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Oxidation of linezolid by permanganate in acidic medium: Pd(II) catalysis, kinetics and pathways

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ABSTRACT

The uncatalysed and Pd(II)-catalysed oxidation of linezolid (LNZ) by permanganate (PMGT) in acidic medium was carried out in the pH range from 3.0 to 6.0. The second order rate constants were found to decrease with increase in pH. The apparent second order rate constants for the uncatalysed reaction were, for example, $k''_{app} = 6.32 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at pH 3.0 and $k''_{app} = 2.64 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at pH 6.0 and at $25 \pm 0.2 \text{ }^\circ\text{C}$ and for the Pd(II)-catalysed reaction the total apparent second order rate constants were $k''_{app} = 75.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at pH 3.0 and $k''_{app} = 45.66 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at pH 6.0 and at $25 \pm 0.2 \text{ }^\circ\text{C}$. The rate constant of the Pd(II)-catalysed reaction was thus ten times higher than for the uncatalysed reaction. The oxidation products of the reaction were identified using high resolution LC-MS. The reaction progresses *via* formation of a Pd-LNZ complex, which reacts with acidic PMGT to form an intermediate compound, which then decomposes to give oxidised products. The dependence of the rate of reaction on various parameters, such as pH, temperature, [LNZ], [PMGT], [Pd(II)], dielectric constant and ionic strength were studied and activation parameters for the reaction were evaluated and discussed.

KEYWORDS: permanganate, kinetics, linezolid, catalysis, palladium, emerging environmental pollutants

1. INTRODUCTION

Potassium permanganate (PMGT) finds application in water and waste water treatment processes. The main role of PMGT is to control the odour, colour, taste and biological growth. It also plays an important role in controlling the formation of disinfection by-products by oxidising precursors and minimising the consumption of other disinfectants [1]. PMGT is a potent oxidising agent at all pH values [2,3]. PMGT also plays an important role as an oxidising agent in synthetic organic chemistry and analytical chemistry [4,5]. In oxidation by PMGT, the mechanism of the reaction depends not only on [PMGT] but also on [substrate] and pH of the medium [6]. The oxidation by PMGT ion gained more importance in synthetic organic chemistry after the discovery of phase transfer catalysis [7,8].

Several drinking water sources are found to be polluted with hazardous chemicals, pesticides, pharmaceuticals, plasticisers, and other microcontaminants [9,10]. Because of its incomplete metabolism in the human body, a large portion of an antibacterial dose is released into public

waste water systems. It is the primary route for the entry of such pharmaceutical moieties into the aquatic environment [11]. Antibacterial resistant microorganisms are identified in civil waste water effluents, sewage-affected surface between chronic water systems, and also in drinking water. Amongst pharmaceuticals, the antibacterial classes are very important, since they have been recognised as emerging environmental pollutants [12,13].

Linezolid (LNZ) has a 1,3-oxazolidinone moiety containing an acetamide sub group at the 5-methyl group position. Linezolid has been widely used in recent decades in human and veterinary drugs for the treatment of diseases and other health-hazardous aspects and to provide for enhancement supports for growth, and to improve the body mass of consumable animals [14]. Linezolid has weak basic properties (pK_a 1.80) [15] and is slightly soluble in water at pH values between 5.0 and 9.0. The solubility of linezolid increases at a pH value below 3.00 and at higher temperatures [16,17]. Linezolid is active against a variety of aerobic Gram-positive microorganisms, with vancomycin- and penicillin-resistant bacteria [18].

The d-block elements are used as catalysts to catalyse many oxidation and reduction reactions, since they show variable oxidation states [19]. 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) have been used extensively as catalysts [2,20]. The reduction potential of the Pd(IV)/Pd(II) couple in acidic medium is 0.532 V. There are several reports on Pd(II) catalysis in the literature [21,22,23]. The reaction mechanism involving Pd(II) depends on the oxidant and substrate used. The Pd(II) usually forms an activated complex with the substrate molecule before forming the final products [24,25].

In the present work, we report the kinetic and mechanistic investigation of the oxidation of LNZ with PMGT in the presence of Pd(II) in aqueous acidic medium. Preliminary experimental results indicated that the reaction in acidic media becomes facile in the presence of micro-amounts of Pd(II) catalyst. Therefore, Pd(II) has been selected as a catalyst in the present investigations [26]. The objectives of the study were to elucidate the catalytic behaviour of Pd(II), to study the kinetics of oxidation of LNZ by Pd(II)-catalysed PMGT, to identify oxidation products, to propose the plausible mechanism, to deduce rate law and to calculate the activation parameters.

2. EXPERIMENTAL

2.1 Materials and methods

All chemicals were used of analytic quality and solutions were prepared in double distilled water and used to carry out the experimental work. The stock solution of linezolid (Dr. Reddy Laboratories) was made by dissolving an appropriate quantity of sample in double distilled water. The PMGT (Merck Specialties Pvt. Ltd.) solution was made and standardised with oxalic acid with a standard procedure [27]. 0.02 mol dm⁻³ acetate (pH 3–5) and phosphate (pH 6.0) were used to maintain constant pH.

