KINETICS AND MECHANISM OF THE OXIDATION OF ORANGE II BY PERMANGANATE ION IN AQUEOUS ACIDIC MEDIUM

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ABSTRACT

The kinetics and mechanism of the oxidation of orange II (here and thereafter referred to as OII^-) by permanganate ion has been studied in aqueous sulphuric acid medium at an ionic strength, I = 0.50 mol dm^{-3} (Na_2SO_4), $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3} (HCl), T = 25 ± 1^{o}C and λ = 484 nm. The redox reaction displayed a stoichiometry of 2:1. The reaction showed a first order dependence on [oxidant] and [reductant]. Study on the effect of ionic strength on the rate of the reaction showed that the rate of the reaction obeyed positive Bronsted - Debye salt effect, implying that the activated complex is composed of reactants of like charges. Plot of $\log k_2$ against $I^{1/2}$ gave a slope of unity. The rate of the reaction increased with increase in hydrogen ion concentration in the range $(0.5 – 10.0) \times 10^{-2}$ mol dm^{-3}. Results of the Michaelis – Menten's plot gave no evidence of intermediate complex formation during the course of the reaction. Based on the results obtained, the reaction is probably proceeding through the outersphere mechanistic pathway.

Keywords: Intermediate; Michaelis - Menton's; Outersphere; Redox

INTRODUCTION

Acid Orange 7 (AO7) or OII^- (C.I. 15510) is produced by coupling reaction between 2-Naphthol, or β-naphthol and diazonium compound of sulfanilic acid [1]. It is a mono-azo acidic dye, which is soluble in water and is widely used in dyeing, weaving, tanning and paper industries [2]. The dye has high photo- and thermal stability. Degradation of S^- dye has been widely studied mostly through the photocatalytic method [3]. Comparative study on the decolorization of OII^- by zero-valence tin in citric and hydrochloric acid has been reported [4]. It was found that zero-valence tin reductively degraded a persistent azo dye (OII^-), to produce colourless aromatic amines.

Despite the studied on the degradation of this dye mostly by photocatalytic method, there is need for detail investigation of the kinetics of its electron transfer reaction in aqueous sulphuric acid medium.

Mn(VII) is a potent oxidizing and hydroxylating agent [5]. Its wide application as an oxidizing agent in synthetic as well as in analytical chemistry has been reported in the literature [6]. The explanation for the positive $[H^+]$ dependence on the rate of MnO_4^- oxidation has been rationalized in terms of the protonation of MnO_4^- in a fast step to give $HMnO_4$, which subsequently reacts with the reductant in a slow step to give the products [7,8]. Despite the rich chemistry of permanganate ions, its redox reaction with OII^- has not been documented. It is our desire to investigate the redox reaction of this oxidant with $OII^-$with a view to examining its mechanistic pathways.

EXPERIMENTAL

Materials

All chemicals and reagents used in this work were analar grade and were used without further purification. $KMnO_4$ was used as the oxidant, H_2SO_4 was used to furnish H^+ to the reaction and Na_2SO_4 was used to maintain a constant ionic strength. Acetone was used to vary the dielectric constant of the reaction medium. OII^-, the oxidant and the other solutions were prepared with distilled water. The λ_{max} (484nm) used for this work was determined by running the spectrum of the dye solution using UV-2500PC series in the wavelength range 350 – 650nm.

Methods

The reaction stoichiometry was determined spectrophotometrically using the mole ratio method [5]. This was accomplished by measuring the absorbance of solutions containing varying concentrations of permanganate ion in the range $(0.1- 2.0) \times 10^{-4})$ mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$mol dm^{-3} and $I = 0.50$ mol dm^{-3} at $\lambda = 484$ nm until a constant absorbance was obtained. A point of inflection on the curve of the absorbance versus mole ratio plot corresponds to the stoichiometry of the reaction.

The kinetic runs were performed under pseudo - first order conditions with the concentration of permanganate ion at least 60-fold greater than that of the dye at T = 25 ± 1°C and ionic strength of reaction medium, I = 0.50 mol dm^{-3} (Na_2SO_4). The reaction was monitored spectrophotometrically by measuring the absorbance at 484 nm using UV-Vis spectrophotometer 6405. The pseudo-first order plots of log (A_t - A_∞) versus time were made (where A_∞ and A_t are the absorbance at the end of the reaction and at time, t respectively).

