

PHOTOOXIDATION OF CERTAIN ORGANICS USING TiO₂ SUSPENSION AS CATALYST

A

REPORT ON

*Laboratory Project submitted for the partial
fulfilment of the degree*

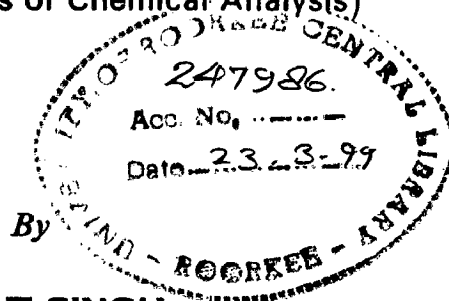
of

MASTER OF PHILOSOPHY

in

CHEMISTRY

(Industrial Methods of Chemical Analysis)



JAGAT SINGH



DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROORKEE
ROORKEE-247 667 (INDIA)

JULY, 1998

18

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Photooxidation of Certain Organics Using TiO_2 Suspension as Catalyst" in partial fulfilment of the requirement for the award of the Degree of **Master of Philosophy** submitted in the **Department of Chemistry** of the University is an authentic record of my own work carried out during a period from ~~January~~ **January 97** to **July 98** under the supervision of **Dr. Anil Kumar**, Associate Professor, Department of Chemistry, University of Roorkee, Roorkee.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

Jagat Singh
(JAGAT SINGH)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Date : July 30 , 1998

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ACKNOWLEDGEMENT

First of all, I would like to express with reverence my deep sense of gratitude and sincere thanks to **Dr. Anil Kumar** for his meticulous guidance, constructive criticism and encouragement during the course of this investigation. His affectionate treatment and keen interest kept me always out of despair and provided me enthusiasm to know more.

I am highly obliged to **Prof. C. L. Sharma, Head of the Chemistry Department, University of Roorkee, Roorkee**, for his helping attitude and providing necessary facilities to carry out this work.

I wish to thank **Mr. Paresh Kumar, Mr. Arvind Kumar Jain** and **Mr. D. P. S. Negi** for their help, and friendly treatment, during my laboratory work. I express my deepest sense of gratitude for them.

I am greatly indebted to **Ms. Vaishali Agarwal** for her encouragement, selfless help, invaluable suggestions and friendly treatment during this work.

I would also like to thank all of my seniors especially Ms. Nidhi Singhal, Ms. Rakesh Yadav, Ms. Rachana Agarwal, Ms. Poonam Malik, Mr. Naveen Singhal, Mr. Vinay Sharma and Mr. Pankaj Kumar.

I am highly thankful of my classmates especially Mr. Sandeep Pokharia, Mr. Akash Deep, Mr. Lokesh Kumar for their step by step help and cooperation rendered to me in one way or the other.

I have no words to express my best regard to my father, brothers and sisters whose blessing always enlighten me in darkness and who are the constant source of inspiration to me, even they are far-far away from me.

Dated : July 30, 1998

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ABSTRACT

TiO₂ sensitized photochemical reaction of ethanolamine has been studied under different experimental conditions and reaction environments. The irradiation of TiO₂ - ethanolamine reaction mixture by the light of wavelength > the band gap energy of TiO₂ (3.2 eV) results in the oxidation of adsorbed substrate to produce HCHO via C-C bond cleavage. In the studied concentration range of ethanolamine, the reaction follows first-order kinetics with respect to ethanolamine. This reaction has been carried out in oxygenated, aerated and nitrogen atmosphere. Oxygen acts as an electron scavenger and enhances the photocatalytic efficiency by about 3 times to that of the aerated reaction samples. In nitrogen atmosphere no reaction product could be detected. In the acidic medium at pH 2.5 the protonation of ethanolamine and TiO₂ surface does not lead to the formation of C-C bond cleavage product. However, the hydroxylation of TiO₂ surface increases the yield of HCHO by about 4 times to that of observed at pH 5.6. The presence of acrylonitrile reduces the reaction yield indicating the operation of free radical mechanism. This reaction could also be initiated by sunlight efficiently. About 12 wt% of silver is found to be the optimum concentration of Ag⁺ as a co-catalyst for the photooxidation of ethanolamine. At high concentration of silver the rate of reaction is retarded. On the basis of these observations a reaction scheme is suggested.

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Chapter 1

INTRODUCTION

INTRODUCTION

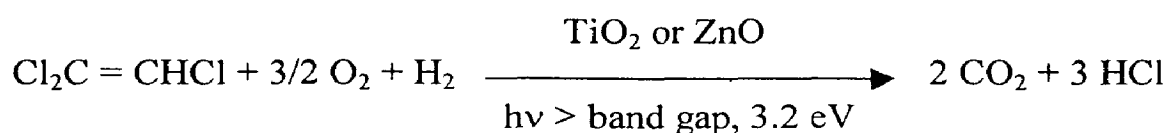
During last two decades there has been a tremendous growth in the field of photochemistry and photobiology. The developments in these areas have contributed several novel applications that are of immense importance to mankind. The time resolved lasers have been successfully used for the treatment of cancer, performing complex surgery in eyes, dentistry and orthopaedics etc. One of the most important process initiated by light in nature is photosynthesis. It is not only crucial for the sustenance of life on earth, but is also important for influencing the global climate.

In view of the scarcity of conventional fuels, lately, the photochemistry has assumed a great significance during last one decade specifically in regard to the development of the efficient solar energy conversion systems. A number of physical and chemical systems have been devised to achieve this objective [1]. Different types of photosensitizers utilized for this purpose comprise a variety of inorganic complexes [2] and semiconductors [3-6].

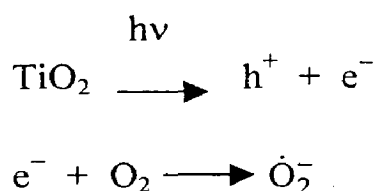
During the last decade there has been an increasing scientific and technical interest in employing photocatalysis initiated by semiconductors to promote the light activated reactions. These systems have been exploited in several ways - for the storage of solar energy, synthetic transformations and also for the removal and mineralisation of pollutants [4,7]. In photocatalysis initiated by semiconductors attention has been focussed mainly on TiO_2 . It has been found to possess the capability to destroy wide range of contaminants. Besides that TiO_2 is chemically

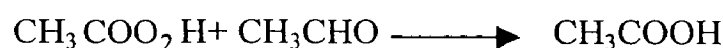
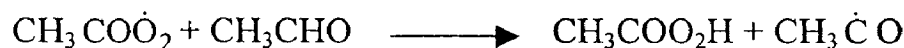
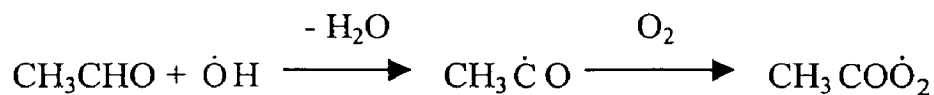
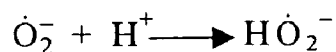
inert, photostable, cheap and can make use of near UV-light to induce the light activated reactions. Several chemical reactions and photomineralisation of large number of pollutants have been sensitized so far by TiO₂ [7]. It is difficult to cover the entire literature in this report. A brief literature survey on the reactions of certain organics is described below :

Trichloroethane is known to be very common human health hazard and is found in ground water supply. The gas phase photooxidation of trichloroethane initiated by photosensitizers such as TiO₂ and ZnO has been studied by Driessen et al. [8]. On clean TiO₂ and ZnO surfaces it produced, CO, CO₂, COCl₂, CCl₂HCO₃, CHCl₃, C₂HCl₅ and HCl as the products. The distribution of products of photooxidation is found to be strongly dependent on the coverage of the adsorbed surfaces of the photocatalyst. The complete oxidation occurs on clean photocatalytic surfaces whereas only partial oxidation takes place on adsorbate surfaces



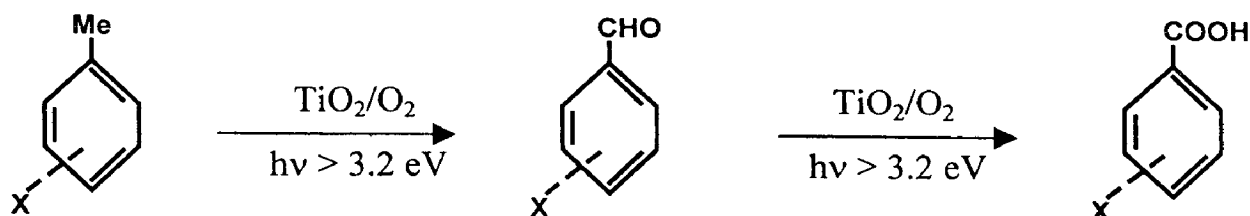
The autooxidation of gas phase acetaldehyde is photocatalysed using TiO₂ thin film [9] under weak UV-illumination. Its main reaction products are acetic acid and CO₂. The initial steps in the gas phase acetaldehyde degradation are given below :





Overall only 0.5 photons participate in generating one molecule of acetic acid.

The aerial oxidation of toluene is photocatalysed by TiO_2 [10]. It results in the formation of substituted benzaldehyde and benzoic acid. The catalytic action of ZnO is significantly improved by the addition of small amounts of acids.



The catalytic effect of H^+ is explained by the adsorption of HSO_4^- like species which act as a surface trap for holes.

The organochlorine pesticide permethrin can be photodegraded into Cl^- and CO_2 in the presence of TiO_2 [11]. The degradation occurred via apparent first-order kinetics with $k = 1.73 \times 10^{-3} \text{ min}^{-1}$ and a half life ($t_{1/2}$) = 400 min. After 20 h of irradiation more than 90% of permethrin had degraded.

Cuendet and Grätzel [12] have observed the efficient reduction of pyruvate to lactate under illumination of aqueous suspensions of TiO₂ powder in a sunlight simulator. Reduction was found to depend on the pH of the medium and electron donor present in the solution. The mechanism of electron transfer reveals that the carbonyl group adjacent to carboxyl group can be catalytically reduced at the TiO₂ surface. The kinetics of reduction has been studied by monitoring the interfacial electron transfer occurring on colloidal TiO₂ using laser flash photolysis. From these data a second order reaction constant of $(680 \pm 50) \text{ M}^{-1} \text{ s}^{-1}$ was computed for interfacial charge transfer.