2.2 Instruments

- (i) For kinetic measurements a CARY 50 Bio UV-Vis Spectrometer (Varian BV, The Netherlands) with a temperature controller and a HPLC system (Agilent 1100 series, USA).
- (ii) For product analysis, a Thermo Scientific Q Exactive high resolution mass spectrophotometer (HRMS) was used as was a Thermo Scientific Hypersil Gold C18 (150 × 4.6 mm–8 μm) column.
- (iii) For pH measurements, a pH meter (Elico model LI 120) was used.

2.3 Kinetic measurements

The oxidation of LNZ by PMGT was carried out under pseudo first-order conditions, where LNZ was taken at a much greater concentration than PMGT at 25 ± 0.2 °C. The initiation of the reaction was done by mixing the reactants, which were kept in the thermostat to maintain constant temperature. The progress of the reaction was followed by monitoring the decrease in the absorbance at 526 nm of PMGT as a function of time in a quartz cell of 1 cm path length using Varian Cary 50 Bio UV–Vis spectrometer. The spectral changes in the oxidation of LNZ by PMGT at 25 ± 0.2 °C are illustrated in Figure 1.

The verification of Beer's law for PMGT was done at 526 nm, giving $\epsilon = 2283 \pm 20$ dm³ mol⁻¹ cm⁻¹ (literature $\epsilon = 2200$ dm³ mol⁻¹ cm⁻¹). It was observed that there is negligible interference from other species at this wavelength [28]. The pseudo-first order rate constants, k'_{obs} were calculated from log (absorbance) vs. time plots at 526 nm. The plots of log (absorbance) vs. time at 526 nm were linear up to 90% completion of the reaction. The experimentally determined rate constants were reproducible within an error margin $\pm 6\%$ as given in Table 1. Product analysis was done by an HPLC system (Shimadzu Prominence) and Thermo Scientific Q Exactive high resolution mass spectrometer (HRMS). Thermo Scientific Hypersil Gold C18 (150 × 4.6 mm–8 μm) column was used.

3. RESULTS AND DISCUSSION

3.1 Product identification method

Linezolid was added to 0.02 mol dm⁻³ pH 6 phosphate buffer to get an initial concentration of 400 mg dm⁻³. PMGT solution was afterwards mixed to start the reaction at oxidant: substrate molar ratios varying at *ca.* 4:1. The reaction mixture was kept for 12 h and the products were analysed using a Thermo Scientific Q Exactive high resolution mass spectrometer (HRMS) with a Thermo Scientific Hypersil Gold C18 (150 × 4.6 mm–8 μm) column. Analytic peaks were identified using pure elutions with changing ratios of 50:50 acetonitrile and double distilled water. MS examination were conducted using positive mode electrospray ionisation (ESI+), with mass scan variation in the range of 100–800 m/z. The flow rate was maintained at 500.00 μ dm⁻³ min⁻¹ and a pressure of 33.20 bar. The observed LC–MS spectra of LNZ and its oxidation products are shown in Figures 2a–c. The identified products are listed in Table 2.

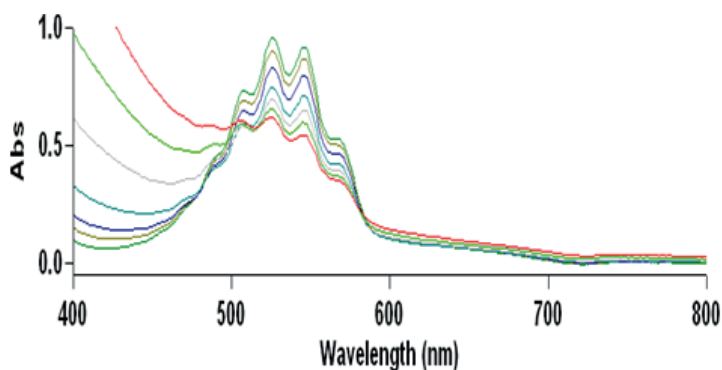


Figure 1 UV-Vis spectral changes during the oxidation of linezolid (LNZ) by PMGT at 25 °C.

Table 1 Influence of variation of [LNZ], [PMGT] and [Pd(II)] on the oxidation of linezolid by PMGT in aqueous acidic medium at 26 °C and $I = 0.01 \text{ mol dm}^{-3}$

