in behaviour between the air and oxygen systems are obvious and significant and this determines that a reaction dependence on oxygen exists in the system.

#### 4.6 Electrochemistry

The evidence suggesting the existence of an electrocatalytic process, after irradiation by the complex necessitated a re-evaluation of the electrochemistry of the system. Using the Ag/Ag<sup>+</sup>, 0.010N NO<sub>3</sub>, 0.100N TEAP (tetraethylammonium perchlorate) reference electrode (+0.532V vs. NHE), voltammetric scans were obtained in non-aqueous as well as in aqueous irradiation solutions (water / acetonitrile mixtures). A comparison between systems helped to determine any behaviours induced primarily by the solution environment.

Preliminary voltammographic scans of dianionic Pt mnt in acetonitrile showed that the complex readily maintains its stability only in the range of potentials lying between -1.0 and +0.4V versus the reference electrode (+0.468 and +0.932V vs NHE). Scanning more anodically results in a significant decomposition process underlined by the appearance of distortions or artifacts in the redox waves due to decomposition products. Stable, reliable scans of the solution require that the scans be limited to the potential range between -1.00 and +0.40 volts versus the reference. The scan of a solution of Pt complex then results in the characteristic voltammograms of the complex. These voltammograms show the highly reversible nature of



the electron-transfer process in this complex.

Relatively concentrated solutions of dianionic Pt mnt  
( $5 \times 10^{-4}$  M) were irradiated under varying conditions to  
determine the effects on the voltammograms. In deaerated  
conditions, the solution doesn't undergo any changes in the  
voltammogram even in the presence of a significant amount  
of water. The presence of oxygen does produce a significant  
change, however, which has nothing to do with  
electrocatalysis. Increasing the sensitivity of the scan  
produces a voltammogram that resembles a solvent wave  
(figures A-11 and 3-15) but is caused, basically, by new  
components generated in the solution during irradiation.  
Previous observations of precipitates appearing in the  
irradiated solutions were never observed here under any  
condition.

#### 4.7 Spectroscopy

The Pt complex and other mnt complexes have  
distinctive and characteristic absorption spectra (figure  
A-3). In ambient conditions, the dianionic and the  
monoanionic forms of the Pt complex consist of the two main  
oxidation forms and they possess differences in spectra  
which are characteristic. A change in the oxidation state  
of the complex during irradiation can, therefore, be  
observed readily. The spectrum of the complex in an

acetonitrile solution also does not change to any extent when water and / or thiosulphate are added to make the irradiation solution (50% aqueous solution of  $5 \times 10^{-4}$  M Pt complex).

The nickel complex does not undergo any change in spectra upon irradiation. The platinum complex spectrum, however, changes significantly when exposed to a light source. The initially bright red solution bleaches to a light orange and, with continuing irradiation, achieves a pale yellow colour. This resembles a decomposition process but the spectra indicate that a relatively intact complex exists. Only a shift in the main absorption band towards the blue occurs. The actual decomposition reaction produces a colourless solution (when excess peroxide added). This yellow form is relatively stable to any further changes during irradiation or upon standing. This species is not the dianionic nor the monoanionic form since these have distinct absorptions and can be manipulated with redox reagents eg. the dianion can be oxidized, the monoanion reduced. The irradiated solution is relatively stable to redox reagents. No change in colour occurs when the system is deoxygenated.

Solution spectra of an irradiated solution containing buffer and thiosulphate show that a rapid change occurs during irradiation. The dianionic main visible absorption band at 470 nm shifts to the new more intense absorption

region at 390 nm. Within the first twenty minutes of irradiation, the absorption band of the dianion rapidly disappears and the new absorption band, distinct from the dianion and monoanion absorption regions, gradually appears. This is a new previously unknown species and the process occurring is clearly not a simple oxidation reaction. The absence of substrate from the irradiated solution allows a small monoanion concentration to appear which indicates that oxidation of the dianion does occur in this solution.

Changes in absorbance at the various wavelengths of importance during the irradiation of a buffer-less and substrate-less solution shows a clear trend in the behaviour of the various components. The particularly significant wavelengths at 390, 465 and 750 nm, corresponding to the new, the dianionic and the monoanionic species, indicate that there is the appearance of a relatively small but constant concentration of monoanion and a decrease in the dianion concentration. The unknown species rapidly increases in concentration. Subsequently, a slow decrease in all concentrations then occurs. This can be interpreted as a general decomposition reaction occurring in the system with continued irradiation.

The behaviour of the unknown species can be readily correlated to the measured photocatalytic activity of the system. The induction period observed during irradiations can then be explained as the time required to generate the

new photocatalytic species. A change in filter from 400 to 420 nm reduces the rate of generation of the new species while increasing the quantity of monoanion. There is also an increase in the observed rate of decomposition in the system. Although the irradiated solution has practically no oxidized complex even in the absence of reducing agents, it is found that the addition of a reducing agent to the solution will, nonetheless, produce a change in the spectra. This indicates the presence of some reducible component.

The reduced alkaline phenolphthalein used to determine the oxidant in solution demonstrated the existence of a generated oxidant during irradiations. Correlation of the absorbance of the indicator with a known concentration of hydrogen peroxide resulted in a concentration versus time plot during the irradiation of a substrate-less and buffer-less solution. It shows the generation of a high concentration of strong oxidant within ten minutes and attaining a relatively steady state.

The intermediate species identified in spectra of irradiated solutions can be isolated by crystallization from a buffer-less and substrate-less solution. A spectrum of the crystals obtained shows the characteristic spectrum of a pure component and supports the existence of this new species as a separate component in the solution. The changes in spectrum obtained in a solution of complex after

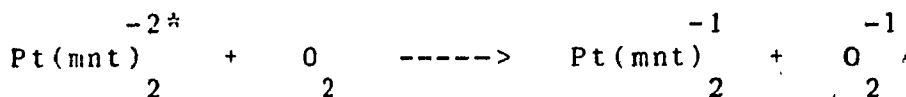
the addition of a significant concentration of hydrogen peroxide suggests that a concentration of a peroxide-like species is generated during irradiation. The dianionic species in solution is oxidized to some extent but it is basically transformed into a new species. The peroxide is generated using oxygen and thus is presumably hydrogen peroxide. This peroxide concentration converts the complex into a peroxo intermediate which then photocatalyzes the ensuing peroxide generation. This new species, appearing at 390 nm, is the same in both the chemical and photochemical reactions. A spectrum of this peroxide-generated component again shows the presence of the intermediate species (at 401 nm). Comparison to sodium mnt (at 367 nm) confirms the distinctly novel species.

Infrared spectra of various components were taken to examine any possible changes in the structures. The Pt mnt dianion (figure 3.29a) shows the characteristic frequencies of this species. Crystallites recovered from an irradiated solution (figure 3.29b) do not show a significant deviation in structure from the dianion structure. The appearance of new peaks at 1530, 1400 and 1210  $\text{cm}^{-1}$  however do represent significant differences. The peroxide-generated component (figure 3.29c) shows a very weak spectrum due to advanced decomposition occurring during crystallization but still exhibits a faint mnt pattern. In all cases, peaks that would be indicative of the presence of oxygen (1145, 770, and 1556  $\text{cm}^{-1}$  representing superoxide, peroxide and

molecular oxygen) are noticeably absent or very weak.

#### 4.8 Mechanism

Despite the similar chemical properties, triplet states and photoactivities (2), the observed photoreactive behaviour of the Pt complex, versus the similar but nonreactive Ni complex is quite different. This may be related to a slightly longer excited-state lifetime, more favourable energy levels or the existence of a higher photoexcitation energy in the Pt complex. The photoexcited



Pt complex will readily donate an electron to available oxygen. In the absence of oxygen, no other photoreactions will occur. The oxygen participates and is necessary to initiate the photocatalytic process in which any appropriate donor species in the solution is oxidized. There is no significant pH dependence and the temperature dependence is difficult to determine. Reaction rate probably increases with temperature but reduced oxygen solubility (the main rate-limiting component) undoubtedly readily counteracts the effects. The photocatalytic process begins with the reduction of oxygen and the formation of

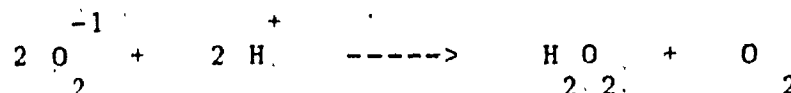
superoxide and / or, hydrogen peroxide. There is, presumably, a change in the oxidation level of the catalyst during catalysis. The cycle continues until the donor population is depleted. The process proceeds regardless of the system and the level of oxygenation determines the rate.

