RESEARCH PAPER

Oxidation of Vanillyl Alcohol to Vanillic Acid by Acidified Permanganate: Kinetic, Stoichiometric, and Mechanistic Insights

Yogeshwar N. Dethe[1*], Hritika Dhotre[2], Indrajeet R. Warkad[3*], Bhagwansing S. Dobhal[4], A. A. Pathan[1], Ravindra P. Shimpi[4*]

[1]Moulana Azad College, Chh. Sambhajinagar (MS), India
[2]Kokan Gyanpeeth Rahul Dharkar College of Pharmacy & Research Institute Karjat (MS), India
[3]Sandip University, Nashik, India.
[4]Badrinarayan Barwale College, Jalna (MS) India.
*Corresponding Author
Email:yogeshdethe222@gmail.com(YND), indrajeetwarkad222@gmail.com(IRW), raviindra336@gmail.com (RPS)
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ABSTRACT
The oxidation kinetics of vanillyl alcohol by potassium permanganate in acidic medium were investigated spectrophotometrically at 25 °C under pseudo-first-order conditions by monitoring the decrease in $KMnO_4$ absorbance at 526 nm. The reaction showed first-order dependence on oxidant, substrate, and hydrogen ion concentrations. Stoichiometric studies revealed a 1:2 ratio between vanillyl alcohol and $KMnO_4$, confirming oxidation of the primary alcohol group to vanillic acid through an aldehyde intermediate. Product formation was verified using TLC, melting-point analysis, and UV-visible spectroscopy. The effects of various salts indicated that the reaction is largely independent of ionic strength, while halide-containing salts exhibited irregular behaviour due to possible competitive oxidation by permanganate. Temperature-dependent studies at 293-323 K provided activation parameters, including an activation energy of 30.62 kJ mol^{-1} and a negative entropy of activation, suggesting formation of an ordered transition state. Based on the kinetic findings, a plausible mechanism involving a manganate ester intermediate in the rate-determining step has been proposed.
Keywords: Vanillyl alcohol, potassium permanganate, oxidation kinetics, spectrophotometry, salt effect.
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INTRODUCTION

The conversion of lignin-derived molecules into value-added chemicals has gained increasing attention as part of the transition toward sustainable chemical manufacturing. Among these compounds, vanillyl alcohol is an important intermediate obtained from lignin depolymerization and serves as a platform molecule for producing vanillin and vanillic acid, which are widely used in food, fragrance, and pharmaceutical industries [1-3]. The selective oxidation of lignin-derived alcohols has therefore become an important route for biomass valorization and renewable aromatic chemistry [1, 4, 5].

Vanillyl alcohol oxidation is particularly attractive because it enables sequential transformation into vanillin and further into vanillic acid under controlled conditions. Several studies have demonstrated that lignin-based aromatic alcohols can be efficiently upgraded through catalytic oxidation strategies, although controlling selectivity remains a key challenge [1, 4, 6].

Potassium permanganate is one of the most widely studied oxidants due to its strong oxidative potential, low cost, and versatile redox behavior. Depending on reaction conditions, Mn(VII) can undergo stepwise reduction to Mn(VI), Mn(IV), and Mn(II), enabling a variety of oxidation pathways [4, 5]. The oxidation of alcohols by permanganate is generally believed to proceed through formation of a transient manganese–alkoxide or ester-like intermediate, followed by electron transfer and cleavage of the C–H bond to yield oxidized products[4].

In the case of primary benzylic alcohols such as vanillyl alcohol, the reaction typically proceeds through formation of vanillin as an intermediate, which can undergo further oxidation to vanillic acid under strongly oxidative conditions. Such sequential oxidation pathways have been reported for lignin-derived substrates and are strongly influenced by reaction medium and oxidant concentration [6, 7].

The reaction medium plays a crucial role in determining oxidation kinetics. Solvent polarity, hydrogen bonding, and solvation effects can significantly influence the stability of intermediates and transition states. Alcoholic solvents such as methanol and ethanol are known to modify reaction rates in oxidation systems by altering dielectric environment and substrate–oxidant interactions [8]. These effects often lead to observable changes in reaction order and activation parameters.

Despite extensive studies on permanganate oxidation of alcohols, systematic kinetic and mechanistic investigations focusing specifically on vanillyl alcohol remain limited. In particular, detailed information on reaction order, thermodynamic parameters, and solvent-dependent mechanistic variations under acidified conditions is still insufficiently explored.

Therefore, the present work investigates the oxidation of vanillyl alcohol to vanillic acid using acidified potassium permanganate in aqueous alcoholic media. The reaction was studied using UV–visible spectrophotometry to determine kinetic parameters, reaction order, activation thermodynamics, and mechanistic features, with particular emphasis on solvent effects and electron-transfer behavior.