pH	$10^4 [\text{PMGT}]$ (mol dm^{-3})	$10^3 [\text{LNZ}]$ (mol dm^{-3})	$10^8 [\text{Pd(II)}]$ (mol dm^{-3})	$10^2 k_T$ (s^{-1})	$10^3 k_U$ (s^{-1})	$10^2 k_C$ (s^{-1})
3.0	1.00	0.50	6.00	3.93	2.98	3.63
	1.00	1.00	6.00	7.03	6.58	6.37
	1.00	1.50	6.00	9.70	8.05	8.89
	1.00	2.00	6.00	13.34	12.48	12.09
	1.00	2.50	6.00	17.89	15.92	16.29
	1.00	3.00	6.00	19.87	18.92	17.97
4.0	1.00	0.50	6.00	3.78	2.75	3.51
	1.00	1.00	6.00	6.30	5.05	5.79
	1.00	1.50	6.00	8.50	7.72	7.73
	1.00	2.00	6.00	11.87	11.02	10.76
	1.00	2.50	6.00	15.46	14.11	14.04
	1.00	3.00	6.00	18.32	16.20	16.70
5.0	1.00	0.50	6.00	3.55	2.55	3.29
	1.00	1.00	6.00	5.78	4.90	5.29
	1.00	1.50	6.00	7.55	7.44	6.81
	1.00	2.00	6.00	10.75	9.61	9.78
	1.00	2.50	6.00	14.39	12.28	13.16
	1.00	3.00	6.00	16.20	14.62	14.73
6.0	1.00	0.50	6.00	3.12	2.47	2.87
	1.00	1.00	6.00	5.36	3.05	5.05
	1.00	1.50	6.00	7.12	5.11	6.60
	1.00	2.00	6.00	9.71	6.08	9.10
	1.00	2.50	6.00	13.58	6.68	12.91
	1.00	3.00	6.00	14.08	7.21	13.36
6.0	0.25	1.00	6.00	6.96	3.48	6.61
	0.50	1.00	6.00	6.82	3.15	6.50
	1.00	1.00	6.00	6.57	3.05	6.26
	1.50	1.00	6.00	6.85	3.95	6.45
	2.00	1.00	6.00	6.46	3.27	6.13
	2.50	1.00	6.00	6.14	3.16	5.82
6.0	1.00	1.00	1.00	1.68	---	1.68
	1.00	1.00	2.00	3.29	---	3.29
	1.00	1.00	4.00	4.88	---	4.88
	1.00	1.00	6.00	6.36	---	6.36
	1.00	1.00	8.00	8.66	---	8.66
	1.00	1.00	10.00	10.11	---	10.11

± 6% error.

3.2 Reaction orders

The oxidation reaction of LNZ with PMGT in acidic medium takes place with a considerable rate without adding Pd(II), and the Pd(II)-catalysed reaction proceeds in an almost identical path involving contributions from the catalysed as well as the uncatalysed reactions. Hence the sum of rate constants of the catalysed (k_C) and uncatalysed (k_U) reactions equals the total rate constant (k_T), *i.e.*, $k_C = k_T - k_U$. Therefore, the reaction

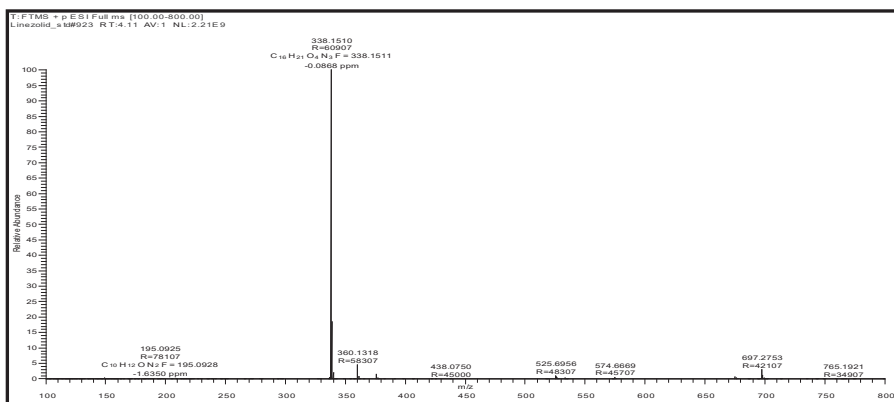


Figure 2a LC-MS spectra of pure LNZ.

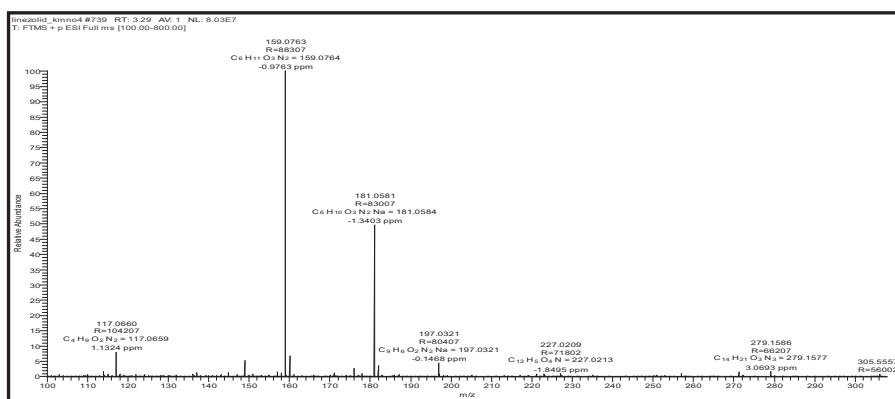


Figure 2b LC-MS spectra of LNZ oxidation products LNZ_P1, LNZ_P2 and LNZ_P3.