The influence of [H^+] on the rate of reaction was investigated using sulphuric acid in the range (0.5 – 10.0) ×10^{-2} mol dm^{-3}, while the [OII^-] and [MnO_4^-] were kept constant at 25 ± 1°C and I = 0.50 mol dm-^{3} (Na_2SO_4).

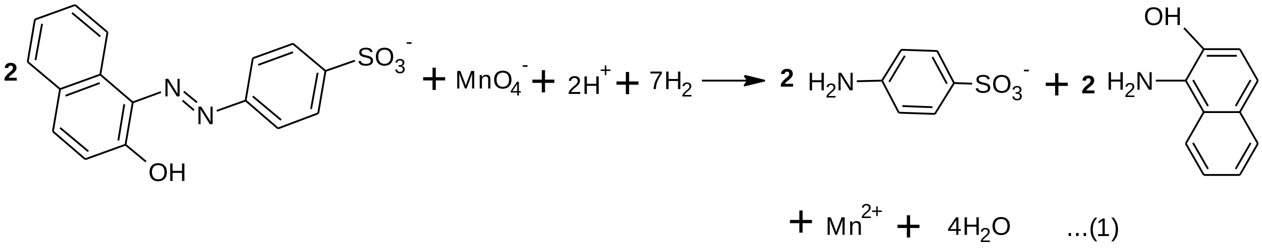
The effect of ionic strength of the reaction medium on the rate of the reaction was investigated in the range of 0.2 - 0.8 mol dm^{-3} (Na_2SO_4) while the concentration of other reactants were kept constant. The effect of added cations and anions were investigated by keeping the concentration of other reactants constant while varying the ions concentrations as follows:

[X^-] = (20.0 – 150) × 10^{-3} mol dm^{-3}, where X = (CH_3COO^- and SO_4^{2-}) and [X] = (10.0 – 100) × 10^{-3} mol dm^{-3}, where X = (Ca^{2+} and Mg^{2+}).

The inorganic product was qualitatively confirmed to be Mn^{2+} by adding 1ml of 6M HNO_3 to few drops of the solution. Sodium bismuthata was also added and stirred.

RESULTS AND DISCUSSION

The stoichiometric study showed that two moles of the dye was consumed by one mole of the oxidant suggesting the overall equation as indicated in equation (1) below.



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A stoichiometry of 1:1was reported for the redox reaction of malachite green and permanganate ion in aqueous acidic medium [5]. Mn^{2+} was confirmed as the inorganic product on addition of sodium hydroxide solution. A white precipitate of manganese (II) hydroxide which was insoluble in excess sodium hydroxide solution was formed. The precipitate oxidised on exposure to air, becoming brown as the result of formation of hydrated manganese dioxide

Sulphanilic acid was confirmed as one of the organic product on addition of few drops of conc. HCl to the reaction solution, followed by solution of sodium nitrite to form a diazonium ion. The reaction was carried out in an ice-bath at 3°C. On addition of the solution of 2-naphthol to the diazonium ion, an orange II dye was formed [9]. On addition of $FeCl_3$ to the reaction solution, a faint green colour was observed. This indicates the presence of 2-naphthol.

Pseudo-first order plots of log (A_t-A_∞) versus time were linear to more than 80% extent of the reaction, suggesting that the reaction is first order with respect to the OII^-. The order of the reaction with respect to $[MnO_4^-]$ was also determined by plotting $\log k_1$ against $\log[MnO_4^-]$ (Fig.1). Slope of one was obtained which indicate that the order of reaction with respect to $[MnO_4^-]$ is first order.

This reaction therefore conforms to the rate law:

$$-d[OII^-]/dt = k_2[OII^-][MnO_4^-] \qquad (2)$$

where k_2 is the second order rate constant.

