



FENTON AND PHOTO- FENTON OXIDATION OF *O*-AMINO BENZOIC ACID

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Article Received on 18/11/2020

Article Revised on 09/12/2020

Article Accepted on 30/12/2020

ABSTRACT

Photo-oxidation of *o*-aminobenzoic acid by Fenton reagent was studied. The effect of various reaction parameters such as concentration of substrate, H₂O₂, Fe²⁺, pH, polarity of solvent and catalyst variation was 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 with overall reaction.

KEYWORDS: Photo-oxidation, *o*-aminobenzoic acid, Photo- Fenton reagent.

INTRODUCTION

o-Aminobenzoic acid, also known as anthranilic acid or 2-aminobenzoate, belongs to amino group substituted benzoic acid at ortho position, is used as an intermediate for production of dyes, pigments and saccharin. It has amino and carboxylic group attached in ring structure. It and its esters are used in preparing perfumes, pharmaceuticals and UV-absorber as well as corrosion inhibitors for metals and mold inhibitors in soya sauce. *o*-Aminobenzoic acid is a potentially toxic compound. Uremic syndrome may affect any part of the body and can cause nausea, vomiting, loss of appetite, and weight loss. Chronic exposure of uremic toxins can lead to a number of conditions including renal damage, chronic kidney disease and cardiovascular disease. It can also cause changes in mental status, such as confusion, reduced awareness, agitation, psychosis, seizures, and coma.

Over the past two decades, a large variety of powerful advanced oxidation processes (AOPs) has attracted increasing interest for the efficient removal of toxic and/or biorefractory pollutants from waters.^[4,2-6] AOPs are environmental friendly chemical, photochemical, photocatalytic, electrochemical and photoelectrochemical methods, which present the common feature of the *in situ* production of hydroxyl radical ([•]OH) as the main oxidant. [•]OH has so high standard reduction potential ($E^{\circ}(\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V vs. SHE}$) that non-selectively reacts with most organics yielding dehydrogenated or hydroxylated derivatives, which can be in turn mineralized to CO₂, water and inorganic ions.^[4,6] The simplest and most typical chemical AOP is the Fenton method in which a mixture of Fe²⁺ and H₂O₂ (Fenton's reagent) is used to degrade organics. The oxidation power of this technique can be significantly improved by illuminating the treated

effluent with UV light (photo-Fenton method) or sunlight (solar photo-Fenton method).^[7] The coupling of the Fenton method with electrochemistry is another way to enhance its decontamination efficiency. These treatment processes are considered as very promising methods for the remediation of contaminated ground, surface and wastewaters containing non-biodegradable organic pollutants. Fenton's oxidation process has been successfully employed to treat landfill leachate^[8], pesticides and phenolic contaminants^[9], textile wastewater^[10,11] and paper pulp wastewater.^[12]

MATERIAL AND METHOD

o-Aminobenzoic acid (Merck, Germany), ferrous sulphate (Merck, India), hydrogen peroxide 30% (Merck, India), sulphuric acid (Merck, India) and methanol (Rankem, India) were used to prepare all the solutions. Besides methanol, the rate of reaction was also studied in solvents like ethanol, acetone and ethyl acetate. All melting points were recorded on Toshniwal melting point apparatus. The pH measurements were done with the help of Systronics-327 Griph (digital) pH meter. An Infra Red spectrum was scanned on SCHIMADZU FTIR-8400S spectrophotometer. Elemental analysis was carried out using Carlo-Erba-1106 automatic analyzer.

o-Aminobenzoic acid (0.30 gm) was dissolved in methanol in a round bottom flask, solution of ferrous sulphate (2.5 ml, 0.1M), hydrogen peroxide (0.35 ml, 30%) and sulphuric acid (0.5N) were added for maintaining 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 concentration of various ingredients in the reaction mixture were:
o-Aminobenzoic acid: 22.0X 10⁻³ M,
 FeSO₄: 2.5 X 10⁻³ M,

H_2O_2 : $31.5 \times 10^{-3} \text{ M}$, 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.

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, two spots corresponding to parent compound and photoproduct were observed. The reaction was allowed for completion (7 h).