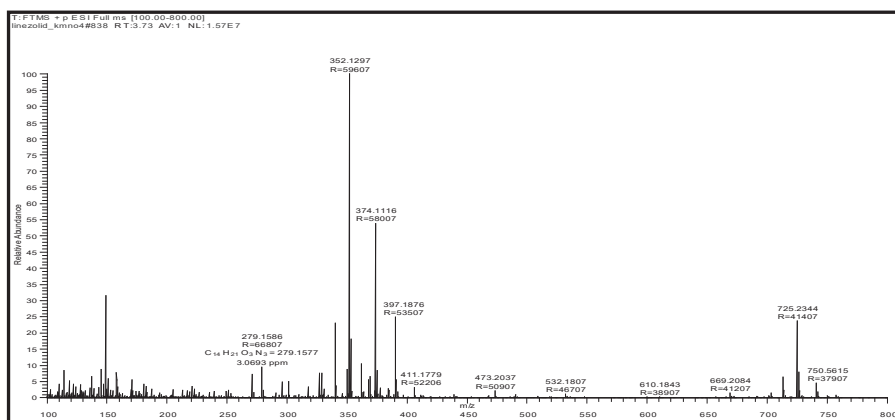


Figure 2c LC-MS spectra of LNZ oxidation products LNZ_P4.

orders have been calculated from the slopes of $\log k_{obs}$ vs. \log (concentration) by changing the concentrations of LNZ, PMGT, and Pd(II), while keeping the other experimental conditions constant.

Table 2 Analysis of LCMS spectra and identification of products of LNZ oxidation by PMGT

LNZ Products	t_R (min) ^a	(Ex) [M + H] ⁺ measured	(Th) Theoretical mass (Da)	Molecular formula	Difference Ex – Th	Degradation site moiety
LNZ_P1	3.29	159.07	158.00	C ₆ H ₁₀ O ₃ N ₂	+1.07	Morpholine
LNZ_P2	3.29	181.05	180.00	C ₁₀ H ₁₁ NOF	+1.05	Oxazolidinone
LNZ_P3	3.29	197.03	196.00	C ₉ H ₅ O ₂ NF	+1.03	Oxazolidinone and fluoro-substituted phenyl of morpholine
LNZ_P4	3.73	352.12	351.00	C ₁₆ H ₁₈ O ₃ N ₃ F	+1.12	Morpholine

^a t_R (min) indicates retention time in minutes.

The uncatalysed reaction was followed under the same reaction conditions, changing the concentrations of LNZ and PMGT, while maintaining the others conditions constant. The rate constant of the uncatalysed reaction (k_U) was found from the plot of $\log k'_{obs}$ vs. time.

3.3 Influence of [potassium PMGT]

The PMGT concentration was varied from of 2.50×10^{-5} mol dm⁻³ to 2.50×10^{-4} mol dm⁻³ maintaining other reaction conditions constant for both Pd(II)-catalysed and uncatalysed reactions. The plots of \log [PMGT] vs. time, for different initial concentrations of PMGT in both uncatalysed and catalysed reactions, were found to be linear and identical in slope, indicating the order with respect to PMGT was in unity. The pseudo-first order rate constant remains constant as shown in Table 1.

3.4 Influence of [LNZ]

The influence of LNZ concentration on the reaction rate was carried out by maintaining constant concentrations of PMGT and at constant pH with an ionic strength of 0.01 mol dm⁻³ at 25 ± 0.2 °C. The concentration LNZ was changed from 5.00×10^{-4} mol dm⁻³ to 3.00×10^{-3} mol dm⁻³ in both uncatalysed and Pd(II)-catalysed reactions Table 1. The rate constant, k'_{obs} was found to increase with increasing LNZ concentration. The plot of $\log k'_{obs}$ vs. \log [LNZ] indicated that the order with respect to LNZ was found to be less than one (0.60) ($R_2 > 0.993$) for the uncatalysed reaction, and for the Pd(II)-catalysed reaction it was 0.85 ($R_2 > 0.970$).

3.5 Influence of pH

The pH of the reaction mixture was varied from 3.00 to 6.00 (acidic medium) by using acetate and phosphate buffers, keeping the other experimental conditions constant. The rate constants were found to decrease with increase in pH of the reaction medium (Table 1). The second order rate constants were also evaluated from the plot of k'_{obs} vs. [LNZ] for corresponding pH values is shown in Figure 3. A graph of k''_{app} vs. pH (Figure 4) shows the pH-dependence of the apparent second-order rate constants for the total Pd(II)-catalysed oxidation reaction with linezolid.

The pH-dependent apparent second order rate constant for the catalysed and uncatalysed reactions were calculated from the plot of $k''_{app} = (k_{obs} / [\text{LNZ}]T)$. The variation in k''_{app} from pH 3.00 to 6.00 can be attributed to the varying importance of specific reaction amongst the individual acidic conditions of LNZ and PMGT.

