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Photochemical Oxidation of *o*-Toluidine by Fenton Reagent

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Photo chemical oxidation of *o*-toluidine by Fenton reagent was studied. The effect of different reaction parameters such as concentration of substrate, H_2O_2, $FeSO_4$, pH, polarity of solvent and catalyst variation was studied. The progress of the reaction was observed by TLC. Photo-product was characterized by physical, chemical and spectral methods. A tentative mechanism has been proposed with overall reaction.

Key Words: Photo chemical oxidation, *o*-Toluidine, Photo Fenton reagent.

INTRODUCTION

Hydroxyl radicals are extraordinarily reactive and unstable species that attack most of the organic pollutants. The theme of the work is to offer a view for photo-initiated reaction of *o*-toluidine in presence of Fenton and photo-Fenton reagent. *o*-Toluidine containing compounds are present in industrially and biologically important chemicals such as fertilizers, pesticides, herbicides, weedicides and soil conditioning agents, drugs and dyes[1] *etc*. Due to the increasing use of these compounds in present time, traces of these compounds are passing to environment. These traces may harm biota if they are not degraded. The improper handling of these toxic chemicals has serious impact on the natural water bodies, land in the surrounding area, health and safety of workers.

Fenton reagent (H_2O_2/Fe^{2+}) in presence of light was found to be very effective in treatment of various industrial wastewater compounds like hydrocarbons[2], polyethylene glycol[3], salicylic acid[4], 2-chlorophenol[5], phosphorus compounds[6], metronidazole[7], insecticide chlorfenvinphos[8], methyl-*tert* butyl ether[9] *etc*. In the light of the above, the title investigation has been undertaken.

EXPERIMENTAL

o-Toluidine (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. Photo oxidation was carried out in borosil glass wares and all the reactions were performed using dried equipments. 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-Toluidine (0.20 mL) was dissolved in methanol in a round bottom flask, solution of ferrous sulphate (3 mL, 0.1 M), hydrogen peroxide (0.25 mL, 30 %) and sulphuric acid (0.5 N) 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*-toluidine 2.3×10^{-2} M, $FeSO_4$ 3.0×10^{-3} M, H_2O_2 2.7×10^{-2} M and the pH of the solution was found to be 2.3.

The reaction mixture was irradiated with light source (Tungsten lamps, 2 × 200 W, 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 [2.01 min^{-1}] was continuously bubbled through the reaction mixture. This served two purposes: (I) continuous stirring of the reaction mixture and (II) availability of oxygen.

The progress of the reaction was monitored 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 Table-1.

TABLE-1
EFFECT OF SUBSTRATE CONCENTRATION
$[H_2O_2] = 2.7 \times 10^{-2}$ M, $[Fe^{2+}] = 3.0 \times 10^{-3}$ M, pH = 2.3, solvent = methanol

[Substrate] (M)	Yield of photoproduct (%)
1.4×10^{-2}	18.0
1.9×10^{-2}	22.1
2.3×10^{-2}	32.7
2.8×10^{-2}	31.0
3.3×10^{-2}	29.0

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, it may start acting like a filter for the incident light. Hence, on increasing the concentration of substrate, 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 presented in Table-2.

TABLE-2
EFFECT OF HYDROGEN PEROXIDE CONCENTRATION
[Substrate] = 2.3×10^{-2} M, [Fe^{2+}] = 3.0×10^{-3} M, pH = 2.3, solvent = methanol

[H_2O_2] (M)	Yield of photoproduct (%)
1.8×10^{-2}	19.9
2.3×10^{-2}	22.7
2.7×10^{-2}	32.7
3.2×10^{-2}	30.9
3.6×10^{-2}	28.2

As the concentration of hydrogen peroxide was increased, the yield of photoproduct also increases. This is explained by the effect of the additional production of $OH^•$ radical. 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 $OH^•$ 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] = 2.3×10^{-2} M, [H_2O_2] = 2.7×10^{-2} M, pH = 2.3, solvent = methanol

[Fe^{2+}] (M)	Yield of photoproduct (%)
2.0×10^{-3}	19.6
2.5×10^{-3}	23.4
3.0×10^{-3}	32.7
3.5×10^{-3}	31.3
4.0×10^{-3}	28.6

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 $OH^•$ radical. In this case, Fe^{2+} reacts with $OH^•$ 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] = 2.3×10^{-2} M, [H_2O_2] = 2.7×10^{-2} M, [Fe^{2+}] = 3.0×10^{-3} M, solvent = methanol

pH	Yield of photoproduct (%)
1.7	17.3
2.0	22.4
2.3	32.7
2.6	28.6
2.9	25.7

These observations are showing that the rate of reaction increases up to a certain limit of pH (2.3). 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 into 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 summarized in Table-5.