Effect of changes in ionic strength of the reaction medium indicated that change in ionic strength of the reaction medium increases the reaction rate (Table 1). Pot of $\log k_2$ against $I^{1/2}$ gave a slope of one. (R^2 =0.99) (Fig 2). This obeys a positive Bronsted - Debye salt effect, implying that the activated complex is formed from reactant of similar charges. This observation is consistent with equation (6) in the reaction mechanism.

The result in Table 1 shows that the rate of reaction increases with increase in $[H^+]$ in the acid range investigated. Plot of $\log k_1$ versus $\log[H^+]$ gave a slope of half, which is an indication that the order with respect to acid is half order. Also, plot of k_2 versus $[H^+]$ was linear with an intercept conforming with equation (3).

$$k_2 = a + b[H^+]^{1/2} \qquad (3)$$

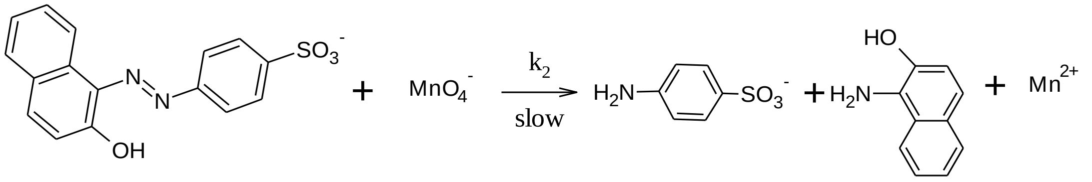
The acid dependence of this nature shows that there is a rapid pre-equilibrium between the protonated and non-protonated forms and both forms are reactive [5].

The overall rate equation in the acid range investigated is given as:

$$-d[OII^-]/dt = (a + b[H^+]^{1/2})[OII^-][MnO_4^-] \qquad (4)$$

Added cations (Ca^{2+} and Mg^{2+}) and anions (CH_3COO^- and SO_4^{2-}) inhibited the rate of reaction. This inhibitive effect by the ions shows the characteristic of the outersphere mechanism [10]. Addition of acrylonitrile to a partially reacted mixture in the presence of excess methanol did not lead to gel formation. This shows that the participation of free radicals is unlikely. The spectrum of the reaction mixture when compared to that of the dye (OII^-) alone showed no shift in λ_{max} suggesting absence of an intermediate complex during the reaction .Plot of $1/k_1$ versus $1/ [MnO_4^-]$ gave a straight line that passed through the origin. (Figure 3). This further suggests the absence of the formation of intermediate complex thereby supporting the outersphere mechanism. On the basis of the above findings, the probable mechanism below is proposed for this reaction

$$MnO_4^- + H^+ \overset{K_1}{\rightleftharpoons} HMnO_4 \qquad ...(5)$$



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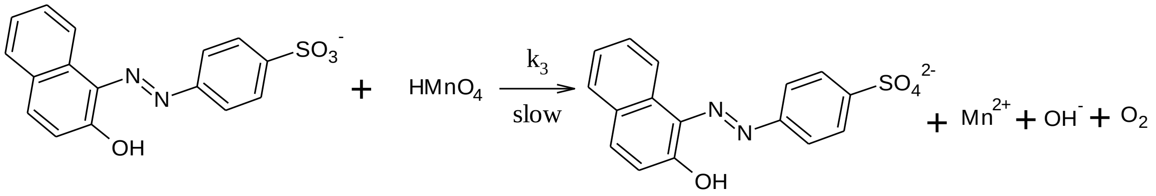

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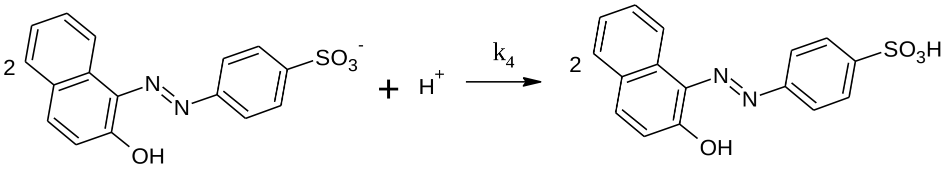

