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PD (II) Catalyzed Chlorination of Levofloxacin during Water Treatment: Kinetics and Mechanism

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***Abstract** – The kinetics and mechanism of the Pd (II) ion catalyzed reaction of levofloxacin (LFC) by free available chlorine (FAC) during water chlorination processes was investigated for the first time between the pH values 4.0 and 9.0. The pH dependent second order rate constants were found to decrease with increase in pH. (e.g. Apparent second order rate constant; $k''_{app} = 105.45\ dm^3\ mol^{-1}\ s^{-1}$ at pH 4.0 and $k''_{app} = 16.93\ dm^3\ mol^{-1}\ s^{-1}$ at pH 9.0 and at 25 ^oC). The reaction rates revealed that Pd (II) catalyzed reaction was faster than the uncatalyzed reaction. The products of the reaction were determined by Liquid chromatography and high resolution mass spectrometry. The reaction proceeds via formation of intermediate complex between Pd (II) ion and levofloxacin, then HOCl reacts with the complex to form chlorinated product. The effect of catalyst, effect of initially added product, effect of dielectric constant and effect of ionic strength on the rate of reaction was also studied. The effect of temperature on the rate of the reaction was studied at four different temperatures and rate constants were found to increase with increase in temperature and the thermodynamic activation parameters E_a, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ were evaluated for the reaction and discussed.*

***Key words:** Kinetics, Chlorination, Levofloxacin, Mechanism, Palladium (II), Catalysis, Oxidation.*

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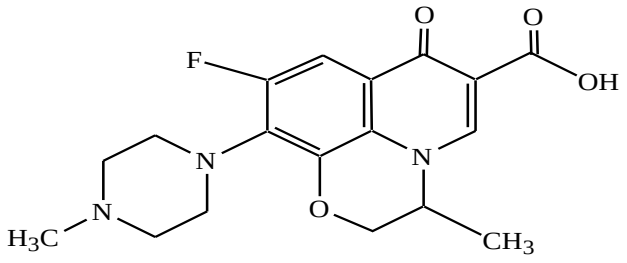
I. INTRODUCTION

Levofloxacin (LFC) belongs to fluoroquinolone class of antibacterials. Antibiotics are the very important compounds used for ef fective medication. Despite the fact that, antibacterial agents have been applied in large quantities for last few decades, the presence of these substances in the aquatic environment has attracted little attention until recently. The antibacterial classes of pharmaceuticals are very important, since they have been recognized as emerging environmental pollutants [1-2].

Fluoroquinolones are broad-spectrum antibacterial agents used to treat the bacterial infections in human beings [3]. An enormous portion of the totally, clinically approved fluoroquinolones dosages are released in the domestic sewage due to partial metabolism of these molecules in the body of human [4]. This represents a main route for entry of such pharmaceutical compounds into natural aquatic environment [5-6]. Micrograms to nanogram per litre of fluoroquinolones have been detected in municipal waste water and effluents from sewage treatment plants [7-8].



Structure of levofloxacin(LFC)

Information on palladium catalyzed chlorination of pharmaceutical compounds is scarce. Hence, the Pd (II) catalyzed chlorination of levofloxacin was studied with the objective of quantifying kinetics, to arrive at transformation mechanism, identify reaction products

and to evaluate and discuss the thermodynamic activation parameters of the reaction.

The d-block elements were used as catalysts to catalyze many oxidation and reduction reactions, because they show variable oxidation states. Recently, d-block metal ions including Ag(I)/Ag(II), Pd(II)/Pd(IV), Os(IV)/Os(VIII), Ru(II)/Ru(III), Ir(IV)/Ir(VI), Rh(II)/ Rh(VI) and are widely used as catalysts due to their strong catalytic influences in various reactions. Alone metals or as aqueous salt solution, acts as catalysts in various oxidation and reduction reactions has involved extensive interest. The reaction mechanism of catalysis is dependent on the nature of the reactant, oxidant and experimental condition; it has been proved that metal ions can catalyze by one of form such as the complex formation by combining with substrates (reactants) or oxidation of the reactant (substrate) itself or by free radicals formation [9].

Palladium (II) most probably used as either a catalyst or as a reductant having the reduction potential of the palladium (IV)/palladium (II) couple in dilute acid as 0.532 V. Most of the studies employed the palladium (II) as in the form of palladium (II) chloride as a catalyst. Several studies performed using palladium (II) because of the commercial importance of palladium (II) catalyzed reactions. The reaction mechanism involving Pd (II) depends the oxidant and substrate used. The Pd (II) usually forms an activated complex with substrate molecule before forming the final products [10].