In a novel experiment Dunn et al. [13] reported the synthesis of amino acids (viz. glycine, alanine, aspartic acid, glutamic acid) from methane, ammonia and water in contact with irradiated suspensions of platinized TiO₂. A mechanism of the reaction based on the involvement of free radical, initiated by $\dot{\text{O}}\text{H}$ produced at the irradiated catalyst was proposed.

In a classic reaction the heterogeneous photocatalytic decomposition of acetic acid on n-type TiO₂ was reported by Kraeutler and Bard [14] to yield almost exclusively methane and carbon dioxide.



In this system the absorption of sunlight on a semiconductor powder suspended in a liquid promotes electron transfer reactions of substances in solution. Apparently the TiO₂ powder acts in a dual function causing the photooxidation of acetate and the reduction of intermediately formed methyl radicals, a property not found at

metal electrodes under the Kolbe conditions where the electrode potential is maintained at a very positive value.

A number of transition metal ions such as iron, ruthenium, rhodium, platinum, silver etc., have been observed to enhance the catalytic efficiency of TiO_2 . Various reasons for the increase in photoactivity have been described in the literature (4). In the present work silver ion has been used as a co-catalyst, the literature on some of the earlier investigated silver doped TiO_2 systems is given below :

Ohtani et al. [15] reported the effect of surface adsorbed 2-propanol on the photocatalytic reduction of silver and/or nitrate ions in acidic TiO_2 suspension. The initial rate of acetone formation, as well as silver deposition followed formal Langmuir equation as a function of the concentration of 2-propanol. The rate was proportional to the surface concentration of 2-propanol used as a hole scavenger. In the absence of silver in the suspension, nitrate ion was reduced to the ammonia together with acetone formation. The photodeposition of silver metal on TiO_2 enhanced the photocatalytic production of ammonia.

The photocatalytic activity of TiO_2 is found to improve the dehydrogenation or oxidation of 2-propanol [16]. This was interpreted to be the beneficial effect of silver in removing the electrons and performing the reduction of oxygen. At higher than optimum silver content, a detrimental increase in the probability of the capture of charge at the numerous silver particles was noted. The photoassisted reduction of silver ion leads to metallic deposition on TiO_2 powder.

The initial rate of deposition varied with the starting concentration of silver according to Langmuir-Hinshelwood's mechanism.

The above literature survey reveals that the mechanism of TiO_2 initiated reaction is not very well understood. It is therefore, needed to study more photochemical reactions at the interface of TiO_2 particles before a general mechanism of this system can be elucidated. In the present work we have examined the reaction of ethanolamine on illuminated TiO_2 suspensions. The product of this reaction has been analysed by using chromatography and electronic spectroscopy and has been followed kinetically under different experimental conditions. The effect of doping of silver on the reactivity of photogenerated charge carriers has been analysed.

Chapter 2

EXPERIMENTAL

EXPERIMENTAL

The physical and chemical properties of semiconductors are known to be affected considerably by adding traces of impurities. For this reason a special care has been exercised in designing of different experiments in the present work. All solutions were freshly prepared in double distilled water and the chemicals used were of high purity. Reagents of L. R. grade were purified by distillation.

A. REAGENTS

The grade and make of chemical used are listed below:

<i>Reagents</i>	<i>Make</i>	<i>Grade</i>
Titanium dioxide powder	Degussa	-
Ethanolamine	Merck	L.R.
Acrylonitrile	SRL	L.R.
p-Rosaniline hydrochloride	G. S. Chemical Testing Lab & Allied Inds.	L.R.
2,4-Dinitrophenylhydrazine	G. S. Chemical Testing Lab & Allied Inds.	L.R.
Chloroform	Qualigens	Excelsa R
Carbon tetrachloride	Merck	G.R.
Chromotropic acid	Merck	G.R.
Silver nitrate	Merck	Anala R
Sodium hydroxide	Merck	Anala R
Sodium metabisulphite	BDH	Anala R
Silica gel – G	Merck	Anala R
Hydrochloric acid	Merck	Anala R
Sulphuric acid	Merck	Anala R
Perchloric acid	Merck	Anala R

B. PURIFICATION OF SUBSTRATE

Ethanolamine and acrylonitrile were purified by distillation. The distillation was carried out under reduced pressure and their purity were checked by recording their boiling points. The values of observed and reported boiling points are given below :

<i>Substrate</i>	<i>Boiling point (°C)</i>	
	<i>Observed</i>	<i>Reported</i>
Ethanolamine	170°C	170°C
Acrylonitrile	77°C	77°C

C. EQUIPMENTS/ TECHNIQUES

(i) *Photolysis assembly*

The photochemical experiments were carried out on 'Oriel' continuous photolysis unit. It was equipped with 200 watt Mercury Xenon arc lamp, power supply and stand alone ignitor. The solutions and glass cut filter (UV-30) were used to select light in the desired wavelength range. All samples were photolysed by light of wavelength > 300 nm.

Some of the samples were directly irradiated by sunlight in stoppered pyrex glass conical flask.

(ii) *Scanning Electron Microscope (SEM)*

The particle size of used TiO₂ powder was determined on a scanning electron microscope "SCM Phillips 501".

(iii) Spectrophotometer

The absorption spectra of the product and absorbance data were recorded on Beckman DU-6 and Shimadzu UV-2100/s spectrophotometers.

(iv) pH meter

The pH of the reactants and reaction mixture were measured on CL-54 Toshniwal pH meter. The pH adjustment was carried out by using dilute solutions of sodium hydroxide and perchloric acid.

(v) Thin layer chromatography (TLC)

TLC was used for the isolation of different components of the products. TLC separation was performed on the glass plates coated with the silica gel G. Silica gel was employed as an adsorbent to provide the stationary phase. It contained 10% of calcium sulphate as binder.

Preparation of TLC plate

The plates were prepared by spreading a slurry of silica gel G in water in a ratio of 1:2 by Stahl's type of applicator. The thickness of layer was maintained at about 0.5 mm. The coated plates were activated by keeping them overnight at about 65°C in the oven [17].

D. METHODOLOGY

(i) Preparation of the photocatalyst solution

The solution of photocatalyst was prepared by suspending 25 mg of the titanium dioxide powder in 100 ml of double distilled water.

(ii) Determination of Particle Size

The TiO₂ suspension were dried under vacuum and were applied on the specimen stub using double sided tape. The photographs of the particles were taken for different magnifications ranging from 20-2500. A typical photograph obtained with a magnification of 320 × 100 μ is shown in Fig. 1. This picture depicts several large clusters along with a number of isolated particles. The size of the isolated particles was estimated to be about 90 nm.

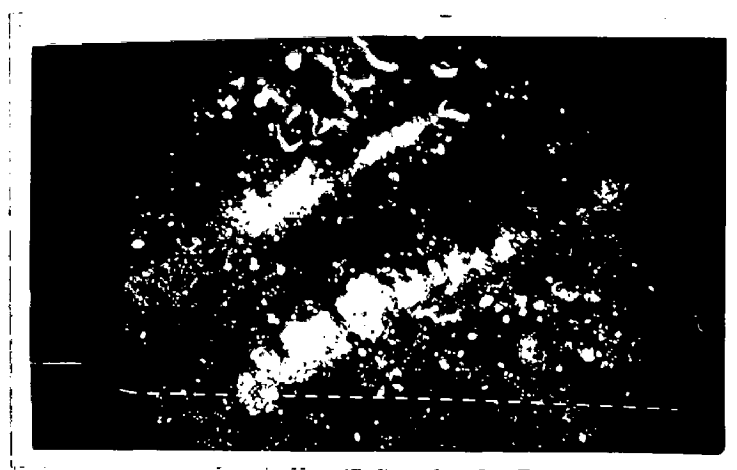


Fig. 1 : SEM photograph of TiO₂ suspension

(iii) Preparation of the reaction sample

The reaction samples were prepared by mixing the catalyst and substrate on mechanical shaker for about an hour before measurements. The pH of the reaction mixture was maintained by adjusting the pH of the used reactants.

(iv) Preparation of the 2,4-dinitrophenylhydrazine (2,4-DNPh) solution

The 0.25g of 2,4-DNPh was dissolved in a mixture of 42 ml conc. hydrochloric acid and 50 ml of water by warming on a water bath. This solution was further diluted to 250 ml with water. The reagent is known to be effective for

Chapter 3

RESULTS
&
DISCUSSION

RESULTS AND DISCUSSION

1. ANALYSIS OF THE PRODUCT AND ITS CHARACTERIZATION

The reaction mixture containing TiO_2 -ethanolamine $2.5 \times 10^{-1} \text{ mol dm}^{-3}$ was irradiated with light of wavelength $> 300 \text{ nm}$ using glass and solution cut filters. The product of the reaction in bulk was prepared by illuminating the reaction sample by sunlight in pyrex vessel. The product from the reaction mixture was separated by centrifugation. The suspensions of TiO_2 settled in the centrifuge tube and were discarded. The filtrate gave positive test for the presence of aldehyde by Schiff's reagent.

For the analysis of product, its 2,4-dinitrophenylhydrazone derivative was prepared as per the literature method described for water soluble aldehyde [18]. The mixing of 2,4-DNPh solution with the reaction product produced orange yellow precipitates. The reaction mixture was allowed to stay for few hours and warmed for the completion of reaction. The resulting precipitates were separated by filtration under washing with cold water to remove the unreacted 2,4-DNPh solution. This sample though still contained the unreacted 2,4-DNPh as was indicated by TLC. For its removal, the product was recrystallized by ethanol. The insoluble portion contained the 2,4-DNPh (Table-1). The filtrate consisted of the 2,4-dinitrophenylhydrazone of the product.

The product was subjected to TLC analysis. The chromatogram was developed by solvent mixture having chloroform and carbon tetrachloride. The best separation was obtained with the solvent mixture containing CHCl_3 and CCl_4

in the ratio of 1:1. This chromatogram exhibited only one spot having R_f value of 0.67. It suggests that only one product is formed. The R_f value of this product matched with the 2,4-dinitrophenylhydrazone of the authentic formaldehyde. The separation data is given in Table-1.

Table-1 : TLC separation of the 2,4-dinitrophenylhydrazone of the oxidation product(s)

Substrate	Colour	R_f Value
Ethanolamine	Orange	0.21
	Yellow	0.67
2,4-dinitrophenylhydrazine	Orange	0.21
	Yellow	0.67

The electronic spectra of 2,4-dinitrophenylhydrazone of unknown sample and authentic formaldehyde are shown in Fig. 2. These spectra are very similar and depicted two peaks at 260 and 346 nm. This suggests that the product of the studied reaction may be formaldehyde.