The species responsible for the photocatalytic activity is not the dianionic or the monoanionic form of the complex. A new intermediate species, absorbing at 390 nm, appears rapidly during irradiation in the presence of oxygen. The photocatalytic activity and the induction period observed in the irradiated systems can be correlated to the appearance of this new unknown species. The detection of a peroxide-like component generated during irradiation can also be correlated to the appearance of this species. There are, possibly, two steps to the reaction: a pH-dependent initial photoreaction (reduction of oxygen, generation of intermediate) and a subsequent pH-independent photocatalytic process involving the new species (generation of peroxide).

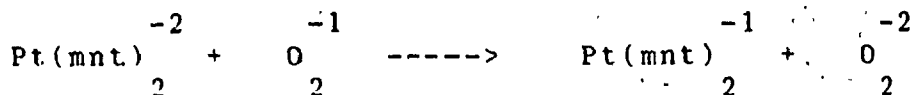
The species can also be generated chemically by exposing the dianionic form to hydrogen peroxide. It can be re-crystallized and isolated from both the irradiated solution and the peroxide-generated solution. It is a reddish-brown, thermally-unstable solid. A high concentration of peroxide is required to decompose the Pt

mnt complex. The Ni mnt complex, on the other hand, rapidly decomposes with any amount of hydrogen peroxide (all chromophores in the solution are destroyed). An intermediate Pt mnt complex species must therefore exist. The infrared spectra indicates that the new species does not vary greatly in structure from the parent compound.

After the initial reduction of oxygen and the generation of superoxide, the simplest mechanism for the reaction consists of the formation of peroxide via disproportionation of the superoxide. The rapid and



complete disproportionation which normally occurs in aqueous solution ( $K = 4 \times 10^{20}$  at pH 7) (60) is not, however, observed in the system. The low superoxide concentration generated cannot sustain a significant peroxide level by this pathway. The reaction may also occur via the reduced complex which could itself reduce the superoxide to peroxide.



These mechanisms are unlikely to be significant, however, in irradiated solutions. The complex can be



observed to undergo significant and irreversible changes. The changes in absorption and the presence of an induction period in the reaction also suggest that a transformation of the complex has occurred. A mechanism of interest is adduct formation. The existence of superoxide-complex would imply that a dissociation is a possible rate-limiting step. The dissociated complex could reduce bound superoxide. The very low concentration of this species in irradiated solutions would thus help explain the slow rate.

A more detailed reactive sequence for the reaction occurring in irradiated systems containing the Pt complex can be obtained by examining known reactions of other transition metal bis-dithiolenes. Reaction mechanisms have been forwarded for some dithiolenes such as the dianionic rhodium mnt complex (theoretical) (figure 4.2) (61). There

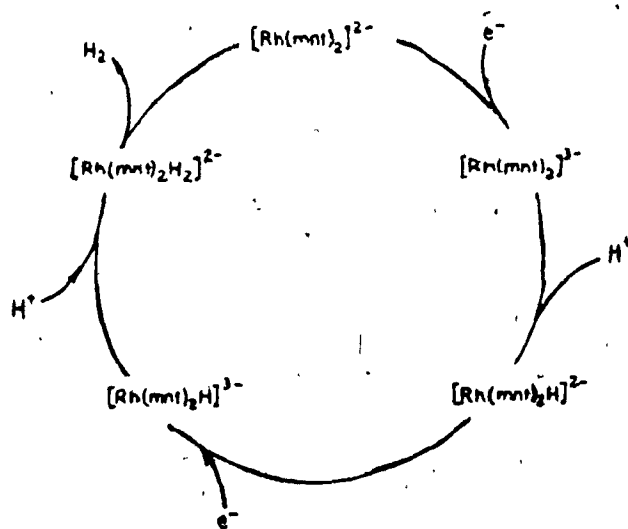


Fig. 4.2 Hydrogen Generation Scheme  
for a Dithiolene

have also been some reports of dithiolene photocatalytic water reduction (62,63), however, the promise of these dithiolenes has so far remained unfulfilled. The reactions of dithiolenes can, nonetheless, be used to determine the mechanisms occurring in our system. The reactions with dithiolenes can proceed either via an attack on the sulfur

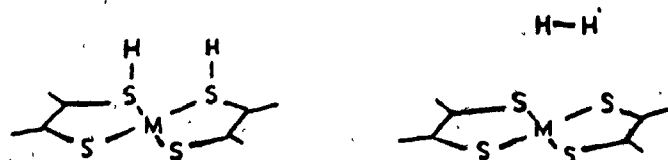


Fig. 4.3 Reaction Using a Sulfur  
Centre

atoms (figure 4.3) or an attack via the metal centre (figure 4.4) (61). Assuming that the process occurring

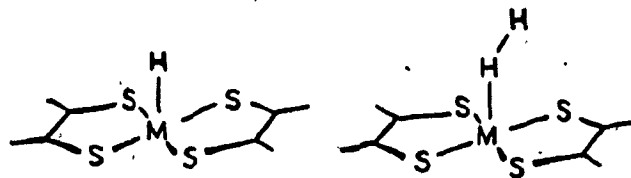


Fig. 4.4 Reaction Using the Metal  
Centre

during irradiation follows one of these reaction pathways,

an attack on the metal centre can be considered more likely since an attack on the sulfur would presumably lead to a rapid decomposition.

Many complexes can react with oxygen to form adducts, sometimes reversibly eg. if the resulting bonds are long enough, the reaction may be reversible (64). A strong oxidant, oxygen's reactions are subject to the inherent kinetic limitations due to spin restrictions and the large free energy requirements for the first of its four one-electron reduction stages (65,66). The activation of oxygen is often effected and controlled via transition-metal centres. Reactions of metal complexes with oxygen are, therefore, often related to biological and industrial catalytic oxygenation (67). Diamagnetic, monomolecular oxygen is known to complex reversibly with platinum metal centers forming triangular complexes with the two oxygen atoms bound equivalently (67). This coordinated oxygen is more reactive and can oxidize many compounds of interest including sulfur dioxide. The stoichiometric reaction of coordinated oxygen with sulfur dioxide to form coordinated sulfate is a reaction characteristic of these oxygen complexes. Free oxygen can also react with a metal-sulfur dioxide complex (67). The new species may be an ionic salt of superoxide; such salts (superoxo complex) are yellow to orange solids and are known to occur in certain metal centres (60).. Superoxo complexes are known to reduce each

another giving a peroxo complex. These are usually unstable and undergo further reactions to give oxides or hydroxides (60).

Among relevant catalytic processes, a reaction occurring in systems containing the dianionic Co mnt complex yields results similar to those obtained (68,69). This

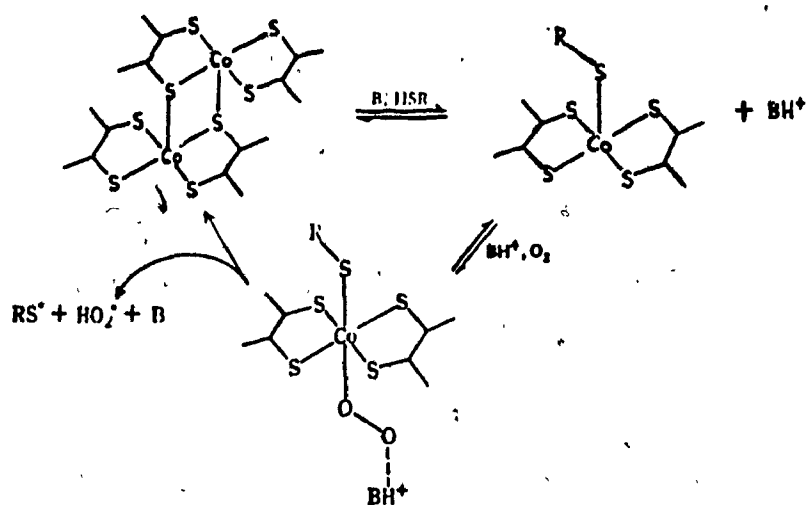


Fig. 4.5 The Autocatalyzed Oxidation of Substrates

complex, closely resembles the Pt complex, and also promotes the autocatalyzed oxidation of several reductant substrates (figure 4.5). A kinetic activation of molecular oxygen is involved. The dithiolene complex catalyst activates the reductant and the oxidant by coordination, transmitting one electron (via the coordinated oxygen) (69). The reaction is dependent on a bimolecular catalytic complex, buffer and the inert salt present (69). Water has

little effect or influence on the stoichiometry. There is no catalytic effect by either  $\text{CoCl}_2$ ,  $\text{mnt}^{-2}$  or  $(\text{mnt})_2$  (decomposition products). These and the following are among characteristics very similar to the Pt mnt system. There is a change in spectrum during reaction which is also related to the generation of an intermediate and attributable to binding onto the complex. Subsequently, there is a facilitated binding of dioxygen to the metal centre. A distinct catalyst deactivation also occurs which accelerates once the substrate is used up. The deactivation is related to substitution by peroxide in a manner analogous to substitution occurring with other nucleophiles (70). Of the two types of mechanisms for catalysed redox reactions (ping-pong or via separate oxidation levels of catalyst; reactants react separately and sequential coordinative; one oxidation level and activation by coordination), the sequential coordination mechanism is considered to be the most likely process (68). It is not assumed that substrate binding occurs but a similar mechanism undoubtedly occurs in the Pt mnt systems.