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$$\text{Rate} = k_2[\text{OII}^-][\text{MnO}_4^-] + k_3[\text{OII}^-][\text{HMnO}_4] \qquad (9)$$

$$[\text{MnO}_4^-]_t = [\text{MnO}_4^-] + [\text{HMnO}_4] \qquad (10)$$

$$[\text{HMnO}_4^-] = \frac{K_1[\text{H}^+][\text{MnO}_4^-]_t}{1+K_1[\text{H}^+]} \qquad (11)$$

$$\text{Rate} = k_2[\text{OII}^-][\text{MnO}_4^-] + \frac{k_3K_1[\text{MnO}_4^-]_t[\text{OII}^-][\text{H}^+]}{1+K_1[\text{H}^+]} \qquad (12)$$

Table 1: Pseudo – first order and second order rate constants for the reaction of OII$^-$ and MnO$_4^-$ at [OII$^-$] = 5.0 × 10^{-5} mol dm^{-3}, λ = 484 nm and T = 25 ± 1°C

10^3[MnO$_4^-$], mol dm^{-3}	**10^2[H$^+$], mol dm^{-3}**	**10^1I, mol dm^{-3}**	**10^3k$_1$, s^{-1}**	**k$_2$, dm^3 mol^{-1} s^{-1}**
3.0	5.0	5.0	0.840	0.280
3.5	5.0	5.0	0.987	0.282
4.0	5.0	5.0	1.12	0.280
4.5	5.0	5.0	1.26	0.280
5.0	5.0	5.0	1.38	0.276
6.0	5.0	5.0	1.70	0.283
4.0	0.5	5.0	0.780	0.195
4.0	2.0	5.0	0.968	0.242
4.0	4.0	5.0	1.05	0.262
4.0	5.0	5.0	1.12	0.280
4.0	6.0	5.0	1.18	0.296
4.0	8.0	5.0	1.25	0.313
4.0	10.0	5.0	1.28	0.320
4.0	5.0	1.0	1.93	0.483
4.0	5.0	2.0	0.592	0.148
4.0	5.0	3.0	0.768	0.192

4.0	5.0	5.0	1.13	0.283
4.0	5.0	6.0	1.23	0.308
4.0	5.0	7.0	1.58	0.390
4.0	5.0	8.0	1.93	0.483

Table 2: Rate data for the effect of added cations (Ca^{2+} and Mg^{2+}) on the rate of reaction of OII^- and MnO_4^- at $[OII^-] = 5.0 \times 10^{-5}$ mol dm^{-3}, $[MnO_4^-] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 484 nm and T = 25 ± 1 °C

Ion	10^3 [ion], mol dm^{-3}	10^3 k_1, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
	0.0	1.12	0.280
Ca^{2+}	10.0	1.08	0.270
	20.0	1.00	0.250
	40.0	0.772	0.193
	60.0	0.568	0.142
	80.0	0.480	0.120
	100.0	0.392	0.098
	0.0	1.124	0.281
Mg^{2+}	10.0	1.09	0.273
	20.0	1.06	0.265
	40.0	0.92	0.230
	60.0	0.752	0.188
	80.0	0.628	0.157
	100.0	0.412	0.103

Table 3: Rate data for the effect of added anions (CH_3COO^- and SO_4^{2-}) on the rate of reaction of OII^- and MnO_4^- at $[OII^-] = 5.0 \times 10^{-5}$ mol dm^{-3}, $[MnO_4^-] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 484 nm and T = 25 ± 1 °C

Ion	10^3 [ion], mol dm^{-3}	10^3 k_1, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
	0.0	1.13	0.282

CH_3COO^-	20.0	1.07	0.268
	40.0	0.932	0.233
	60.0	0.744	0.186
	80.0	0.60	0.150
	100.0	0.512	0.128
	150.0	0.328	0.082
	0.0	1.12	0.280
SO_4^{2-}	20.0	1.05	0.263
	40.0	0.912	0.228
	60.0	0.652	0.163
	80.0	0.480	0.120
	100.0	0.320	0.080
	150.0	0.104	0.026