II. EXPERIMENTAL

A. Materials and Method

The chemicals used in the experiment were of analytical quality and used with no purification. Levofloxacin (a gift sample from Dr. Reddy Laboratories) stock solution of was prepared by taking calculated quantity in doubly distilled water. A stock solution of Free Available Chlorine was prepared by diluting calculated volume of 5% NaOCl (Thomas Baker) in distilled water according to the procedure described in the literature [11-12]. Standardization of the stock solution FAC by DPD-FAS titrimetry and iodometric respectively [13]. A stock solution of palladium chloride ($PdCl_2$) of known concentration was prepared in chlorine free distilled water. 0.02 $mol.dm^{-3}$ acetate (pH 4.0-6.0), phosphate (pH 7.0), and borate (pH 8.0-9.0) buffer solutions were used to keep constant pH throughout the experiments conducted in reagent water system.

B. Instruments Used

(i) UV-Vis Spectrophotometer (CARY 50 Bio, Varian BV, The Netherlands) with a temperature controller and HPLC system (Agilent 1100 series, USA) were used for kinetic studies.

(ii) Product analysis was carried out, by using LC/MSD Trap systems (Agilent 1200 series, USA).

(iii) pH meter (Elico model LI 120) was used for pH measurements.

C. Kinetic procedure

All the reactants were kept in a thermostatic bath at 25.0 ± 0.2 ^{o}C for at least 30 minutes to attain thermal equilibrium. The kinetic study was followed in pseudo first order condition with [FAC]: [LFC] ≥10:1 by maintaining the constant ionic strength using 0.01 $mol.dm^{-3}$ buffers in both uncatalyzed and catalyzed reactions. Reaction was initiated with addition of LFC, $PdCl_2$, FAC solutions and with the necessary volume of buffers thermostat. Reaction progress was studied conveniently by monitoring the absorbance of LFC at 295 nm, which decreases with time. Spectral changes during the chlorination of LFC by FAC in the presence of Pd (II) catalyst as shown in UV–Vis spectra as shown in Fig.

The verification of Beer's law for LFC at λ_{max} 295 nm, giving ε = 59475 dm^3 mol^{-1} cm^{-1}. Pseudo first-order rate constants, k'_{obs}, were evaluated from the graph plot of log (A_t-A_∞) Vs. time. The first order plots are in most of the instances were extending along straight line up to 60-80% reaction being completed and k'_{obs} values were reproducible within an error margin of ±7% (Table 1). The Parent compound loss was also checked by HPLC system (Agilent 1100 series, USA) with RX-C18 column (4.6 mm × 250 mm, 5 µm) with UV diode array detector. The observed rate constants from HPLC method were in good agreement with UV visible methods. FAC concentration was measured by DPD – colorimetry or DPD-FAS titrametry [12] on the conclusion of each kinetic measurement.

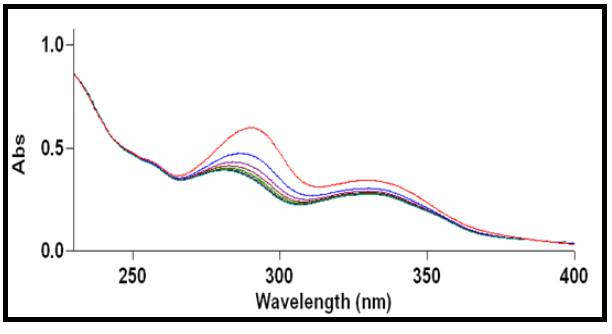


Fig. 1 UV-Visible spectral changes during the chlorination of LFC by FAC with Pd (II) catalyst at 25 ± 0.2˚C

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TABLE 1 INFLUENCE OF VARIATION OF [FAC] ON THE RATE OF CHLORINATION OF LEVOFLOXACIN, AT DIFFERENT pH (VARIATION AT pH 4.00 AND 9.00). I = 0.01 mol dm^{-3} AT 25 ^{o}C.

pH	10^4 [FAC] (mol dm^{-3})	10^5 [LFC] (mol dm^{-3})	10^8[Pd(II)] (mol dm^{-3})	$10^3 k_T$ (s^{-1})	$10^4 k_U$ (s^{-1})	$10^3 k_C$ (s^{-1})
4.0	0.44	0.40	2.00	10.0	8.98	9.10
	0.77	0.40	2.00	14.0	16.58	12.3
	1.10	0.40	2.00	16.6	19.05	14.69
	1.43	0.40	2.00	19.2	22.48	16.95
	1.76	0.40	2.00	24.8	25.92	22.20
5.0	0.44	0.40	2.00	5.16	3.60	4.80
	0.77	0.40	2.00	7.33	5.47	6.97
	1.10	0.40	2.00	8.00	8.80	7.12
	1.43	0.40	2.00	10.78	10.4	9.74
	1.76	0.40	2.00	12.76	13.9	11.37
6.0	0.44	0.40	2.00	2.16	2.55	1.91
	0.77	0.40	2.00	3.33	4.95	2.84
	1.10	0.40	2.00	5.00	7.44	4.26
	1.43	0.40	2.00	6.78	8.61	5.92
	1.76	0.40	2.00	8.76	10.08	7.75
7.0	0.44	0.40	2.00	1.52	1.11	1.49
	0.77	0.40	2.00	2.71	2.90	2.42
	1.10	0.40	2.00	3.74	3.18	3.42
	1.43	0.40	2.00	5.40	6.15	4.79
	1.76	0.40	2.00	7.44	8.08	6.63
8.0	0.44	0.40	2.00	1.01	0.90	0.92
	0.77	0.40	2.00	2.61	1.10	2.50
	1.10	0.40	2.00	3.56	1.82	3.37
	1.43	0.40	2.00	4.44	2.05	4.24
	1.76	0.40	2.00	6.02	5.85	5.44
9.0	0.44	0.40	2.00	0.84	0.45	0.80
	0.77	0.40	2.00	0.96	0.65	0.89
	1.10	0.40	2.00	1.11	0.84	1.03
	1.43	0.40	2.00	2.21	0.98	2.11
	1.76	0.40	2.00	3.01	1.15	2.90

