



PHOTOCHEMICAL DEGRADATION OF NEUTRAL RED USING POTASSIUM TRISOXALATOFERRATE (III) AS AN OXIDANT

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ABSTRACT

The photochemical degradation of neutral red by potassium trisoxalatoferate (III) has been investigated. The rate of photocatalytic degradation of dye was observed spectrophotometrically. The effect of variation of different parameters like pH, concentrations of complex and dye, amount of light intensity, etc. on the rate of photochemical degradation was also observed. A tentative mechanism for the photochemical oxidative degradation of neutral red has been proposed.

Key words: Photochemical degradation, Neutral red, Potassium trisoxalatoferate (III).

INTRODUCTION

Photochemical reactions form a basis for the development of the world in its present form, having Sun as the central figure. Initially, Sun was the source of energy but with the passage of time, nature developed various other photobiological reactions and thus, provided a way for the self propagation of life. Photochemistry has been developed only to a very little extent than desired; perhaps because chemists have been attracted by some other problems, which seemed more urgent. So, it happened that while thermochemistry and electrochemistry have already reached a high degree of development, photochemistry is still in its early age.

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The reactions like dissociation, isomerization and optical emission of electronically excited species are the central features of photochemistry. On the other hand, physical chemists may be interested in the detailed dynamics of a photodissociation process and of the processes on a time scale of less than pico second, while organic chemists may seek an improved understanding through the examples that photochemistry affords of the relationship between reactivity, electronic and molecular structure.¹

Photosensitized reactions are widely used in many technical and biological areas. Recent studies on photosensitized reactions have given methods to graft copolymerization^{2,3}. Balazani and Carassiti⁴ have reviewed the photochemistry of coordination compounds quite extensively, while the volumes edited by Adamson and Fleischaure⁵ can be cited as an important milestone in the evolution of inorganic photochemistry in recent times.

Inorganic photochemistry has progressed through several stages i.e., Eder's reaction⁶, the photoredox decomposition of HgCl₂ in the presence of oxalate ions, uranyl oxalate actinometry⁷, and the classic blue printing process, where photoreduction of ferric citrate to Fe (II) in the presence of ferricyanide ions leads to the formation of Turnbull's blue. Photoredox decomposition of Co (III) complexes was studied by Vraeck⁸, Schwarz and Tede⁹ and Linhard and Weigel¹⁰.

Chen *et al.*¹¹ observed the electrochemical degradation of bromopyrogallol red in presence of cobalt ions while Lunak *et al.*¹² reported the photocatalytic effects of halogenopentaammine cobalt (III) complexes and H₂O₂. The photochemistry of complexes of number of metals like Cr, Fe, Co, Pt, M and W has been studied extensively by Zhang *et al.*¹³ Photocatalytic reaction by Fe (III)-citrate complex and its effect on the photodegradation of atrazine in aqueous solution was observed by Ou *et al.*¹⁴ Pretzer *et al.*¹⁵ explained the effect of Pt oxidation state and concentration on the photocatalytic removal of aqueous ammonia with Pt-modified titania. Sharma *et al.*¹⁶ reported ferrate enhanced photocatalytic oxidation of pollutants in aqueous TiO₂ suspensions.

EXPERIMENTAL

Preparation of potassium trisoxalatoferrate (III)

15 g ferrous ammonium sulfate was dissolved in 50 mL of hot distilled water, which is already having 1 mL of 4N H₂SO₄ in a 250 mL beaker. The solution was stirred using a magnetic stirrer and slowly, 7 mL of 10% oxalic acid solution was added to it. The beaker was removed and heated to boiling with stirring the solution all the time, with a glass rod. A precipitate of ferrous oxalate was formed, which is allowed to settle down. The supernatant

solution was decanted completely without disturbing the precipitate as far as possible. Now 50 mL of hot distilled water was added to the precipitate and it was stirred. The precipitates were allowed to settle down once again and the supernatant solution was decanted very carefully.