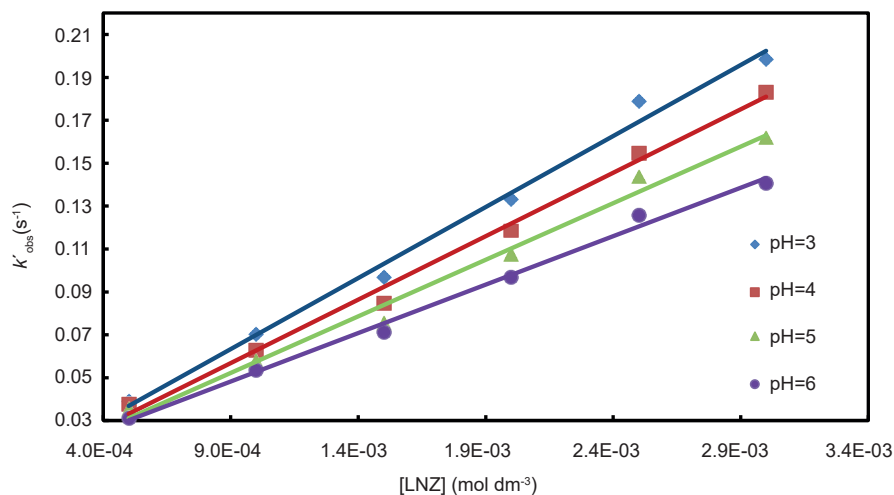


Figure 3 Second order plot of k'_{obs} vs. $[LNZ]$.

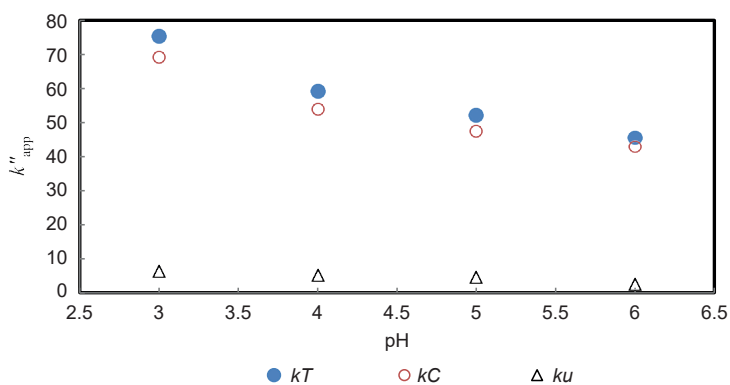


Figure 4 The second order rate constants catalysed, uncatalysed and total reaction plot of k''_{app} vs. pH.

3.6 Influence of ionic strength

The influence of ionic strength (I) was studied by changing the buffer concentration (pH 6) from $0.002 \text{ mol dm}^{-3}$ to $0.012 \text{ mol dm}^{-3}$ by maintaining other conditions constant. The calculated rate constants were observed to remain almost constant *i.e.* there is no significant influence of ionic strength on the rate constant [29].

3.7 Influence of dielectric constant

The influence of dielectric constant (D) was determined by changing the tertiary butanol–water volume content present in the reaction mixture keeping other conditions constant. The reaction rate decreases with increase in the volume of tertiary butanol. In the present study a decrease in the rate with decrease in the dielectric constant of the medium was observed in both uncatalysed and Pd(II)-catalysed reactions. The plot of $\log k_{obs}$ vs. $1/D$, $R^2 > 0.984$ and $R^2 > 0.967$ for uncatalysed and catalysed respectively was linear with a negative slope [37] (Figure 5).

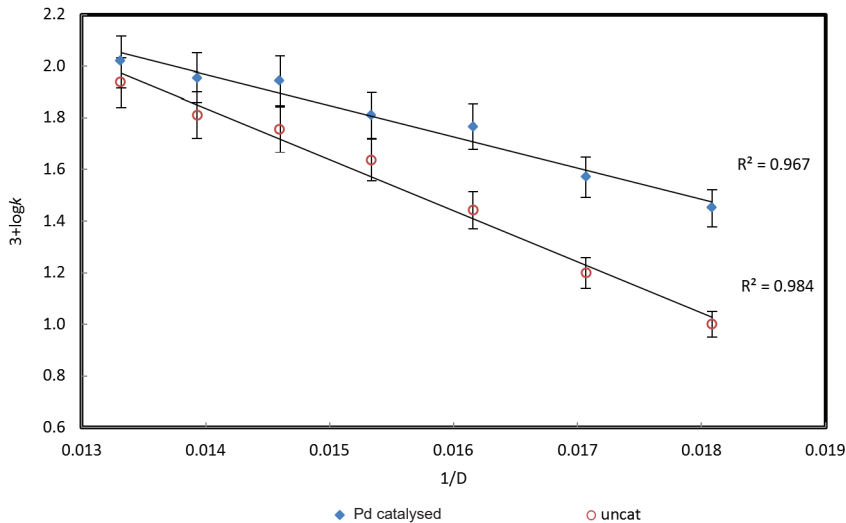


Figure 5 Influence of dielectric constant on the uncatalysed and Pd(II)-catalysed oxidation of linezolid by PGMT.

3.8 Influence of varying [Pd(II)]

The influence of the palladium catalyst concentration was determined by varying [Pd(II)] from 1.00×10^{-8} to 1.00×10^{-7} mol dm⁻³, at constant concentrations of PMGT, LNZ and ionic strength. The reaction rate increases with an increase in Pd(II) concentration as shown in Table 1. The order with respect to [Pd(II)] was found to be less than unity (0.342) from the plot of $\log k_{obs}$ vs. \log [Pd(II)].

