

Light Induced Hydrogen Production From Ethanolic Aqueous Solutions Sensitized By 2,4-Dimethoxy Benzylidene-2- Hydroxy Aniline And Some of Its Metal Complexes

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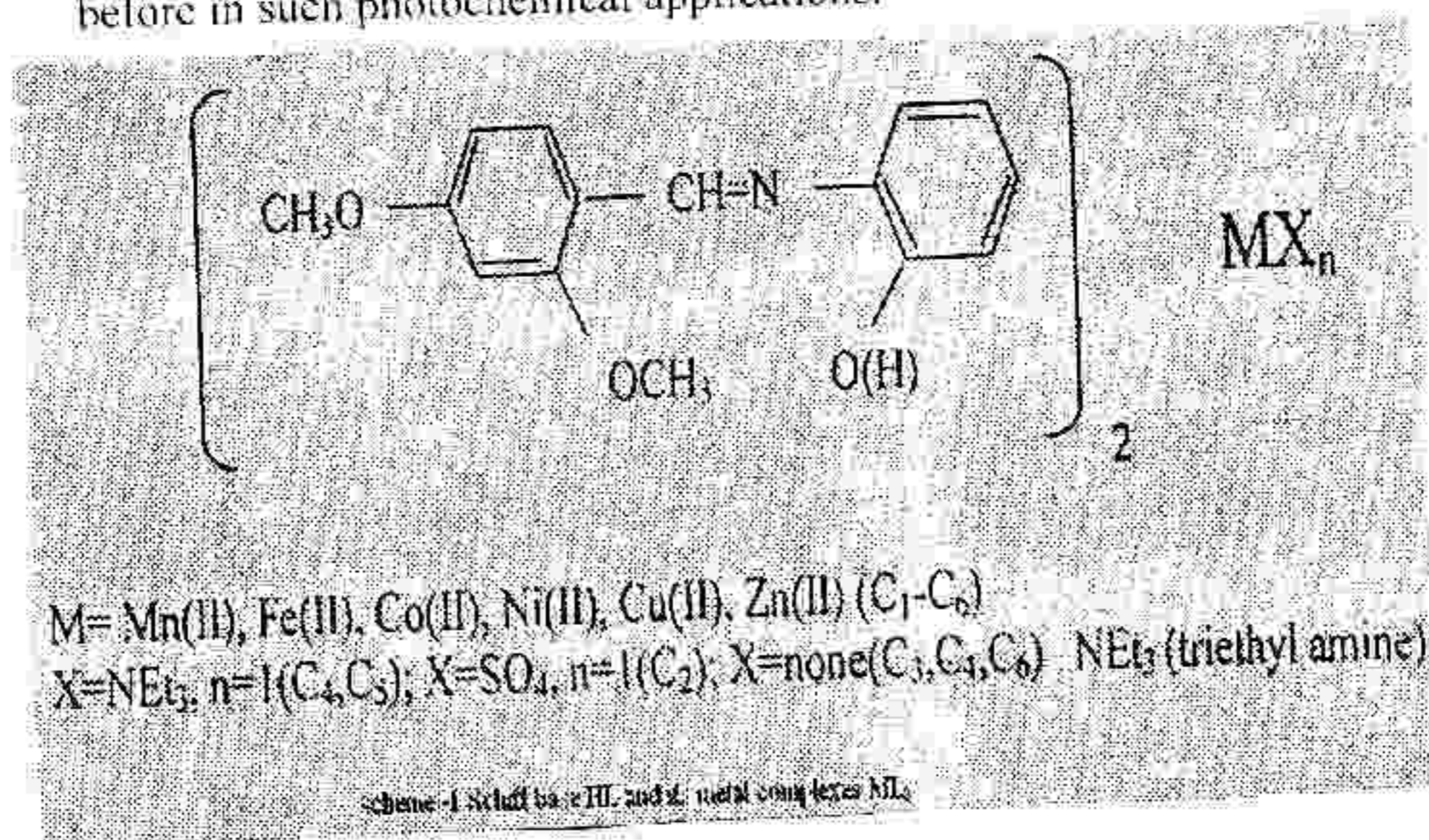
Abstract

Hydrogen productions were achieved by irradiating ethanolic aqueous solutions (20%, v/v) containing mixtures of the ligand 2,4-dimethoxybenzylidene-2-hydroxy aniline (HL) or one of its complexes (ML_2) with the following divalent ions: Mn (II), Fe(II), Co(II), Ni(II), Cu(II) and Zn (II), as photosensitizers, methyl viologen (MV^{2+}) as electron acceptor, ethylene diamine tetraacetic acid disodium salt (EDTA) as a sacrificial electron donor, in presence of platinum poly (vinyl alcohol) (Pt-PVA) or platinized TiO_2 (Pt/ TiO_2), (200 and 45 micron) as reduction catalysts, using white light from 250 W xenon arc lamp at room temperature 25 ± 2 °C. Oxidation Potentials of the ligand and its complexes were determined by cyclic voltammetry. The efficiency of the photoreduction of MV^{2+} and hydrogen production by HL and metal complexes was mainly dependant on pH, type and particle size of catalyst, as well as metal ion in case of ML_2 . Best performances were recorded by the free ligand.

Introduction

Certain metal complexes such as ruthenium (II) trisbipyridyl $Ru(bip)_3^{2+}$ metal phthalocyanines (MPc) and metal porphyrins (MP) were reported to be more efficient photosensitizers than the original ligands in light induced electron transfer reactions leading to hydrogen production (1-12).

In the present work a comparison is made between using the Schiff base 2,4-dimethoxybenzylidene - 2-hydroxy aniline (HL), and its complexes (ML_2) with some bivalent ions (Scheme 1) in photosensitization of hydrogen production from 20% v/v ethanolic aqueous solutions in presence of MV^{2+} as an electron acceptor, EDTA as a sacrificial electron donor and Pt/PVA or Pt/TiO₂ as reduction catalysts. Neither the ligand nor its complexes have been studied before in such photochemical applications.



