

KINETICS AND MECHANISM OF OXIDATION OF P-ANISIDINE BY FE(III) SOLUTION IN ACIDIC MEDIUM

MOHAMED A. MANSOUR

*Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt***Abstract**

Kinetics of oxidation of p-anisidine by Fe(III) ion was studied spectrophotometry in acidic medium. The rate constant was found to increase with increasing p-anisidine and hydrogen ion concentrations. The order of reaction was found to be first order with respect to both Fe(III) ion and p-anisidine concentration. The suggested mechanism involves the interaction of the reactive species of the reactants to form the activated complex which decompose in a rate determining step to products. The rate law was derived and activation parameters are calculated to be $\Delta H^* = 47 \text{ kJ mol}^{-1}$ and $\Delta S^* = -148.6 \text{ JK}^{-1} \text{ mol}^{-1}$

Introduction

Complexation and redox reactions of Fe(III) ion with chelating ligands such as cysteine¹, thioglycolate², and several other mercaptocarboxylic acids³⁻⁵ have been extensively studied, where intermediates were formed and undergo redox decomposition to products. The kinetic of oxidation of aromatic amines by peroxomonosulfate⁶, N-chloroacetanilide⁷, N-bromoacetamide⁸ and peroxidate⁹ were reported.

In all cases, an amine-oxidant complex is first formed in a rapid and reversible step which is followed by a rate determining decomposition to products.

In the present work, we extend our studies to the reaction of ferric ion with p-anisidine which contain groups toward which Fe(III) ion is highly specific.

Experimental

All chemicals were obtained from B.D.H., The kinetic measurements were performed using a unicam Helios α spectro-photometer equipped with a water-jacketed cell holder. The reactants were thermostated for ca 15 min then mixed thoroughly and quickly transferred to an absorption cell. The pH of the reaction was measured using a radiometer M62 pH meter fitted with a glass-calomel electrode.

The kinetics runs were made with the Fe(III) ion concentration changed from $5 \times 10^{-4} \text{ M}$ to $8.33 \times 10^{-4} \text{ M}$ while the p-anisidine concentration was varied from $8 \times 10^{-3} \text{ M}$ to $20 \times 10^{-3} \text{ M}$. The reaction kinetics were followed by observing the growth in

absorbance associated with the formation of the products at 541 nm. The ionic strength of the medium was adjusted to be 0.5 M with potassium nitrate solution.

Results And Discussion

The kinetics of oxidation of p-anisidine by Fe(III) ion was investigated at several initial concentrations of the reactants in acid media at constant pH with p-anisidine concentration in excess. Plots of $\ln(A_{\infty}-A_t)$ versus time are linear, as shown in (Fig.1), indicating that the reaction is first order in Fe(III) ion concentration. This is confirmed by obtaining a constant value of the observed first order rate constants with different Fe(III) ion concentration. The pseudo first-order rate constants obtained from the slopes of these plots are collected in Table 1. The values of rate constants are increasing with increasing p-anisidine concentration and reached a limiting value at high p-anisidine concentration (Fig. 2).

It is observed also that the pH changes have a marked effect on the rates of oxidation of p-anisidine. The rate constants dependence on the hydrogen ion concentration is presented in Fig. 3, where the rate of reaction increases with increasing the hydrogen ion concentration. A plot of k_{obs}^{-1} versus $(\text{H}^+)^{-1}$, at different p-anisidine concentrations, gave straight lines with positive intercepts (Fig. 3).

The first order dependence of the rate on ferric ion and p-anisidine suggests the interaction between the effective species of the reactants forming the activated complex followed by a rate determining decomposition to products.