Activity of catalyst

It was observed by Moelwyn–Hughes [30] when both uncatalysed and catalysed reactions proceed simultaneously, then

$$k_T = k_u + K_C [\text{Pd(II)}]^x \quad (1)$$

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 run were considered to be less than unity (0.342). Afterwards, the value of K_C can be calculated using eqn. (2). The average value of K_C for the reaction was found to be 20 ± 2.0 .

$$K_C = \frac{[k_T - k_u]}{[\text{Pd(II)}]^x} = \frac{k_C}{[\text{Pd(II)}]^{0.342}} \quad (\text{Where } k_T - k_u = k_C) \quad (2)$$

3.9 Influence of initially added products

The concentration of manganate ion was varied from 2.50×10^{-5} mol dm⁻³ to 2.50×10^{-4} mol dm⁻³ by maintaining remaining conditions constant. It was observed that initially added manganate ion has no significant effect on the rate constant. The rate law for the experimental results are summarised as follows.

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k [\text{MnO}_4^-]^1 [\text{LNZ}]^{0.85} [\text{H}^+]^{0.1} [\text{Pd(II)}]^{0.34} \quad (3)$$

3.10 Polymerisation study

The possible intermediacy of free radicals was examined by adding acrylonitrile monomer to the reaction mixture, which was kept in an inert atmosphere for 24 h. This reaction mixture was diluted with methyl alcohol but no precipitate was observed, which suggests that free radicals were not involved in the reaction [31].

3.11 Influence of temperature

The influence of temperature on the reaction rate was determined at four different temperatures: 283 K, 288 K, 296 K and 299 K at pH 6.00. The activation energy related to these rate constants was calculated by Arrhenius plot of $\log k'_{obs}$ vs. $1/T$ ($R^2 > 0.920$) for the uncatalysed reaction and for the Pd(II)-catalysed it was $R^2 > 0.954$. From the rate constants other activation parameters were obtained (Table 3).

The PMGT reactive species in acidic media can be obtained from the order of $[H^+]$ in the reaction medium. If the order is less than unity with $[H^+]$ then this indicates the PMGT ions formed permanganic acid, which is a more powerful oxidant species than PMGT ion [32]. If the rate of reaction attains a limiting value at a very low pH then the protonation is almost complete, indicating that only the protonated form, *i.e.* permanganic acid, is active. The following equation shows the acid–PMGT equilibrium [Eqn (4)].



The value of the equilibrium constant for protonation of PMGT (MnO_4^-), *i.e.* K_I is reported as $3.05 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$ at 25 °C. The value of K_I is also in concurrence with a pK_a value of $HMnO_4$, as reported earlier.

In this study, the stoichiometry of the reaction between PMGT and LNZ was found to be 1:1 with unit order dependence on PMGT and fractional order dependences on $[Pd(II)]$, $[LNZ]$ and $[H^+]$. On the basis of the experimental data, a mechanism can be proposed accommodating all the observed orders in each reactant, [oxidant], [reductant], [catalyst] and $[H^+]$. It is evident from the increase in rate with increase in $[H^+]$ in the pre-equilibrium step, H^+ reacts with MnO_4^- to form the $HMnO_4$ species. $HMnO_4$ formation has been well documented in earlier studies [33]. LNZ reacts with the active species Pd(II) in the second equilibrium step to form a complex (C),

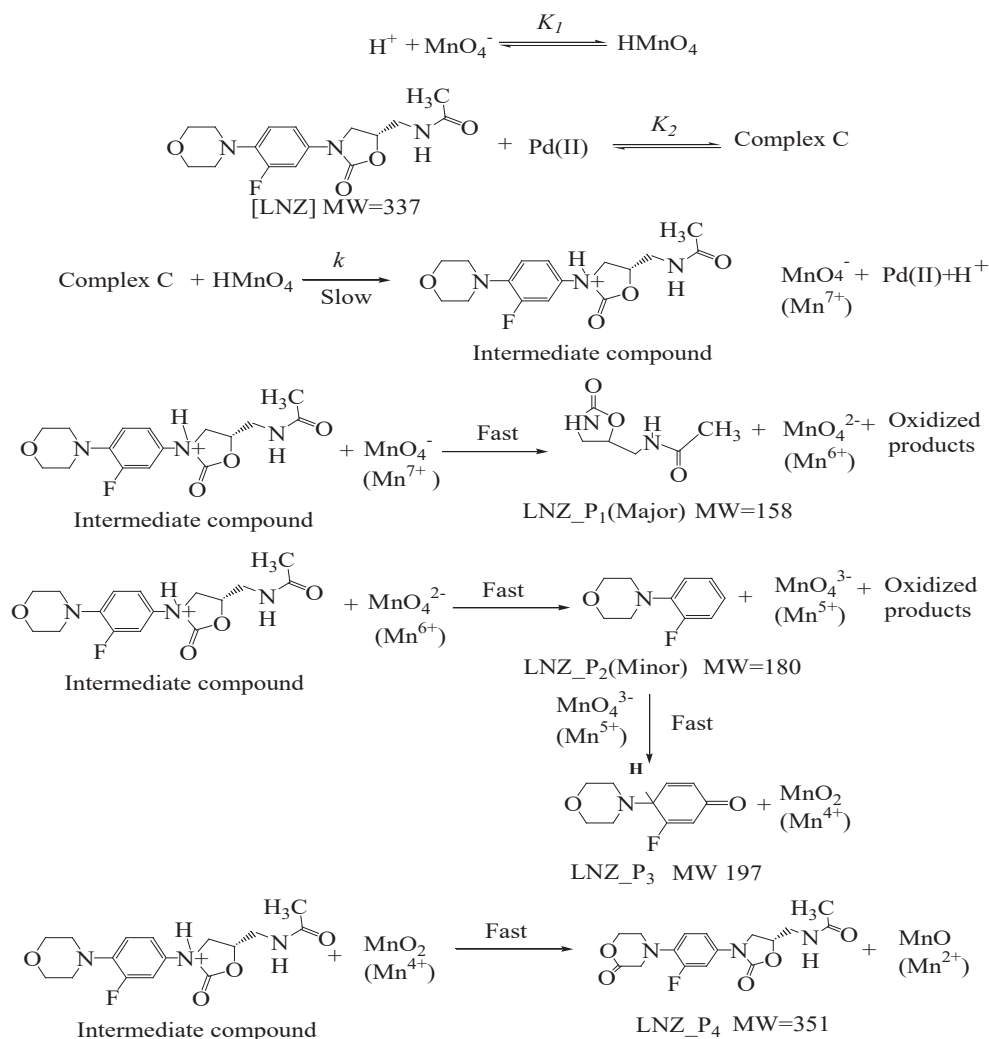
Table 3 Activation parameters for the Pd(II)-catalysed oxidation of linezolid by permanganate in aqueous acidic medium