Experimental

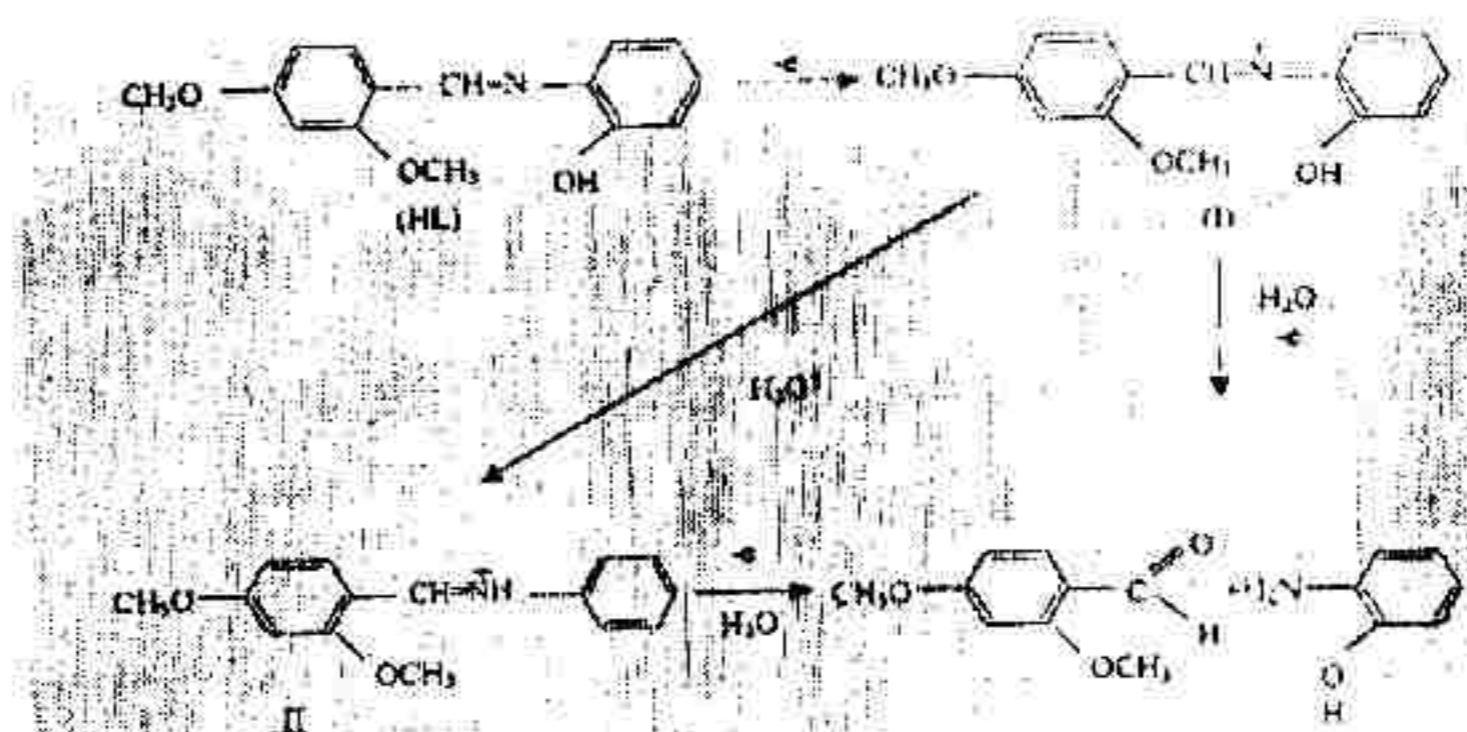
The preparation and characterization of the ligand and its complexes were reported in a previous work (13). Colloidal platinum (Pt-PAV₄₉₀₀₀) and platinized TiO₂ (Pt/TiO₂) were prepared as reported earlier (126). Anodic oxidation of these compounds (4.8×10^{-4} M) were carried out in aqueous ethanolic solutions (20%) containing potassium sulphate (0.1M) as a supporting electrolyte. Measurements were recorded by using a three electrode system with a CV-27 BAS scanning potentiostat supplied with a cell stand type CIB-240 and an X-Y recorder Omnigraph Houston Instrument, scan rate 0.1V/s. Irradiation experiments were performed with a 250W xenon arc lamp (Applied Photophysics Ltd.), connected to a thermostatic unit Photoreduction. Of MV^{2+} was carried out in 5 ml quartz cell, fitted with a 1cm² irradiation window. Hydrogen production reactions were carried out in a 30 ml irradiation cell fixed with a water cooling jacket.

and a 2cm diameter quartz irradiation window. The following reactant concentrations were used : HL or MI_2 , 3.4×10^{-4} ; MV^{2+} , 3.4×10^{-3} ; and EDTA, 10^{-2} M with different concentrations and loadings of Pt-PVA and Pt/TiO₂ respectively at different pH and at room temperature (25 ± 2 °C). Intensity of Incident light (150 ± 5 m W/cm²) was measured by using a Centronic Optical system photometer radiometer model 210. Detection of hydrogen gas evolution was recorded on a Pye-Unicam 304 gas chromatograph supplied with carbosieve 5A. column 1 inch in diameter and 3ft length with a thermal conductivity detector. column temperature 60°C, injection temperature 100°C and a flow rate 20 ml min⁻¹. U. v- visible spectra of irradiated solutions with time were recorded on a Cecil type CF 599 and Lambda 9 Uv-visible-Nir spectrophotometer.