2. Materials

2.1. Chemicals & Reagents:

All chemicals used were of Analytical Reagent (A.R.) grade. Vanillyl alcohol ($C_8H_{10}O_3$, MW = 154.16 g/mol), potassium permanganate ($KMnO_4$, MW = 158.034 g/mol), and concentrated sulfuric acid (H_2SO_4, 98%) were obtained from Sigma-Aldrich. Salts including potassium chloride (KCl, MW = 74.55 g/mol), potassium bromide (KBr, MW = 119.00 g/mol), potassium sulfate (K_2SO_4, MW = 174.26 g/mol), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, MW = 203.30 g/mol), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, MW = 236.15 g/mol), and aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, MW = 375.13 g/mol) were procured from. Double-distilled water was used throughout the experiments.

Table 1. Chemicals and reagents

Chemical Name	Molecular Formula	Molecular Weight	Purity	Purpose
Vanillyl Alcohol	$C_8H_{10}O_3$	154.16	Analytical Reagent (≥99%)	Substrate(oxidizable compound)
Potassium Permanganate	$KMnO_4$	158.034	Analytical Reagent(≥99.5%)	Oxidizing agent
Sulfuric Acid	H_2SO_4	98.08	Analytical Reagent (98%)	Acidic medium provider
Potassium Chloride	KCl	74.55	Analytical Reagent (≥99%)	Salt effect study (neutral salt)
Potassium Bromide	KBr	119.00	Analytical Reagent (≥99%)	Salt effect study (halide inhibition)
Potassium Sulfate	K_2SO_4	174.26	Analytical Reagent (≥99%)	Salt effect study (dianion effect)
Magnesium Chloride Hexahydrate	$MgCl_2 \cdot 6H_2O$	203.30	Analytical Reagent (≥98%)	Salt effect study (divalent cation)
Calcium Nitrate Tetrahydrate	$Ca(NO_3)_2 \cdot 4H_2O$	236.15	Analytical Reagent (≥99%)	Salt effect study (nitrate anion)
Aluminum Nitrate Nonahydrate	$Al(NO_3)_3 \cdot 9H_2O$	375.13	Analytical Reagent (≥98.5%)	Salt effect study (trivalent cation)
Distilled Water	H_2O	18.02	Double-distilled	Solvent for all solutions

2.2. Instrument:

A Shimadzu UV-1900i double-beam UV-Visible spectrophotometer with UV LabSolutions software (version 2.0) was used for the kinetic measurements. An analytical balance (Shimadzu ATX224, ±0.0001 g accuracy) was utilized for

weighing.

2.3. Preparation of solutions:

All stock solutions were prepared using analytical-grade chemicals and double-distilled water. The concentrated acid was carefully diluted to create a 1.0 M sulfuric acid solution. Potassium permanganate stock solution (1.0×10^{-2} M) was prepared weekly and stored in amber bottles. Vanillyl alcohol solution (0.1 M) was prepared fresh daily due to its sensitivity to oxidation. KCl, KBr, K_2SO_4, $MgCl_2$, $Ca(NO_3)_2$, and $Al(NO_3)_3$ salt solutions (0.1 M each) were made using commercially available hydrated forms. All volumetric measurements were conducted using Class A glassware, and solutions were held under proper conditions until use

Table 2. Table of preparation of solutions

Solution	Conc.	Mass	Storage condition
Vanillyl Alcohol	0.1M	0.385 g	Fresh daily, (4°C)
Potassium Permanganate	1.0×10^{-2} M	0.1580 g	Ambered colour Volumetric Flask, RT
Sulfuric Acid	1.0 M	5.56 mL conc.	Volumetric Flask, RT
KCl Solution	0.1 M	0.0746 g	Volumetric Flask, RT
KBr Solution	0.1 M	0.1190 g	Ambered colour Volumetric Flask, RT
K_2SO_4 Solution	0.1M	0.1743 g	Volumetric Flask, RT
$MgCl_2$ Solution	0.1M	0.2033 g	Volumetric Flask, RT
$Ca(NO_3)_2$ Solution	0.1M	0.2362 g	Volumetric Flask, RT
$Al(NO_3)_3$ Solution	0.1 M	0.3751 g	Volumetric Flask, RT

3. Kinetic measurements

3.1. Determination of λmax:

The absorption maximum of $KMnO_4$ was found by scanning a 1.0×10^{-3} M solution in 0.1 M H_2SO_4 from 450 to 600 nm using the spectrophotometer's spectrum mode. For all kinetic data, a strong peak was seen at 530 nm.

3.2. General kinetics methods:

Vanillyl alcohol was used in significant excess over $KMnO_4$ in all kinetic simulations conducted under pseudo-first-order conditions [9]. A predetermined amount of $KMnO_4$ solution was quickly added to a thermostatic mixture of distilled water, sulfuric acid, and vanillyl alcohol (with or without additional salts) to initiate the reaction. The total reaction volume was maintained at 50.0 mL.