To confirm the above identified product, a specific reagent for formaldehyde, chromotropic acid was employed. The unknown product with this reagent formed a coloured product which showed λ_{max} at 572 nm. This was identical to the absorption spectrum obtained by treating the authentic sample of the formaldehyde under similar experimental conditions. It thus confirms that the product of TiO_2 - photosensitized ethanolamine reaction is formaldehyde.

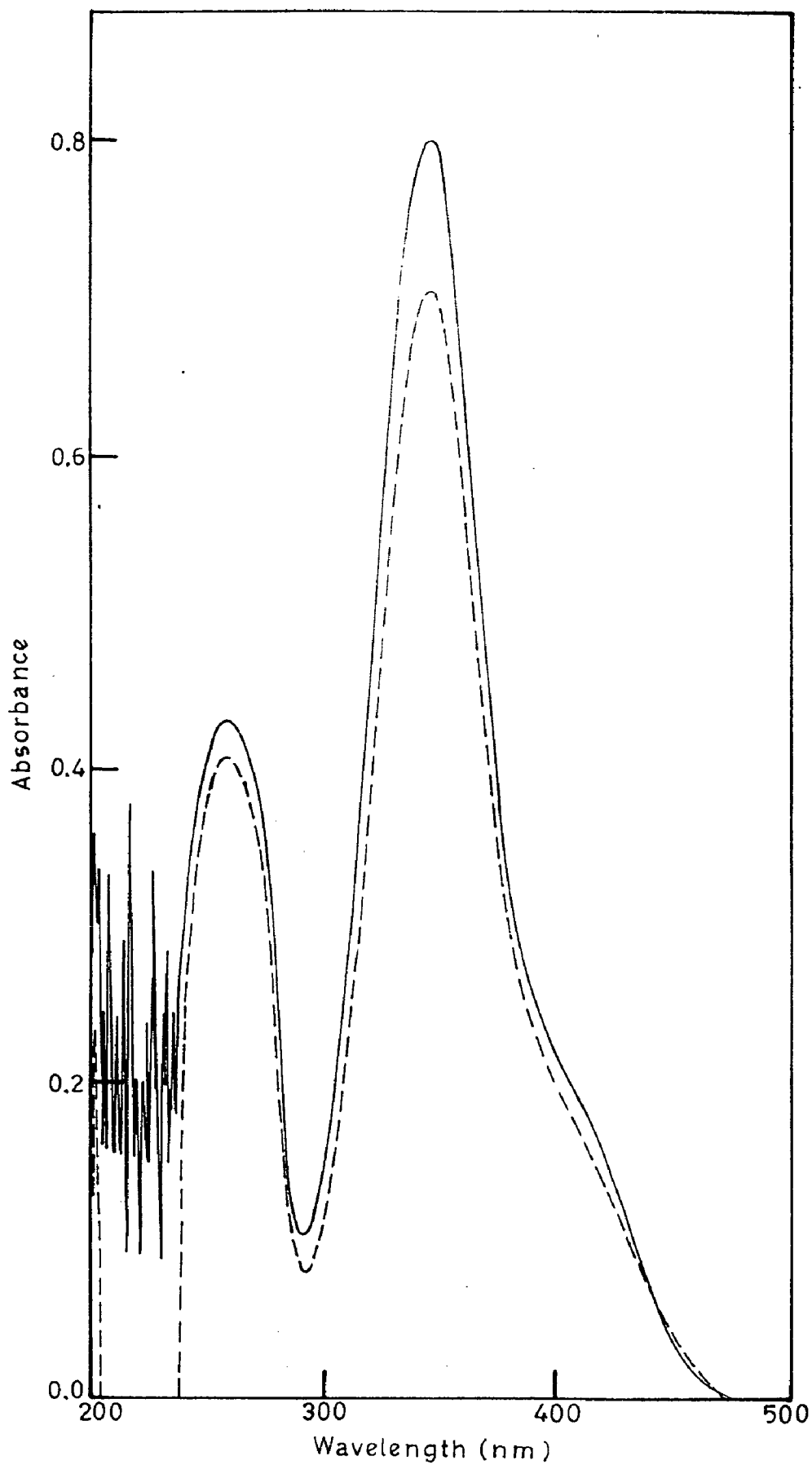


Fig. 2 : Electronic spectra of 2,4-dinitrophenylhydrazone of the product obtained upon irradiation of TiO_2 -ethanolamine reaction mixture (-----); and 2,4-dinitro-phenylhydrazone of HCHO(—)

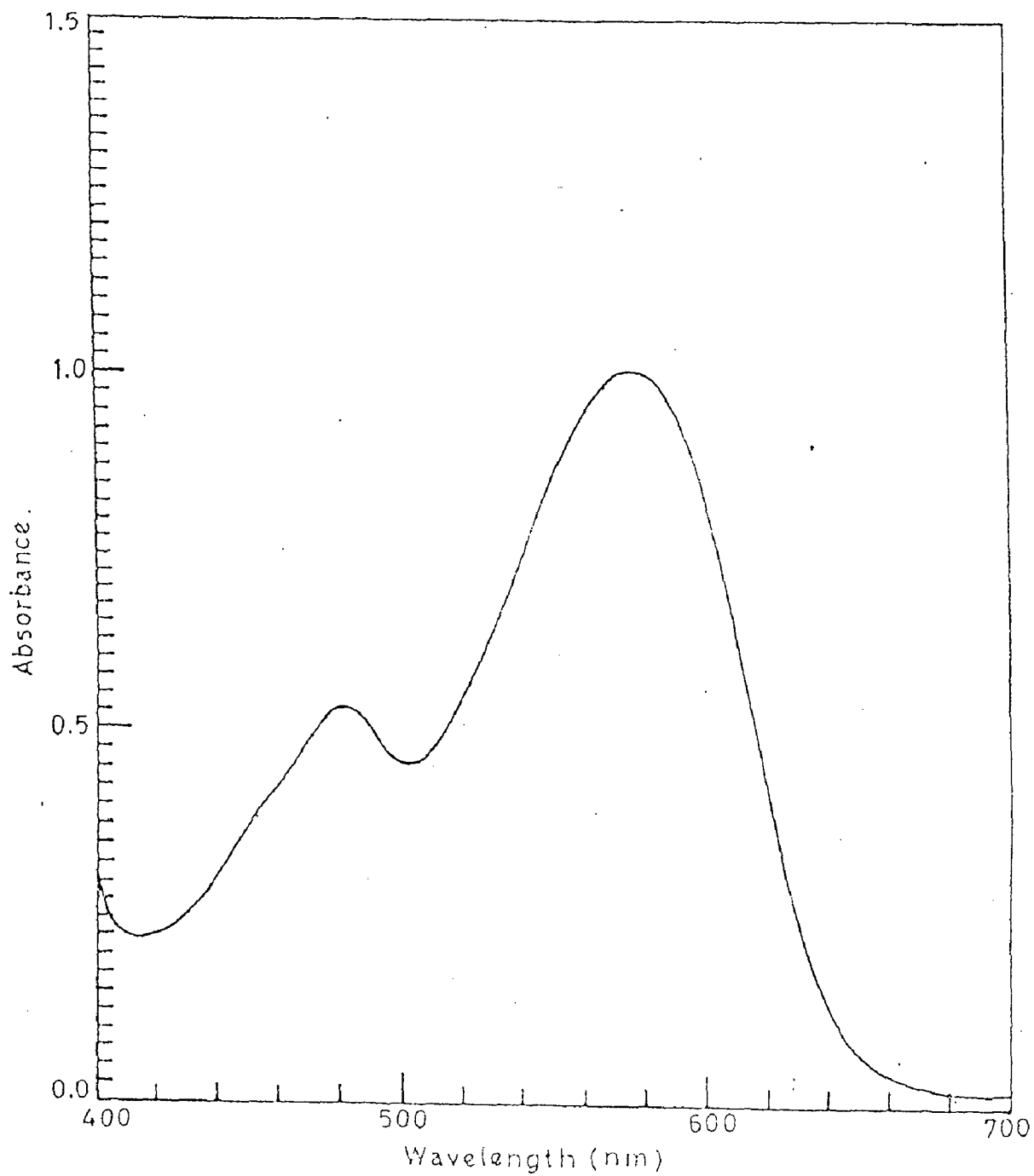


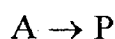
Fig. 3: Electronic spectrum of the product obtained upon irradiation of TiO_2 -ethylene glycol reaction mixture after treating with chromotropic acid

2. KINETIC STUDY

2.1 Determination of order with respect to the substrate

The order with respect to ethanolamine was determined by following the product kinetically at different [ethanolamine] (1×10^{-1} to 2.5×10^{-1} mol dm⁻³). The kinetic data of these runs are summarized in Table-2. The plots of product formation as a function of time are depicted in Fig. 4. From the early portion of these curves, the initial rate values at different concentrations of ethanolamine were evaluated. These values are given in Table-3. The initial rate increases regularly with an increase in [ethanolamine].

The following Vant-Hoff's equation was used to determine order with respect to ethanolamine :



$$\frac{-d[A]}{dt} (R_o) = k (c)^n$$

where,

R_o is the initial rate for the decomposition of the reactant

k = rate constant

n = order of the reaction

c = initial concentration of the reactant

The plot of $\log (R_o)$ vs \log [ethanolamine] is shown in Fig. 5. It gives a straight line with the slope of unity. It suggests that order with respect to ethanolamine is unity in the studied concentration range.