As a result, it is reasonable to assume that the photoexcited Pt complex binds oxygen forming a superoxo-complex (figure 4.6). This relatively stable species is then subject to further reduction and excitation and peroxide is generated.

Only a simple electron-transfer occurs between thiosulphate and the Pt complex species. Bisulfite will,

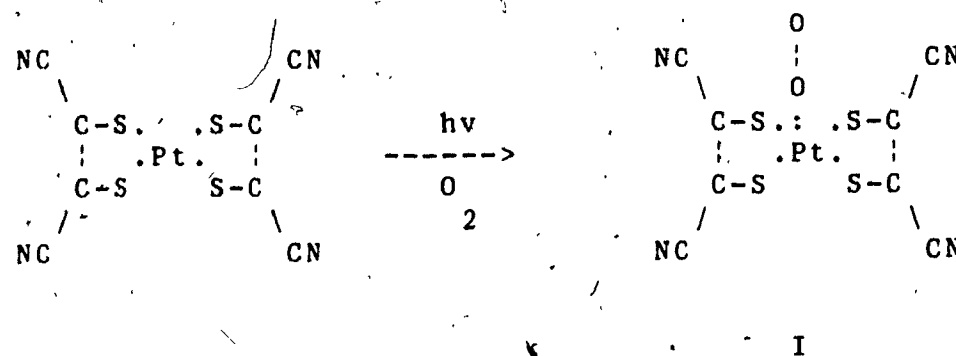
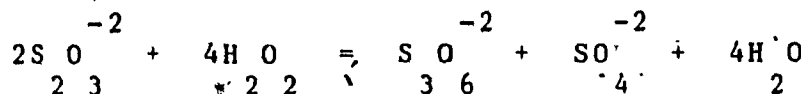


Fig. 4.6 Formation of the Intermediate or Oxygen Adduct. (I)

however, actually bind to the activated dioxygen in order to produce sulfate (the oxidation product of bisulfite in the pH range 4 - 8 is primarily sulfate). The product of sulfite and hydrogen peroxide is primarily sulfate too (71). In the system examined, we find that sulfate is the main reaction product produced in the reaction. The product of thiosulphate and peroxide is also generally sulfate ( $k = 5.5 \times 10^{-1} \text{ lit. mol}^{-1} \text{ sec}^{-1}$ ,  $E_a = 17 \text{ kcal mol}^{-1}$ ) and involves the stoichiometry :



In our system, however, we find that sulfate isn't produced. Hydrogen peroxide reacts with sulfite producing almost exclusively sulphate (the two peroxide oxygens are

transferred). This probably proceeds via a nucleophilic displacement by the peroxide on bisulfite to form a peroxomonosulfurous acid intermediate which then undergoes a rate-determining rearrangement (73). The primary oxidation product is sulfate (not dithionate, therefore this is not a radical pathway) (71). The reaction between oxygen and bisulphite in the presence of a catalyst usually displays an induction period where little or no reaction occurs. This is followed by an almost linear decrease in the bisulphite concentration. This as well as its complex kinetic behaviour can be explained by the existence of a chain mechanism involving a series of cobalt complex intermediates (73). Sulphite and bisulfite are known to be an excellent complexing agents and they will coordinate easily to a metal atom (through the sulfur atom) (71).

A decomposition of the catalytic species occurs slowly during irradiation. The decomposition proceeds much more rapidly when the donor concentration has been depleted. The generated intermediate is attacked by unused peroxide product destroying its chromophoric properties

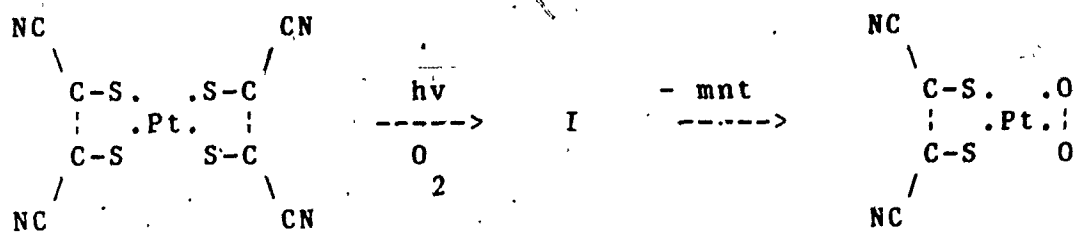


Fig. 4.7 Decomposition Process via Ligand Substitution

(figure 4.7).

The evidence has contributed to help elucidate the type of processes occurring in the irradiated systems containing the dianionic Pt mnt complex. We have found a system that photogenerates a peroxide concentration via a superoxo intermediate. The photoactivation of oxygen occurs by coordination at the metal site and uses electrons from available reductants.



## CHAPTER 5

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### CONCLUSION

A relatively stable, photocatalytic redox process has been established in a homogeneous solution containing the dianionic Pt mnt complex and a suitable electron donor species during irradiation with visible light. In the systems examined, several mild reductants were used to maintain the reaction. These included the thiosulfate and the bisulfite species and may presumably also include any other reductant species which can effectively reduce the mononanionic form of the complex. These electron donors are able to sustain a photoreaction whose extent in the presence of a small quantity of complex clearly indicates that the process is catalytic. The driving force of the reaction is the photoinduced activation of oxygen.

In their present state, the systems investigated cannot produce hydrogen to any measurable extent upon irradiation with visible light. Also, a clean, oxygen-free solution of the dianionic Pt complex does not exhibit electrocatalytic activity. The precipitation of Pt mnt complex aggregates reported to occur after irradiation is

likewise not readily observed. It is clear, however, that a photocatalytic consumption of oxygen occurs. During irradiation, there is the generation of a peroxide-like species. In the photoexcited state, the dianionic complex slowly reduces all available oxygen. The product, a peroxide species bound or unbound to the platinum complex activates the complex producing a new, previously unreported intermediate species. The appearance of this species can be related to the accelerated photocatalytic activity since the increase in the rate of photoactivation of oxygen can be related to its formation. The appearance of the intermediate is accompanied by the rapid disappearance of the dianionic form. A significant concentration of peroxide is generated in the solution and rapidly consumes all reductant species. The previous suggestions that processes observed in the system were related to quenching and electrocatalysis can now be attributed to strictly oxygen-dependent processes.

The photocatalytic species generated in the homogeneous system during irradiation must be an adduct of superoxide or peroxide since (i) there is no fundamental change in infrared spectral positions indicating little actual structural change, (ii) a similar system has already been reported to exist with dioxygen involving a closely related complex (Co mnt) and (iii) the photocatalyst is gradually degraded during irradiation due to the presence

some destructive agent. This also helps explain the changes in absorption and the existence of an induction period. Hydrogen peroxide quickly degrades the nickel complex on exposure while degradation of the platinum complex occurs in the presence of a sufficiently high concentration. Hydrogen peroxide in close proximity to the complex would have the effect of a high concentration and is, therefore, the leading candidate for the peroxide species generated.

In conclusion, solutions of the dianionic Pt mnt complex will rapidly generate a high concentration of peroxide when irradiated with visible light. This behaviour provides a convenient method to generate a controlled concentration of peroxide in solution eg. for synthesis, degradation, sterilization, etc. It has also been found to readily degrade sulfur dioxide present in solution to its sulfate product. The system can be of some interest to oxygen-metal studies.

There is a possibility of optimization of the desirable characteristics in the dithiolenes. As such, a better light-harvesting ability eg. higher extinction coefficient, lower wavelength absorption and better properties eg. more efficient electron transfer, greater selectivity towards a particular desirable process ( $H_2O_2$  generation or detoxification abilities) would be highly desirable features for a potential photocatalyst. A variety of such modifications to dithiolene systems are possible. The already great number of known dithiolene structures

possess a good variety of chemical properties, can absorb at a variety of wavelengths and undergo redox reactions over a wide range of potentials. With further investigations, the desirable characteristics of a potential system could be optimized by design helping achieve an ability to plan the evolution of increasingly efficient and selective photoactive catalytic systems and furthering the ultimate objectives of photocatalytic research.