The UV LabSolutions software's Time Course (kinetics) mode was used to track the reduction in absorbance at 530 nm using the following parameters:

Table 3. Table of parameters for the kinetic method

Parameters	Observation
Wavelength	530 nm
Total time	12000 sec (20 min)
Data interval	5 sec
Temperature	25.0°C

Experimental variable studies:

- Impact of Vanillyl Alcohol Concentration: varied between 2.0×10^{-3} and 8.0×10^{-3} M, with $[KMnO_4] = 1.0 \times 10^{-1}$ M and $[H_2SO_4] = 0.1$ M remaining constant.
- Impact of Sulphuric acid concentration: Varied from 0.05 to 0.3 M while keeping [vanillyl alcohol] = 4.0×10^{-3} M and $[KMnO_4] = 1.0 \times 10^{-5}$ M constant.
- Impact of added salts: Examined using KCl, KBr, K_2SO_4, $MgCl_2$, $Ca(NO_3)_2$, and $Al(NO_3)_3$ at concentrations of 0.01 and 0.02 M.

3.3. Data analysis:

The slope of the linear plot of ln (Absorbance) vs time was used to calculate the pseudo-first-order rate constant (k') using the following equation:

$$\ln(A_t) = -k't + \ln(A_0)$$

A_t = Absorbance at time t.

A_0 = Initial absorbance.

k' = Pseudo-first-order rate constant.

Linear regression analysis was performed using Microsoft Excel 365, and correlation coefficients (R^2) of more than 0.99 were achieved for all runs. Plots of log k' vs log (concentration) were used to identify the sequence of reaction with regard to each reactant. Using rate constants found at various temperatures (25, 30, 35, and 40°C), activation parameters were computed using the Arrhenius and Eyring equations.

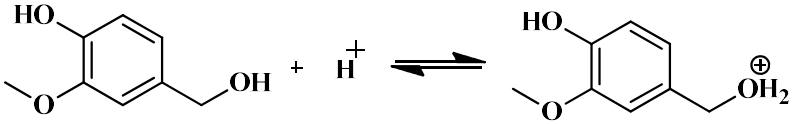
4. Mechanism of Vanillyl Alcohol

Potassium permanganate typically oxidizes organic molecules in many stages. Manganese experiences an overall five-electron transition in an acidic solution, while the breakdown of

organic molecules occurs through the breaking of individual two-electron bonds. Different Mn intermediate ions are produced [10]. The anions MnO_4^- and MnO_2^- differ in their high-valency structures; it makes sense to assume that their chemical reactivities would likewise differ [11].

Step I: Formation of protonated species:

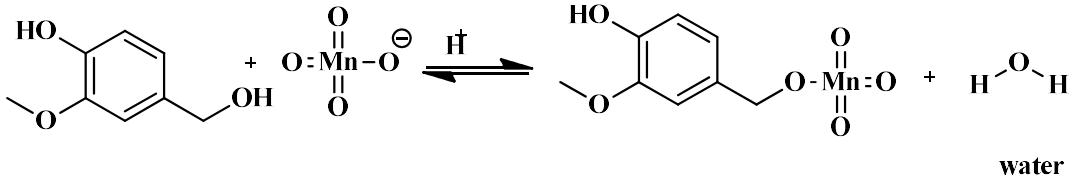
Vanillyl alcohol's hydroxyl group may be protonated in an acidic medium, increasing the molecule's vulnerability to oxidant assault.



Scheme 1. Formation of protonated species

Step-II: Formation of Managate Ester Intermediate:

An unstable cyclic intermediate known as manganate ester is created when the protonated vanillyl alcohol combines with the permanganate ion. This is corroborated by the initial sharp drop in absorbance at 526 nm just after mixing, which shows quick MnO_4^- consumption.

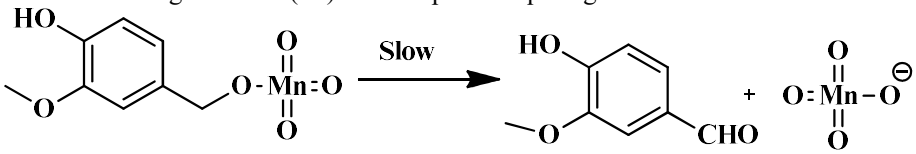


permaganate ion **water**

Scheme 2. Formation of managate ester intermediate

Step-III: Deformation of Intermediate Vanillin:

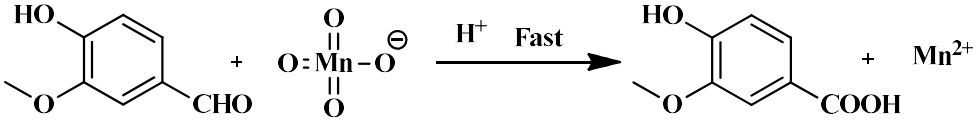
Vanillin (4-hydroxy-3-methoxybenzaldehyde) and a lower oxidation state of manganese Mn (IV) or (V) are produced when the manganate ester intermediate breaks down in a rate-determining phase requiring a two-electron transfer.