Table-2 : Effect of concentration of Ethanolamine on the yield of product upon illumination of oxygenated TiO₂-ethanolamine reaction mixture as a function of time.

pH = 12.0

[Ethanolamine] $\times 10^1$ (mol dm^{-3})	1.0		1.5		2.0		2.5	
	O.D. at 572 nm	[HCHO] $\times 10^5$ (mol dm^{-3})	O.D. at 572 nm	[HCHO] $\times 10^5$ (mol dm^{-3})	O.D. at 572 nm	[HCHO] $\times 10^5$ (mol dm^{-3})	O.D. at 572 nm	[HCHO] $\times 10^5$ (mol dm^{-3})
30	0.119	0.16	0.125	0.17	0.177	0.20	0.191	0.23
60	0.135	0.17	0.147	0.18	0.228	0.27	0.258	0.30
120	0.215	0.25	0.238	0.28	0.354	0.43	0.398	0.48
180	0.313	0.36	0.370	0.45	0.417	0.50	0.427	0.50
240	0.374	0.45	0.419	0.48	0.514	0.62	0.518	0.62
300	0.502	0.60	0.540	0.65	0.613	0.71	0.621	0.75

Table-3 : Data of Vant-Hoff's plot for the determination of order with respect to ethanolamine.
pH = 12.0

[Ethanolamine] $\times 10^1$ (mol dm ⁻³)	O.D. at 572 nm	[HCHO] $\times 10^5$ (mol dm ⁻³)	(R ₀) $\times 10^5$ * (mol dm ⁻³ /min)	log[Ethanolamine]	log (R ₀)
1.0	0.073	0.0831	0.04155	-1.000	-6.38
1.5	0.095	0.1080	0.05400	-0.824	-6.26
2.0	0.117	0.1371	0.06855	-0.699	-6.16
2.5	0.127	0.1496	0.07480	-0.602	-6.12

* Initial rate has been calculated after 15s of illumination assuming 1 mol of ethanolamine produces 2 mol of formaldehyde

Table-4 : Data of plot of (1/R₀) Vs $\frac{1}{[\text{Ethanolamine}]_i}$

pH = 12.0

[Ethanolamine] _i $\times 10^1$ (mol dm ⁻³)	O.D. at 572 nm	[HCHO] $\times 10^5$ (mol dm ⁻³)	(R ₀) $\times 10^5$ (mol dm ⁻³ /min)	$\frac{1}{[\text{Ethanolamine}]_i}$ (mol ⁻¹ dm ³)	(1/R ₀) $\times 10^5$
1.0	0.073	0.0831	0.04155	10	24.09
1.5	0.095	0.1080	0.05400	6.7	18.51
2.0	0.117	0.1371	0.06855	5	14.59
2.5	0.127	0.1496	0.07480	4	13.36

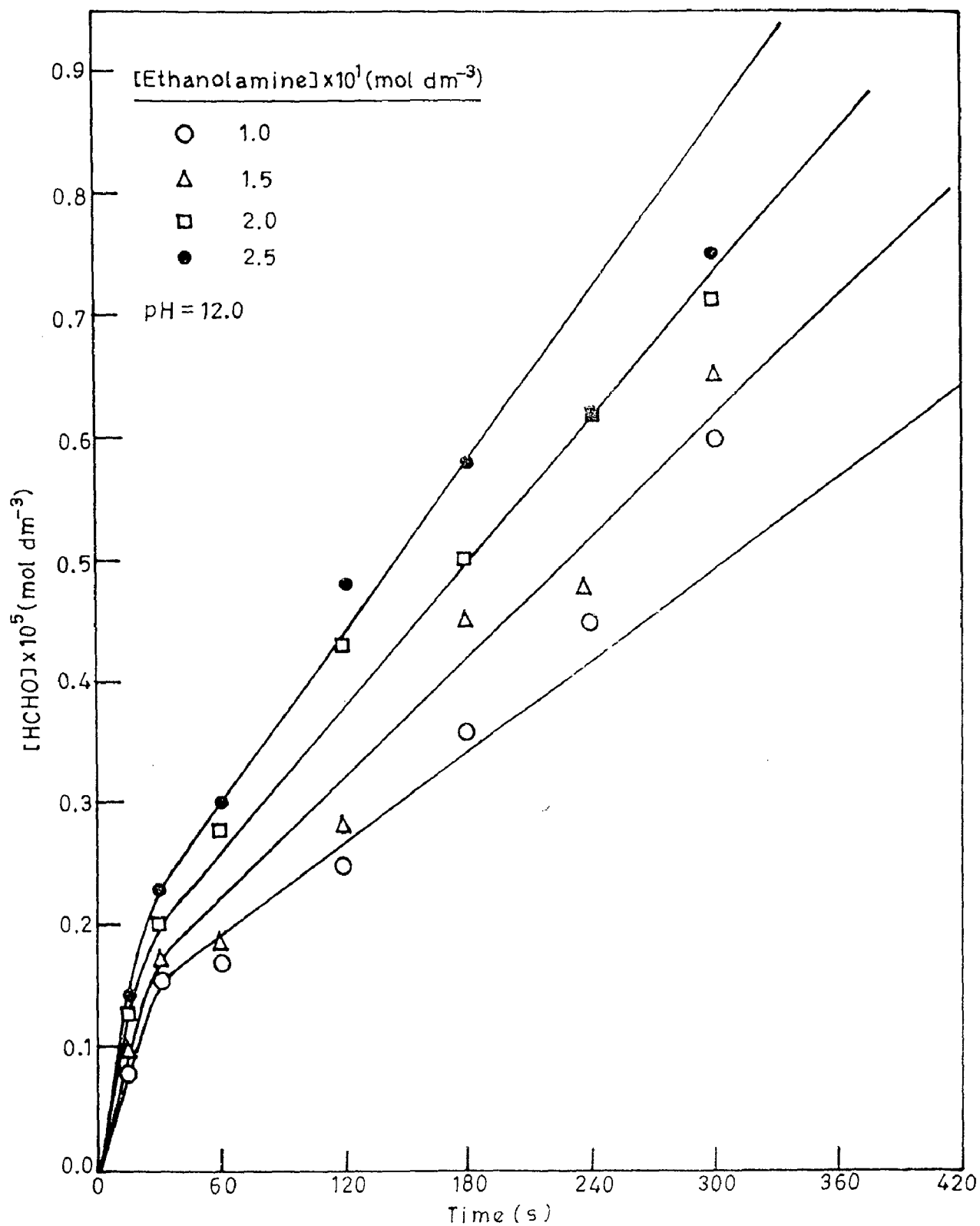


Fig. 4 : Effect of concentration of ethanolamine on the yield of product upon illumination of oxygenated TiO₂-ethanolamine reaction mixture as a function of time.

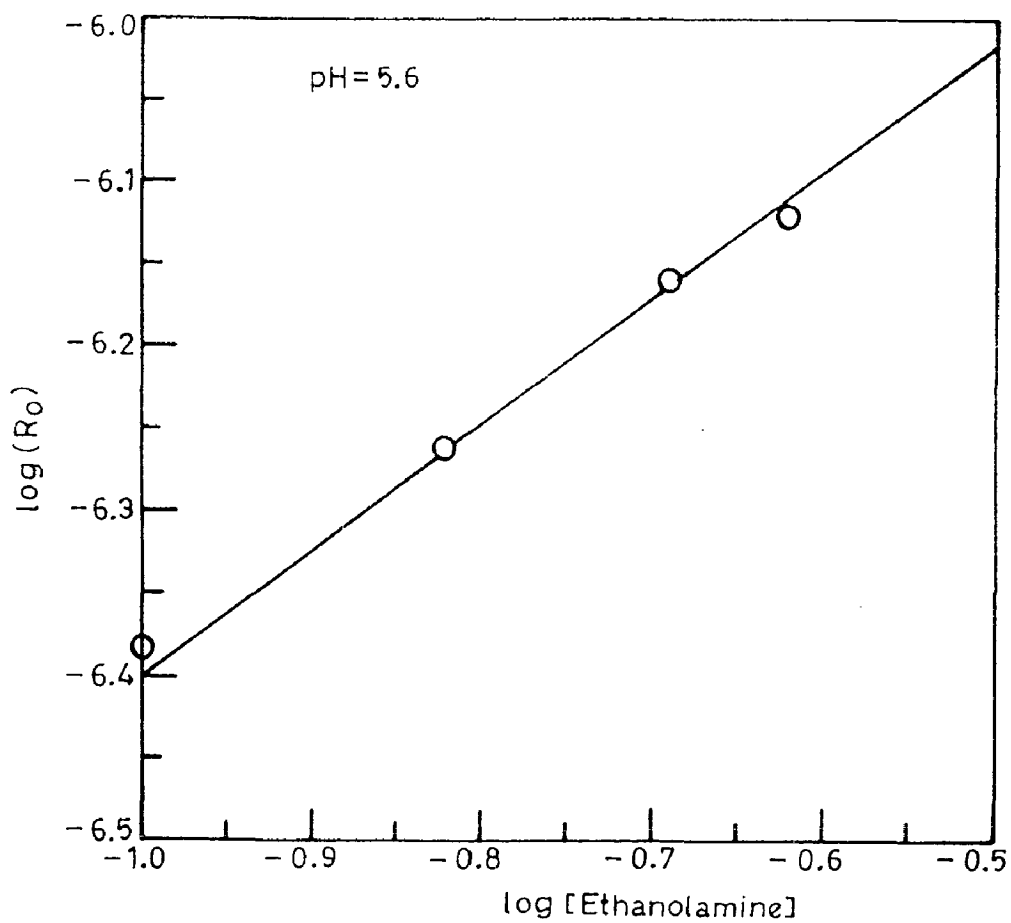


Fig. 5 : Vant-Hoff's plot for the determination of order with respect to ethanolamine