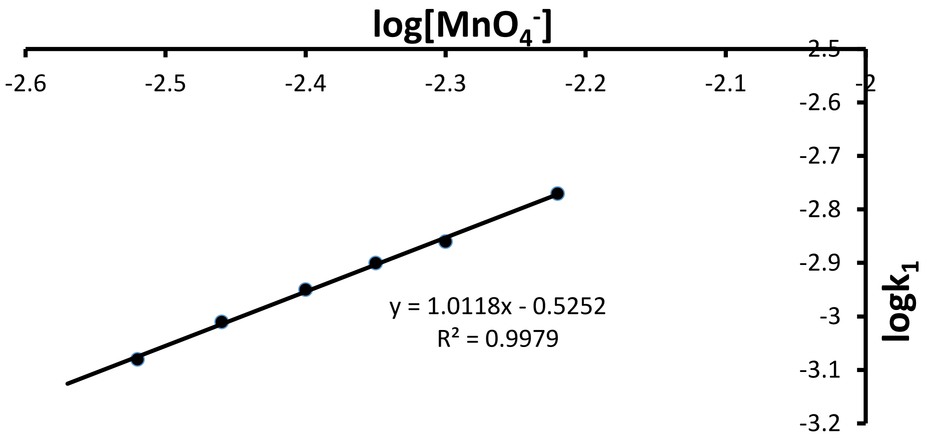

Figure 1: Plot of log k_1 versus log[MnO_4^-] for the redox reaction of OII^- with MnO_4^- at [OII^-] = 5.0×10^{-5} mol dm^{-3}, [MnO_4^-] = $(3.0 – 6.0) \times 10^{-3}$ mol dm^{-3}, [H^+] = 5.0×10^{-2} mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 484 nm and T = 25 ± 1°C

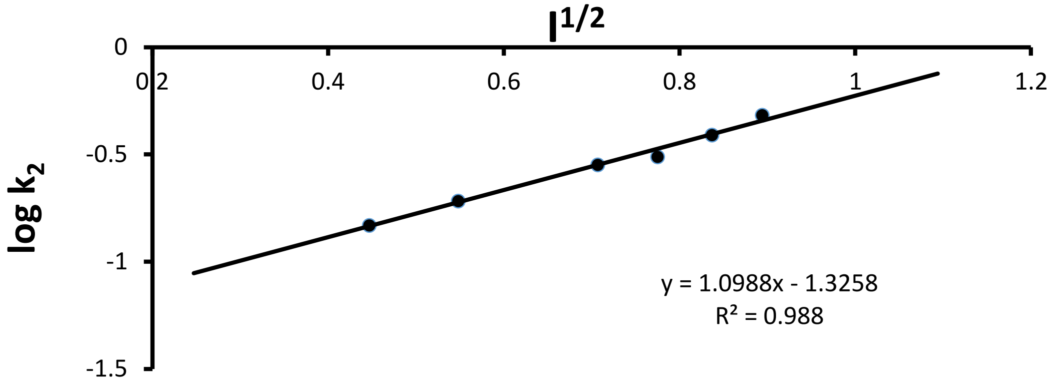

Figure 2: Plot of logk_2 versus $I^{1/2}$ for the redox reaction between OII^- and MnO_4^- at $[OII^-] = 5.0 \times 10^{-5}$ mol dm^{-3}, $[MnO_4^-] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, I = 0.50 mol dm $^{-3}$, $\lambda = 484$ nm and T= 25 ± 1 °C