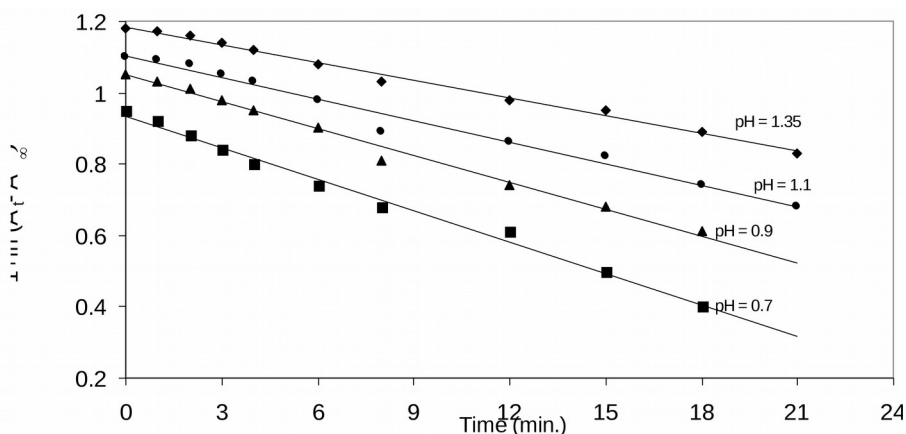
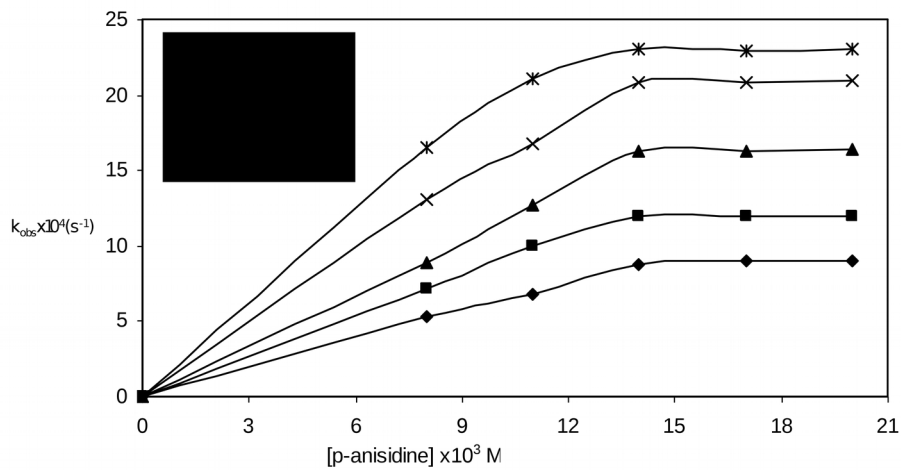
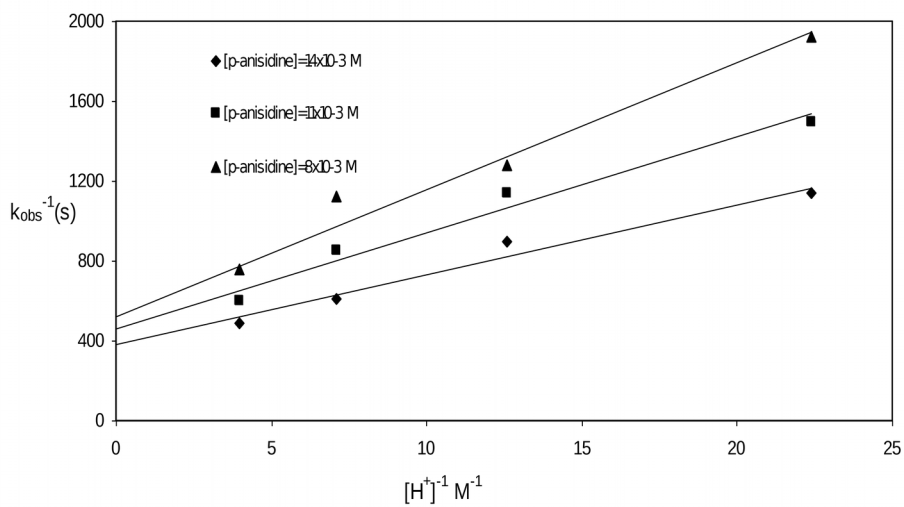


Fig. (1): Pseudo-first order plot for oxidation of p-anisidine by Fe (III) at different pH values at 35 °C, $[\text{Fe (III)}] = 6.67 \times 10^{-4} \text{ M}$, and $[\text{p-anisidine}] = 14 \times 10^{-3} \text{ M}$



Fig(2): Variation of the rate constant with p-anisidine concentrations at different pH at 35 °C



Fig(3): Variation of k_{obs}^{-1} versus $[H^+]^{-1}$ at different p-anisidine concentrations at 35°C

Table (1) Rate constants for reaction of p-anisidine with Fe(III) solution at various pH and temperatures.