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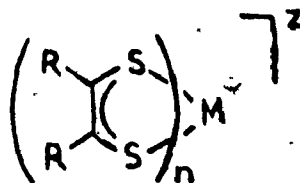
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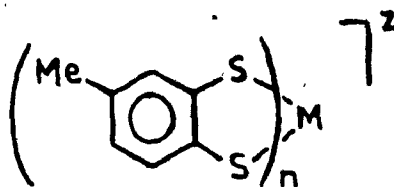
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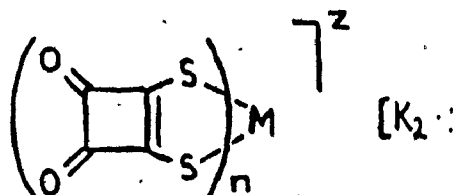
APPENDIX  
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i



ii



iii

Fig. A-1 Metal Dithiolene Complexes of Interest  
to Photocatalysis

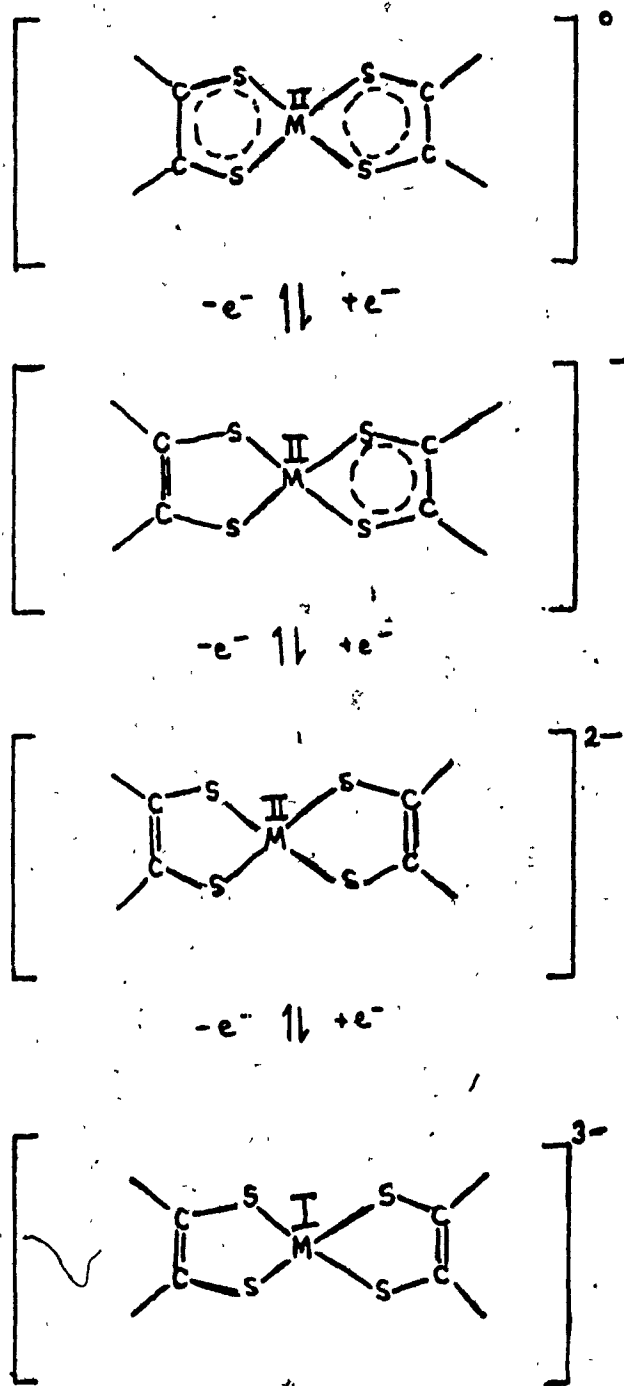


Fig. A-2 Various Oxidation States Available  
to the Metal Dithiolenes (22,72)

Table A-3 Electronic Absorption Spectra of Several  
Relevant Metal mnt Complexes in Acetonitrile (1)

| Complex                               | Wavelength<br>( nm ) | $\epsilon$ |    | Assignments   | Ref. |
|---------------------------------------|----------------------|------------|----|---|------|
|                                       |                      | 3 -1       | -1 |   |      |
|                                       |                      | dm M       | cm |   |      |
| Ni(mnt)<br><sup>-2</sup> <sub>2</sub> | 855                  | 30         |    | <sup>2</sup> <sub>x</sub> - <sup>2</sup> <sub>y</sub> --> xy  | 51   |
|                                       | 571                  | 570        |    | xz --> xy   | 51   |
|                                       |                      |            |    | n --> M   | 52   |
|                                       | 519                  | 1,250      |    | <sup>2</sup> <sub>x</sub> - <sup>2</sup> <sub>y</sub> --> Ln* | 51   |
|                                       |                      |            |    | n --> M   | 51   |
|                                       | 476                  | 3,800      |    | xz --> Ln*  | 51   |
|                                       | 378                  | 6,600      |    | Ln --> xy   | 51   |
|                                       | 319                  | 30,000     |    | Ln --> Ln*  | 51   |
| Pt(mnt)<br><sup>-2</sup> <sub>2</sub> | 270                  | 50,000     |    | Lo --> xy   | 51   |
|                                       | 694                  | 49         |    | <sup>2</sup> <sub>x</sub> - <sup>2</sup> <sub>y</sub> --> xy  | 51   |
|                                       | 639                  | 56         |    | xz --> Ln*  | 51   |
|                                       | 540                  | 1,220      |    | <sup>2</sup> <sub>x</sub> - <sup>2</sup> <sub>y</sub> --> xy  | 51   |
|                                       |                      |            |    | <sup>2</sup> <sub>x</sub> - <sup>2</sup> <sub>y</sub> --> Ln* | 51   |
|                                       | 473                  | 3,470      |    | xz --> Ln*  | 51   |
|                                       | 336                  | 15,600     |    | Ln --> Ln*  | 51   |

| Complex            | Wavelength | e                  | Assignments                            | Ref. |
|--------------------|------------|--------------------|--|------|
|                    | ( nm )     | 3 -1 -1<br>dm M cm |  |      |
| Ni(mnt)<br>-1<br>2 | 309        | 13,400             | Ln --> Ln *                            | 51   |
|                    | 260        | 17,000             |  |      |
|                    | 228        | 43,500             | Lo --> xy                              | 51   |
|                    | 1,200      | 329                | xz --> x <sup>2</sup> - y <sup>2</sup> | 51   |
|                    |            |                    | M --> n (                              | 52   |
|                    | 848        | 8,000              | Ln --> x <sup>2</sup> - y <sup>2</sup> | 51   |
|                    |            |                    | M --> n                                | 52   |
|                    | 600        | 668                |  | 51   |
|                    |            |                    | n --> M                                | 52   |
|                    | 545        | 798                |  | 51   |
|                    |            |                    | n --> n                                | 52   |
|                    | 477        | 2,490              | Lo --> x <sup>2</sup> - y <sup>2</sup> | 51   |
|                    |            |                    | n --> n                                | 52   |
|                    |            |                    | n --> M                                | 52   |
|                    | 370        | 7,114              | Ln --> xy                              | 51   |
|                    |            |                    | M --> n                                | 52   |
|                    | 311        | 33,873             | Ln --> Ln *                            | 51   |
|                    |            |                    | n --> n                                | 52   |
|                    | 270        | 34,017             | Lo --> xy                              | 51   |
|                    | 230        | 19,093             |  |      |

Table A-4 Cyclic Voltammetric Parameters for Several  
Metal mnt-Complexes at Pt Electrode in Acetonitrile  
vs Ag / Ag<sup>+</sup> Redox Couple (1)

| Complex = |   | M (mnt) <sup>n</sup>                |       |                      |      |      |      |
|-----------|---|-------------------------------------|-------|----------------------|------|------|------|
|           |   | 2                                   |       |                      |      |      |      |
| M         |   | E <sub>1/2</sub>                    |       | Δ E <sub>P</sub>     |      |      |      |
|           |   | 1/2                                 |       |                      |      |      |      |
|           |   | +1 ⇌ 0   0 ⇌ -1   -1 ⇌ -2   -2 ⇌ -3 |       | 0/-1   -1/-2   -2/-3 |      |      |      |
| Ni        | - | +0.82                               | -0.14 | -1.94                | -    | 0.13 | -    |
| Cu        | - | +0.96                               | -0.03 | -1.07                | -    | 0.06 | 0.10 |
| Pd        | - | +0.48                               | +0.04 | -2.17                | 0.38 | 0.16 | -    |
| Pt        | - | +0.72                               | -0.16 | -2.68                | 0.07 | 0.07 | -    |
|           | - | -                                   | -     | -2.97                | -    | -    | -    |

\* Values differ (8,23)

