



PHOTO-ASSISTED OXIDATION OF *p*-ANISIDINE BY FENTON REAGENT

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ABSTRACT

Organo-nitrogen compounds play an important role in the industrial and biological chemistry. Photo-assisted oxidation of *p*-anisidine by Fenton reagent has been studied. The effect of different reaction parameters such as concentration of substrate, H₂O₂, FeSO₄, pH and polarity of solvent were studied. The progress of the reaction was observed by TLC. Photoproduct was characterized by physical, chemical and spectral methods. A tentative mechanism has been proposed for overall reaction.

Key words: Photo-assisted oxidation, *p*-Anisidine, Photo-Fenton reagent

INTRODUCTION

Photocatalysis is widely explored for the decontamination of polluted water. The polluting sources may be pesticides, fertilizers, pharmaceuticals, dyes, textile industries¹, etc. The progress of removal of amines from industrial wastewater is of great importance because of well known amines resistance to microbial degradation and their ability of accumulation in the environment as well as possible carcinogenic and mutagenic properties.

Fenton reagent (H₂O₂/Fe²⁺) represents one of the most common treatment methods for the detoxification and degradation of many organic wastes like EDTA², dimethyl phthalate³, fenitrothion⁴, herbicide trifluraline⁵ azo dye⁶ and phenolic compounds⁷⁻⁹ etc. The oxidation of these pollutants is based on the generation of hydroxyl radicals that is considered as advanced oxidation processes (AOPs). Hydroxyl radicals are extraordinarily reactive and unstable species that attack most of the organic pollutants. The attack by hydroxyl radical in presence of oxygen initiates an oxidative reaction leading to degradation.

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The aim of the present investigation is to determine the efficiency of Fenton's reaction for the removal of amines from polluted waste water.

EXPERIMENTAL

p-Anisidine (Merck, India), ferrous sulphate (Merck, India) hydrogen peroxide 30% (Merck, India), sulphuric acid (BDH) and methanol (Rankem, India) were used to prepare the solutions. Besides methanol, the rate of reaction was also studied in solvents like ethanol, acetone and ethyl acetate. Photooxidation was carried out in Borosil glasswares and all the reactions were performed using dried equipments. All melting points were recorded on Toshniwal melting point apparatus. The pH measurements were made with the help of Systronics-327 Griph (digital) pH meter. Infra-red spectrum was scanned on Perkin-Elmer Spectrum RX I spectrometer. The spectrophotometric studies were performed on Systronics-106 (MK-II) spectrophotometer. Elemental analysis was carried out using Carlo-Erba-1106 automatic analyzer. *p*-Anisidine (0.15 g) was dissolved in methanol in a round bottom flask and then solution of ferrous sulphate (3.0 mL, 0.1M), hydrogen peroxide (0.25 mL, 30%) and sulphuric acid (0.5 N) were added at maintained pH. Total volume of the reaction mixture was made 100 mL by adding methanol. All the chemicals used in the investigation were purified according to the recommended methods.

The concentrations of various ingredients in the reaction mixture were:

$$[p\text{-Anisidine}] = 12.2 \times 10^{-3} \text{ M}$$

$$[\text{FeSO}_4] = 3.0 \times 10^{-3} \text{ M}$$

$$[\text{H}_2\text{O}_2, 30\%] = 22.5 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.2$$

The reaction mixture was irradiated with light source (Tungsten lamps, 2 x 200W, Philips) at a distance of 30 cm from the reaction vessel. A water filter (15 cm thick) was placed between light source and the reaction vessel to cut off thermal radiations. Oxygen gas [2.0 L min^{-1}] was continuously bubbled through the reaction mixture. This served two purposes –

- (i) Continuous stirring of the reaction mixture
- (ii) Availability of oxygen.

The progress of the reaction was observed with the help of TLC at every 2 h interval and the product was identified by its usual tests. In initial stages of reaction, only a single spot corresponding to parent compound was observed when the TLC plate was

placed in iodine chamber. After 4 h, later two spots corresponding to the parent compound and photoproduct were observed. The reaction was allowed for completion (7 h).

RESULTS AND DISCUSSION

After the completion of photo-chemical reaction, the photoproduct was characterized by its usual chemical tests^{10, 11}.