Results and Discussions

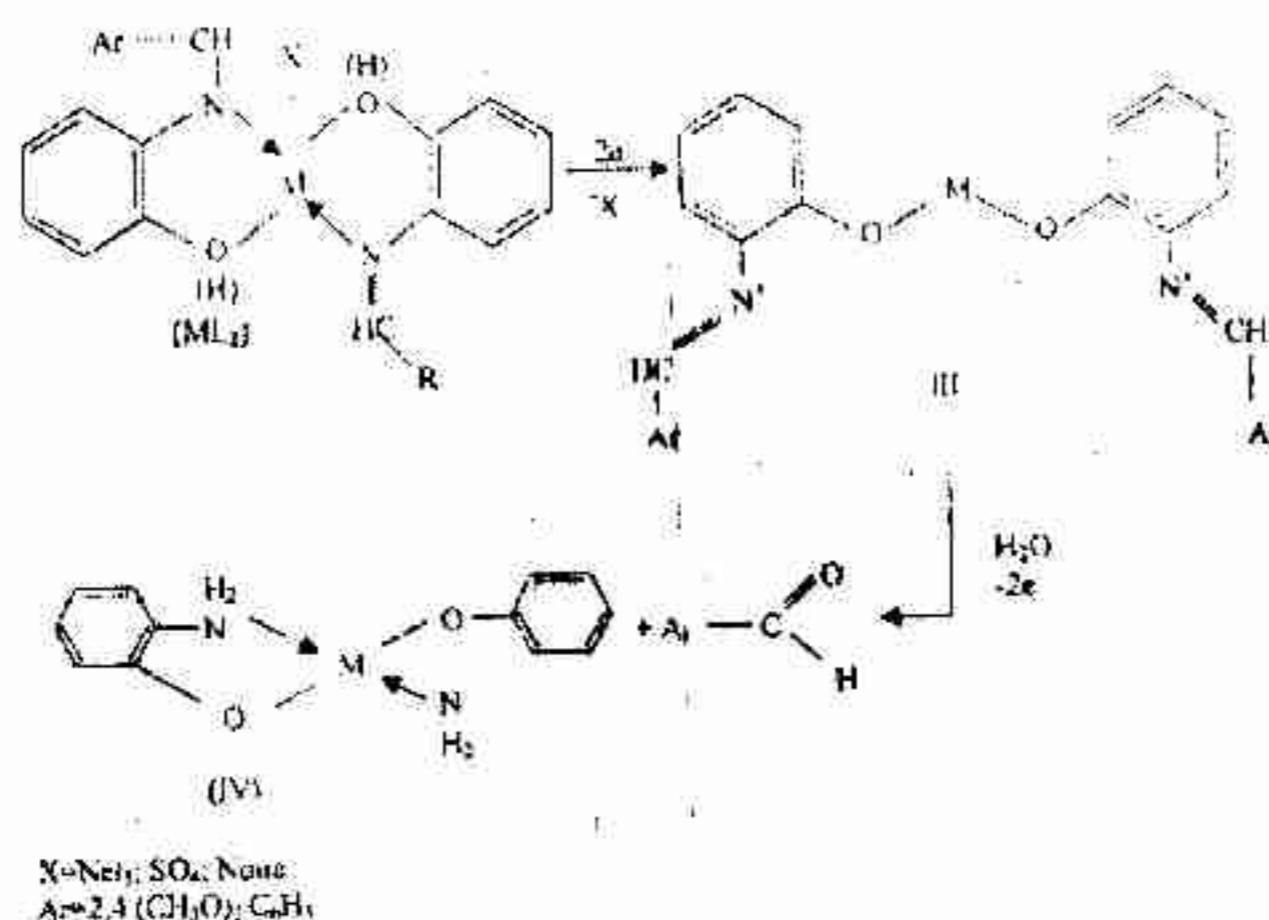
- Cyclic Voltammetry

Table (1) describes the peak potentials (EP) and peak current (ip) resulted from anodic oxidation of HL and MI_2 molecules. The Ligand exhibited two irreversible oxidation peaks Fig. (1). The first peak (E_{p1}) may be attributed to oxidation of HL forming a radical cation (I) through one electron process (14,15). In presence of traces of acid, I is converted to the species II (Scheme-2). The second oxidation peak (E_{p2}) was assigned to further oxidation of both species I and II, leading to the formation of 2,4-dimethoxy benzaldehyde and 2-aminophenol as final products through one electron process (14,15). The whole mechanism is shown in Scheme -2.



Metal complexes, in general, showed two oxidation peaks, the positions of which were metal dependent. The first peak (Ep_1) appeared at the region 1.150 – 1.290 V may be attributed to an electron loss from the coordinated azoethine moiety, depending on nature of bonding with the metal ion, giving the dicationic radical III (Scheme-3). The second peak (Ep_2) appeared at the region 1.403 – 1.658V may be attributed to further oxidation of III to the corresponding aldehyde and two phenoxyamino fragments bonded to the metal ion (IV).

A third oxidation peak (Ep_3) was exhibited by C_1 , C_2 , C_3 and C_5 . These were attributed to the oxidation of Net_3 in C_1 and C_5 (15), and to irreversible oxidation of metal ions in C_2 and C_3 (15-18). Voltammograms of HL, C_1 , C_3 and C_6 are shown in Fig. (1).



Scheme-3 Anodic oxidation of Schiff base metal complexes

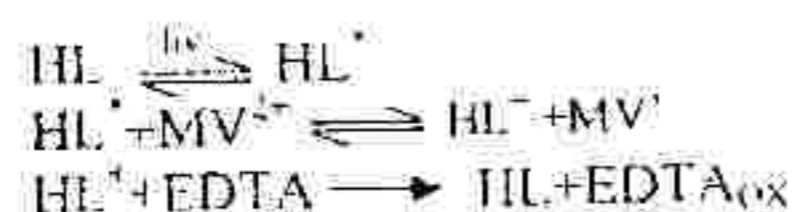
- Photochemical Reactions

a. Photoreduction of methyl viologen

Fig. (2a) shows the variation of u. v-visible spectra with time on irradiating mixtures of HL or ML_2 , MV^{2+} , and EDTA in 20% ethanolic solutions at pH=5 for 30 min. Build up of reduced acceptor molecules was detected by the gradual appearance of the blue colour characteristic of $MV^{\cdot+}$, radical cations and by the increased appearance of their characteristic absorption peak at 602 nm (6,12,19-22) with time of irradiation. The photoreduction of MV^{2+} by HL and ML_2 refers to the occurrence of electron transfer reactions, mediated by

light, from photoexcited ligand or complex molecules to MV^{2-} molecules to form the blue radical cations. Such reaction could not proceed in the absence of EDTA. Leaving the irradiated mixtures in the dark, gave the original spectra before irradiation. Irradiating the ligand or its complexes in absence of MV^{2-} and EDTA showed no change in the spectra for 6h, which refers to their stability towards light and hydrolysis. The presence of the two methoxy groups at 2- and 4- positions plays a good role in stabilization of the irradiated molecules. The electron transfer reactions occur when the molecules (HL or ML_2) absorb light energy that leads to an excited singlet or triplet state and when the latter acquires a redox potential that allows for reducing the suitable electron acceptor. The photoreduction of MV^{2+} by HL and ML_2 refers to the existence of such properties. As a result, the excited sensitizer is oxidized. The presence of the methoxy group will help in spreading the positive charge along the oxidized species (23) and hence increasing their stability. The presence of OH group in HL at the ortho position of imino group offers further contribution to resonance structure stabilization compared with metal complexes (24-27).

The presence of EDTA is very important in providing electrons to the oxidized photosensitizers and in inhibiting backward reaction. The mechanism of light-induced photoreduction of MV^{2+} by HL , may be summarized by the following equations (22,28,29).

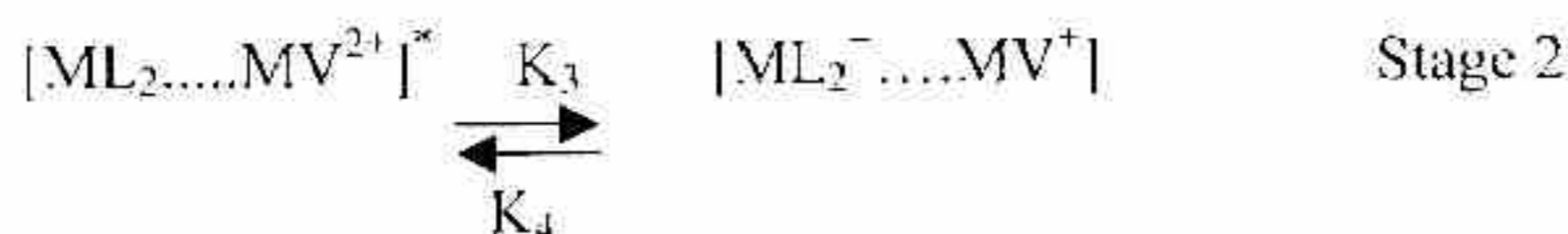


Rate constants of photoreduction (k) for HL , are listed in Table (2). Values were found to fit first order reactions (30) and were pH dependent. The build up of $MV^{\bullet+}$ radicals sensitized by metal complexes was observed after the complete disappearance of the absorption bands located mainly in the visible region at (410-480 nm) (13), Fig. (2b,c). In spite of their stability towards hydrolysis, metal complexes showed lower photoreduction efficiencies than the original ligand, with best performance exhibited by C_4 and C_6 . This may be attributed to the overlapping of the lone pair on imino nitrogen of HL with the empty orbitals of metal ions which decreases the donation property of the molecule to MV^{2+} molecules. The degree of inhibition of electron transfer depends directly on polarization ability applied by