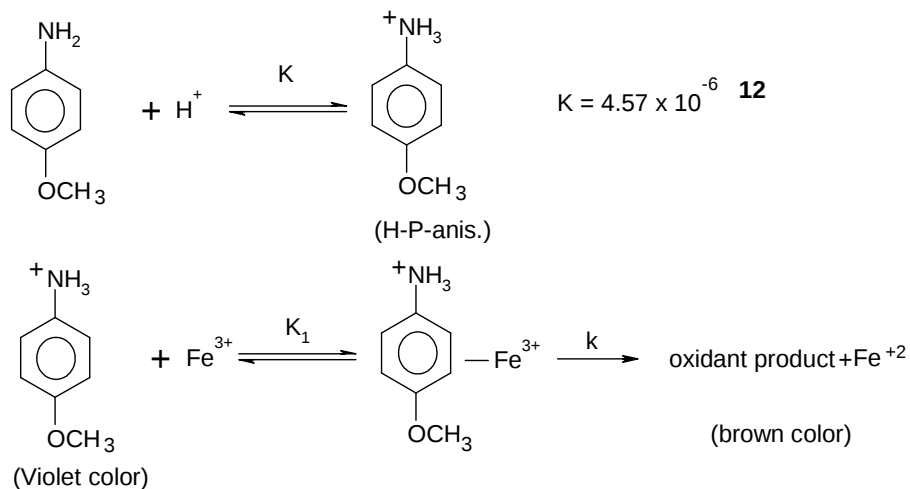
[Fe³⁺] = 6.67x10⁻⁴ M

Temp	pH	(p-anis.) x 10 ³ M	k _{obs} x 10 ⁴ (s ⁻¹)
25°C	0.70	14	15-3
	0.85	14	11.3
	1.10	14	7.6
	1.35	14	5.8
35°C	0.30	8	16.8
	0.70	8	20.7
	0.85	8	16.8
	1.10	8	11.8
	1.35	8	8.8
	0.30	11	18.8
	0.60	11	16.7
	0.85 ^a	11	20.6
	0.85	11	12.7
	0.85 ^b	11	12.5
	1.10	11	8.8
	1.35	11	6.70
	0.30	14	23.0
	0.60	14	22.8
0.85	14	16.3	
1.10	14	11.2	
40°C	1.35	14	8.8
	0.70	14	25.0
	0.85	14	20.2
	1.10	14	15.3
	1.35	14	13.0

Where: (a) [Fe⁺³] = 5x10⁻⁴M (b) [Fe³⁺] = 8.33x10⁻⁴M

In acid media, the reaction mixture changes from violet to brown color. The violet color is attributed to the protonation of the amine group of the p-anisidine. The protonated p-anisidine is reacted with Fe(III) ion to give the brown product color. This observation was also reported by Michael D. Johnson¹⁰ and A.K. Ghosh et al¹¹ in the study the reaction between Fe(III) ion and p-anisidine.

Therefore, the following scheme is proposed to account for the different steps involved.



Where (H-p-anis.) is protonated p-anisidine, K is protonation constant of p-anisidine, K_1 is equilibrium constant of formation of activated intermediate and k is rate constant of decomposition of the activated intermediate

And the observed first-order rate constant is

$$\begin{aligned}
 \text{Rate} &= k K_1 [\text{H-p-anis.}] [\text{Fe}^{3+}] \\
 &= k K_1 K [\text{p-anis.}] [\text{H}^+] [\text{Fe}^{3+}] \\
 [\text{Fe}^{3+}]_{\text{T}} &= [\text{Fe}(\text{H}_2\text{O})_6^{3+}] + [\text{Fe-H-p-anis.}] \\
 &= [\text{Fe}(\text{H}_2\text{O})_6^{3+}] + K_1 [\text{H-p-anis.}] [\text{Fe}(\text{H}_2\text{O})_6^{3+}] \\
 &= [\text{Fe}(\text{H}_2\text{O})_6^{3+}] \{1 + K_1 [\text{H-p-anis.}]\} \\
 &= [\text{Fe}(\text{H}_2\text{O})_6^{3+}] \{1 + K_1 K [\text{p-anis.}] [\text{H}^+]\}
 \end{aligned}$$

$$\therefore [\text{Fe}(\text{H}_2\text{O})_6^{3+}] = \frac{[\text{Fe}^{3+}]_{\text{T}}}{1 + K K_1 [\text{p-anis.}] [\text{H}^+]}$$

$$\therefore \text{Rate} = \frac{k K_1 K [\text{H}^+] [\text{p-anis.}] [\text{Fe}^{3+}]_{\text{T}}}{1 + K K_1 [\text{p-anis.}] [\text{H}^+]}$$

$$\therefore k_{\text{obs}} = \frac{kK_1K[\text{H}^+][\text{p-anis.}]}{1 + KK_1[\text{p-anis.}][\text{H}^+]}$$

$$\therefore \frac{1}{k_{\text{obs}}} = \frac{1}{kK_1K[\text{p-anis.}][\text{H}^+]} + \frac{1}{k}$$