± 7 % Error

III. RESULTS

A. Product identification method

100 mg dm^{-} amount ^{3} of Levofloxacin was added with 0.01 mol.dm^{-3} pH 7.00 phosphate buffers with necessary volume used to starting reaction concentration. Free available chlorine solution was then subsequently added to begin reactions at oxidant: substrate molar ratios varying from 1:02 to 5:10. The reaction mixture was kept for 12 hrs and the products were analyzed using LC/MSD Trap system equipped with RX-C18 column (250 x 4.6 mm, 5 µm), column temperature was 25 ^{0}C and UV diode array detector (Agilent 1200 series, USA) Analytical peaks were resolved using gradient solvent with changing ratios of 0.2% (v/v) acetic acid to pure acetonitrile. MS investigation was performed with positive mode Electro Spray Ionization (ESI^{+}); over a mass scan variation range of 50-1000 m/z. The mass spectrometer fragmentation potential difference was normally adjusted to 80.0 eV. Spray chamber temperature and drying gas flow were adjusted to 320 ^{o}C and 10 dm^{3} min^{-1} respectively. The observed peak of LC/MS spectrum (Fig.2) interprets in agreement with the proposed structure of the product. The major identified product in the reaction is shown below (Scheme1 and 2).

B. Reaction order

The chlorination of LFC with FAC taking place with a measurable rate without using Pd (II) and with Pd (II) catalyzed reaction. It is observed that both reactions are taking place in an almost parallel path. Hence the sum of rate constants of the catalyzed (k_C) and uncatalyzed (k_U) reactions are equal to total rate constant (k_T) so $k_C = k_T - k_U$.

A plot of log k'_{obs} Vs. log [FAC] was linear with a slope of unity at different pH as shown in Fig.3. indicating that chlorination of levofloxacin can be their first order with respect to FAC. The reaction LFC/FAC can be elucidating as a second order, bimolecular reaction.

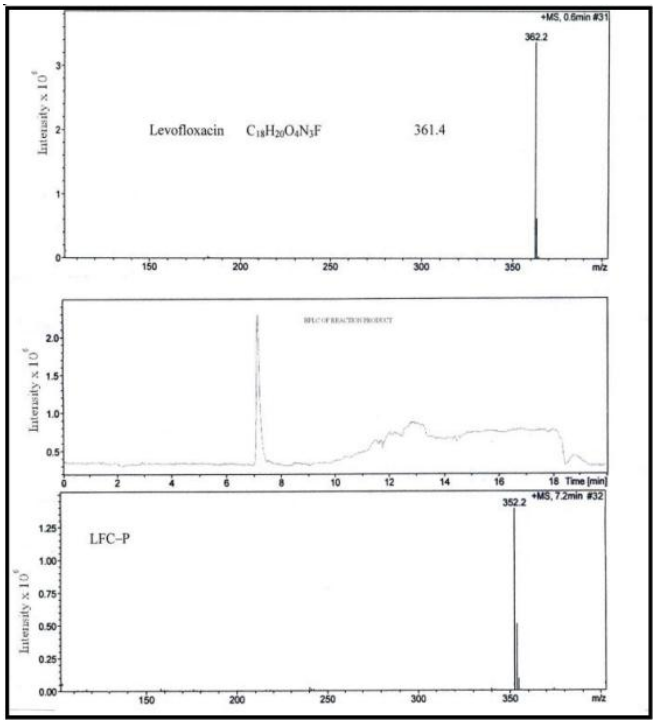
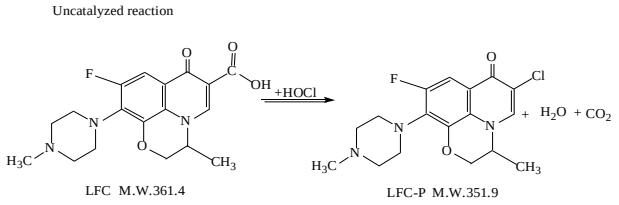


Fig. 2. LC/MS spectra levofloxacin and levofloxacin chlorination major product

SCHEME 1. PROPOSED REACTION FOR MAJOR PRODUCT LFC /FAC REACTION BASED ON LC/MS.