10 g of potassium oxalate was dissolved in 30 mL of hot distilled water and slowly ferrous oxalate precipitates were added. The beaker was kept in a steam bath; then slowly and continuously 25 mL 20 vol. H₂O₂ was added. The solution was regularly stirred. The temperature of the solution was kept above 40°C, by keeping the beaker in the water bath. The solution may have some traces of ferric hydroxide precipitates at this stage and therefore, the beaker was kept on a wire gauze and the solution was heated to boiling. It was constantly stirred and in boiling solution, very rapidly 10 mL of 10% oxalic acid solution was added. Then 3 mL more 10% oxalic acid solution was added to it drop by drop. The hot solution was filtered through a previously weighed sintered crucible G3. At this stage, if any crystals are formed, these were dissolved in 30 mL of warm ethyl alcohol. The filtrate was collected and kept aside for crystallisation in dark. Some bright green coloured crystals were obtained, which were then filtered through the sintered crucible. These were washed with 50% ethyl alcohol and then with a small quantity of acetone. The suction was continued until the crystals become dry. The crystals were further dried.

As the crystals are extremely photosensitive; these were preserved in dark and exposure to light was avoided.

Photochemical degradation of neutral red

1.0×10^{-3} M Neutral red solution was prepared by dissolving 0.0288 g of the dye in 100 mL of doubly distilled water and 1.0×10^{-3} M solution of potassium trisoxalatoferate (III) was prepared by dissolving 0.0436 g of it in 100 mL of double distilled water. These were used as stock solutions and further diluted as and when desired.

The absorption maximum of the dye was determined with the help of spectrophotometer (Systronics Model 106). It was found to be 533 nm. The dye solution was placed in equal amounts in four beaker.

- (i) The first beaker containing neutral red blue solution was kept in dark.
- (ii) The second beaker containing neutral red solution was exposed to light.
- (iii) The third beaker containing equal amounts of neutral red solution and potassium trisoxalatoferate (III) was kept in dark.

- (iv) The fourth beaker containing equal amounts of neutral red solution and potassium trisoxalatoferate (III) solution was exposed to light.

After keeping these beakers for some time, the optical density of the solution in each beaker was measured with the help of spectrophotometer. No change in the optical density was found for the solution of first three beakers, but a decrease in initial value of optical density was observed in the fourth beaker. From these observations, it is clear that this reaction required presence of both; light as well as the complex potassium trisoxalatoferate (III). Hence, this reaction is a photocatalytic reaction.

4.5 mL of 10^{-4} M neutral red solution was taken and 2.0 mL of 10^{-4} M potassium trisoxalatoferate (III) and 23.5 mL of water was added to it. The pH of the reaction mixture was adjusted to 5.0. Then the solution was exposed to a 200 W tungsten lamp. An aliquot of 2.0 mL was taken out from the reaction mixture and its optical density was measured at 535 nm at regular time intervals.

It was observed that the optical density of neutral red solution decreases with increasing time of exposure.

A plot of $1 + \log OD$ against time was found to be linear. The rate constant was determined with expression.

$$k = 2.303 \times \text{slope} \quad \dots(1)$$

A typical run has been presented in Table 1 and graphically presented in Fig 1.

Table 1: A typical run

[Neutral Red] = 1.50×10^{-5} M		pH = 5.0
[Trisoxalatoferate (III)] = 6.66×10^{-6} M		Light intensity = 60.0 mW cm^{-2}
Time (min)	Optical density (O.D)	$1 + \log O.D.$
0.0	0.309	0.4899
20.0	0.282	0.4502
40.0	0.260	0.4150
60.0	0.239	0.3784

Cont...

Time (min)	Optical density (O.D)	1 + log O.D.
80.0	0.224	0.3502
100.0	0.209	0.3201
120.0	0.188	0.2741
140.0	0.178	0.2504
160.0	0.162	0.2095
180.0	0.151	0.1790
200.0	0.138	0.1399
220.0	0.129	0.1106
240.0	0.118	0.0719