Values of k and K_1 at different p-anisidine concentrations, were obtained from the intercepts and slopes of straight lines of Fig. 3 and summarized in Table 2. Also the value of ΔH^* is obtained from the relation

$$\ln k = \frac{-\Delta E}{RT} + \text{constant}$$

and from Arrhenius plot and the value of ΔS^* are obtained from the equation:

$$k = \frac{RT}{Nh} e^{\frac{-\Delta H^*}{RT}} \cdot e^{\frac{\Delta S^*}{R}}$$

Where N is Avogadro's number and h is Planck's constant.

The values of ΔH^* and ΔS^* are included in Table 2, the negative values of ΔS^* reflect the formation of a stable intermediate. In the oxidation of p-chloroaniline with periodate¹³, a value of $3.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 25°C was obtained which is smaller than the obtained value in our study ($k = 1.25 \text{ M}^{-1} \text{ s}^{-1}$ at 40°C). This can be attributed to the inductive effect of chlorine atom which decrease the electron density on the aminonitrogen and reducing the possibility of the intermediate formation, whereas in our study the electrophilic attack of Fe^{3+} on the nitrogen atom of the amine increase by the electron releasing effect of methoxyl group which increase the electron density on the nitrogen atom. This conclusion was confirmed by Dalhlgren and Rand¹⁴, where the observed rate constants for periodate oxidation of 2-(methylamino) ethanol ($k_{\text{obs}} = 14.4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 50°C) was higher than that for 2-amino ethanol ($k_{\text{obs}} = 5.08 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 50°C).

Table (2) Summary of the kinetics data and activation parameters for the reaction of Fe(III) and p-anisidine at 35°C

[p-anisidine] (M)	K_1 (M^{-1})	k (s^{-1})
8×10^{-3}	3.9×10^6	0.0255
11×10^{-3}	8×10^6	0.0520

$$\Delta H^* = 47 \text{ kJ mol}^{-1}$$

$$\Delta S^* = - 148.57 \text{ JK}^{-1} \text{ mol}^{-1}.$$

Conclusion

The kinetics study of oxidation of p-anisidine with Fe(III) solution in acidic medium was studied in pseudo -unimolecular condition with excess of p-anisidine concentration. The reaction is first order for both reactants and directly proportional to H⁺ concentration. The values of K₁ equilibrium constant of intermediate formation and k, is the rate constant of decomposition the activated intermediate complex at different p-anisidine concentrations were obtained. The values of ΔH^* and ΔS^* were also obtained, and the negative values of ΔS^* reflect the formation of a stable intermediate.

References

1. D. LEUSSING, J.P. MISLAN and R.J. GOLL, J. Am. Chem. Soc., 84, 1070 (1960).
2. H. LAMFRAM AND S.O. NIELSEN, J. Am. Chem. Soc., 79, 1966 (1956).
3. A. MCAULEY and K.J. ELLIS, J. Chem. Soc. (A), 1533 (1973).
4. A. MCAULEY and G. LAPPIN, J. Chem. Soc., Dalton Trans., 1560 (1975).
5. A. MCAULEY, G. LAPPIN and K.J. ELLIS, J. Chem. Soc., Dalton Trans., 1930 (1975).
6. R.M. SATYANARAYAN, K.C. RAJANNA and N. AHMED, Int. J. of Chem. Kinet., 27(12), 1143 (1995).
7. K. ARUN and B. GUNUDAS, J. Indian Chem. Soc., 89 (9), 523 (1991).
8. P.R. SHARADAMANI and V. JAGANNADHAM, Indian, J. Chem., 29A, 700 (1990).
9. S.S. ANIS and MOHAMED A. Mansour, Afinidad 56 (484), 388 (1999).
10. MICHAEL D JOHNSON and Brooks J.Hornstein, *Inorg. Chem.*, (21), pp 6923–6928 (2003)
11. A.K. GHOSH, K.N. MITRA, G. MOSTAFA, S. GASWAMI. European J. of Inorg. Chem. Vol. 2000, 1961-1967 (2000).
12. Dissociation Chemistry of Organic Acids. Institute of Fundamental Science, Massery University 1998-2008
13. S.P. SRIVASTAVA, G. BHATTACHARJEE and P. MALIK, J. Indian Chem. Soc., 67, 347 (1990).
14. G. DAHLGREN AND E.M. RAND, J. Phys. Chem. 71, 1955, (1967).