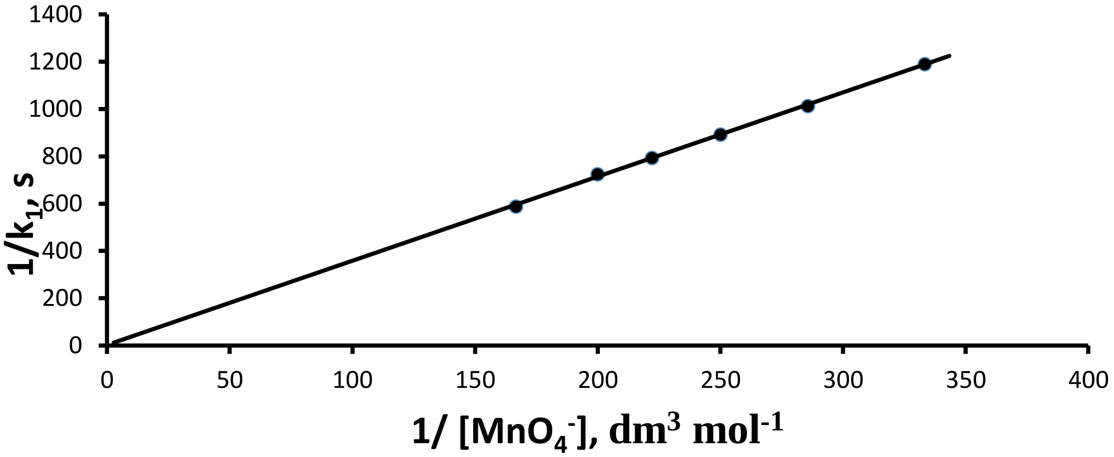

Figure 3: Michaelis - Menten plot for the redox reaction between OII^- and MnO_4^- at $[OII^-] = 5.0 \times 10^{-5}$ mol dm^{-3}, $[MnO_4^-] = (3.0 – 6.0) \times 10^{-3}$ mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, I = 0.50 mol dm $^{-3}$, $\lambda = 484$ nm and T= 25 ± 1 °C

CONCLUSION

The study of rhe redox reaction between OII^- and permanganate ion in aqueous acidic solution revealed a stoichiometry of 2:1, and first order with respect to oxidant and reductant concentrations. The rate of the reaction increased with increase in acid concentration as well as in the ionic strength of the reaction medium. Added ions inhibited the rate of the reaction and addition of acrylonitrile to a partially reacted mixture in the presence of excess methanol did not lead to gel formation. The result from the spectroscopic study indicated no significant shift from the absorption maximum of 484nm characteristic of OII^-. Plot of $1/k_1$ versus $1/[MnO_4^-]$ gave a straight line which passed through the origin. Based on the above results, it is proposed that the reaction is most probably operates through the outersphere mechanism.

REFERENCES

1. Booth, G. (2000). Dyes, General Survey, Wiley-VCH. *DOI: 10.1002/14356007.a09_073*
2. Daneshvar, N., Aber, S. & Hosseinzadeh, S. (2008). Study of C.I. acid orange 7 removal in contaminated water by photo oxidation processes, *Global NEST Journal*, 10 (1), 16-23
3. Bandara, J., Morrison, C., Kiwi, J., Pulgarin, C. & Peringer, P (1997). Dyanamics of oxidants addition as a parameter in the modeling of dye mineralization (orange II) via advanced oxidation technologies, *Journal of water science and technology*, 35(4), 87-93.
4. Shizuo, N. & Makoto, S. (2012). Comparative Study on the Decolorization of Orange II by Zero-valence Tin in Citric and Hydrochloric Acids, Energy *and Environment Research*, 2(1), 1-12
5. Mohammed, Y., Iyun, J. F. & Idris, S. O. (2009). Kinetic approach to the mechanism of the redox reaction of malachite green and permanganate ion in aqueous acidic medium, *African Journal of Pure and Applied Chemistry*, 3(12), 269-274.
6. Hiremath, G.A., Timmanagondar, P.L., Nandibewoor, S.T. (1996). Kinetics of oxidation of Thallium (I) by permanganate in aqueous hydrochloric acid medium using the stopped – flow Technique, *Transition Metal Chemistry*, 21: 560.
7. Hassan, R.M. (1991). Kinetics and mechanism of oxidation of DL –alanine by permanganate ion in acid perchlorate media, *Canadianm Journal of Chemistry,* 69: 2018.
8. Sen, P.K., Sanyal, A., Gupta, K.K.S. (1995). Evidence of protonation during the oxidation of some aryl alcohols by permanganate in perchloric acid medium and mechanism of the oxidation processes. *Int. J. Chem. Kinet.* 27: 379.
9. Stephanie (2008). Practical organic chemistry, 3rd year Students part 1, Jazan University, Faculty of Science, Chemistry Department. Pp 38
10. Mayer, T.J. & Taube, H. (1987). *Comprehensive coordination chemistry*: The synthesis, reactions, properties and application of coordination compounds, Pergamon Press U.K, pp. 384.