- (i) Nitrogen was found to be present.
- (ii) Black precipitates with Mulliken – Barker test confirm the presence of $-\text{NO}_2$ group.
- (iii) The photoproduct *p*-nitroanisole was separated as its trinitro derivative (recrystallized, M.P. 120 °C)

The control experiments were performed. The reaction was carried out in the presence of –

- (i) Oxygen and light (no Fenton reagent was added).
- (ii) Oxygen and Fenton reagent (no exposure to light).
- (iii) Light and Fenton reagent (no oxygen was purged).

It was observed that no photoproduct was formed in the first two cases and the yield was very low in third case. So it was concluded that both; light and Fenton reagent are necessary for the photo-reaction and presence of oxygen increases the rate of reaction. Involvement of free radicals has been confirmed by adding acrylamide in the reaction mixture, where a resinous mass is obtained.

The rate of the oxidation depends on the concentration of various parameters like substrate, H_2O_2 , pH, FeSO_4 and the polarity of solvent. The results of these variations are as follows –

Effect of substrate concentration

The effect of concentration of substrate on this reaction was studied by using variable amounts of substrate. The yield of the photoproduct was determined and the results are summarized in the Table 1.

Table 1. Effect of substrate concentration

$[H_2O_2] = 2.25 \times 10^{-2} \text{ M}$

$[Fe^{2+}] = 3.0 \times 10^{-3} \text{ M}$

pH = 2.2

Solvent = Methanol

Time of irradiation = 7 h

[Substrate] x 10³ M	Yield of photoproducts (%)
4.1	19.0
8.1	21.6
12.2	26.2
16.2	29.1
20.0	30.3

It has been observed that as the concentration of substrate was increased, the yield of photoproduct was also found to increase, ultimately attaining an optimum level.

Effect of hydrogen peroxide concentration

The effect of concentration of hydrogen peroxide on the yield of photoproduct was investigated using different concentrations of H_2O_2 . The results are summarized in Table 2.

Table 2. Effect of hydrogen peroxide concentration

$[Substrate] = 1.22 \times 10^{-2} \text{ M}$

$[Fe^{2+}] = 3.0 \times 10^{-3} \text{ M}$

pH = 2.2

Solvent = Methanol

Time of irradiation = 7 h

[H₂O₂] x 10³ M	Yield of photoproduct (%)
13.5	20.6

Cont...

$[\text{H}_2\text{O}_2] \times 10^3 \text{ M}$	Yield of photoproduct (%)
18.0	22.0
22.5	26.2
27.0	28.2
31.5	29.1

As the concentration of hydrogen peroxide was increased, the yield of photoproduct also increases. Results indicate that the rate of reactions is directly proportional to the concentration of H_2O_2 , and it reaches to optimum value at a certain level.

Effect of ferrous ion concentration

The effect of Fe^{2+} concentrations was also studied using various concentrations of Fe^{2+} ions. The results are reported in Table 3.

Table 3. Effect of ferrous ion concentration

[Substrate] = $1.22 \times 10^{-2} \text{ M}$

$[\text{H}_2\text{O}_2] = 2.25 \times 10^{-2} \text{ M}$

pH = 2.2

Solvent = Methanol

Time of irradiation = 7 h

$[\text{Fe}^{+2}] \times 10^3 \text{ M}$	Yield of photoproduct (%)
2.0	20.2
2.5	22.3
3.0	26.2
3.5	29.0
4.0	30.1

From above observations, it can be concluded that as the concentration of Fe^{2+} ions was increased, the rate of reaction also increases.

Effect of pH variation

Keeping all the other conditions identical, the effect of pH on the photooxidation was studied. The results are reported in Table 4

Table 4. Effect of pH variation

[Substrate] = 1.22×10^{-2} M

[H₂O₂] = 2.25×10^{-2} M

[Fe²⁺] = 3.0×10^{-3} M

Solvent = Methanol

Time of irradiation = 7 h

[pH]	Yield of photoproduct (%)
1.8	19.2
2.0	22.4
2.2	26.2
2.4	23.2
2.6	20.3

These observations indicate that the rate of reaction increases up to a certain limit of pH. With further rise in pH, the yield of the photoproduct decreases.

Effect of polarity of solvent

The effect of polarity of solvent was observed using a wide range of solvents with different polarities. The results are summarized in Table 5.