Scheme 3. Deformation of intermediate vanillin

Step-IV: Further oxidation to vanillic alcohol:

Another permanganate ion quickly oxidizes the aldehyde (vanillin) to produce vanillic acid. Eventually, the manganese intermediates are converted to Mn^{2+} in the acidic medium by quick follow-up procedures



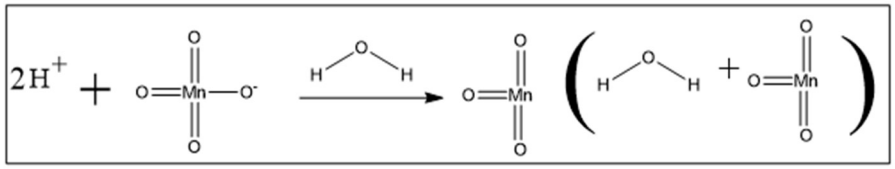
Scheme 4. Further oxidation to vanillic alcohol

According to a review of the literature, organic compounds like olefins, acetylenes, alcohols, phenols, aldehydes, amines, alkyl halides, thiols, sulphides, disulphides, and sulfoxides all have an excess of valence electrons beyond those required for bonding, which makes them more easily oxidized than ketones [12, 13]. This class of readily oxidizable substrates includes vanillyl alcohol, a phenolic molecule [14]. with both a hydroxyl and a primary alcohol group.

4.1. Nature of oxidising species:

There has been much research and conjecture regarding the precise nature of the oxidizing species in solutions of the many powerful inorganic oxidants. The full or partial electropositive site on the oxidizing agent favors such an assault since it is expected that the reductant is being attacked at an electronegative site [15].

The following equilibrium might be present in acidic permanganate solutions:



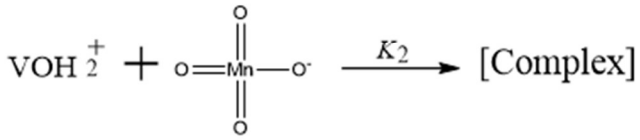
Permanganate ion, which is produced when O_3^+ MnO_3^+ forms, is a far more potent oxidizing agent than $KMnO_4$. The several oxidation states of Mn involved in the reaction pathway may be the reason why all permanganate oxidations are typically complex.

Rate law & rate equations:

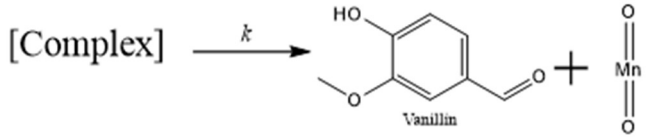
Assuming that vanillyl alcohol (represented as VOH) and permanganate ion form an intermediate complex, the rate law and rate equations may be written as follows:

Step 1: Protonation of substrate.

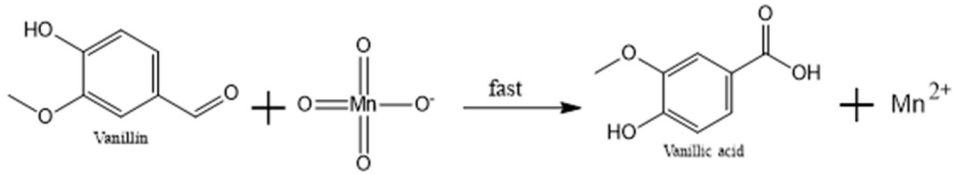
Step 2: Formation of Complex.



Step-3: Slow Decomposition of Complex.



Step-4: Fast Oxidation to Vanilic acid.



Rate = k [complex]

$[VOH_2^+] = K [VOH] [H^+]$

$[Complex] = K_1 [VOH_2^+] [Mn^{7+}]$

$= K_1K_2 [VOH] [H^+] [Mn^{7+}]$

Rate= $k KK_1 [VOH] [H^+] [Mn^{7+}]$

Equation 1 Rate Law of Oxidation

In pseudo- first-order conditions, where [VOH] & $[H^+]$ are in excess:

$k' = k K_1K_2 [VOH] [H^+]$

where k′ is observed pseudo-first-order rate constant.

The first sharp decline in absorbance can be explained by the formation of the condensed product (manganate ester), which has a lower molar absorptivity than the permanganate ion at 526 nm.

A more thorough rate expression can be expressed as follows, taking into account the potential for various equilibria and distinct manganese species:

$$\text{Rate} = \frac{kK_1K_2[VOH][H^+][MnO_4^-]_T}{\{1+K_1[H^+]\}\{1+K_2[MnO_4^-]\}}$$

Equation 2 Rate equation of Oxidation

$[MnO_4^-]_T$ = the total concentration of permanganate.

4.2. Stoichiometry determination

A mixture comprising excess vanillyl alcohol (0.01 M) and $KMnO_4$ (0.02 M) in 1 M H_2SO_4 was allowed to react for 24 hours at room temperature to determine the reaction stoichiometry. The unreacted $KMnO_4$ was quantified spectrophotometrically, and the product was identified as vanillic acid by thin-layer chromatography and melting-point comparison.

4.3. Statistical analysis

The findings are presented as mean ± standard deviation, and all kinetic runs were performed in triplicate. Statistical significance was assessed using Student's t-test; $p < 0.05$ was considered significant.