SCHEME2. DETAILED SCHEME FOR Pd(II) CATALYZED CHLORINATION OF LEVOFLOXACIN BY FAC.

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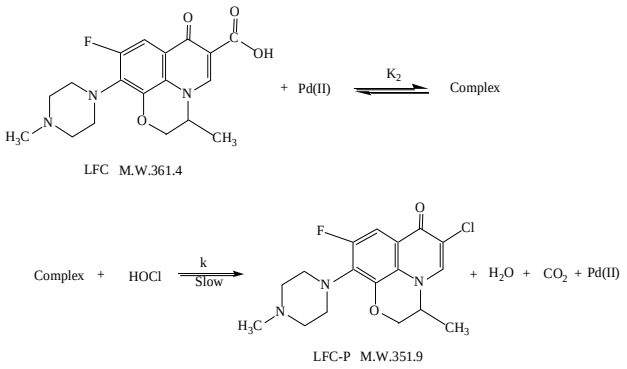

C. Influence of [LFC]

The LFC concentration variation was carried out in the range of 0.2 × 10^{-5} moldm^{-3} to 1.0 × 10^{-5} mol dm^{-3} with constant concentrations of FAC, 1.00 × 10^{-4} mol dm^{-3}, and catalyst Pd (II), 2.00 ×10^{-8} mol dm^{-3} at constant ionic strength of 0.01 mol dm^{-3} for both uncatalyzed and catalyzed reactions. The pseudo-first order rate constant remains constant. The k'_{obs} values (shown in table 2) indicating that the order with respect to [LFC] was found to be unity.

TABLE 2. INFLUENCE OF VARIATION OF [LFC] ON THE RATE OF CHLORINATION OF LEVOFLOXACIN AT 25 ^{O}C. I = 0.01 mol.dm^{-3}

pH	10^4[FAC] (mol dm^{-3})	10^5[LFC] (mol dm^{-3})	k_{obs} x 10^3 (s^-)
7	1.00	0.20	3.09
	1.00	0.40	3.46
	1.00	0.60	3.73
	1.00	0.80	3.01
	1.00	1.00	3.90

D. Influence of [FAC]

The FAC variation was carried out in the range of 0.44 ×10^{-4} moldm^{-3} to 1.76 x 10^{-4} moldm^{-3} with maintaining the concentrations of LFC, 0.40 × 10^{-5} mol.dm^{-3}, Pd (II), 2.00 × 10^{-8} mol.dm^{-3} and at constant ionic strength of 0.01 mol.dm^{-3}. The pseudo-first order rate constants; k'_{obs} values (Table 1) indicated that the order with respect to [FAC] was found to be unity. It is observed that the pseudo-first order rate constants k'_{obs} increase with increases in concentration of FAC. The plots of k'_{obs} Vs. [FAC], with varying initial concentrations of FAC are found to be linear (Fig.3).

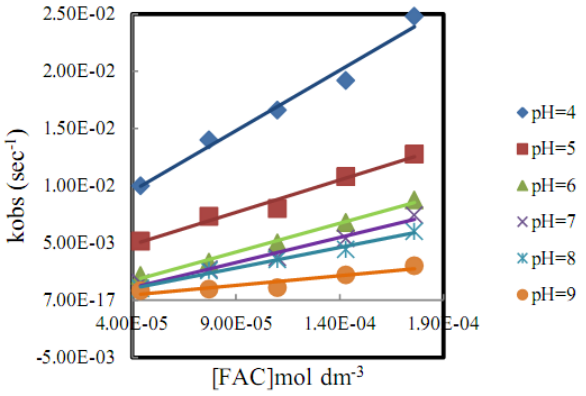

Fig. 3- Second order plot of k'_{obs} Vs. [FAC]

E. Influence of pH

The pH of the reaction mixture was varied from pH = 4.00 to 9.00 by using acetate, phosphate and borate buffers, keeping the other reaction conditions constant. The rate constant was observed to be decreasing with increasing pH values. A plot of apparent second order rate constant, k''_{app} Vs. pH for uncatalyzed, catalyzed and total reaction is as shown in the Fig.4.

The pH dependent apparent second order rate constant for the catalyzed and uncatalyzed reaction were calculated from the plot of $k''_{app} = (k'_{obs.} / [FAC]_T)$. The variation in $k''_{app.}$ from pH 4.00 to 9.00 can be ascribed to the varying significance of specific reaction between the individual acid -base conditions of LFC and FAC.