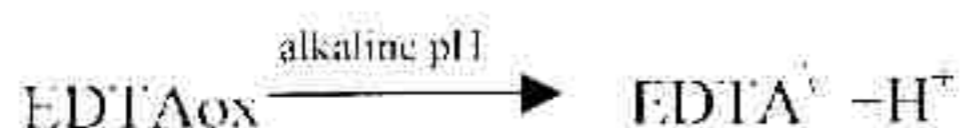
the metal ions on the imino nitrogen (31). Accordingly, the photosensitization process by ML_2 was suggested to proceed through two stages. Stage I may include the formation of an excited charge transfer complex between the excited metal complex and MV^{2+} molecules (32) as shown in the following equations :



The second stage (stage 2) may include the formation of ion pairs leading to the build up of MV^+ radicals in presence of EDTA (29,32-34).



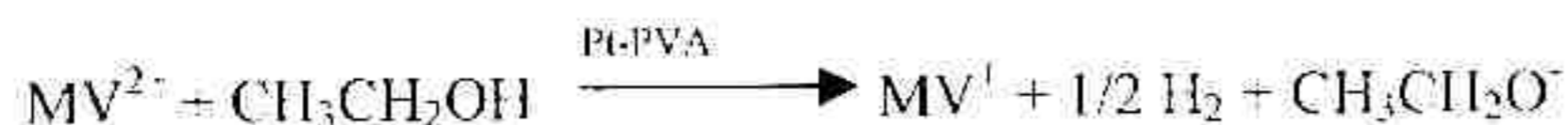
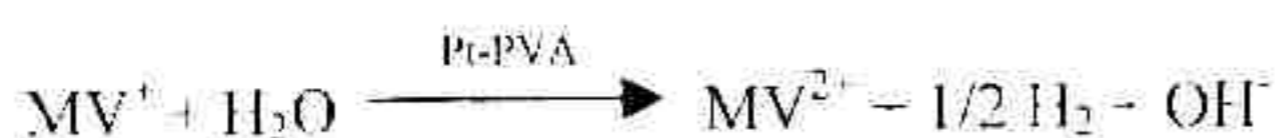
The rate constants (K_1 , K_2) and K_3 for stage 1 and 2 respectively were found to fit first order reaction (30) Table (3 and 4 respectively) while those of K_4 represent second order reactions (19, 33,34). Fig. (3) shows the linear relationship for first order kinetics using C_3 as a photosensitizer. Better performances were exhibited by the ligand and its complexes in alkaline pH than in acidic media. This may be attributed to decrease of electron donation property of both the photosensitizer and EDTA as a result of protonation of both molecules, which inhibits the forward electron transfer reactions (12,22). Whereas in alkaline solutions the electron donor activity of EDTA is increased for being converted to a strong reducing carbon centered radical (EDTA) (12,22), as a result of hydrogen abstraction from EDTAox. and hence additional reduction of MV^{2+} by EDTA will take place as shown by the following equations:



b. Hydrogen Production

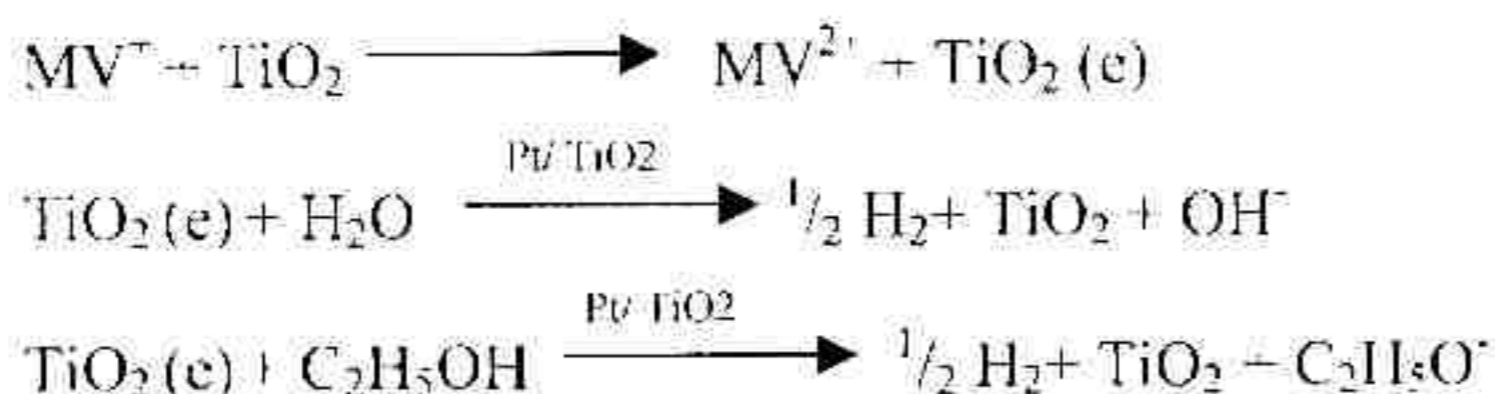
i. Catalysis by Pt-PVAA:

Table (5) describes the yields, and turnover numbers (TN) of hydrogen gas evolution on irradiating the previously specified ethanolic aqueous solutions of HL and ML_2 in presence of MV^{2+} , and EDTA with white light for 5h at pH=5 at room temperature using different concentrations of Pt-PVA (13) as a reduction catalyst. Results were directly related to those obtained in the photoreduction of MV^{2+} . Ligand molecules exhibited higher performance than metal complexes, which were metal dependent. Best results were recorded by C_4 and C_6 . Optimum yields were observed at $[\text{Pt-PVA}] = 3.2 \times 10^{-4}$ and $2.6 \times 10^{-4} \text{M}$ for HL and ML_2 respectively. The photochemical processes may be summarized by the following equations (22,35-37).



ii. Catalysis by Pt/TiO₂

The same previously mentioned irradiation processes and conditions were repeated but instead of Pt-PVA, two mesh sizes of Pt/TiO₂ particles were used for catalysis: 200 micron, and 45 micron with different loadings at pH=5, the yields were much higher than those catalyzed by Pt-PVA, especially with mesh size of 45 micron. The TiO₂ particles offer more efficient charge separation through formation of holes and electrons which provide more active centers for photoelectron transfer reactions towards hydrogen production (14,28). In this process electrons are injected from $\text{MV}^{\cdot-}$ radicals into conduction band of TiO₂ particles to form the electron carriers $\text{TiO}_2(e^-)$ (10,28,38-40). The latter transfer their electrons to deposited platinum to achieve hydrogen production as illustrated by the following equations.