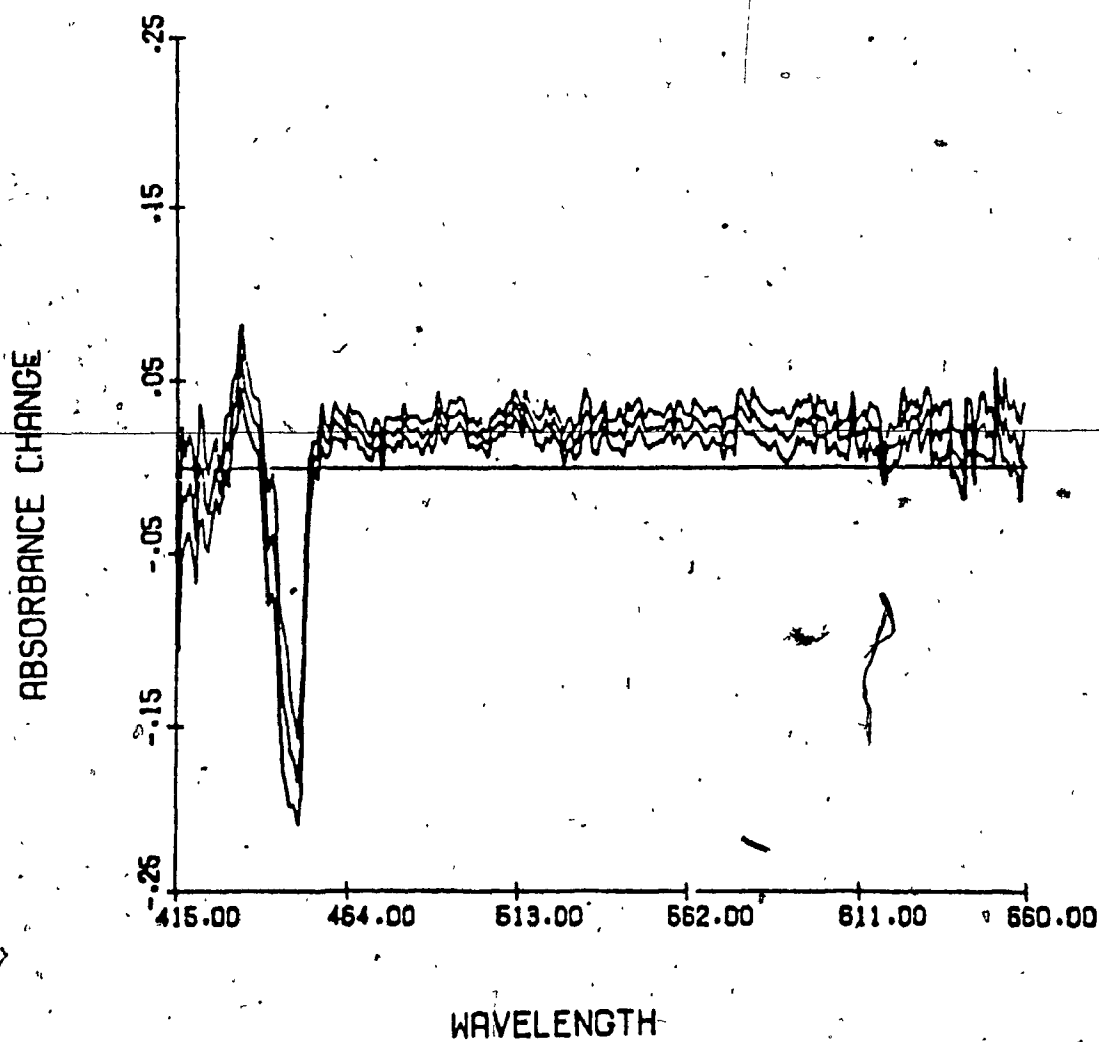


Fig. A-5 Transient Behaviour of Acetonitrile at Pulse  
Delay of 10 nsec



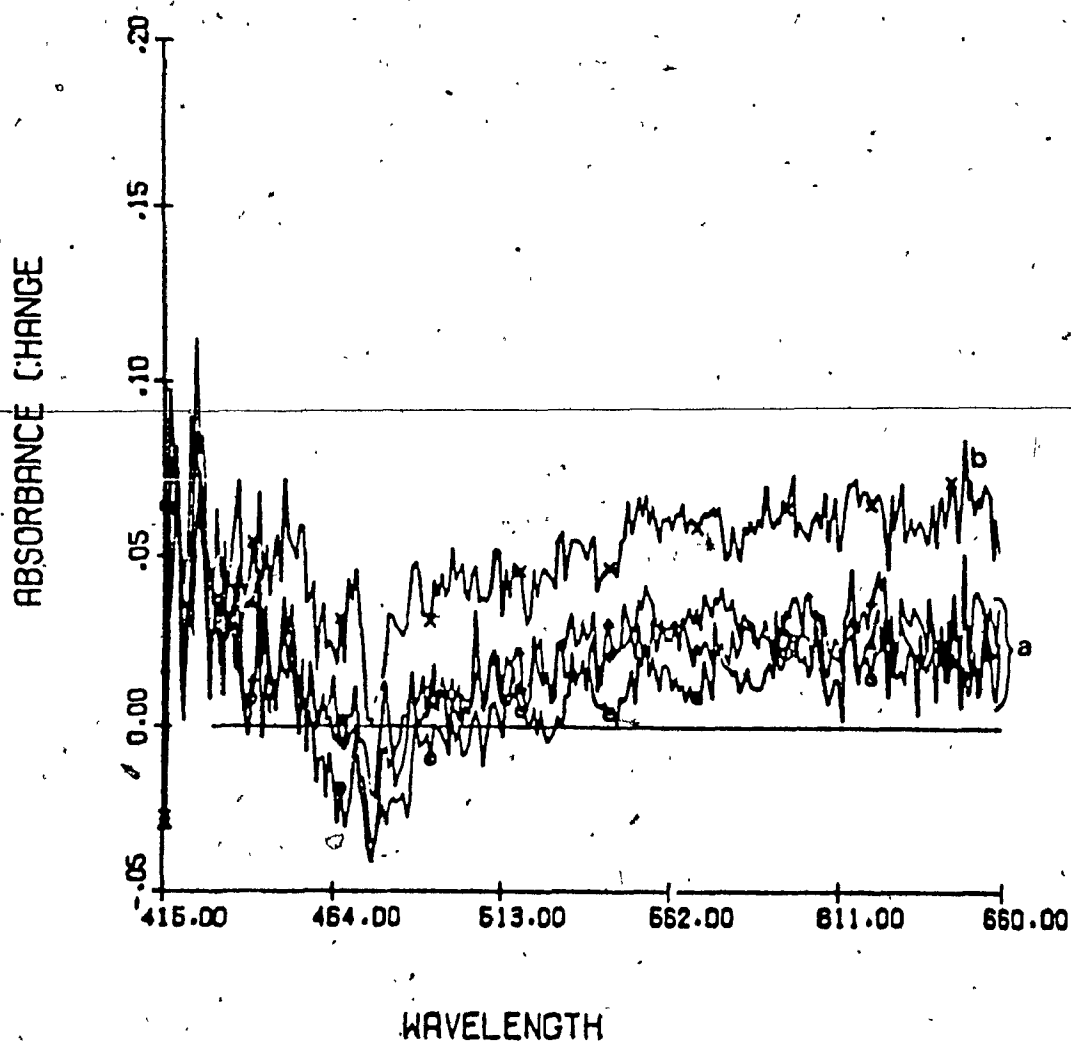


Fig. A-6 Transient Absorption Spectrum and Bleaching of  
 $\text{Ni(mnt)}_2$  in Acetonitrile at Probe Pulse Delay of:  
 (a) 3 to 7 nsec (b) 10 nsec