TABLE-5
EFFECT OF POLARITY OF SOLVENT
[Substrate] = 2.3×10^{-2} M, [H_2O_2] = 2.7×10^{-2} M, [Fe^{2+}] = 3.0×10^{-3} M, pH = 2.3

Solvent	Yield of photoproduct (%)
Ethyl acetate ($\varepsilon = 6.3$)	17.2
Acetone ($\varepsilon = 21.4$)	22.6
Ethanol ($\varepsilon = 24.5$)	26.1
Methanol ($\varepsilon = 33.6$)	32.7
Ethyl acetate ($\varepsilon = 6.3$)	17.2

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. The results are reported in Table-6.

TABLE-6
EFFECT OF CATALYST VARIATION
[Substrate] = 2.3×10^{-2} M, [H_2O_2] = 2.7×10^{-2} M, [Fe^{2+}] = 3.0×10^{-3} M,
[UO_2^{2+}] = 3.0×10^{-3} M, solvent = methanol, pH = 2.3

Catalyst	Yield of photoproduct (%)
H_2O_2	26.4
$H_2O_2 + Fe^{2+}$	32.7
$H_2O_2 + UO_2^{2+}$	35.6
$H_2O_2 + UO_2^{2+} + Fe^{2+}$	41.2

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[10,11]. (i) Nitrogen was found to be present. (ii) Black precipitates with Milliken Barker test confirm the presence of -NO_2 group. (iii) The photoproduct *o*-nitrotoluene was separated as its dinitro derivative (recrystallized, m.p. 72 ºC).

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 two cases and the yield was very low in 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 acrylamide in the reaction mixture where a resinous mass is obtained.

The IR spectrum shows the peak at 1530 and 1350 cm^{-1} which confirms the presence of NO_2 group. There is no absorption in region 3500-3300 cm^{-1} (N-H stretching) and 1640-1560 and 800 cm^{-1} (N-H bending) confirms the absence of NH_2 group in the photoproduct[12,13].

The structure was further confirmed by quantitative elemental analysis of the photoproduct *o*-nitrotoluene found:

	C (%)	H (%)	N (%)
Found	60.30	5.62	10.05
Calculated	61.31	5.15	10.21

On the basis of spectral data, physical and chemical analysis the photoproducts were characterized as *o*-nitrotoluene.

On the basis of the above, the following mechanism (Fig. 1) has been proposed for the photo catalytic reaction of *o*-toluidine with Fenton reagent. The generally accepted mechanism for the Fenton process identifies the hydroxyl radical ($^{\bullet}OH$) 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).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet} \qquad (1)$$

Hydrogen peroxide decomposes catalytically by Fe(III) and generates hydroperoxy radicals and Fe^{2+} (reactions 2 and 3).

$$Fe^{3+} + H_2O_2 \rightarrow H^+ + [Fe\text{-}HO_2]^{2+} \qquad (2)$$

$$[Fe\text{-}HO_2]^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \qquad (3)$$

The hydroxyl radical and hydroperoxy radical reacts with substrate to give the product, respectively by reaction 4 and 5. The $OH^{\bullet}$ radical formed from the photolysis brings about a radical chain mechanism forming $HO_2^{\bullet}$, O_2, $OH^{\bullet}$ *etc.*, which are used for the oxidation of substrate[14,15].

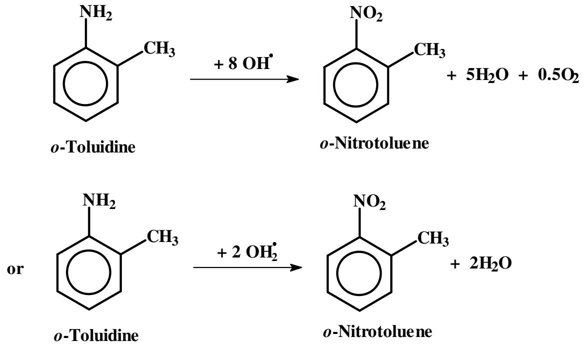

Fig. 1. Mechanism of photo catalytic oxidation of *o*-toluidine by Fenton reagent

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