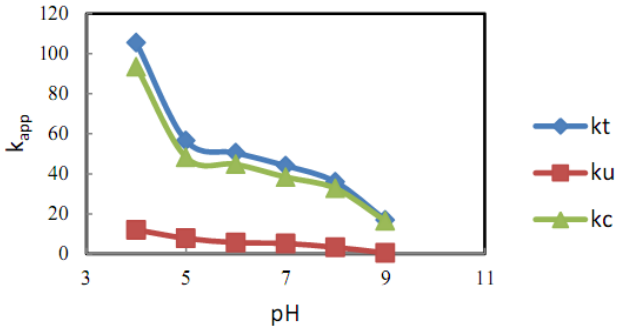

Fig.4 Influence of pH on the palladium catalyzed chlorination of levofloxacin at 25 ^{0}C

F. Influence of ionic strength

The effect of ionic strength (I) at 25˚C temperature was studied by varying the buffer concentration from 0.001 to 0.01 mol.dm^{-3}at pH 7.00 conditions was carried out. The rate constants were found to remain almost constant (Table 5.4). It was observed that no significant effect of ionic strength on the rate constant.

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TABLE 3 .INFLUENCE OF IONIC STRENGTH ON THE CHLORINATION OF LEVOFLOXACIN AT pH 7.0 AND 9.00 at 25˚C

pH	10^4[FAC] (mol dm^{-3})	10^3[LFC] (mol dm^{-3})	buffer×10^3	$k_{obs} \times 10^3$ (s^{-})
7	1.0	0.4	1.00	3.15
	1.0	0.4	3.00	3.00
	1.0	0.4	5.00	3.30
	1.0	0.4	7.00	2.90
	1.0	0.4	10.0	3.40

I. Influence dielectric constant

The effect of dielectric constant (D) was studied by varying the tertiary butyl alcohol water content in the reaction mixture with all other conditions being maintained constant. The D values were calculated from the equation, $D = D_W V_W + D_B V_B$, where D_W and D_B are dielectric constants of pure water and tertiary butyl alcohol respectively, and V_W and V_B are the volume fractions of components water and t-butyl alcohol, respectively, in the total volume of the mixture. The solvent tertiary butyl alcohol did not react with FAC under experimental conditions [14].

The rate constant k'_{obs} decreases with decrease in the dielectric constant of the medium. The plot of log k'_{obs} Vs. 1/D with was linear with a negative slope of 246.13 and $R^2 \geq 0.985$ (Fig.5).

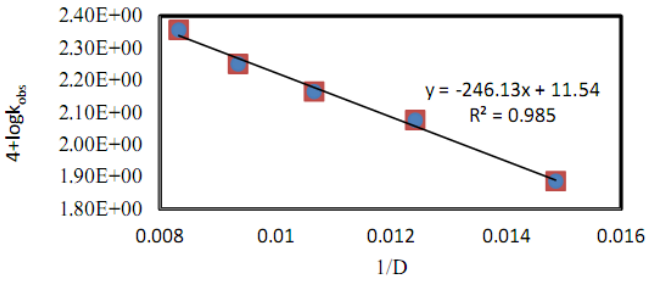


Fig.5. - Influence of dielectric constant on the chlorination of LFC in the presence of Pd(II) catalyst.

J. Polymerization Study

For both uncatalyzed and catalyzed reactions, the possible interference of free radicals was examined by adding acrylonitrile to the reaction mixture, which was kept in an inert atmosphere for 24 h. This reaction mixture was diluted with methanol and no precipitate was observed, which suggests that free radicals were not involved in the reaction [15].

K. Influence of temperature

The kinetics was studied for both catalyzed and uncatalyzed reactions at four different temperatures with varying [FAC] by keeping other experimental conditions constant, the rate constant was found to increase with increase in temperature. The first order rate constants at four different temperatures 10, 20, 30 and 40 ˚C for uncatalyzed and catalyzed reactions were obtained and listed in Table 4a. respectively. The activation energy is related to these rate constants was calculated using Arrhenius plot of $logk'_{obs}$ Vs. 1/T) and from this other activation parameters were obtained as shown in table 4b.

TABLE 4. INFLUENCE OF TEMPERATURE ON THE CHLORINATION OF LEVOFLOXACIN AT DIFFERENT TEMPERATURES. (WITH CATALYST) AT 7.00 pH

(A)EFFECT OF TEMPERATURE

Temperat)ure (Kelvin)	10^2k(s^{-1})
283	9.38
293	10.57
303	17.03
313	21.00

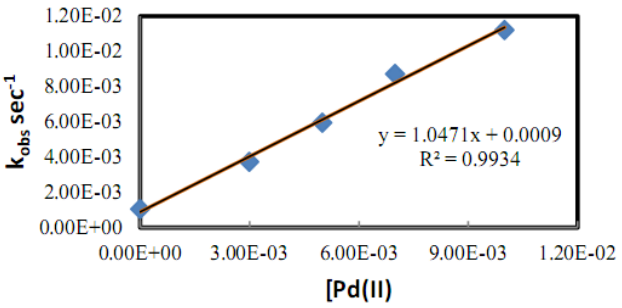
(B)ACTIVATION PARAMETERS

Activation parameters	Pd(II) Catalyzed reaction	Uncatalyzed reaction
Ea (kJ mol^{-1})	15.33±2.0	28.6 ± 3.0
ΔH (kJ mol^{-1})	12.86±1.0	26.1 ± 2.7
ΔS ±(Jk^{-1} mol^{-1})	-30.16±2.5	-12.4 ± 1.5
ΔG ±(kJ mol^{-1})	13.10±1.0	29.8 ± 3.0