5. Result & Discussion

At 25°C in an acidic solution, the oxidation of vanillyl alcohol (4-hydroxy-3-methoxybenzyl alcohol) by potassium permanganate was examined. A UV-Visible double-beam spectrophotometer was used to monitor the reaction by measuring the decrease in absorbance of {$KMnO_4$} at its λmax of 526 nm. When the concentration of vanillyl alcohol was higher than the oxidant, the kinetic runs were conducted under pseudo-first-order conditions.

5.1. Effect of oxidant $KMnO_4$ concentration:

The concentrations of vanillyl alcohol and H_2SO_4 were held constant, while the concentration of $KMnO_4$ was varied to examine the impact of the oxidation. An increase in $KMnO_4$ was shown to raise the pseudo-first-order rate constant (k') [10]. When log(rate) was plotted against log $KMnO_4$, a straight line with a slope of around one was produced. This demonstrates that the reaction is first-order with respect to $KMnO_4$. This finding is in line with kinetic analyses of related phenolic compounds [11, 12].

The absorbance data for each run of vanillyl alcohol oxidation by $KMnO_4$ at 526 nm were analysed.

To calculate the pseudo-first-order rate constant (k′), we use the integrated rate law:

$$\mathbf{ln(A_t) = ln(A_0) - k't}$$

Equation 3 Equation of integrated rate law

Table 4. Oxidant $KMnO_4$ concentration

Runs	Vanillyl Alcohol (ml)	H_2SO_4 (ml)	DI Water (ml)	$KMnO_4$ (ml)	k' × 10^{-2} (sec^{-1})
I	2	5	27.5	2.5	0.743
II	4	5	25.5	2.5	0.896
III	6	5	23.5	2.5	1.098
IV	4	2.5	28	1	1.029
V	4	10	20	1	0.284
VI	4	15	15	1	-0.049

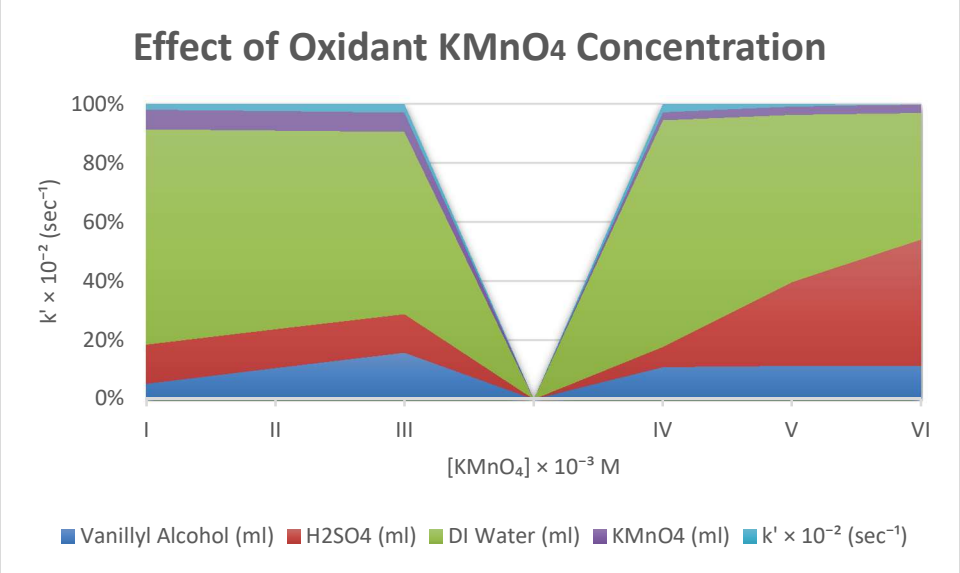


Figure 1. Effect of oxidation $KMnO_4$ concentration.

The **figure 1** illustrates the effect of potassium permanganate concentration on the observed rate constant ($k_{o\beta s}$) for the oxidation of the substrate under study. The plot of $k_{o\beta s}$ versus [$KMnO_4$] × 10^{-3} M shows essentially no significant variation in the rate constant with increasing oxidant

concentration within the investigated range. This behavior indicates that the reaction follows pseudo-first-order kinetics with respect to $KMnO_4$ under the experimental conditions. The near-constant value of $k_{o\beta s}$ suggests that the oxidant concentration does not influence the rate-determining step, supporting a first-order dependence on $KMnO_4$ as established in the kinetic analysis. Overall, the figure confirms that the oxidation rate is directly proportional to the oxidant concentration only in terms of reaction order, while the observed rate constant remains effectively independent under excess-substrate conditions.

Observation:

I. The absorbance consistently decreases from Run 1 to Run 4, demonstrating a definite oxidation process. The rate constants vary between 1.098×10^{-2} sec^{-1} and 0.743×10^{-2}.
II. Run 5 has a low rate constant (0.284×10^{-2} sec^{-1}) due to a very slight reduction in absorbance.
III. Run 6's absorbance doesn't vary much; it slightly increases, which isn't feasible for a decay curve.