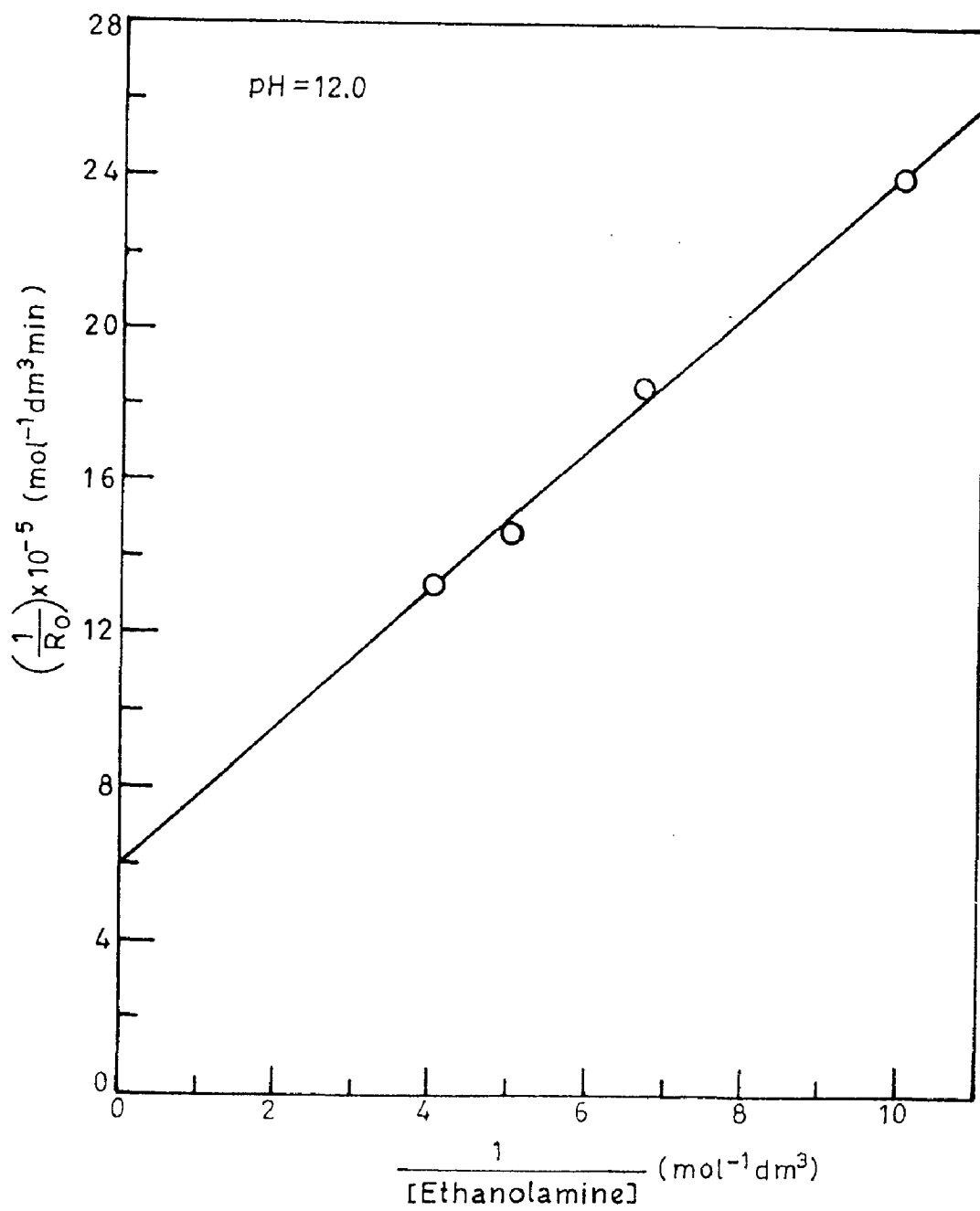


Fig. 6 : Plot of $(1 / R_0)$ vs $\frac{1}{[\text{Ethanolamine}]}$

2.2 Effect of the reaction environment on the rate of photooxidation

In the literature most of the TiO_2 - illuminated photochemical reactions have been performed in the presence of air. The role of oxygen in these reaction has lately been analyzed by Vinodgopal et al. [20]. In these systems the oxygen acts as the electron acceptor and hydrogen peroxide is eventually formed via dioxygen radical formation in the presence of suitable electron donor. In order to examine the earlier observations, we have carried out the effect of concentration of oxygen on the rate of formation of product. The amount of formaldehyde formed was determined as a function of irradiation time in different reaction environments, namely nitrogen, air and oxygen. Data of these runs are summarized in Table-5. Their plots are given in Fig. 7. An examination of these data reveal that the highest yield is obtained in oxygenated reaction mixture. On the contrary negligible amount of product is formed in the nitrogen atmosphere. In the presence of air the amount of product was in between the inert and oxygenated atmosphere. These observations can be understood by the fact that oxygen act as a electron acceptor on the illuminated TiO_2 - powder. It thus reduces the electron - hole recombination and the hole is increasingly scavenged by the added substrate.

Table-5 : Effect of O₂ content on the yield of product as a function of illumination time for TiO₂-ethanolamine reaction mixture.

[Ethanolamine] = 2.5×10^{-1} mol dm⁻³

pH = 12.0

Reaction Environment	Nitrogen		Air		Oxygen	
	O.D. at 572 nm	[HCHO] × 10 ⁵ (mol dm ⁻³)	O.D. at 572 nm	[HCHO] × 10 ⁵ (mol dm ⁻³)	O.D. at 572 nm	[HCHO] × 10 ⁵ (mol dm ⁻³)
30	-	-	-	-	0.191	0.22
60	-	-	-	-	0.258	0.31
120	0.048	0.05	0.160	0.19	0.398	0.49
180	-	-	-	-	0.427	0.50
240	-	-	-	-	0.518	0.62
300	0.050	0.05	0.250	0.30	0.621	0.74
600	0.047	0.05	0.398	0.49	-	-

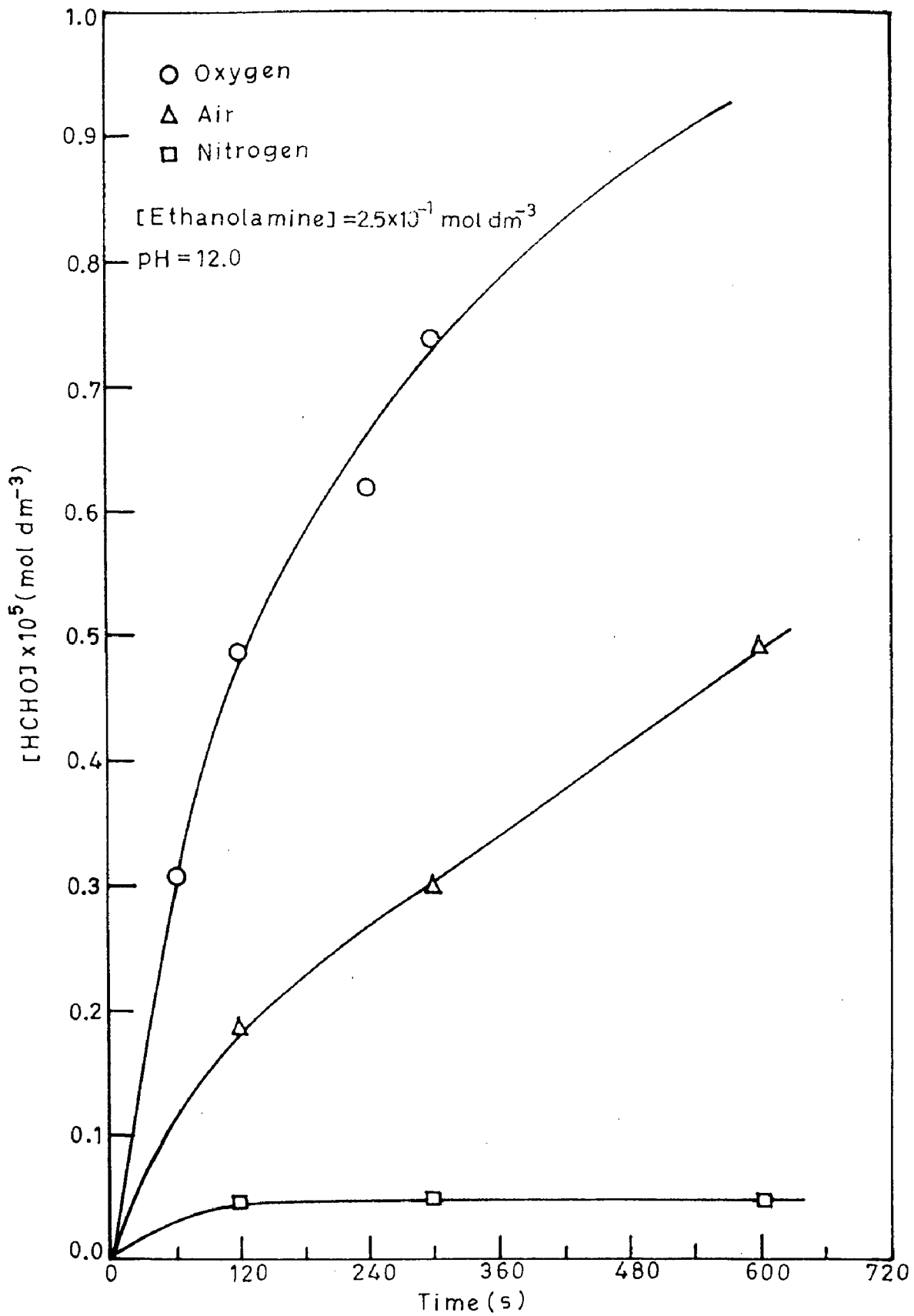
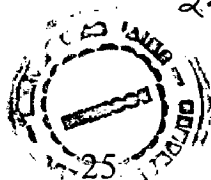


Fig. 7 : Effect of O₂ content on the yield of product as a function of illumination time for TiO₂-ethanolamine reaction mixture.

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2.3 Effect of pH on the rate of reaction

The pH of the reaction mixture has been reported to affect significantly the rate for TiO₂ - initiated photochemical reactions. The pH of solution may effect the TiO₂ - particles in various ways, e.g., it may change the energies of conduction and valence band, charge of the particle, and the size of aggregates. To examine these possibilities we have investigated the effect of pH on the studied reaction. These experiments were performed with oxygenated reaction mixture and the pH was varied between 2.5 to 12.0 only. The yield of product was followed as a function of irradiation time. These data are summarized in Table-6. The plots of the amount of product vs time are shown in Fig. 8. An examination of this figure reveals that an increase in pH enhance the yield of product significantly. Interestingly, at pH 2.5 the amount of product was very less in contrast to earlier observations [21] with 1, 2-ethanediol. At higher pHs, an increase in basicity regularly increased the amount of product. The isoelectric point of TiO₂ in water is known to be around 6. Thus at low pH the surface of TiO₂ will be positively charged and at high pH it will be negatively charged. The pK of ethanolamine is reported to be 9.5 [22]. Therefore, as the pH increases, an increasing amount of ethanolamine may possibly bind the TiO₂ surface. On the other hand at high pH OH⁻ will also be preferentially adsorbed on the surface of TiO₂ - particles. Thus the observed changes in the amount of product as a function of pH can be rationalised by the cumulative effect of the enhanced adsorption of these two species on the surface of TiO₂ -particles.

This reaction could also be carried out by sunlight efficiently. A plot of this run is shown in Fig. 9. This data reveals that the general behaviour of photooxidation of ethanolamine is very similar to that of recorded using light source.

Table-6 : Effect of pH on the yield of product upon illumination of oxygenated TiO₂-ethanolamine reaction mixture.