L. Influence of catalyst

The [Pd (II)] catalyst concentrations were varied from $1x10^{-8}$ to 10 $x10^{-8}$ $moldm^{-3}$ range, keeping other conditions constant and at constant ionic strength of 0.01 $mol.dm^{-3}$ constant ionic strength. The reaction rate increases with increasing in the concentration of Pd (II). The order with respect to [Pd (II)] was found to be unity from the linearity of the plot of k_C Vs. [Pd(II)] as shown in Fig .6.

Fig.6. Influence of catalyst for the reaction of LFC and FAC at different concentrations of Pd (II)



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Activity of catalyst

For both the uncatalyzed and catalyzed reactions which proceeds simultaneously, it is observed by Moelwyn–Hughes [16]

$$k_T = k_U + K_C[Pd(II)]^x$$

Pseudo first order rate constants in the presence of Pd(II) catalyzed reaction is k_T, k_U is for uncatalyzed and K_c is the catalytic constant and 'x' the order of the reaction with respect to Pd(II). In the current investigation, x values for the standard reaction run was considered to be one.

$$K_C = \frac{[k_T - k_U]}{[Pd(II)]^x} = \frac{k_C}{[Pd(II)]^{1.02}} \text{ (Where } k_T - k_U = k_C)$$

DISCUSSION

Kinetics of FAC reactions with LFC

When sodium hypochlorite is dissolved in water, it hydrolysis rapidly and combines with H^+ ions according to the equation 3 and 4

$$NaOCl \rightleftharpoons Na^+ + OCl^- \quad (1)$$

$$HOCl \overset{K_{a\ HOCl}}{\rightleftharpoons} H^+ + OCl^- \quad (2)$$

$$K_a = \frac{[H^+]\,[ClO^-]}{[HOCl]} \quad (3)$$

Hypochlorous acid is weak acid; it undergoes partial ionization as shown in equation (5). Where K_a is called dissociation constant, $[H^+]$, $[OCl^-]$ and [HOCl] are the concentration of H^+, OCl^- and HOCl respectively, with $K_{a,HOCl} = 10^{-7.5}$ [17]. The pKa value of HOCl is 7.54 at 25 ^oC and pKa value of HOCl is 7.82 at 0 ^oC [18]. The decrease in the extent of k''_{app} above pH 7.00 can be ascribed toward decomposition of hypochlorous acid to give up OCl^-, it is usually a weaker electrophile than hypochlorous acid [19]. At lower pH HOCl dominant active species & at higher pH OCl^- dominant weaker species. Hence, rate of reaction decreases with increase in pH. The major product identified by LC/MS spectrum was LFC-P, which has an LFC structure, in that the quinolone carboxylic group was displaced by a Chlorine atom. Elimination of carboxylic acid group ensuing in a mass reduction of 45 daltons and addition of chlorine atom (leads to mass gain of 35 daltons) would give up a net reduction of 10 daltons relating to the parent levofloxacin molecule, corresponding to the mass variation between LFC and LFC-P. Electrophilic halodecaboxylation is reported for enrofloxacin (EF) with FAC reaction [20] and is quite well documented for bromination and chlorination reactions [21-23] but only for specific types' substrates [24-25]. A variety of mono and dihydroxy benzoic acid species have been undergoing elimination of carboxylic acid group during treatment with aqueous bromine or chlorine species. Previous investigation as well suggests that HOCl can elimination of carboxylic acid group from aliphatic β-keto acids (via halogenation of their enol tautomers) [26-27].

Confirmation for complex formation was explained from the UV–Visible spectrum of reaction mixtures where hypsochromic change of 5 nm from 294 to 289 nm and hyperchromicity was observed at 289 nm.