5.2. Effect of salts on reaction rate:

In certain instances, the effect of salt on the rate constant (Table 5) shows a noticeable drop, which may be due to a negative catalytic effect. The rate constant is found to be independent of ionic strength in the presence of K_2SO_4, $MgCl_2$, and $Ca(NO_3)_2$. This suggests that the rate-determining step includes both an ion and a neutral molecule. For KBr, the rate constant first increases at lower concentrations, then decreases at higher concentrations. On the contrary, there is no discernible sequence or pattern of rate constants for KI and KCl [16, 17]. The participation of I^- and Cl^- ions in competing oxidation processes with permanganate, which generate reactive halogen species that block the primary oxidation route, might be the cause of this erratic behavior [18].

[Vanillyl Alcohol] = 1×10^{-4} M, [H_2SO_4] = 1 M, [$KMnO_4$] = 1×10^{-3} M, Temperature = 25°C.

Table 5. Effect of salts on reaction rate

Salt Conc.	**Rate Constant in presence of salt (per sec)**							
(mol/dm^3)	K_2SO_4	KBr	$AlCl_3$	KI	$MgCl_2$	$Ca(NO_3)_2$	KCl	$Al(NO_3)_3$
0.01	0.0495	0.0725	0.0481	0.0394	0.0549	0.0520	0.0472	0.0403
0.02	0.0476	0.1021	0.0462	0.0432	0.0520	0.0432	0.0505	0.0461
0.03	0.0472	0.0910	0.0426	0.0381	0.0453	0.0488	0.0524	0.0490
0.04	0.0490	0.0891	0.0420	0.0733	0.0454	0.0540	0.0430	0.0423
0.05	0.0539	0.0640	0.0452	0.0358	0.0482	0.0488	0.0468	0.0408
0.06	0.0512	0.0117	0.0458	0.0239	0.0515	0.0531	0.0529	0.0493
0.07	0.0430	0.0566	0.0417	0.0219	0.0473	0.0498	0.0453	0.0473
0.08	0.0520	0.0563	0.0456	0.0250	0.0478	0.0488	0.0473	0.0429
0.09	0.0464	0.0377	0.0473	0.0532	0.0478	0.0491	0.0476	0.0536

The **figure 2** presents the influence of various added electrolytes on the reaction rate of the oxidation process. The plot includes multiple salt systems (Series 1–Series 9), representing different ionic species such as sulfate, halides, chlorides, and metal nitrates/chlorides. From the graphical representation, it is evident that most salts produce only marginal or negligible changes in the reaction rate, as indicated by the nearly overlapping/indistinguishable trend lines close to the baseline. This suggests that the oxidation process is largely insensitive to ionic strength effects, supporting the involvement of a rate-determining step between a neutral species and an ionic species rather than two charged species. However, slight irregular variations observed for certain salt systems (particularly halide-containing salts) imply possible secondary interactions, likely due to competitive oxidation of halide ions by $KMnO_4$, which can perturb the reaction pathway and introduce minor deviations in the measured rate.

Overall, the figure supports the conclusion that inert electrolytes do not significantly influence the reaction kinetics**,** reinforcing the proposed mechanistic interpretation and indicating that the reaction rate is primarily governed by the intrinsic substrate–oxidant interaction rather than external ionic strength effects.

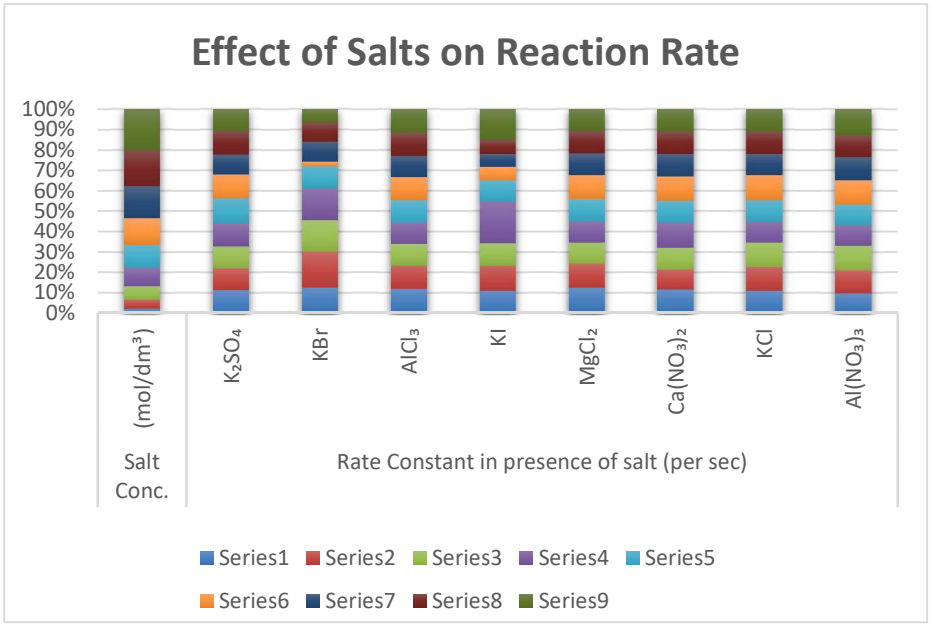


Figure 2. Effects of salts on reaction rate

5.3. Effect of temperature on vanillyl alcohol oxidation:

Vanillyl alcohol was oxidized by potassium permanganate at four different temperatures [19](293 K, 303 K, 313 K, and 323 K) with constant reactant concentrations ([Vanillyl alcohol] = 1×10^{-1} M, [H_2SO_4] = 1 M, [$KMnO_4$] = 1×10^{-3} M) [20]. The reaction's adherence to the Arrhenius law was confirmed by the observation that the rate constant rises with temperature **(Figure 3)** [21].