Smaller particle sizes of TiO₂ (45 micron) provide more active centers and bigger surface area for charge separation and hence lead to higher yield of hydrogen molecules than bigger particles. Results obtained from both particle sizes 200 and 45 micron are described in Tables 6 and 7 respectively. Optimum yields were obtained on using 50 mg. and 30 mg of catalysts respectively. Results were closely similar to those obtained in presence of Pt/PVA, as HL gave the highest yield of hydrogen evolution while C₄ and C₆ showed the best yields among metal complexes. The amount of hydrogen gas was recorded after abstracting the amount of gas evolved in absence of HL and metal complexes.

Conclusions

Because of their stability towards light and hydrolysis in 20% aqueous ethanolic solutions HL and ML₂ can be recommended as photosensitizers in photoproduction of hydrogen. The presence of electron donating groups such as OCH₃ and OH increased the donor activity of HL in the process. The performance of metal complexes was lower than that of HL and was inversely proportional to the degree of polarization exerted by metal ion on the lone pair of imino nitrogen.

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Table (1) Anodic oxidation potentials (Ep, volt)and peak currents (ip, mA) of HL and its metal complexes by cyclic voltammetry in 20%, V/Vaqueous ethanol containing 0.1 M of K₂SO₄

| Formula Symbol | Ep ₁ V | Ip ₁ mA | Ep ₂ V | Ip ₂ mA | Ep ₃ V | Ip ₃ mA |
|--|-------------------|--------------------|-------------------|--------------------|-------------------|--------------------|
| (HL)[C ₁₅ H ₁₁ NO ₂] | 1.150 | 0.056 | 1.625 | 0.162 | | |
| (C ₁)[MnL ₂ (Et ₃ N)] | 1.268 | 0.068 | 1.658 | 0.155 | 0.975 | 0.030 |
| (C ₂)[Fe(HL) ₂ .SO ₄] | 1.260 | 0.043 | * | * | 0.657 | 0.035 |
| (C ₃)[CoL ₂].3H ₂ O | 1.250 | 0.055 | * | * | 1.109 | 0.043 |
| (C ₄)[NiL ₂] 0.5 EtOH | 1.291 | 0.061 | 1.610 | 0.157 | | |
| (C ₅)[CuL ₂ (Et ₃ N) ₂ .0.5H ₂ O | 1.200 | 0.025 | 1.403 | 0.046 | 0.963 | 0.019 |
| (C ₆)[ZnL ₂] 0.5 H ₂ O | 1.213 | 0.067 | 1.605 | 0.155 | | |

* unidentifed peak

Table (2) Rate constant values K (s^{-1})* of photoreduction of MV^{+} (3.4×10^{-3} M) sensitized by HL (3.4×10^{-4} M) in presence of EDTA (10^{-2} M) in aqueous ethanol (20%) at different pH

| pH | $K/s \times 10^{-2}$ |
|----|----------------------|
| 3 | 2.00 |
| 5 | 2.66 |
| 7 | 3.28 |
| 9 | 3.40 |

* calculated according to the following equation ⁽³²⁾

$$\ln(A_{\infty} - A_t) = \ln A_{\infty} - kt$$

A_{∞} = Absorbance of MV^{+} at $t = \infty$

A_t = Absorbance of MV^{+} at irradiation time intervals $t=t$

K = rate constant (s^{-1}), t = irradiation intervals (s)

Table (3) Rate constant values* (s^{-1}) for photoinduced charge transfer complex formation (k_1) between ML_2 and MV^{+2} and their decay (k_2) at pH=5 (stage 1)

| Comp No. | $K_1/s \times 10^{-4}$ | $K_2/s \times 10^{-3}$ |
|-------------------------|------------------------|------------------------|
| C ₁ [Mn(II)] | 50.20 | 15.30 |
| C ₂ [Fe(II)] | 4.80 | 9.82 |
| C ₃ [Co(II)] | 43.00 | 11.20 |
| C ₄ [Ni(II)] | 98.00 | 6.61 |
| C ₅ [Cu(II)] | 5.33 | 4.24 |
| C ₆ [Zn(II)] | 100.00 | 5.01 |

*Rate constant was calculated according to the following equations ⁽³²⁾

$$\ln(A_{\infty} - A_t) = \ln A_{\infty} - kt$$

$$\ln A_t = \ln A_0 - kt$$

where A_{∞} = Absorbance of MV^{+} at $t = \infty$

A_t = Absorbance of MV^{+} at irradiation time intervals $t-t$

A_0 = initial absorbance of MV^{+} at $t = 0$

Table (4) Rate constant values (K_3 , s^{-1}) for photosensitized reduction of MV^{+2} through charge transfer complexation with excited ML_2 (C₁-C₆) at different pH(stage 2)

| Complex no. | Rate constant K_3 (s^{-1}) | | | |
|----------------|----------------------------------|--------------------------|--------------------------|--------------------------|
| | (PH =3) $\times 10^{-3}$ | (PH =5) $\times 10^{-2}$ | (PH =7) $\times 10^{-2}$ | (PH =9) $\times 10^{-2}$ |
| C ₁ | 5.8 | 1.4 | 2.0 | 2.3 |
| C ₂ | 4.7 | 1.19 | 1.98 | 2.21 |
| C ₃ | 10.0 | 1.20 | 2.1 | 2.5 |
| C ₄ | 10.1 | 1.58 | 2.4 | 2.6 |
| C ₅ | 8.31 | 1.49 | 2.23 | 2.4 |
| C ₆ | 12.1 | 1.60 | 2.0 | 2.8 |

Table (5) Total volume (ml/L). no. of moles, and turnover numbers (TN)* of hydrogen evolution on irradiation mixtures of HL or its complexes (3.4×10^{-4} M) with MV^{+2} (3.4×10^{-3} M) and EDTA (10^{-2} M) in aqueous ethanol (20%v/v) for 5h at pH=5 catalysed by different concentrations of Pt – PVA