The rate law can be derived from the proposed palladium catalyzed mechanism is

$$\frac{\text{Rate}}{[LFC]} = k_{obs} = \frac{kK_1K_2\ [OCl^-]\ [H^+]\ [Pd^{2+}]}{1 + K_1[OCl^-]\ + K_1[H^+]} \quad ----(4)$$

$$\frac{[Pd^{2+}]}{k_C} = \frac{1}{kK_1K_2[OCl^-][H^+]} + \frac{1}{kK_2[H^+]} + \frac{1}{kK_2[OCl^-]} \quad ---(5)$$

From the plot Arrhenius of log k'_{obs} Vs. 1/T, gives a straight line. With the help of the plot activation energy and other activation parameters like enthalpy, entropy and Gibbs free energy changes, can calculated and these values are given in Table 4 .both uncatalyzed and Pd (II) catalyzed reactions. The results indicate the average value of activation energy (Ea) was found to be 15.33 $kJmol^{-1}$ for palladium (II) catalyzed oxidation and for uncatalyzed was found to be 28.60 $kJ.mol^{-1}$, entropy of activation $\Delta S^{\#}$ is -30.16 $JK^{-1}\ mol^{-1}$ for palladium catalyzed oxidation and for uncatalyzed was found to be -12.40 $JK^{-1}\ mol^{-1}$ and free energy of activation($\Delta G^{\#}$) is 13.10 $kJ.mol^{-1}$ for palladium catalyzed oxidation and for uncatalyzed was found to be 29.80 $kJ.mol^{-1}$ and the value of enthalpy of activation ($\Delta H^{\#}$) is 12.86 $kJmol^{-1}$ for palladium catalyzed oxidation and for uncatalyzed was found to be 26.10 $kJ.mol^{-1}$. The positive value of $\Delta H^{\#}$ and $\Delta G^{\#}$ (Table) indicates that the transition state is highly solvated, increases the size of transition state the average values of $\Delta H^{\#}$ and $\Delta G^{\#}$ were together consenting for electron transfer processes [27]. The negative value of $\Delta S^{\#}$ denotes that transition state is highly ordered than the reactants. The activation parameters evaluated for both catalyzed and uncatalyzed reactions make clear the catalytic influence on the reaction. The catalyst Pd(II) forms a complex (C) with substrate, which increase the reduction property of the reactant compared with without using catalyst. Hence, the Pd(II) catalyst changes the reaction pathway by decreasing the activation energy. A catalyst does work by providing a different path, by lowering Ea, for the reaction. The presence of a catalyst allows a greater extent of the reactants to obtain enough

energy to pass through the transition state and become products [27].

The observed insignificant influence with the variation of ionic strength on the rate of reaction indicates that the reaction is between two neutral species or a neutral and a charged species [28].

The influence of solvent polarity on the reaction rate has been explained in detail in well known monographs of Amis [29]. In the present study the rate constant at pH 7 decreases with decrease in dielectric constant of the medium. This is due to the zero angle approach between two dipoles or an ion dipole system, Amis has shown that a plot log k'_{obs} Vs. 1/D shows the straight line with the slope of negative value due the interaction between negative ions and dipole or two dipoles.

CONCLUSION

In drinking water treatment, toxic organic compounds could combines with chlorine. pH plays an important factor in affecting the chlorination process. Levofloxacin reacts rapidly with chlorine over the range of pH 4.0 to 9.0 with different rates. It undergoes faster reaction in acidic medium and becomes slower in basic medium by maintaining conventional chlorination conditions are probable to be noticed in conventional water chlorination methods. The observed product the formation of major product involves electrophilic halodecarboxylation of quinolone moiety and hence, it may retain the antibacterial activity as observed in ciprofloxacin and enrofloxacin. Further toxicological studies on the degradation products of LFC are required to understand the environmental implications of the LFC reaction with FAC[30].

REFERENCES

M.S. Gudaganatti, M.S. Hanagadakar, R.M. Kulkarni, R.S. Malladi, R.K. Nagarale, Transformation of levofloxacin during water chlorination process: Kinetics and pathways, Prog. React. Kinet. Mech. 37 (2012) 366–382.

R. M. Kulkarni, D. C. Bilehal and S T Nandibewoor, Deamination and decarboxylation in the chromium(III)-catalyzed oxidation of L-valine by alkaline permanganate and analysis of chromium (III) in microscopic amounts by a kinetic method. Trans. Met. Chem., Vol.28, 2003, pp. 199-208.

A. K. Singh, S. Srivastava, J. Srivastava, R. Srivastava and P. Singh, Studies in kinetics and mechanism of oxidation of D- glucose and D-fructose by alkaline solution of potassium iodate in the presence of Ru (III) as homogeneous catalyst. J. Mol. Catal. A: Chem., Vol. 278 (1-2), 2007, pp.72-81.

S. Wilkinson, Chem. Eng. News, Vol.77, 1999, pp. 27–28.

7. E. Cao, A. Gavriilidis, W. B. Motherwell, Oxidative dehydrogentation of 3-methyl-2-buten-1-ol in micro reactors, Chem. Eng. Sci., Vol.59, 2004, pp.4803–4808.

A. Prakash, P. Dwivedi, M.N. Srivastava and B Saxena, National academy of Science Letters. Vol.2, 1988, pp.107.

J. P. Taquet, O. Siri , J. P. Collin , A. Messaoudi and P. Braunstein ,One-electron oxidation-induced dimerising C-C coupling of a 2,5-diamino-1,4-benzoquinonediimine: a chemical and electrochemical investigation, New J. Chem. 2005, 29; 188–192.