$$k = 5.04 \times 10^{-5} \text{ sec}^{-1}$$

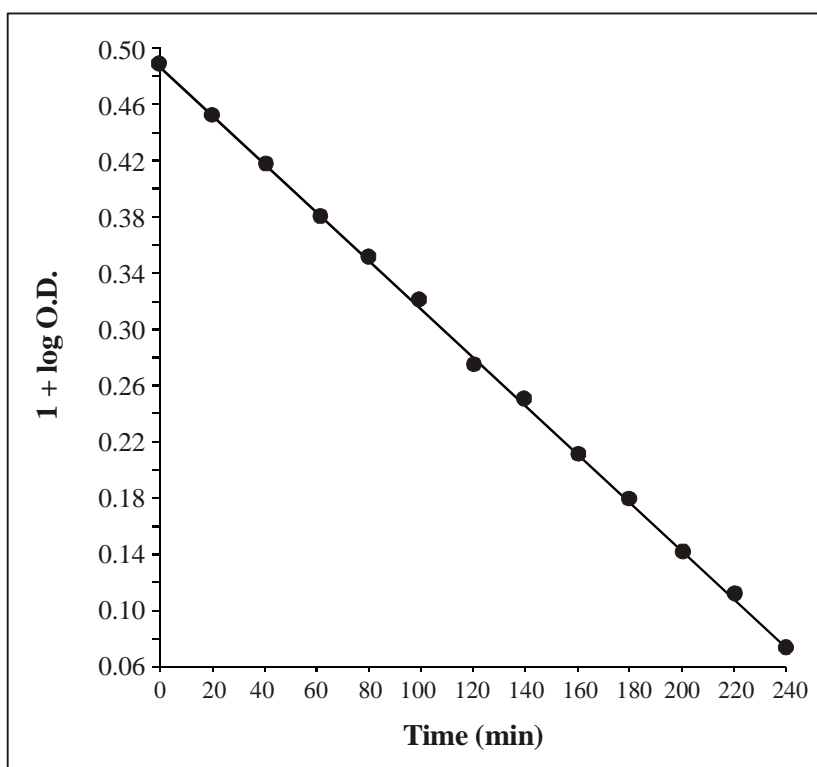


Fig. 1: A typical run

Effect of pH

The pH of the reaction medium is likely to affect the bleaching of the dye neutral red and hence, the effect on the rate of degradation was investigated in the pH range (3.0 - 7.5). The results are reported in Table 2.

It was observed that the rate of bleaching of neutral red increases with increasing pH of the solution upto 5.0, but a decrease in the rate of reaction was observed on increasing the pH of the medium further, i.e. above pH 5.0.

Table 2: Effect of pH

[Neutral Red] = 1.50×10^{-5} M Light intensity = 60.0 mW cm^{-2}
 [Trisoxalatoferate (III)] = 6.66×10^{-6} M

pH	Rate constant $k \times 10^5 \text{ (sec}^{-1}\text{)}$
3.0	0.85
3.5	1.88
4.0	2.72
4.5	3.61
5.0	5.04
5.5	4.20
6.0	3.26
6.5	2.30
7.0	1.23
7.5	0.48

Effect of neutral red concentration

The effect of dye concentration on the rate of bleaching of neutral red was investigated in the concentration range (0.33×10^{-5} M – 2.14×10^{-5} M). The results are summarized in Table 3.

Table 3: Effect of neutral red concentration

[Trisoxalatoferrate (III)] = 6.66×10^{-6} M pH = 5.0
 Light intensity = 60.0 mW cm^{-2}

[Neutral Red] $\times 10^5$ M	Rate constant $k \times 10^5$ (sec ⁻¹)
0.33	1.59
0.50	1.92
0.67	2.33
0.83	2.86
1.02	3.37
1.17	3.90
1.33	4.35
1.50	5.04
1.66	3.81
1.92	2.78
2.14	1.82

It has been observed that the rate of bleaching of dye, neutral red in presence of potassium trisoxalatoferrate (III) and light increases with an increase in the concentration of the dye upto 1.50×10^{-5} M. A decrease in the rate of reaction was observed on increasing the concentration of dye above a particular limit i.e. 1.50×10^{-5} M.

Effect of oxidant concentration

The rate of bleaching of trisoxalatoferrate (III) may be also affected by the change in concentration of oxidant, potassium trisoxalatoferrate (III) and hence, the effect of concentration of potassium trisoxalatoferrate (III) was also observed in the concentration range 3.33×10^{-6} M – 15.00×10^{-6} M. The results are given in Table 4.

It has been observed from the experimental data that there was an increase in the rate of bleaching of dye on increasing the concentration of potassium trisoxalatoferrate (III). The rate reaches its optimum at concentration of oxidant = 6.66×10^{-6} M. On increasing the concentration of potassium trisoxalatoferrate (III) further, an adverse effect on the rate of reaction has been observed.