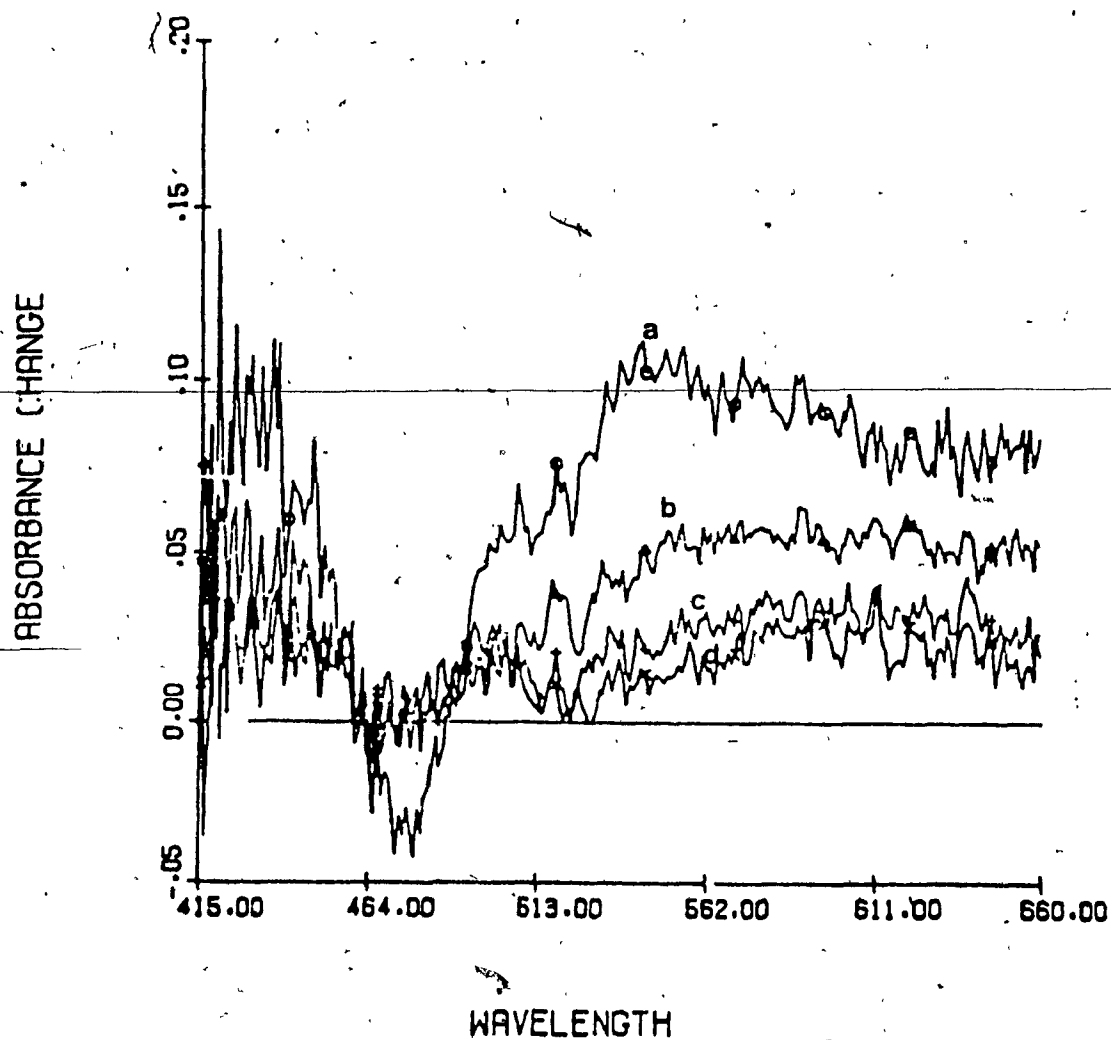


Fig. A-7 Transient Absorption Spectrum and Bleaching of  
 $\text{Ni(mnt)}_2$  in Acetonitrile at Probe Pulse Delay of:  
 (a) 20 psec (b) 50 psec (c) 100 psec  
 and (d) 200 psec

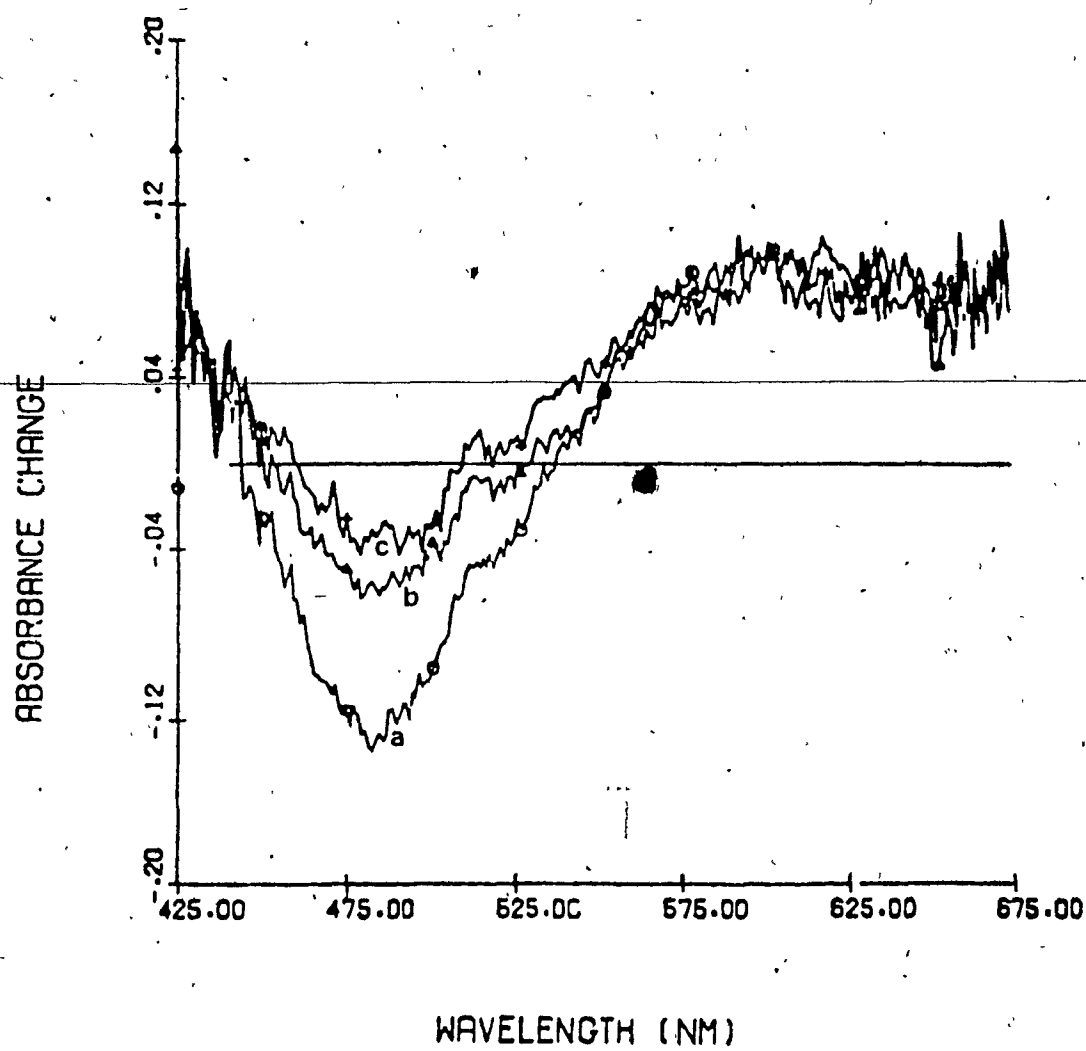


Fig. A-8 Transient Absorption Spectrum and Bleaching of  
 $\text{Pt(mnt)}^{-2}$  in Dry Acetonitrile at Probe Pulse Delay of:  
 (a) 500 psec (b) 5 nsec (c) 10 nsec