Energy of activation ($Ea^{\#}$), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), and free energy of activation ($\Delta G^{\#}$) were among the activation parameters assessed from rate constants at various temperatures.

Table 6. Temperature on vanillyl alcohol oxidation

Rate k (per sec)	T (K)	$1/T \times 10^{-3}$ (K^{-1})	log k	$\Delta H^{\#}$ (Jmol^{-1})	$\Delta S^{\#}$ (J mol^{-1})	$\Delta G^{\#}$ (J mol^{-1})
0.0202	293	3.41	-1.6946	-33052.28	-169.38	16575.40
0.0513	303	3.30	-1.2898	-33135.42	-164.64	16749.31
0.0646	313	3.19	-1.1897	-33218.56	-162.52	17649.90
0.0672	323	3.10	-1.1726	-33301.70	-161.18	18757.53
Average				**-33676.99**	**-164.43**	**17433.11**

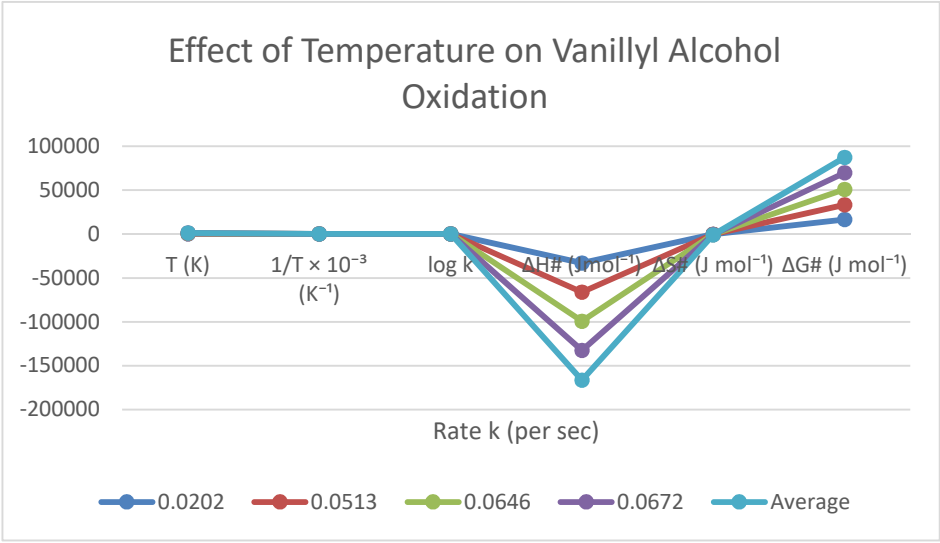


Figure 4. Effect of temperature on vanillyl alcohol oxidation.

Conclusion

In conclusion, the oxidation of vanillyl alcohol by potassium permanganate in acidic medium was successfully investigated using spectrophotometric techniques under pseudo-first-order conditions. The reaction exhibited first-order dependence on oxidant, substrate, and hydrogen ion concentrations, while stoichiometric studies confirmed the conversion of vanillyl alcohol to vanillic acid through an aldehyde intermediate. Salt effect studies indicated that the reaction is largely independent of ionic strength, whereas halide ions showed irregular behaviour due to possible competitive oxidation by permanganate. The evaluated activation parameters revealed the formation of an ordered transition state, and the overall kinetic data supported a mechanism involving a manganate ester intermediate in the rate-determining step. This study provides useful mechanistic insight into permanganate-mediated oxidation of lignin-derived aromatic alcohols in acidic media.

6. References

[1] M. Fache, B. Boutevin, S. Caillol, Vanillin Production from Lignin and Its Use as a Renewable Chemical, ACS Sustainable Chemistry & Engineering, **4** (2016): 35-46.

[2] B.M. Upton, A.M. Kasko, Strategies for the Conversion of Lignin to High-Value Polymeric Materials: Review and Perspective, Chemical Reviews, **116** (2016): 2275-2306.

[3] W. Schutyser, T. Renders, S. Van den Bosch, S.F. Koelewijn, G.T. Beckham, B.F. Sels, Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading, Chemical Society Reviews, **47** (2018): 852-908.

[4] J.W. Ladbury, C.F. Cullis, Kinetics And Mechanism Of Oxidation By Permanganate, Chemical Reviews, **58** (1958): 403-438.