(a) Effect of temperature		
Temperature (K)	$10^3 k_U \text{ s}^{-1}$	$10^2 k_C \text{ s}^{-1}$
283	2.51	5.46
288	4.41	7.35
296	5.49	9.34
299	6.68	12.91

(b) Activation parameters		
Activation parameters	Values (Uncatalysed)	Values Pd(II)-catalysed
E_a (kJ mol ⁻¹)	39.08 ± 2.00	34.90 ± 2.00
ΔH^\ddagger (kJ mol ⁻¹)	36.66 ± 1.00	31.97 ± 1.00
ΔS^\ddagger (J K ⁻¹ mol ⁻¹)	-160.06 ± 1.00	-150.24 ± 1.00
ΔG^\ddagger (kJ mol ⁻¹)	83.32 ± 2.00	75.77 ± 2.00

which undergoes further reaction with HMnO_4 in a slow step to form the intermediate product MnO_4^- (Mn^{7+}), and an H^+ species with regeneration Pd(II) . In a fast step, the intermediate product of the LNZ decomposes to give the major product LNZ_P_1 , MnO_4^{2-} (Mn^{6+}). In the next fast step, the intermediate compound undergoes reaction with MnO_4^{2-} to give the LNZ_P_2 , MnO_4^{3-} (Mn^{5+}) and other oxidised products. Further, the LNZ_P_2 is oxidised with MnO_4^{3-} (Mn^{5+}) to form LNZ_P_3 , and in the fast reaction, the intermediate compound reacts with MnO_2 (Mn^{4+}) to form LNZ_P_4 . The results can be understood from Scheme 1 [33,34].

The spectral interaction of linezolid with Pd(II) was attained from the UV-Vis spectra of LNZ ($1.50 \times 10^{-3} \text{ mol dm}^{-3}$), Pd(II) ($6.00 \times 10^{-8} \text{ mol dm}^{-3}$) and a mixture of these. UV-Vis Spectral evidence for the formation of a $\text{Pd(II)}-\text{LNZ}$ complex was obtained from the blue shift of 3 nm from 252 nm to 249 nm. The corresponding Michaelis–Menten plot provides the evidence for complex formation between catalyst and LNZ, which explains the order with respect to $[\text{LNZ}]$



Scheme 1

being less than unity. Such complex formation between a catalyst and substrate has also been observed in previous studies [33].

According to Scheme 1

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k[\text{Complex C}][\text{HMnO}_4] = k K_1 K_2 [\text{LNZ}]_f [\text{Pd(II)}]_f [\text{MnO}_4^-] [\text{H}^+] \quad (5)$$

The total concentration of $[\text{MnO}_4^-]_T$ is given by,

$$\begin{aligned} [\text{MnO}_4^-]_T &= [\text{MnO}_4^-]_f + [\text{HMnO}_4] + [\text{Complex C}] \\ &= [\text{MnO}_4^-]_f + K_1 [\text{H}^+] [\text{MnO}_4^-]_f + K_1 K_2 [\text{LNZ}] [\text{H}^+] [\text{MnO}_4^-]_f \\ &= [\text{MnO}_4^-]_f \{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{LNZ}]\} \end{aligned}$$

and T and f refer to the total and free concentrations.

$$[\text{MnO}_4^-]_f = \frac{[\text{MnO}_4^-]_T}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{LNZ}]} \quad (6)$$

Similarly,

$$\begin{aligned} [\text{H}^+]_T &= [\text{H}^+]_f + [\text{HMnO}_4] \\ &= [\text{H}^+]_f + K_1 [\text{H}^+] [\text{HMnO}_4^-] \end{aligned}$$