Table 4: Effect of oxidant concentration

[Neutral Red] = 1.50×10^{-5} M pH = 5.0
 Light intensity = 60.0 mW cm^{-2}

[Trisoxalatoferrate (III)] $\times 10^6$ M	Rate constant $k \times 10^5$ (sec ⁻¹)
3.33	0.48
4.16	1.97
5.00	3.36
6.66	5.04
8.10	4.11
10.20	3.25
11.66	2.40
13.33	1.63
15.00	0.81

Effect of light intensity

The effect of intensity of light was also observed on the rate of bleaching of dye neutral red by changing the distance between the light source and the surface of the solution. The results are summarized in Table 5.

Table 5: Effect of light intensity

[Neutral Red] = 1.50×10^{-5} M pH = 5.0
 [Trisoxalatoferrate (III)] = 6.66×10^{-6} M

Light Intensity (mW cm ⁻²)	Rate constant $k \times 10^5$ (sec ⁻¹)
10.0	0.38
20.0	1.28
30.0	2.20
40.0	3.18
50.0	4.06
60.0	5.04
70.0	4.81
80.0	4.22

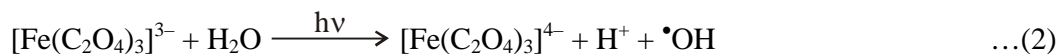
It was observed that there is a direct relationship between the intensity of light and rate of bleaching of the dye. As the light intensity was increased, there was a corresponding increase in the rate of reaction and it goes on increasing with the intensity of light; however, higher light intensities were avoided assuming that it may cause some thermal effects.

RESULTS AND DISCUSSION

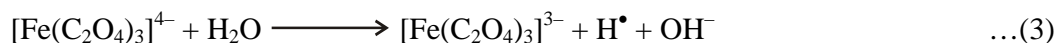
Effect of pH

It was found that the rate of bleaching of dye increases on increasing the pH of reaction medium upto a certain limit 5.0 for neutral red. But after a particular pH, any further increase in the pH of the medium caused a decrease in the rate of reaction between dye and potassium trisoxalatoferate (III).

It may be attributed to the fact that potassium trisoxalatoferate (III) may accept an electron from water molecule in presence of light and as a consequence, corresponding trisoxalatoferate (II) complex is formed along with generation of proton and hydroxyl radicals. It decreases the pH of the reaction mixture. Thus, on decreasing pH of the medium, this reaction is driven in the backward direction due to large excess of protons in the solution and as a result, further reaction is retarded.



On increasing the pH of the reaction mixture in the higher pH range, more OH^- ions are available, which may donate the electron back to trisoxalatoferate (II); thus, regenerating trisoxalatoferate (III), along with hydroxyl ions and hydrogen radical. This hydrogen radical may dimerize immediately to yield hydrogen.



As the OH^- are generated in equation (3), it may not be favoured at higher pH and therefore, regeneration of trisoxalatoferate (III) is retarded, which ultimately results in the decrease in the rate of bleaching of dye by trisoxalatoferate (III).

Effect of dye concentration

It was observed that initially, the rate of reaction increases on increasing the concentration of the dye but after obtaining an optimum rate at a particular concentration of

dye i.e. 1.50×10^{-5} M for neutral red, rate of reaction decreases on increasing the concentration of dye further.

It may be explained on the basis that as the dye concentration was increased, a large number of dye molecules were available for excitation and consecutive oxidation of the dye resulting into its bleaching. As a result, the rate of reaction increases. But a decrease in the rate of reaction was observed on increasing the concentration of dye beyond this particular limit, which may be due to the fact that dye is a coloured material and it starts acting as an internal filter and absorbs a major portion of incident light in its path. Thus, the desired light intensity will not reach the molecules present in the bulk of the solution and as a consequence, a corresponding decrease in the rate of bleaching of the dye has been observed.

Effect of oxidant concentration

It was found that the rate of bleaching of dye was increased on increasing the concentration of potassium trisoxalatoferate (III), which acts as a photochemical oxidant in this reaction. But a reverse trend was observed above a particular concentration of the potassium trisoxalatoferate (III) i.e. 6.66×10^{-6} M, where a decrease in the rate of reaction was observed on increasing the concentration of oxidant.