[Ethanolamine] = 2.0×10^{-1} mol dm⁻³

pH	2.5		5.6		9.0		12.0	
	O.D. at 572 nm	[HCHO] × 10 ⁵ (mol dm ⁻³)	O.D. at 572 nm	[HCHO] × 10 ⁵ (mol dm ⁻³)	O.D. at 572 nm	[HCHO] × 10 ⁵ (mol dm ⁻³)	O.D. at 572 nm	[HCHO] × 10 ⁵ (mol dm ⁻³)
30	0.013	0.01	0.052	0.07	0.093	0.11	0.177	0.20
60	0.010	0.01	0.065	0.09	0.114	0.15	0.228	0.27
120	0.016	0.01	0.098	0.13	0.152	0.18	0.354	0.43
180	0.026	0.02	0.111	0.15	0.172	0.20	0.417	0.49
240	0.043	0.03	0.132	0.17	0.215	0.25	0.514	0.61
300	0.041	0.03	0.167	0.19	0.273	0.33	0.613	0.73

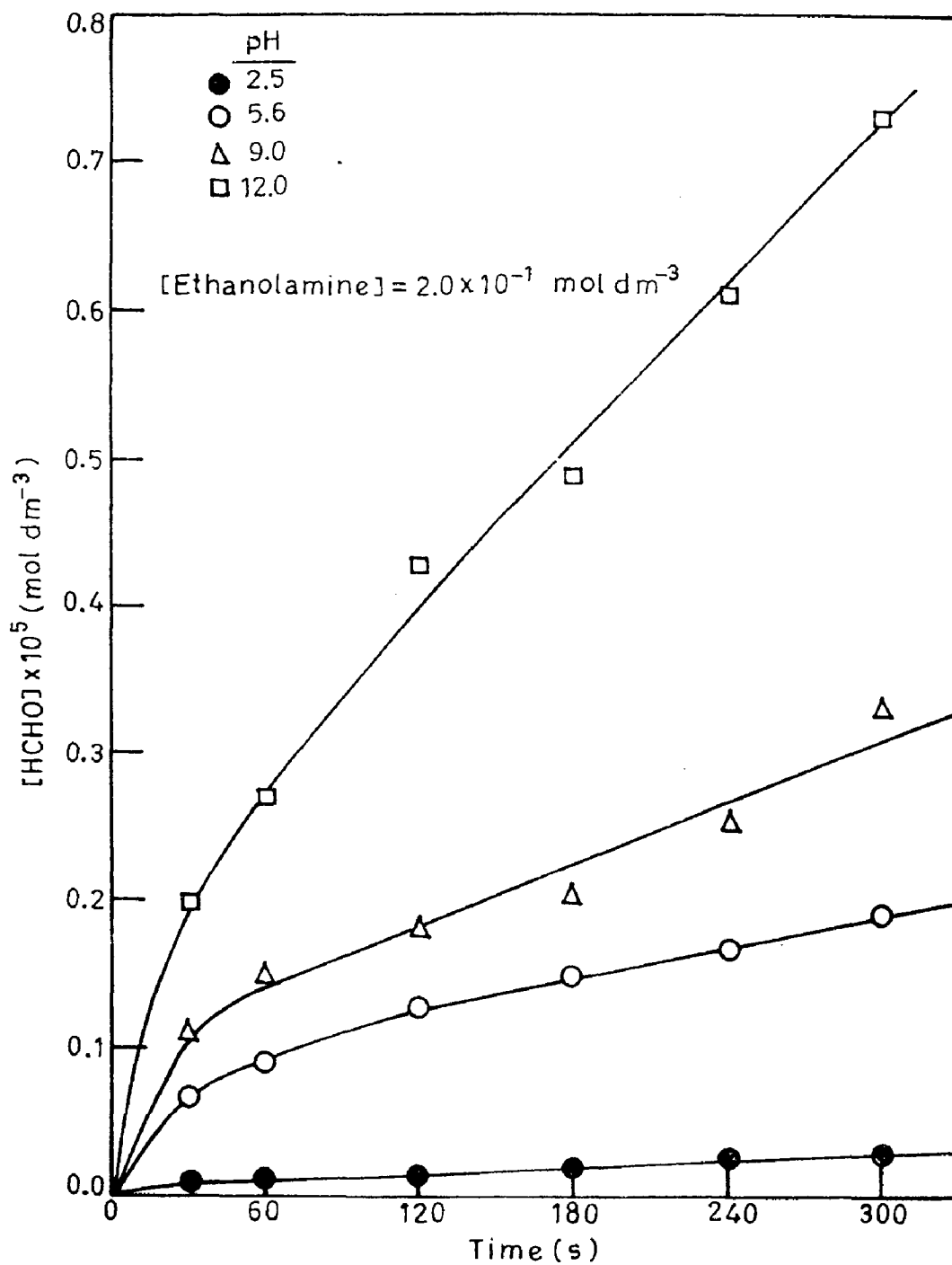


Fig. 8 : Effect of pH on the yield of product upon illumination of oxygenated TiO_2 -ethanolamine reaction mixture.

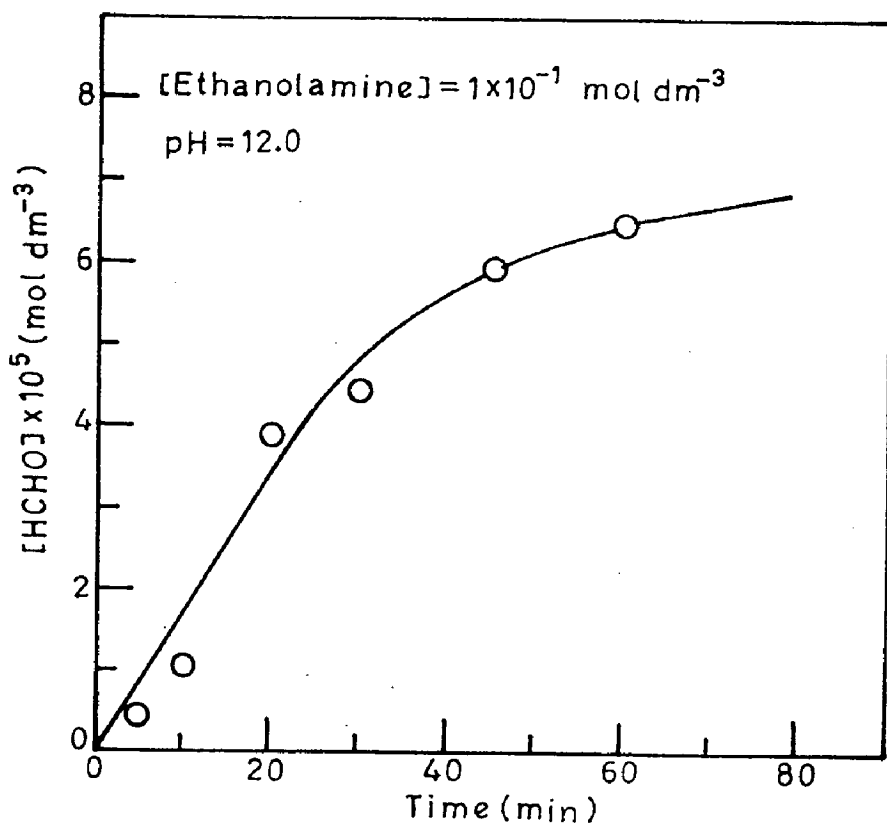


Fig. 9 : Amount of product formed with time upon irradiation of aerated TiO_2 -ethanolamine reaction mixture by sunlight.

2.4 Effect of the free radical scavenger on the photocatalytic activity of TiO_2

The photoirradiation of TiO_2 in the presence of oxygen is considered to involve initially the formation of $\dot{\text{O}}\text{H}$ radical. In order to examine the possibility of involvement of free radicals in reaction scheme, we carried out the TiO_2 - sensitized reaction of ethanolamine in the presence of acrylonitrile. The data of these experiments are presented in Table-7 and the respective kinetic plots are shown in Fig. 10. The presence of acrylonitrile caused a decrease in the yield of product.

This finding suggests the operation of free radical mechanism. It may, however, be noted that a decrease in the yield of HCHO was not substantial and amounts to only 10%. It is very likely that the free radicals formed in the reaction remained attached to the surface of particles and are not released in the solution. Therefore acrylonitrile may not scavenge the radical intermediate effectively.

Table-7 : Effect of radical scavenger on the yield of product upon irradiation of oxygenated TiO₂-ethanolamine reaction mixture.

[Ethanolamine] = 2.5×10^{-1} mol dm⁻³

pH = 12.0

[Acrylonitrile] $\times 10^2$ (mol dm ⁻³)	0		1.0		2.5	
	O.D. at 572 nm	[HCHO] $\times 10^5$ (mol dm ⁻³)	O.D. at 572 nm	[HCHO] $\times 10^5$ (mol dm ⁻³)	O.D. at 572 nm	[HCHO] $\times 10^5$ (mol dm ⁻³)
30	0.182	0.21	-	-	0.166	0.19
60	0.259	0.31	0.249	0.30	0.227	0.27
120	0.369	0.44	0.362	0.43	0.353	0.42
180	0.591	0.71	0.557	0.67	0.525	0.63
240	0.625	0.75	0.617	0.73	0.572	0.70
300	0.690	0.82	0.647	0.77	0.642	0.76