Table 5. Effect of polarity of solvent

[Substrate] = 1.22×10^{-2} M

[H₂O₂] = 2.25×10^{-2} M

[Fe²⁺] = 3.0×10^{-3} M

pH = 2.2

Time of irradiation = 7 h

Solvent	Yield of photoproduct (%)
Ethyl acetate ($\epsilon = 6.3$)	15.5

Cont...

Solvent	Yield of photoproduct (%)
Acetone ($\epsilon = 21.4$)	19.2
Ethanol ($\epsilon = 24.5$)	21.2
Methanol ($\epsilon = 33.6$)	26.2

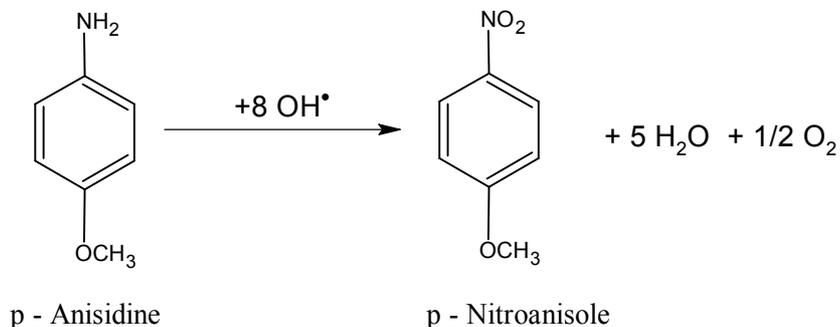
It was observed that the rate of photooxidation increases with the increase in the polarity of the solvent.

The I.R. spectrum of the product shows peaks at 1530 cm^{-1} and 1350 cm^{-1} , which confirm the presence of NO_2 group. There is no absorption in region $3500\text{-}3300\text{ cm}^{-1}$ (N-H stretching) and $1640\text{-}1560\text{ cm}^{-1}$ and 800 cm^{-1} (N-H bending) confirming the absence of NH_2 group in the photoproduct^{12, 13}.

The structure was further confirmed by quantitative elemental analysis of the photoproduct (*p*-nitroanisole) –

	C (%)	H (%)	N (%)
Found	54.25	4.61	9.05
Calculated	54.90	4.60	9.15

On the basis of spectral data, physical and chemical analysis, the photoproduct was characterized as *p*-nitroanisole.



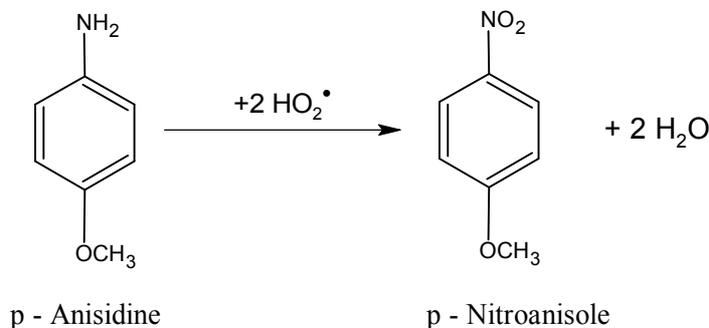


Fig. 1: Mechanism of photo-assisted oxidation of p-anisidine by Fenton reagent

Initially, ferrous ions (Fe^{2+}) react with hydrogen peroxide to form Fe^{3+} ions, a hydroxyl radical and a hydroxide anion (Step-1). The hydroxyl radical reacts with substrate to give the product (Step-3). The hydroperoxy radical formed by the reaction of Fe^{3+} ion with H_2O_2 in presence of light (Step-2), reacts directly with substrate to give the product (Step-4). The generally accepted mechanism for the Fenton process is that the OH^\bullet radical formed from the photolysis brings about a radical chain mechanism¹⁴⁻¹⁶.

ACKNOWLEDGEMENTS

The authors are thankful to Dr. U. C. Bansal (Principal), Dr. R. L. Pitliya, Dr. V. K. Vaidya and Dr. J. P. N. Ojha (Vice Principal), M. L. V. Govt. College, Bhilwara, Dr. P. K. Jain (Head, Chemistry Department), Dr. S. K. Sharma, Dr. R. K. Khandelwal, Dr. Rekha Chandak and all other members of Department of chemistry, M.L.V. Govt. College, Bhilwara, for continuous encouragement in accomplishing this work.

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Accepted : 18.11.2007