It may be attributed to the fact that as the concentration of potassium trisoxalatoferate (III) was increased, more and more hydroxyl radicals are produced due to photochemical reduction of ferric state to ferrous state, i.e. reduction of Fe (III) oxidation state to Fe (II) oxidation state in presence of water and light. This type of reduction may be considered as an alternate to photo-Fenton reagent. The generation of a large number of hydroxyl radicals will increase the rate of bleaching of dye molecules involving hydroxyl radicals as an active oxidising species. The participation of hydroxyl radicals as active oxidising species was confirmed by using specific hydroxyl radical scavenger i.e. 2-propanol. It was observed that when this reaction was carried out in presence of 2-propanol (isopropanol), then the reaction rate was drastically reduced.

After a particular concentration of the potassium trisoxalatoferate (III), if its concentration was further increased, then there was a decrease in the rate of bleaching of dye. As the complex potassium trisoxalatoferate (III) is yellowish green in colour, it may absorb a major portion of incident light in the path and due to this absorption of light, there is a decrease in the intensity of light reaching the reactant molecules present in the bulk of solution. Thus, a corresponding decrease in the rate of bleaching of dye was observed on increasing the concentration of oxidant i.e. potassium trisoxalatoferate (III).

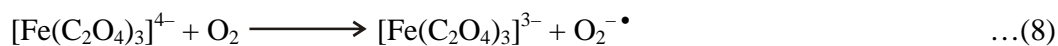
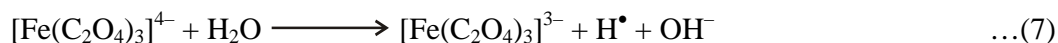
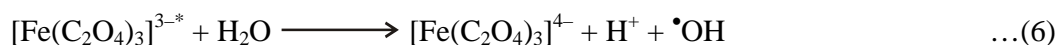
Effect of light intensity

An almost linear behaviour between the rate of reaction and intensity of light was observed.

It may be explained on the basis that as the intensity of light was increased, more photons were there to excite the dye or oxidant molecules per unit area and time. Thus, more oxidant molecules were excited to participate in the reaction generating more hydroxyl radicals, and as a result, higher rate of bleaching of dye molecules was observed at higher light intensities. However, there is a possibility of having some side thermal reactions at higher intensities and therefore, higher light intensities beyond 60.0 mW cm⁻² were avoided.

MECHANISM

Based on experimental observations, a tentative mechanism for the bleaching of dye (Dye) i.e. neutral red has been proposed.



Potassium trisoxalatoferrate (III) is excited by absorbing light of suitable wavelength and it reacts in its excited state with water generating hydroxyl radicals and proton. It is itself reduced to trisoxalatoferrate (II), which further reacts with water to regenerate trisoxalatoferrate (III) alongwith hydroxyl ions and hydrogen radical; thus, making this process cyclic like photo-Fenton reagent or it may react with dissolved oxygen to regenerate

trisoalatoferrate (III) alongwith superoxide anion radical. The superoxide anion radical may decompose water to release oxygen again and producing hydroxyl ions and hydrogen radicals. These hydrogen radicals may undergo dimerisation producing hydrogen gas, which was seen in the form of some bubbles during this process.

Dye is also coloured and therefore, it may absorb light radiations to give excited state of the dye, which is more reactive than its corresponding ground state. The excited form of the dye is easily oxidised to its leuco-form by reacting with hydroxyl radicals. The leuco-form being unstable, degrades into final products. The products were confirmed as carbon dioxide and nitrate ions by their usual tests.

Thus, it may be concluded that potassium trisoalatoferrate (III) is a photochemical oxidant and it can degrade dyes and can be used as an alternate effective reagent for the treatment of waste water containing dyes, particularly in effluents from printing, dyeing, textile and paint industries. Secondly, it can also be used in place of photo-Fenton reagent as it is regenerated in this process and utilises only water and oxygen in place of hydrogen peroxide; making this process cost-effective and eco-friendly also. Not only this, it also decomposes (reduces) water into hydrogen, which is predicted and advocated as a fuel of future. However, the hydrogen is produced at a very smaller concentration at present, may be micro or nano-moles, but time is not far off, when such system will find commercial viability in years to come, giving an additional strength to human society to combat against rapidly emerging energy crisis and ever increasing water pollution all over the globe.

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Accepted : 19.06.2010