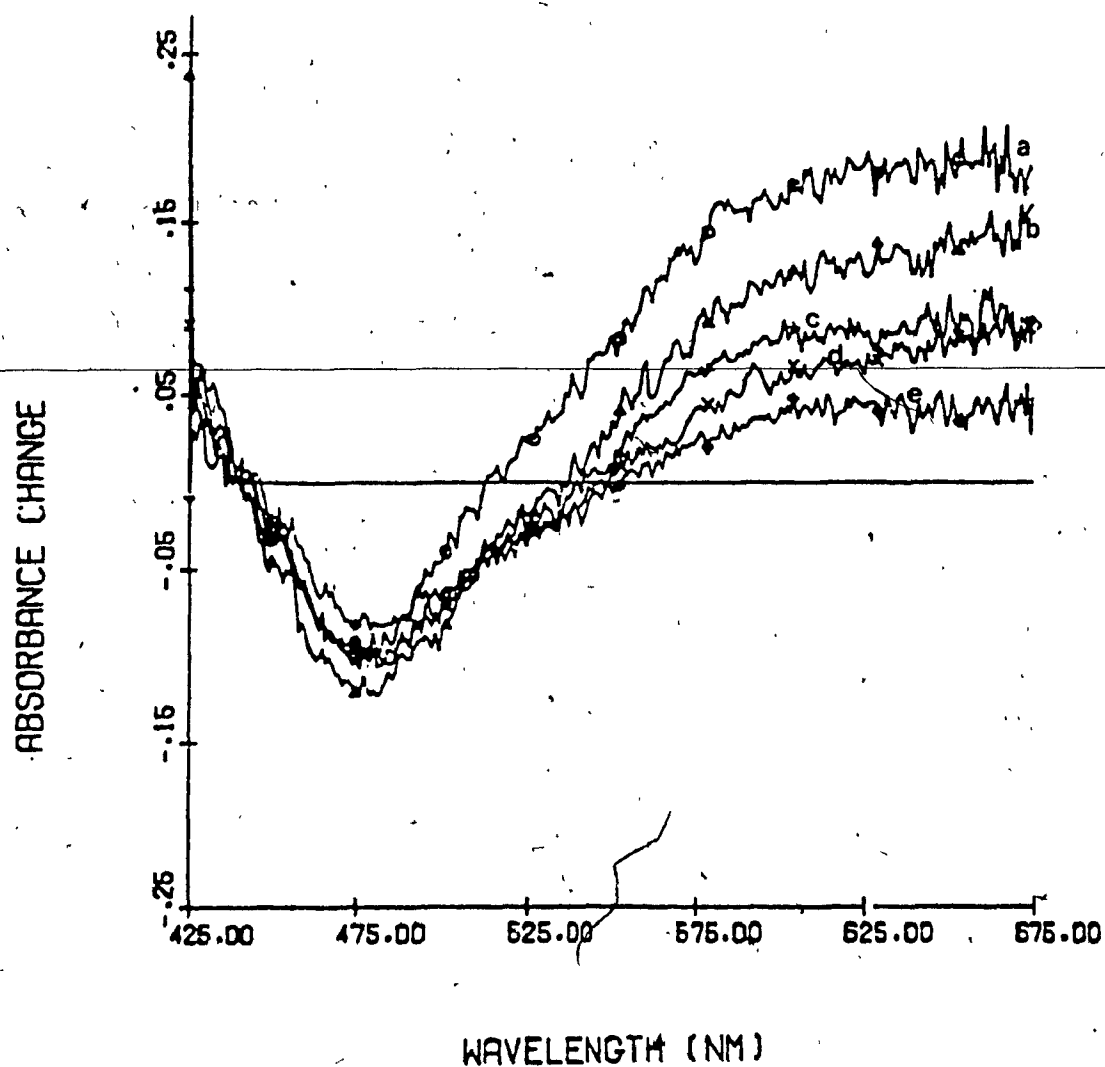


Fig. A-9 Transient Absorption Spectrum and Bleaching of  
 $\text{Pt(mnt)}_2$  in 30% Aqueous Acetonitrile at Probe Pulse  
 Delay of : (a) 50 psec (b) 1 nsec (c) 3 nsec  
 (d) 5 nsec and (e) 10 nsec

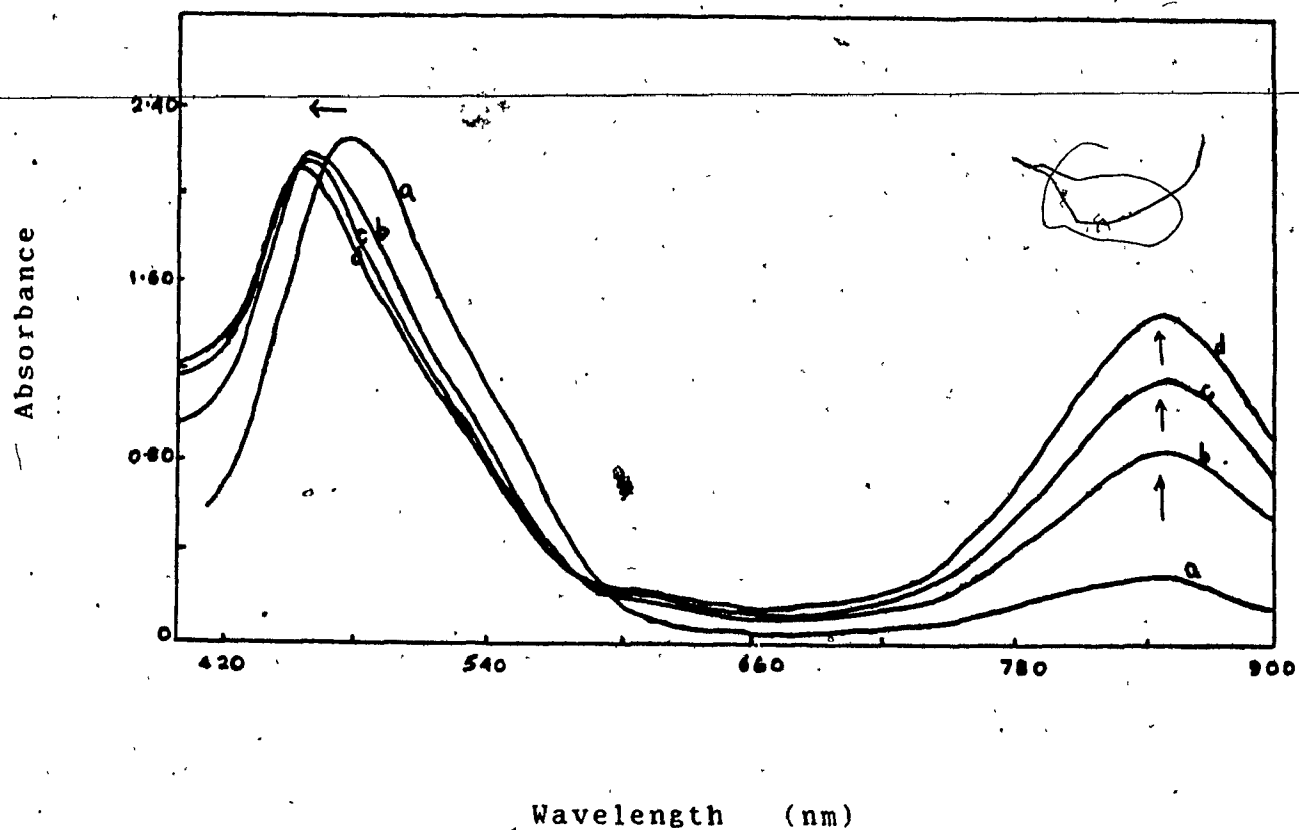


Fig. A-10 Changes in the Absorption Spectrum of An Aqueous  
 $\text{Pt(mnt)}_2$  in Acetonitrile During Irradiation  
 for 4, 6 and 8 hours : (a) before photolysis  
 (b), (c), (d) after photolysis (1)

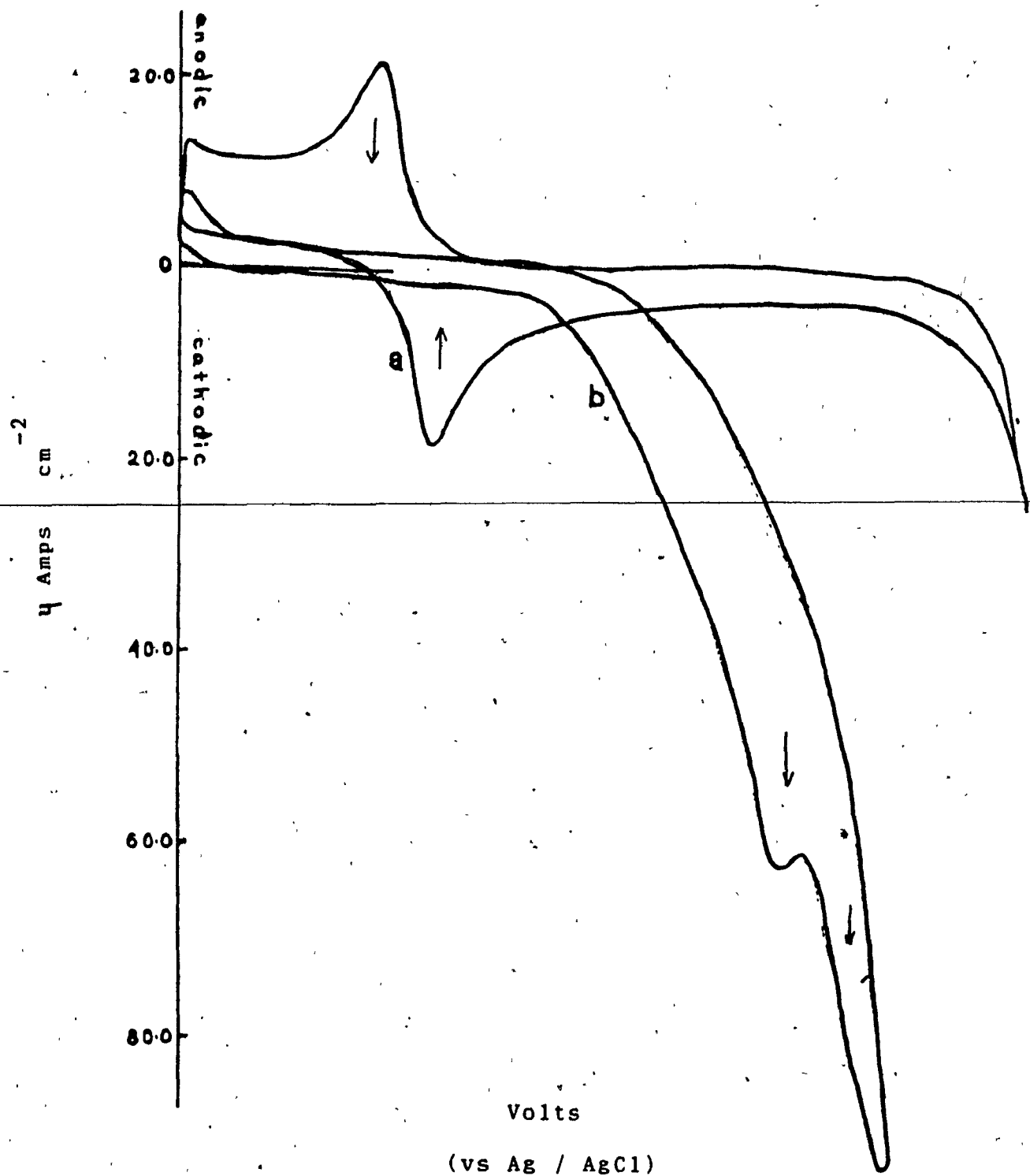


Fig. A-11 Cyclic Voltammogram of  $\text{Pt}(\text{mnt})_2$  in Solution at Pt Electrode in 30% Aqueous, 0.1 M  $\text{NaClO}_4$  / MeCN