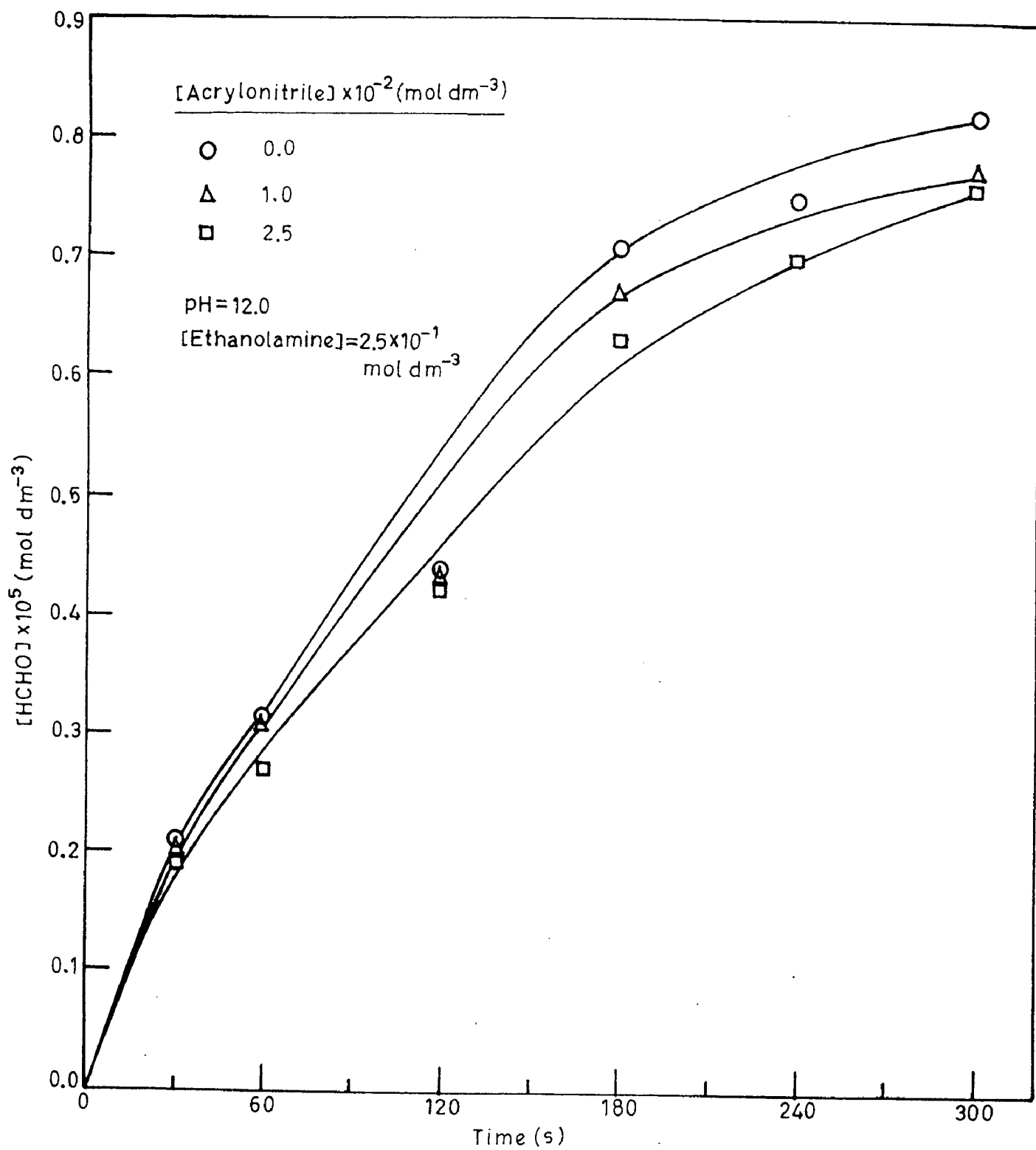


Fig. 10 : Effect of radical scavenger on the yield of product upon irradiation of oxygenated TiO_2 -ethanolamine reaction mixture.

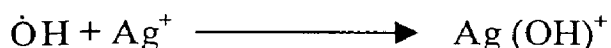
2.5 Effect of doping of transition metal ions on the rate of TiO₂ -sensitized photochemical reaction of ethanolamine

In the present work we have carried out the doping of Fe²⁺ and Ag⁺ ions. The irradiation of reaction mixture in the presence and absence of different concentration of Fe²⁺ did not show any change in photoactivity at pH 4.4. In the basic medium the Fe²⁺ precipitated on the surface of TiO₂ – suspensions. For these reasons these experiments were abandoned.

The influence of Ag⁺ on the photocatalytic activity of TiO₂ was investigated by doping different concentrations of silver ranging from 2.5 x 10⁻⁵ to 10 x 10⁻⁵ mol dm⁻³. The yield of formaldehyde was measured kinetically by illuminating TiO₂ - ethanolamine reaction mixtures in the absence and presence of different concentrations of Ag⁺. These data are presented in Table-8. Their kinetic plots are given in Fig. 11. From this figure, it may be seen that an increase in silver upto about 12 wt. % showed an increase in rate of photooxidation of ethanolamine. A further increase in silver beyond this limit retards the rate of photooxidation.

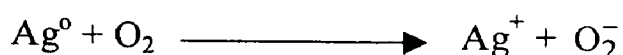
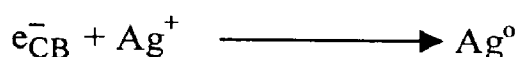
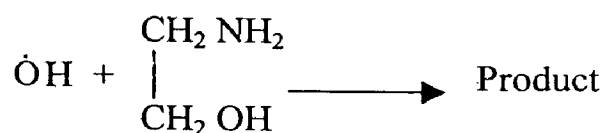
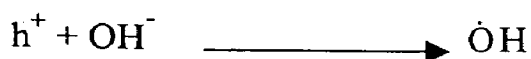
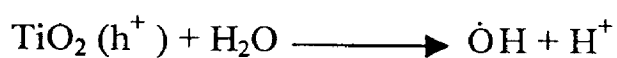
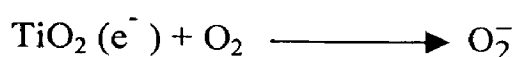
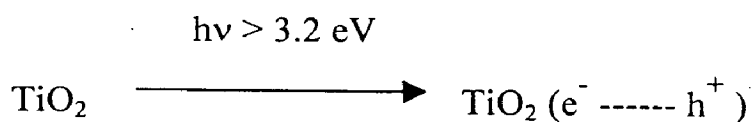
A plot of initial rate of formation of HCHO (R₀) vs wt. % of silver is shown in Fig. 12. This plot shows that the doping of about 12% silver has the maximum catalytic effect on the initial rate of oxidation which is about 2.5 fold to that of in the absence of silver. At higher concentrations of silver a negative effect on the reaction rate is observed. The catalytic effect at low concentrations of silver can be understood by increased scavenging of electrons by these ions which allows holes to react with the adsorbed substrate. Had the holes also been scavenged by silver

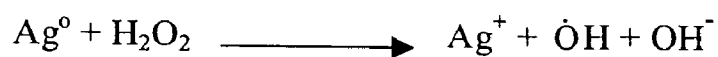
ions then at higher concentrations of silver one would expect the formation of Ag^{2+} .



Silver (II) is reported to oxidize ethanolamine to yield HCHO [23]. The decrease in the reaction efficiency at high concentrations of Ag^+ apparently rules out this possibility. This was also confirmed by adding bipyridyl to the silver doped TiO_2 catalyst. The irradiation of this reaction sample did not produce Silver (II) bipyridyl (Fig. 13). Silver (II) bipyridyl is known to absorb at 357 and 454 nm [24].

The used TiO_2 suspension, being having particle size of about 90 nm, provide large surface to the substrate. In view of the above observed kinetic effects, the mechanism of TiO_2 - induced photooxidation of ethanolamine can be outlined in the following steps:





The above shown reaction steps demonstrate that the photogenerated charge is separated in the presence of oxygen. An increase in concentration of OH^- would enhance the production $\dot{\text{O}}\text{H}$, which would eventually increase the amount of product. The doping of silver at its low concentration (≤ 12 wt%) increases the rate of formation of product by scavenging the conduction band electron but at high concentrations of silver (> 12 wt%) the holes possibly start to interact with silver particles as a result of which the yield of product is reduced.

Table -8 : Effect of $[Ag^+]$ on the yield of product upon irradiation of oxygenated TiO_2 -ethanolamine reaction mixture.

$[Ethanolamine] = 2.0 \times 10^{-1} \text{ mol dm}^{-3}$

$pH = 5.6$

$[AgNO_3]$ $\times 10^5$ (mol dm^{-3})	0		2.5		5.0		7.5		9.0		10.0	
	O.D. at 572 nm	$[HCHO]$ $\times 10^5$ (mol dm^{-3})	O.D. at 572 nm	$[HCHO]$ $\times 10^5$ (mol dm^{-3})	O.D. at 572 nm	$[HCHO]$ $\times 10^5$ (mol dm^{-3})	O.D. at 572 nm	$[HCHO]$ $\times 10^5$ (mol dm^{-3})	O.D. at 572 nm	$[HCHO]$ $\times 10^5$ (mol dm^{-3})	O.D. at 572 nm	$[HCHO]$ $\times 10^5$ (mol dm^{-3})
15	0.034	0.05	0.077	0.10	0.085	0.11	0.095	0.12	0.074	0.10	0.640	0.09
30	0.052	0.07	0.153	0.18	0.167	0.19	0.179	0.21	0.151	0.18	0.121	0.16
60	0.065	0.09	0.161	0.19	-	-	0.185	0.22	0.169	0.19	0.125	0.17
120	0.098	0.13	0.176	0.20	0.185	0.22	0.234	0.28	0.178	0.21	0.141	0.18
180	0.111	0.15	0.187	0.22	0.194	0.23	0.242	0.29	0.188	0.22	0.165	0.19
240	0.132	0.17	0.205	0.24	0.215	0.25	0.270	0.32	0.193	0.23	0.174	0.20
300	0.167	0.19	0.212	0.25	0.264	0.31	0.306	0.36	0.230	0.28	0.184	0.21

Table-9 : Effect of [Ag⁺] on initial rate of formation of product observed after 15 s of illumination of TiO₂-ethanolamine reaction mixture.

[Ethanolamine] = 2.0×10^{-1} mol dm⁻³

pH = 5.6

[AgNO ₃] $\times 10^5$ (mol dm ⁻³)	[Ag ⁺] (wt. %)	O.D. at 572 nm	[HCHO] $\times 10^6$ (mol dm ⁻³)	(R ₀) $\times 10^6$ (mol dm ⁻³ /s)
0	0	0.034	0.45	0.225
2.5	4	0.077	1.00	0.500
5.0	8	0.085	1.10	0.550
7.5	12	0.095	1.20	0.600
9.0	15	0.074	0.98	0.490
10.0	16	0.064	0.90	0.450