| Comp No. | [Pt-PVA] | | | | | | | | | | | | | | |
|----------------|----------------------|-------------------------------|-------|----------------------|-------------------------------|------|----------------------|-------------------------------|------|----------------------|-------------------------------|------|----------------------|-------------------------------|-------|
| | 1.6×10^{-4} | | | 2.6×10^{-4} | | | 3.2×10^{-4} | | | 5.0×10^{-4} | | | 8.0×10^{-4} | | |
| | H ₂ ml/L | No. of moles $\times 10^{-6}$ | TN | H ₂ ml/L | No. of moles $\times 10^{-4}$ | TN | H ₂ ml/L | No. of moles $\times 10^{-4}$ | TN | H ₂ ml/L | No. of moles $\times 10^{-4}$ | TN | H ₂ ml/L | No. of moles $\times 10^{-6}$ | TN |
| HL | 6.00 | 267.0 | 0.78 | 11.60 | 5.17 | 1.52 | 12.00 | 5.35 | 1.57 | 7.80 | 3.48 | 1.00 | 1.20 | 535.0 | 0.15 |
| C ₁ | 0.79 | 35.7 | 0.10 | 3.38 | 1.51 | 0.44 | 2.80 | 1.25 | 0.36 | 1.79 | 0.80 | 0.23 | 0.39 | 17.80 | 0.05 |
| C ₂ | 0.009 | 0.446 | 0.001 | 4.39 | 1.96 | 0.57 | 1.99 | 0.89 | 0.26 | 0.79 | 0.36 | 0.01 | 0.012 | 0.56 | 0.016 |
| C ₃ | 0.0079 | 3.57 | 0.01 | 3.98 | 1.78 | 0.52 | 3.58 | 1.60 | 0.47 | 2.00 | 0.89 | 0.26 | 0.39 | 17.80 | 0.05 |
| C ₄ | 3.80 | 171.0 | 0.50 | 9.97 | 4.46 | 1.31 | 3.38 | 1.51 | 0.44 | 2.09 | 0.37 | 0.27 | 0.59 | 26.70 | 0.076 |
| C ₅ | 0.009 | 0.446 | 0.001 | 4.70 | 2.14 | 0.61 | 1.59 | 0.74 | 0.21 | 1.40 | 0.63 | 0.18 | 0.009 | 0.45 | 0.001 |
| C ₆ | 3.90 | 178.0 | 0.51 | 10.39 | 4.64 | 1.36 | 3.58 | 1.60 | 0.47 | 2.19 | 0.98 | 0.28 | 0.79 | 35.70 | 0.10 |

* TN=moles of hydrogen produced / Moles of photosensitizer

Table (6) Total volume (mL/L), no. of moles, and turnover numbers (TN) of hydrogen production on irradiation HL or its metal complexes (3.4×10^{-4} M) with MV^{+2} (3.4×10^{-3} M) and EDTA (10^{-2} M) in (20%) aqueous ethanol for 5h at pH=5, using different loadings of Pt/TiO₂ (200 mic)

| Comp No. | Pt/TiO ₂ loadings | | | | | | | | | | | |
|----------------|------------------------------|-------------------------------|-------|---------------------|-------------------------------|------|---------------------|-------------------------------|------|---------------------|-------------------------------|------|
| | 30 mg | | | 40 mg | | | 50 mg | | | 60 mg | | |
| | H ₂ ml/L | No. of moles $\times 10^{-6}$ | TN | H ₂ ml/L | No. of moles $\times 10^{-4}$ | TN | H ₂ ml/L | No. of moles $\times 10^{-4}$ | TN | H ₂ ml/L | No. of moles $\times 10^{-5}$ | TN |
| IIL | 1.00 | 446.0 | 1.30 | 16.80 | 7.50 | 2.20 | 19.60 | 8.75 | 2.57 | 9.60 | 42.80 | 1.25 |
| C ₁ | 1.40 | 62.50 | 0.18 | 1.60 | 0.71 | 0.21 | 2.80 | 1.25 | 0.36 | 1.40 | 6.25 | 0.18 |
| C ₂ | 0.01 | 0.45 | 0.001 | 1.60 | 0.71 | 2.17 | 2.60 | 1.16 | 0.34 | 1.40 | 6.25 | 0.18 |
| C ₃ | 0.40 | 17.80 | 0.052 | 4.80 | 2.14 | 0.63 | 5.20 | 2.32 | 0.68 | 2.00 | 8.92 | 0.26 |
| C ₄ | 0.52 | 23.50 | 0.069 | 5.60 | 2.51 | 0.73 | 8.66 | 3.87 | 1.13 | 2.00 | 9.20 | 0.27 |
| C ₅ | 0.029 | 1.33 | 0.004 | 2.80 | 1.25 | 0.36 | 4.00 | 1.78 | 0.52 | 1.60 | 7.10 | 0.20 |
| C ₆ | 0.56 | 250.0 | 0.73 | 5.00 | 2.50 | 0.73 | 8.80 | 3.92 | 1.15 | 2.00 | 8.92 | 0.26 |

Table (7) Total volume (m/L), no. of moles, and turnover numbers (TN) of hydrogen produced on irradiation H₂ aqueous ethanoic solutions (20%) of HL or ML₂ (3.4x10⁻³ M and EDTA (10⁻² M) for five hours at pH=5 using different loading of Pt/TiO₂ (45 micron)

| Comp No. | Pt/TiO ₂ loadings | | | | | | | | | | | | | | |
|----------------|------------------------------|--------------------------------|-------|---------------------|--------------------------------|------|---------------------|--------------------------------|------|---------------------|--------------------------------|------|---------------------|--------------------------------|------|
| | 10 mg | | | 20 mg | | | 30 mg | | | 40 mg | | | 50 mg | | |
| | H ₂ ml/L | No. of moles x10 ⁻⁶ | TN | H ₂ ml/L | No. of moles x10 ⁻⁴ | TN | H ₂ ml/L | No. of moles x10 ⁻⁴ | TN | H ₂ ml/L | No. of moles x10 ⁻⁴ | TN | H ₂ ml/L | No. of moles x10 ⁻⁶ | TN |
| HL | 8.00 | 357.0 | 1.05 | 16.0 | 7.14 | 2.10 | 30.0 | 13.30 | 3.91 | 27.0 | 12.0 | 3.52 | 15.60 | 696.0 | 2.04 |
| C ₁ | 4.40 | 196.0 | 0.40 | 7.00 | 2.67 | 0.78 | 5.60 | 2.50 | 0.73 | 2.80 | 1.25 | 0.36 | 1.60 | 71.40 | 0.21 |
| C ₂ | 6.80 | 300.0 | 0.88 | 10.00 | 4.46 | 1.31 | 8.40 | 3.75 | 1.10 | 4.80 | 2.14 | 0.62 | 2.00 | 0.892 | 0.26 |
| C ₃ | 0.10 | 0.45 | 0.001 | 4.40 | 1.96 | 0.57 | 4.00 | 1.78 | 0.52 | 2.40 | 1.07 | 0.31 | 0.80 | 35.70 | 0.10 |
| C ₄ | 3.84 | 560.0 | 1.64 | 15.70 | 7.00 | 2.05 | 15.30 | 6.80 | 2.00 | 7.00 | 3.14 | 0.91 | 3.60 | 16.00 | 0.47 |
| C ₅ | 1.60 | 71.40 | 0.21 | 6.00 | 2.67 | 0.78 | 4.60 | 2.05 | 0.60 | 2.80 | 1.25 | 0.37 | 0.80 | 0.357 | 0.10 |
| C ₆ | 13.20 | 589.0 | 1.73 | 16.80 | 7.50 | 2.20 | 16.60 | 7.36 | 2.16 | 7.60 | 3.40 | 1.00 | 4.00 | 18.0 | 0.52 |