A.K. Das, Kinetics and mechanistic aspects of metal ion catalysis in cerium (IV) oxidation, Coord. Chem. Rev.,Vol. 213, 2001, pp.307-325.

K. A Thabaj, S.A. Chimatadar and S.T. Nandibewoor, Mechanistic study of oxidation of palladium (II) by cerium (IV) in aqueous acid, Transition Met. Chem., Vol.31, 2006 pp.186-193.

S. A. Chimatadar, S. B. Koujalagi and S.T. Nandibewoor, Kinetics and mechanism of palladium (II) catalyzed chromium (VI) oxidation of mercury (I) in aqueous sulphuric acid, Trans. Met. Chem., Vol.26, 2001, pp.662-667.

M. C. Dodd and C. H. Huang, Transformation of the antibacterial agent sulfamethoxazole in reaction with chlorine: Kinetics, Mechanisms and Pathway. Environmental Science and Technology, Vol.38, 2004, pp.5607-5615.

J.C. Morris, The acid ionization constant of HOCl from 5-35°C, Journal of Physical Chemistry,Vol. 70, 1966, pp.3798-3805.

APHA (American Public Health Association), AWWA (American Water Works Association), and WPCF (Water Pollution Control Facility), Standard Methods for the Examination of Water and Wastewater (20th ed.), Washington DC, USA.1998

D. G. Richard. Introduction to Physical Organic Chemistry. Addison Wesley Publishing Company, London. 1970, 195-202.

S. Bhattacharya, P.Benerjee , Kinetic Studies on the Electron Transfer between Azide and Nickel(IV) Oxime Imine Complexes in

Aqueous Solution, Bull. Chem. Soc. Jpn.1996, 69, 3475.

E. A. Moelwyn-Hughes, Kinetics of Reaction in Solutions, Oxford University Press, London, 1947, pp.297.

C. G. White, Hand book of chlorination and alternative disifections, Fourth edn, John Wiley & Sons, New York, 1998.

F. Ge, L. Zhu and H. Chen, Effects of pH on the chlorination process of phenols in drinking water, Journal of Hazardous Materials, B.,Vol.133,2006, pp.99-105.

C.M. Gerritsen and D. W. Margevum, Non Metal redox kinetics, hypochlorite and hypochlorous acid reactions with cyanide, Inorg. Chem.,Vol. 29, 1990, pp.2757 – 2762.

M.C. Dodd., A.D. Shah, U.von Gunten and C. H. Huang, Interaction of fluroquinolone antibacterial agents with aq. Chlorine reactions kinetics, Mechanism and transformation pathways. Env. Sci Technol, Vol. 39, 2005, pp.7065-7076.

L. H. Farinholt, A. P. Stuart, D. Twiss, The halogenation of salicylic acid, J. Am. Chem. Soc.,Vol. 62, 1940, pp.1237 – 1241.

E. Grovenstein and U.V.Henderson, The kinetics and mechanism of Bromodecarboxylation of 3, 5-dibromo-2-hydroxy benzoic and 3,5-dibromo-4-hydroxy benzoic acids, J. Am. Chem. Soc., Vol.78, 1956, pp.569 – 578.

R.A. Larson and A.L. Rockwell, Chloroform and chlorophenol production by Decarboxylation of natural acids during aqueous chlorination. Env. Sci Technol, Vol. 13(3), 1979, pp. 325-329.

S.D. Boyce, J.F. Hornig. Reaction pathways of trihalomethane formation from the halogenations of dihydroxyaromatic model compounds for humic acid, Environ. Sci. Technol., 17, 1983, pp.202 – 211.

S. I. Itoh, S. Naito and T. Unemoto, Acetoacetic acid as a potential trihalomethane precursor in the biodegradation intermediates produced by sewage bacteria, Water Res., Vol. 19, 1985, pp.1305 – 1309.

L. Pauling, Oxford and IBH publishers. New Delhi, (3rd Ed.). 1969, pp. 496.

N. R. Pai and S. S.Patil, Newer Process Development of Trimetazidine Dihydrochloride, Res. J. Pharm. Technol., Vol.6. (10), 2013, pp.1154-1156.

K. J. Laidler, Chemical Kinetics (3rd Ed.). ISBN -81-297-0268-1 Pearson Education, (Singapore) Pvt. Ltd, Indian Branch, Delhi, India, 183, 2004, pp.198.

E. S. Amis, Solvent effects on reaction rates and Mechanisms, Academic Press; New York, 1966.

L. L. Shen, L. A. Mitscher, P. N. Sharma, T. J. O' Donnel, D. W. T, Chu and C. S. Cooper, Mechanism of inhibition of DNA gyrase by quinolone antibacterial: a cooperative drug-DNA binding model. Biochemistry, 28(9), 1989, pp. 3886-3894.

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