In view of the low concentration of $[\text{H}^+]$ in the second term, it can be neglected. Therefore,

$$[\text{H}^+]_T = [[\text{H}^+]_f] \quad (7)$$

Similarly,

$$[\text{LNZ}]_T = [\text{LNZ}]_f \quad (8)$$

Now,

$$\begin{aligned} [\text{Pd(II)}]_T &= [\text{Pd(II)}]_f + [\text{Complex C}] \\ &= [\text{Pd(II)}]_f + K_2 [\text{LNZ}] [\text{Pd(II)}]_f \\ &= [\text{Pd(II)}]_f \{1 + K_2 [\text{LNZ}]\} \end{aligned}$$

$$[\text{Pd(II)}]_f = \frac{[\text{Pd(II)}]_T}{1 + K_2 [\text{LNZ}]}$$

Since the value of second term in the denominator is less than unity, it can be neglected. Substituting the values of $[\text{MnO}_4^-]_f$, $[\text{LNZ}]_f$, $[\text{H}^+]_f$ and $[\text{Pd(II)}]_f$ into Eqn (5) and omitting the subscripts, we get:

$$\text{Pd(II)}_f = [\text{Pd(II)}]_T \quad (9)$$

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{-dt} = \frac{k K_1 K_2 [\text{MnO}_4^-] [\text{LNZ}] [\text{H}^+] [\text{Pd(II)}]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{LNZ}]} \quad (10)$$

$$\frac{\text{Rate}}{[\text{MnO}_4^-]} = k_c = k_T - k_U = \frac{k K_1 K_2 [\text{MnO}_4^-] [\text{LNZ}] [\text{H}^+] [\text{Pd(II)}]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{LNZ}]} \quad (11)$$

The rate law, Eqn (11) can be rearranged into the following form:

$$\frac{[\text{Pd(II)}]}{k_c} = \frac{1}{k K_1 K_2 [\text{LNZ}] [\text{H}^+]} + \frac{1}{k K_2 [\text{LNZ}]} + \frac{1}{k} \quad (12)$$

The Arrhenius plot was linear and gave activation parameters such as activation energy, enthalpy of activation, entropy of activation and Gibbs free energy of activation (Table 3). The results demonstrate that the average value of activation energy (E_a) was found to be 34.90 kJ mol⁻¹ for the Pd(II)-catalysed oxidation and for uncatalysed was found to be 39.08 kJ mol⁻¹; the entropy of activation ΔS^\ddagger was -150.24 J K⁻¹ mol⁻¹ for the palladium-catalysed oxidation and for the uncatalysed it was found to be -160.06 J K⁻¹ mol⁻¹ while the free energy of activation (ΔG^\ddagger) was 75.77 kJ mol⁻¹ for the palladium-catalysed oxidation and for the uncatalysed it was found to be 83.32 kJ mol⁻¹; the enthalpy of activation (ΔH^\ddagger) was 31.97 kJ mol⁻¹ for the palladium-catalysed oxidation and for the uncatalysed it was found to be 36.66 kJ mol⁻¹. A negative value of the entropy of activation was found, indicating a highly ordered transition state, possibly involving higher solvation compared with the reactant ground states. The energy of activation, free energy of activation and entropy parameters imply that Pd(II) forms the activated complex more easily compared to the uncatalysed reaction. A mechanism consistent with the observed rate laws has been suggested [35,36]. The activation parameters found for the catalysed and uncatalysed reactions elucidates the influence of catalytic activity on the reaction. Pd(II) forms a complex (C) with LNZ, which increases the reducing property of the substrate more than without a catalyst. In addition to this, the Pd(II) catalyst alters the reaction pathway by decreasing the activation energy [34].

The effect of ionic strength had no influence on the rate constant, *i.e.* the added ions did not interact with the reactants under the conditions investigated which indicates that the reaction is between two neutral species or a neutral and a charged species. An Amis plot of $\log k'_{obs}$ versus $1/D$ gave a straight line with a negative slope for both the uncatalysed and Pd(II)-catalysed reactions [37,38]. The slope is negative due to the reaction being between a dipole or two dipoles and a negative ion, and one gets a positive slope for a positive ion-dipole interaction [39–41].

4. CONCLUSION

The kinetics of the PMGT oxidation of linezolid in an acid medium was investigated using the spectrophotometric technique at five different temperatures. The most important reactive active species of PMGT is HMnO₄. The function of hydrogen ion is important to the reaction. The proposed mechanism is consistent with the experimental data. The Pd(II)-catalysed oxidation of linezolid by PMGT was studied. For this reaction, the main active species of PMGT is found to be HMnO₄ and active species of Pd(II). The reaction rates suggest that the Pd(II)-catalysed reaction is about ten-times faster than the uncatalysed reaction. It is clear from carrying out this reaction, the role of reaction medium is important. The overall order explained here is consistent with the products, mechanistic and kinetic studies. The oxidation of linezolid by PMGT was slow in acidic media, but increased in rate in the presence of the Pd(II) catalyst. The observed results were explained by plausible mechanism and the related rate law was deduced. It can be stated that Pd(II) performs as a capable catalyst for the oxidation of LNZ by PMGT in acidic media.

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