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

Effect of substrate concentration

The effect of concentration of substrate on photo catalytic reaction was studied using variable amount of substrate. The yield of the photoproduct was determined and the results are summarized in the table 1:

Table 1: Effect of substrate concentration.

$[\text{H}_2\text{O}_2, 30\%] = 31.5 \times 10^{-3} \text{ M}$
 $[\text{Fe}^{+2}] = 2.5 \times 10^{-3} \text{ M}$
 [pH] = 2.2

Solvent = Methanol

Time of irradiation = 7 h.

Sr. No	[Substrate]	% yield of photoproduct
1.	$14.6 \times 10^{-3} \text{ M}$	21.3
2.	$18.3 \times 10^{-3} \text{ M}$	23.4
3.	$22.0 \times 10^{-3} \text{ M}$	31.2
4.	$25.7 \times 10^{-3} \text{ M}$	30.6
5.	$29.4 \times 10^{-3} \text{ M}$	28.4

It has been observed that as the concentration of substrate increases, the yield of photoproduct was found to increase, up to an optimum level. On further increase in concentration of substrate, yield of photo product was decreased. It may be due to the fact that as the concentration of the substrate was increased, only a fraction of the light intensity will reach the catalyst surface and thus; a decrease in the photocatalytic oxidation of substrate was observed.

Effect of hydrogen peroxide concentration

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

Table 2: Effect of hydrogen peroxide concentration

[Substrate] = $22.0 \times 10^{-3} \text{ M}$, $[\text{Fe}^{+2}] = 2.5 \times 10^{-3} \text{ M}$,
 [pH] = 2.2, [Solvent] = Methanol,
 Time of irradiation = 7 h.

Sr. No.	$[\text{H}_2\text{O}_2, 30\%]$	% yield of photoproduct
1.	$22.5 \times 10^{-3} \text{ M}$	18.5
2.	$27.0 \times 10^{-3} \text{ M}$	20.9
3.	$31.5 \times 10^{-3} \text{ M}$	31.2
4.	$36.0 \times 10^{-3} \text{ M}$	30.4
5.	$40.5 \times 10^{-3} \text{ M}$	29.2

As the concentration of hydrogen peroxide was increased, the yield of photoproduct also increases. However, above a certain H_2O_2 concentration, the reaction rate levels off and is negatively affected. This may be due to auto-decomposition of H_2O_2 to oxygen and water and recombination of OH^\cdot radical.

Effect of ferrous ion concentration

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

Table 3: Effect of ferrous ion concentration.

[Substrate] = $22.0 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{O}_2, 30\%] = 31.5 \times 10^{-3} \text{ M}$,
 [pH] = 2.2, Solvent = Methanol,
 Time of irradiation = 7 h.

S. N.	$[\text{Fe}^{+2}]$	% yield of photoproduct
1.	$1.5 \times 10^{-3} \text{ M}$	21.8
2.	$2.0 \times 10^{-3} \text{ M}$	26.5
3.	$2.5 \times 10^{-3} \text{ M}$	31.2
4.	$3.0 \times 10^{-3} \text{ M}$	29.6
5.	$3.5 \times 10^{-3} \text{ M}$	27.1

From above observations it can be concluded that as the concentration of Fe^{2+} ions is increased the rate of reaction also increases, up to a certain limit. But after reaching on optimum level the efficiency decrease. This may be due to the increase of a brown turbidity that hinders the absorption of the light required for the photo-Fenton process or by the recombination of OH^\cdot radical. In this case, Fe^{2+} reacts with OH^\cdot radical as scavenger.

Effect of pH variation

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

Table 4: Effect of pH variation.

[Substrate] = $22.0 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{O}_2, 30\%] = 31.5 \times 10^{-3} \text{ M}$,
 $[\text{Fe}^{+2}] = 2.5 \times 10^{-3} \text{ M}$, Solvent = Methanol,
 Time of irradiation = 7 h.

S. N.	[pH]	% yield of photoproduct
1.	1.8	19.2
2.	2.0	25.1
3.	2.2	31.2
4.	2.4	28.3
5.	2.6	25.5

These observations are showing that the rate of reaction increases up to a certain limit (2.2.) With further rise in pH, the yield of the photoproduct is decreased. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In this form, iron catalytically decomposes the H_2O_2 in to oxygen and water, without forming hydroxyl radical.