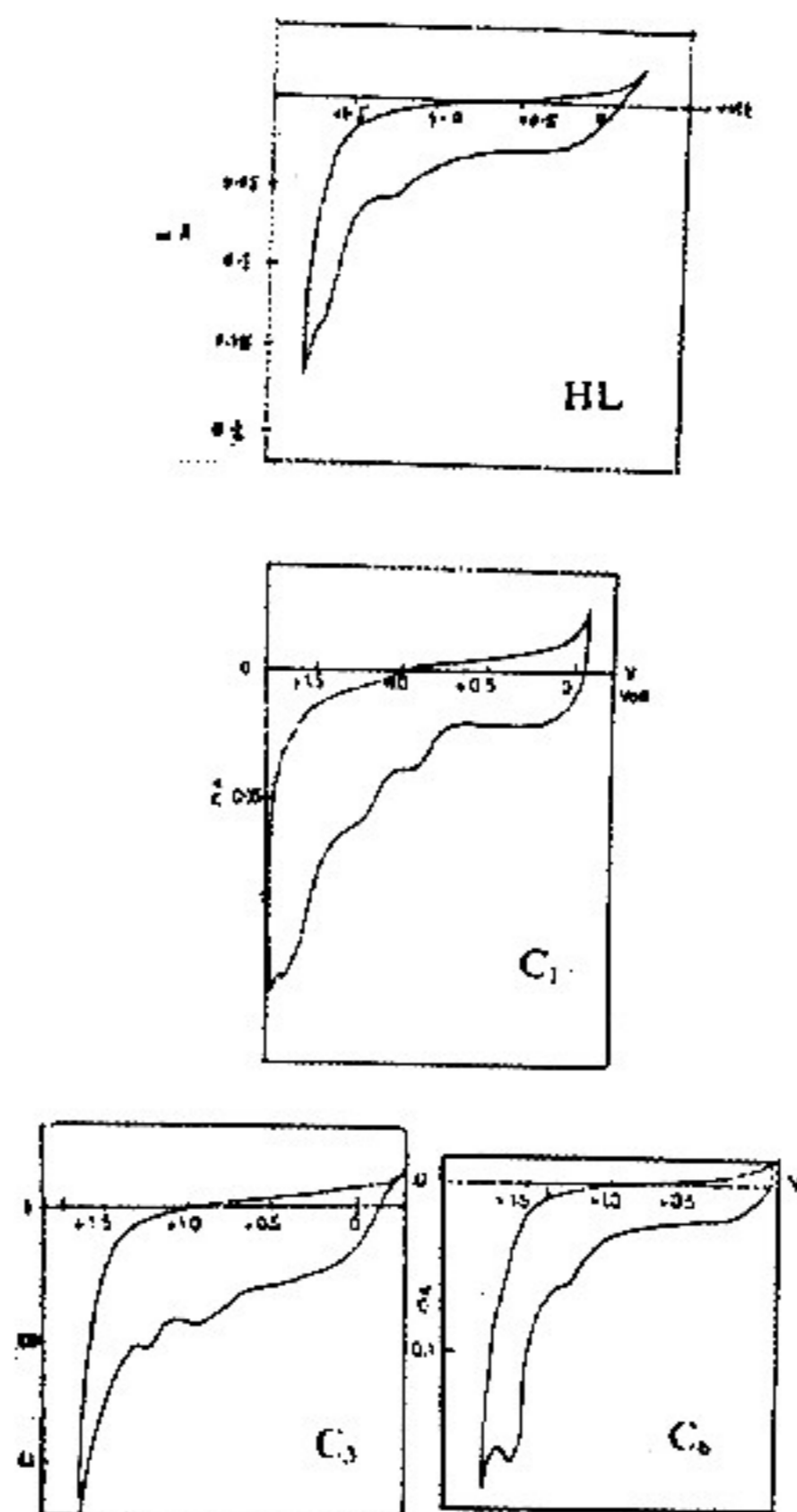


Fig. (1) Cyclic voltammograms of compounds HL, C₁, C₃ and C₆ in 20% aqueous ethanolic solution containing 0.1 M K₂SO₄ at pH= 5