(a) before photolysis

(b) after photolysis

(1)

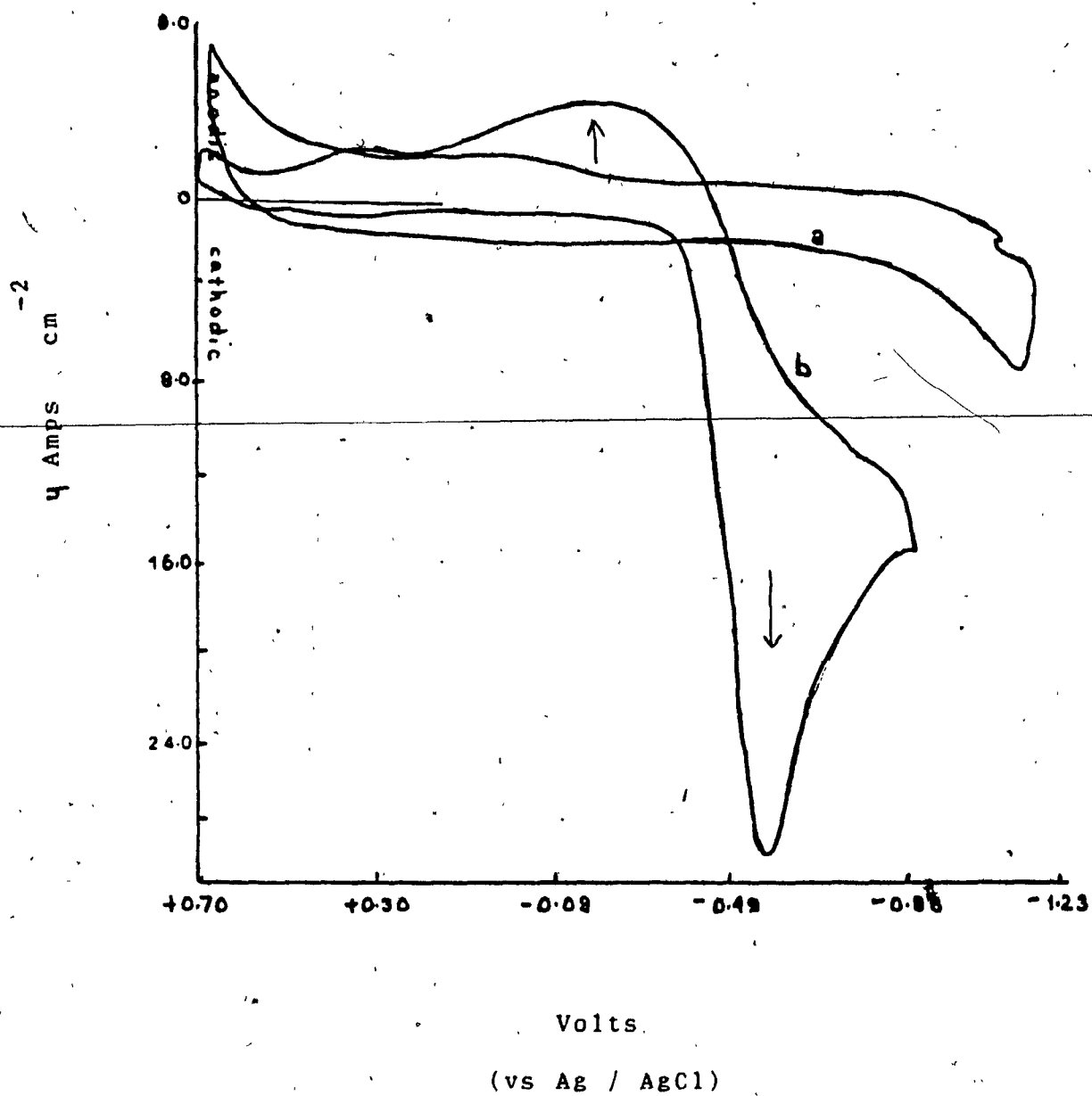


Fig. A-12 Cyclic Voltammogram of  $\text{Pt(mnt)}_2$  Solution at Pt  
Electrode After Irradiation for 2 hours in 30% Aqueous,  
0.1 M  $\text{NaClO}_4$  / MeCN

(a) after 4 hours without stirring

(b) after stirring

(1)

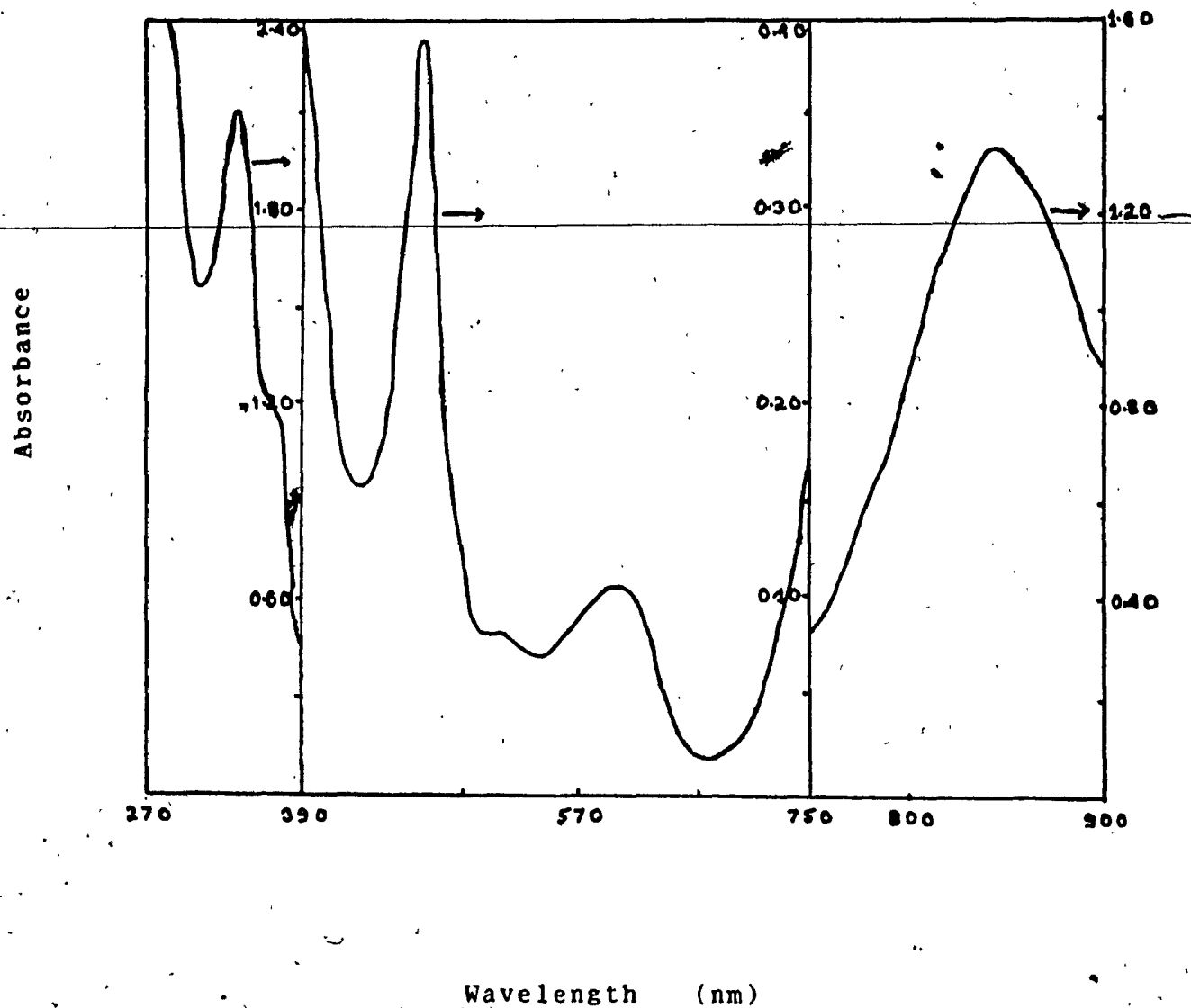


Fig. A-13 Absorption Spectrum of Fine Particulates  
Recovered After the Photolysis  
of the Solution

(1)