Effect of polarity of solvent

The effect of polarity of solvent was observed using a wide range of solvents with different polarity. The results are reported in table 5.

Table 5: Effect of polarity of solvent.

[Substrate]= 22.0×10^{-3} M, [H_2O_2 , 30%]= 31.5×10^{-3} M,
[Fe^{+2}] = 2.5×10^{-3} M, [pH] = 2.2,

Time of irradiation = 7 h.

S. N.	Solvent	% yield of photoproduct
1.	Ethyl acetate ($\epsilon = 6.3$)	13.4
2.	Acetone ($\epsilon = 21.4$)	19.2
3.	Ethanol ($\epsilon = 24.5$)	21.2
4.	Methanol ($\epsilon = 33.6$)	31.2

It was observed that the rate of photo oxidation increased with the increase in the polarity of the solvent.

Effect of catalyst variation

Keeping all the other conditions identical, the effect of catalyst variation on the photo oxidation was studied, those were H_2O_2 , $H_2O_2 + Fe^{2+}$, $H_2O_2 + UO_2^{2+}$ and $H_2O_2 + UO_2^{2+} + Fe^{2+}$. The % yield of photoproduct was 21.7, 31.2, 34.7 and 36.7.

It was observed that when Fe^{2+} ions of Fenton reagent replaced by uranyl ions [UO_2^{2+}], the percentage yield of photoproduct was increased. It may be due to the formation of more hydroxyl free radical which oxidizes the available organic matter.

RESULTS AND DISCUSSION

After the completion of photo catalytic reaction, the photoproduct was characterized by its usual chemical tests.^[13, 14]

- Nitrogen was found to be present.
- Black precipitates with Milliken Barker test confirm the presence of $-NO_2$ group.

- The photoproduct *o*-nitrobenzoic acid was separated as its amide derivative (recrystallized, M.P. $174^\circ C$)

The control experiments were performed. The reaction was carried out in the presence of (i) Oxygen and light (no photo catalyst was added), (ii) Oxygen and photo catalyst (no exposure to light) and (iii) Light and photo catalyst (no oxygen was purged).

It was observed that no photoproduct had formed in the first cases and the yield was very low in second and third case. So it is concluded that both light and photo catalyst are necessary for the photo reaction and oxygen increases the rate of reaction. Involvement of free radicals has been confirmed by adding acryl amide in the reaction mixture where a resinous mass is obtained.

The I.R. spectrum shows the peak at 1530 cm^{-1} and 1350 cm^{-1} which confirms the presence of NO_2 group. There is no absorption in region $3500-3300\text{ cm}^{-1}$ (N-H stretching) and $1640-1560\text{ cm}^{-1}$ and 800 cm^{-1} (N-H bending) confirms the absence of NH_2 group in the photoproduct.^[15, 16]

On the basis of the above, the following mechanism (Fig.1) has been proposed for the photo catalytic reaction of *o*-aminobenzoic acid with Fenton reagent. The generally accepted mechanism for the Fenton process identifies the hydroxyl radical ($\cdot OH$) and hydroperoxy radical ($HO_2\cdot$) as the active oxidizing intermediate in the system. According to this mechanism, the combination of ferrous iron and hydrogen peroxide induces a series of chain reactions initiated by the degradation of peroxide to the Fe^{3+} , hydroxyl radical and the hydroxide ion (reaction 1). Hydrogen peroxide decomposes catalytically by $Fe(III)$ and generates hydroperoxy radicals and Fe^{2+} (reaction 2 & 3). The hydroxyl radical and hydroperoxy radical reacts with substrate to give the product respectively by reaction 4 and 5. The $OH\cdot$ radical formed from the photolysis brings about a radical chain mechanism forming $HO_2\cdot$, $O_2\cdot$, $\cdot OH$ etc. which are used for the oxidation of substrate.^[17,18]



Fig.1: Mechanism of photo-oxidation of *o*-aminobenzoic acid by Fenton reagent.

ACKNOWLEDGEMENT

The author is thankful to Principal and HOD, deptt. of chemistry, M. S. J. Govt. College, Bharatpur (Raj.) for providing the necessary facilities.

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