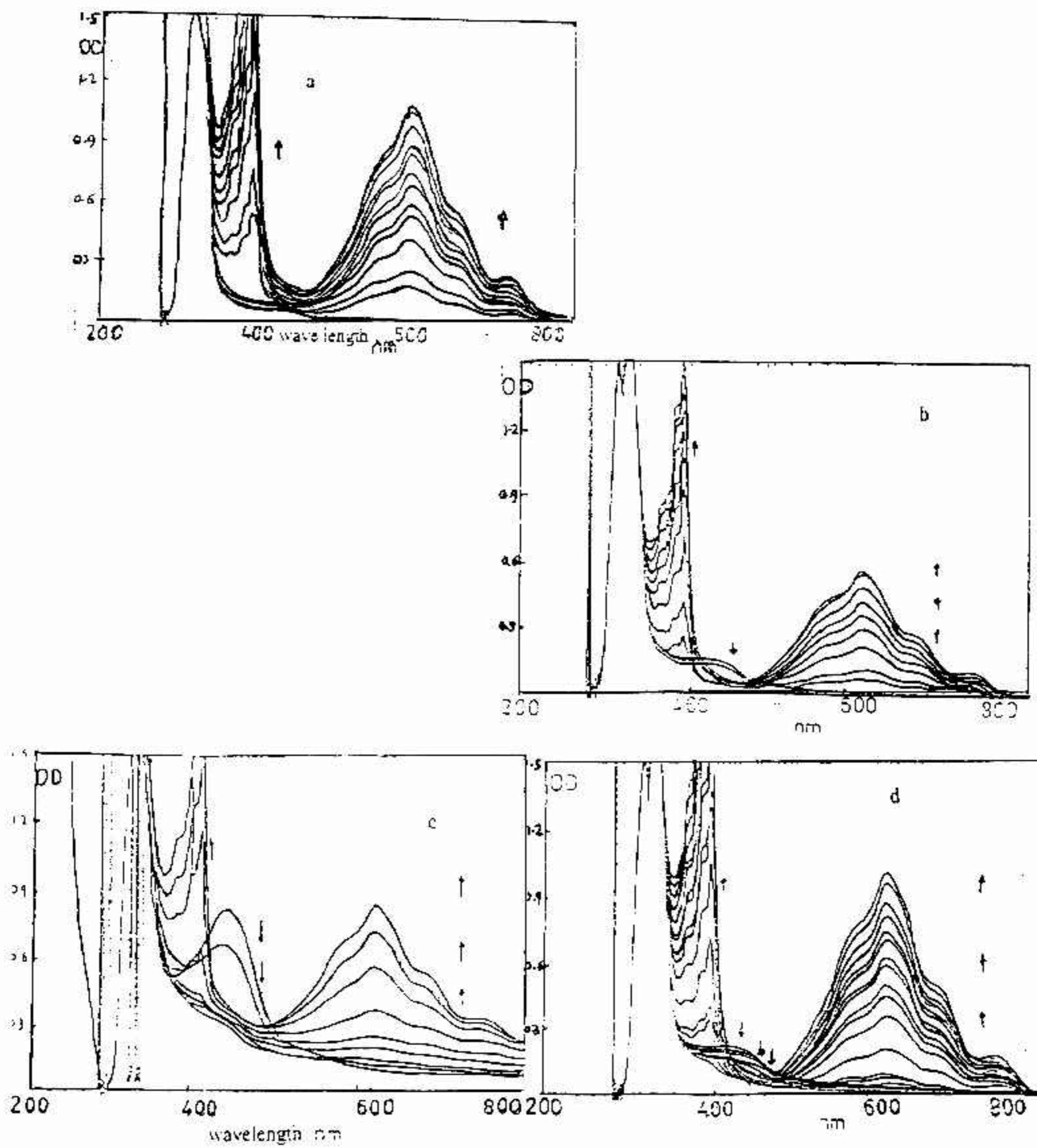


Fig. (2) Photoreduction of MV^{2+} by a) HL b) C_4 , c) C_5 and d) C_6 in aqueous ethanolic solution at pH=5

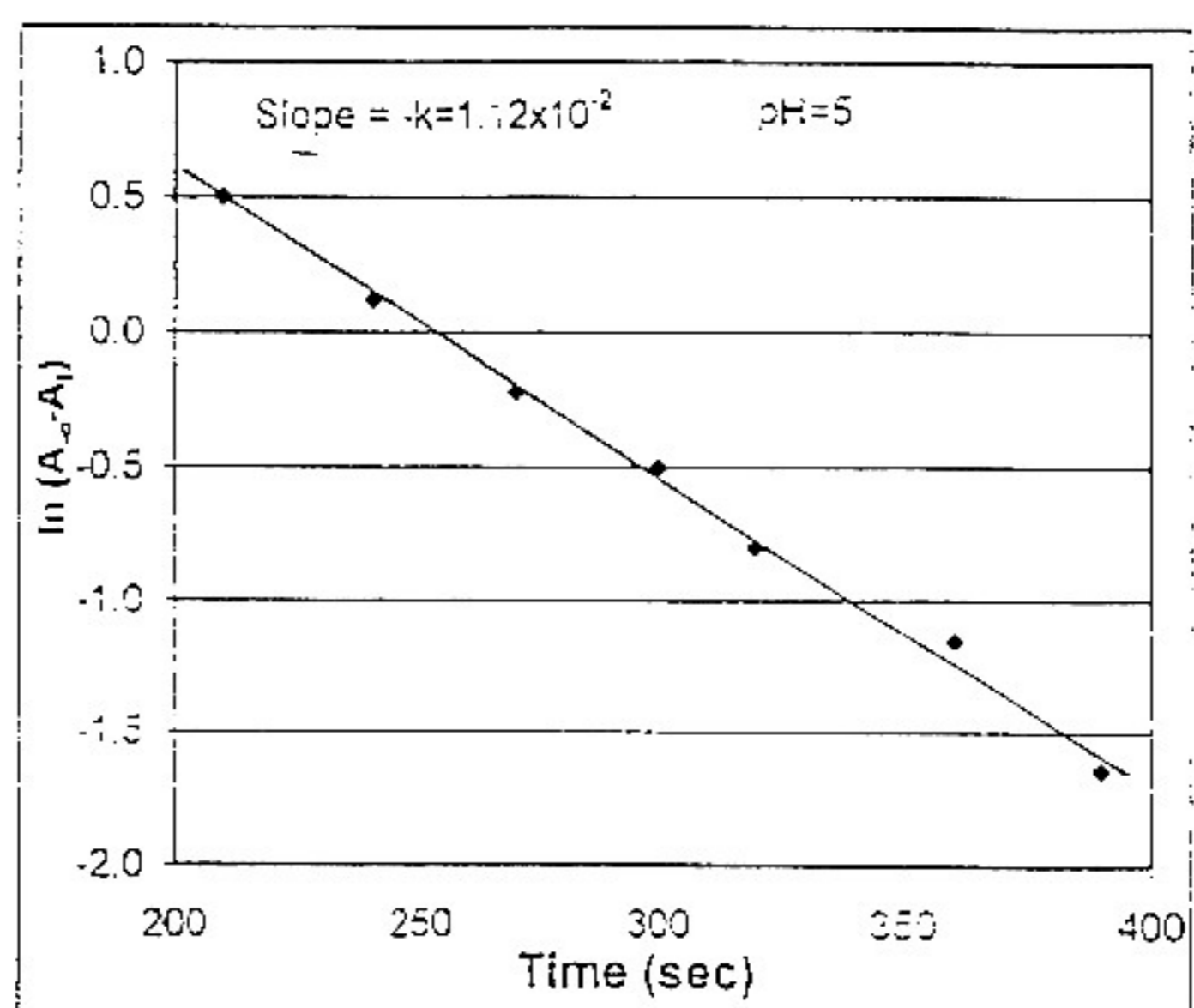


Fig. (3) The linear relationship for first order kinetics using C_3 as a photosensitizer in the photoreduction of MV^{+2} in aqueous ethanolic solutions

انتاج غاز الهيدروجين ضوئيا من المحاليل المائية والمحفز بواسطة 2 و 4 - ثنائي ميتوكسي بنزايليدين -2- هيدروكسي انيلين وبعض معقداته الفلزية

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الخلاصة

انتج غاز الهيدروجين من تشعيع محاليل كحول/ماء (20% حجما) تحتوي على مزيج من الليكاند 2,4 - ثنائي ميتوكسي بنزايليدين -2- هيدروكسي انيلين (HL) او احد معقداته (ML_2) مع الايونات ثنائية التكافؤ التالية: المنغنيز والحديد والكوبلت والنيكل والسنحاس والزنك كمحفزات ضوئية ومثيل الفايلوجين (MV^{2+}) كمستقبل للالكترونات ثنائي الامين رباعي حامض الخليك ملح ثنائي الصوديوم (EDTA) كواهب للالكترونات بوجود متعدد فينيل الكحول - البلاتين (Pt-PVA) او ثنائي اكسيد التيتانيوم المبلتن (Pt/TiO_2) (200 و 45 ميكرون) كعامل مساعد للاختزال. اجري التشعيع باستخدام الضوء الابيض من مصباح الزينون (250 واط) في درجة حرارة $25 + 2^\circ$ م. تم تحديد جهود التأكسد لليكاند ومعقداته الفلزية باعتماد الفولنومترية الحلقية. كانت كفاءة التفاعلات الضوئية تتغير مع تغير pH المحلول ونوع وحجم دقائق العامل المساعد فضلا عن نوع ايون الفلز المركزي للمعقدات المدروسة. سجل الليكاند الاداء الافضل بالمقارنة مع المعقدات الفلزية بينما سجل معقدي النيكل والزنك الاداء الافضل بالمقارنة مع بقية المعقدات.