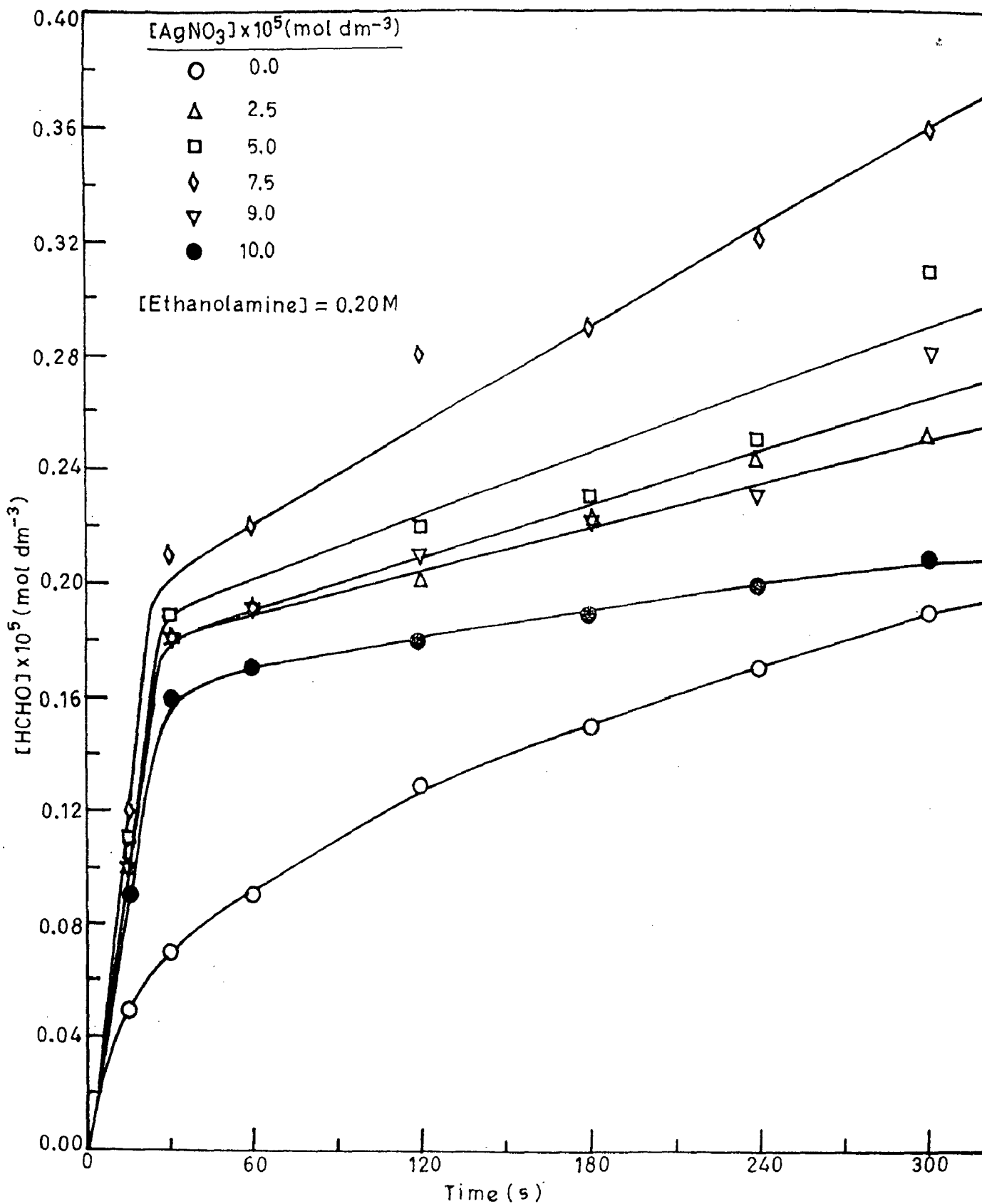


Fig. 11 : Effect of $[\text{Ag}^+]$ on the yield of product upon irradiation of oxygenated TiO_2 -ethanolamine reaction mixture.

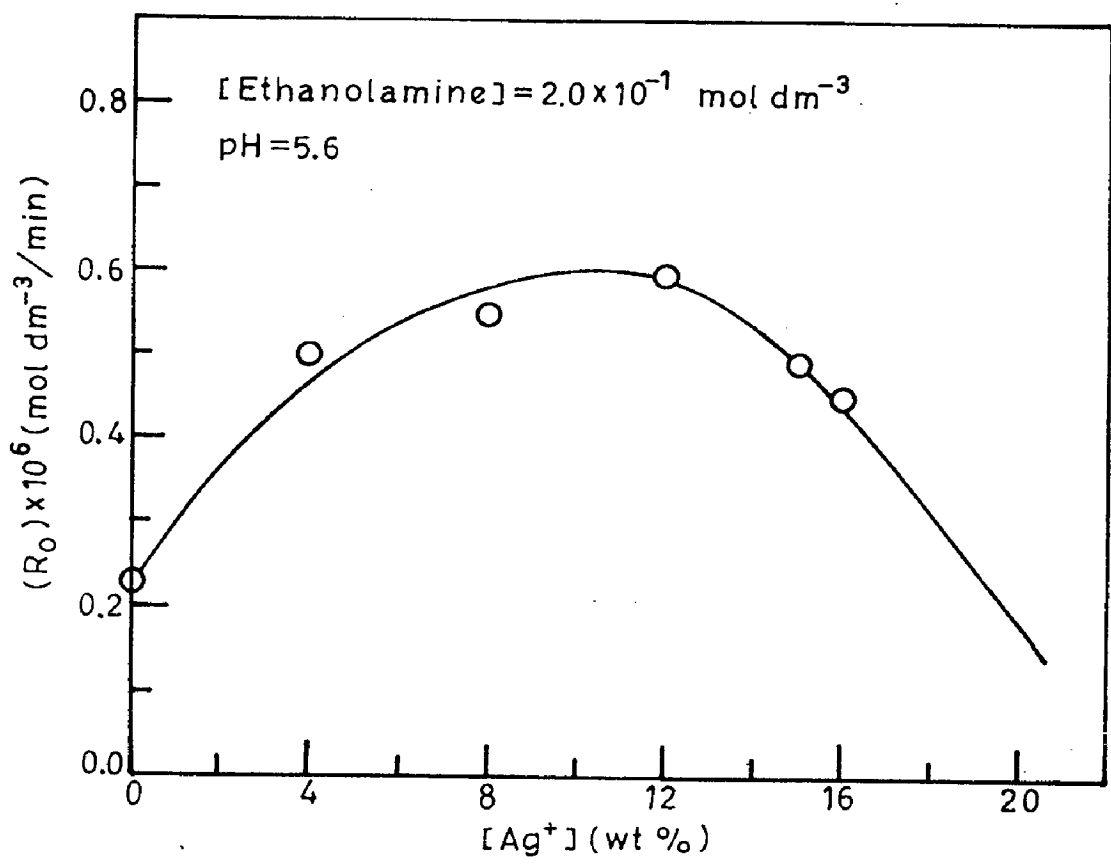


Fig. 12 : Effect of [Ag⁺] on the photocatalytic oxidation of ethanolamine.

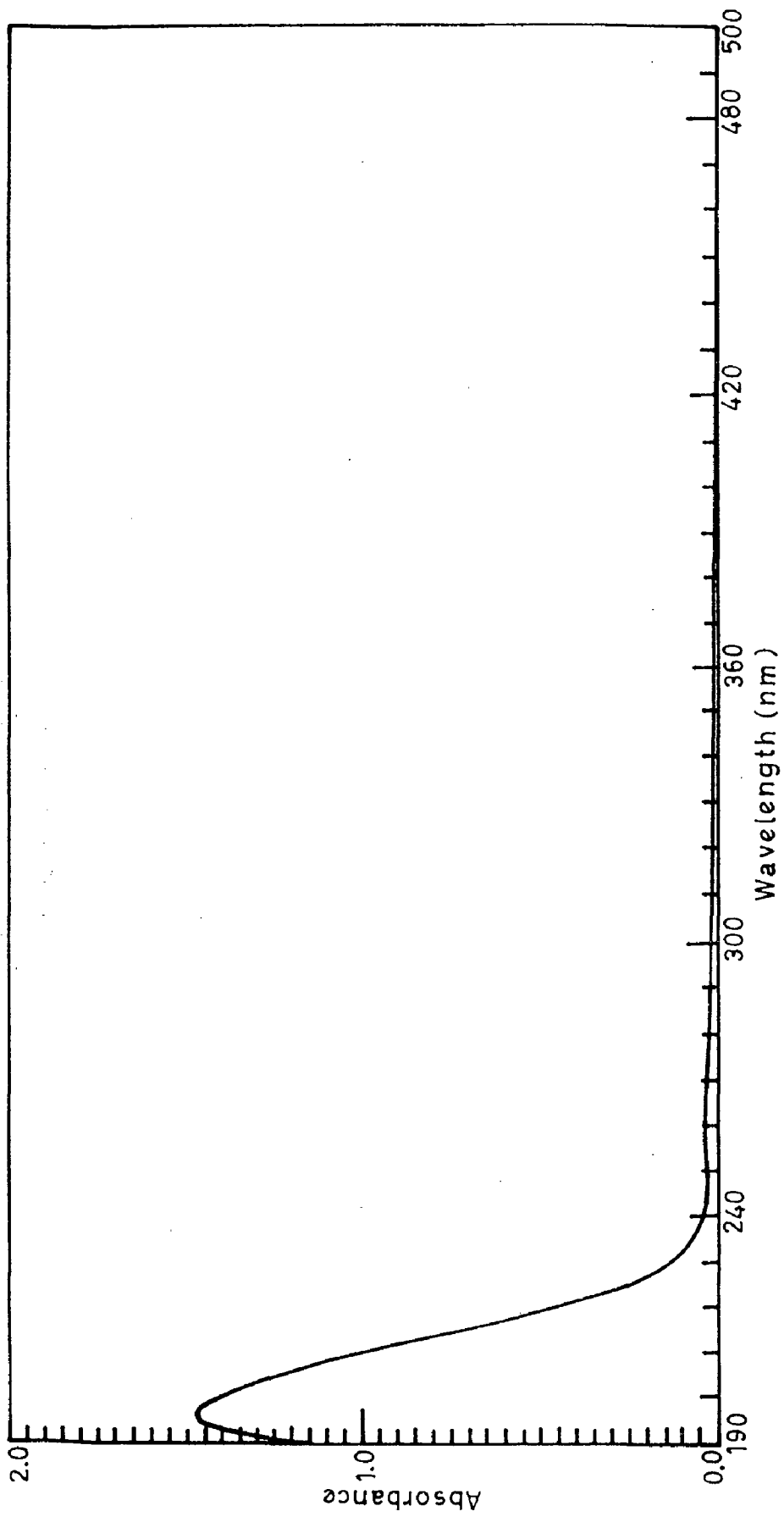


Fig. 13 : Electronic spectrum of illuminated silver doped TiO_2 catalyst in the presence of bipyridyl.

CONCLUSIONS

The TiO_2 induced photooxidation of ethanolamine obeys first-order kinetics with respect to ethanolamine in the studied concentration range. The presence of oxygen is essential for bringing the charge separation in this system. The rate of oxidation is enhanced by an increase in pH. The doping of iron has no effect on the rate of photooxidation whereas the presence of silver significantly enhances the rate of photooxidation.

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