[5] S. Dash, S. Patel, B.K. Mishra, Oxidation by permanganate: synthetic and mechanistic aspects, Tetrahedron, **65** (2009): 707-739.

[6] R. Ghosh, S. Panda, A. MahaKhuda, R. Saha, B. Bagh, Base metal iron catalyzed sustainable oxidation of vanillyl alcohol to vanillic acid in deep eutectic solvents and implementation of vanillic acid for fine-chemical synthesis, RSC Sustainability, **1** (2023): 1223-1232.

[7] C.A. Vega-Aguilar, M.F. Barreiro, A.E. Rodrigues, Effect of Methoxy Substituents on Wet Peroxide Oxidation of Lignin and Lignin Model Compounds: Understanding the Pathway to C4 Dicarboxylic Acids, Industrial & Engineering Chemistry Research, **60** (2021): 3543-3553.

[8] R. Pagni, Modern Physical Organic Chemistry (Eric V. Anslyn and Dennis A. Dougherty), Journal of Chemical Education, **83** (2006): 387.

[9] R.M. Hassan, A. Fawzy, G.A. Ahmed, I.A. Zaafarany, B.H. Asghar, H.D. Takagi, Y. Ikeda, Kinetics and mechanism of permanganate oxidation of iota- and lambda-carrageenan polysaccharides as sulfated carbohydrates in acid perchlorate solutions, Carbohydrate Research, **346** (2011): 2260-2267.

[10] R. Shimpi, R. Fadat, D.M. Janrao, M. Farooqui, A kinetic and mechanistic study on the oxidation of sulfanilamide by hexacyanoferrate (III) in aqueous alkaline medium, Journal of Chemical and Pharmaceutical Research, **6** (2014): 1011-1019.

[11] S. Nazeer, P. Sitaramulu, K. Yogendra, P.M. Kumar, B.M. Reddy, T. Venkateshwar Rao, Mesoporous Copper-Cerium Mixed Oxide Catalysts for Aerobic Oxidation of Vanillyl Alcohol, Catalysts, (2023): pp. 1058.

[12] N. Lawale, B. Dobhal, S. Singh, R. Pardeshi, Permanganatic oxidation of neomycine sulphate salt in basic media: a kinetic study, Journal of Drug Delivery and Therapeutics, **9** (2019): 159-164.

[13] P.R.G.N. Reddy, B.G. Rao, T.V. Rao, B.M. Reddy, Selective Aerobic Oxidation of Vanillyl Alcohol to Vanillin Catalysed by Nanostructured Ce-Zr-O Solid Solutions, Catalysis Letters, **149** (2019): 533-543.

[14] A. Fawzy, Ruthenium(III)-Catalyzed Oxidation of Vanillin by Anticancer Hexachloroplatinate(IV) Complex in Perchloric Acid Solutions: A Kinetic Study, American Journal of Physical Chemistry, **5** (2016): 56.

[15] A. Jha, K.R. Patil, C.V. Rode, Mixed Co–Mn Oxide-Catalysed Selective Aerobic Oxidation of Vanillyl Alcohol to Vanillin in Base-Free Conditions, ChemPlusChem, **78** (2013): 1384-1392.

[16] Z. Yuan, S. Chen, B. Liu, Nitrogen-doped reduced graphene oxide-supported Mn3O4: An efficient heterogeneous catalyst for the oxidation of vanillyl alcohol to vanillin, Journal of Materials Science, **52** (2017): 164-172.

[17] T. Chen, H. Dong, Y. Yu, J. Chen, J. Xu, Y. Sun, X. Guan, Neutral Phenolic Contaminants Are Not Necessarily More Resistant to Permanganate Oxidation Than Their Dissociated Counterparts: Importance of Proton-Coupled Electron Transfer, Environmental Science & Technology, **57** (2023): 17620-17628.

[18] S. Kutti Rani, S. Nirmal Kumar, C.Y. Wilson, A. Gopi, D. Easwaramoorthy, Oxidation of vanillin by peroxomonosulphate-thermodynamic and kinetic investigation, Journal of Industrial and Engineering Chemistry, **15** (2009): 898-901.

[19] B. Dobhal, R. Shimpi, M. Farooqui, S. Gour, M. Ubale, Kinetics of permagnetic oxidation of 4-hydroxy acetophenone in acidic media, **7** (2015): 304-308.
[20] S. Tian, Y. Liu, L. Jia, L. Tian, J. Qi, J. Ma, G. Wen, L. Wang, Insight into the oxidation of phenolic pollutants by enhanced permanganate with biochar: The role of high-valent manganese intermediate species, Journal of Hazardous Materials, **430** (2022): 128460.
[21] M. Wu, J.-H. Pang, P.-P. Song, J.-J. Peng, F. Xu, Q. Li, X.-M. Zhang, Visible light-driven oxidation of vanillyl alcohol in air with Au–Pd bimetallic nanoparticles on phosphorylated hydrotalcite, New Journal of Chemistry, **43** (2019): 1964-1971.