Research article Available online www.ijsrr.org ISSN: 2279–0543

International Journal of Scientific Research and Reviews

# Oxidation of Vanillin by Bromate in Aqueous Acetic Acid Medium: A Kinetic and Thermodynamic Approach

**Sunitha Manjari P., Koteshwar Rao R.*, Sathish T. , Parashuramudu. M**

Department of Chemistry, University College of Science, Saifabad, Osmania University, Hyderabad-500 004, Telangana. INDIA.

## ABSTRACT

The kinetics and mechanism of the oxidation of vanillin by acid bromate (unmixed with $Br_2$) in aqueous acetic acid medium is studied. The reaction exhibits first order in [bromate] and fractional order less than unity in [vanillin] and fractional-order in [acid]. Variation of ionic strength had no effect on the reaction rate. The reaction is failed to induce the polymerization of acrylonitrile. The decrease in the rate of reaction with increase in dielectric constant of the medium is observed The reaction has been carried out at four different temperatures and the activation and thermodynamic parameters were calculated. The mechanism proposed involves the decomposition of vanillin-bromate complex leading to vanillic acid.

**KEYWORDS**: Vanillin, Bromate, Kinetics, Mechanism.

***Corresponding author**

**Koteshwar Rao R.**

Department of Chemistry, University College of Science, Saifabad,

Osmania University, Hyderabad-500 004, Telangana, INDIA.

E. mail: psmanjari76@gmail.com; koti4idealchemy@gmail.com

## INTRODUCTION

Vanillin (4-hydroxy-3-methoxybenzaldehyde), commercially called *p*-vanillin (Van) occurs [1] in nature as a glucoside, which hydrolyses to vanillin and sugar. It is the major flavour component of natural vanilla. Van is a naturally occurring compound found in vanilla beans and may also be released to the environment as a by product in the decay process of plant material. If released to air, the vapor pressure of 0.01599 Pa at 298 K indicates Van will exist solely as a vapor in the ambient atmosphere. Vanillin displays antioxidant and antimicrobial properties and it may be used as a food preservative[2] and is also useful in the synthesis of drugs like Aldomet, L-Dopa[3] and Trimethaprim. It is also used in the preparation of perfume, metal-plating industries and as a catalyst in the polymerization of methyl methacrylate[4]. It is capable of undergoing reactions of both phenolic, aldehydic group and aromatic nucleus. In comparison with most other aldehydes, vanillin is notable for its stability. Van shows up in all sorts of products—in foods and flavoring, obviously, but also in fragrances, cosmetics and aromatherapy.

Oxidation of vanillin has been studied previously by few reagents such as hexacyanoferrate(III)[5], diperiodatoargentate(III)[6], bismuth(V)[7], diperiodato nickelate(IV)[8], periodate catalyzed by ruthenium(III)[9] in alkaline medium and by cerium(IV)[10], peroxomonosulphate[11], ruthenium(III) catalysed hexachloroplatinate(IV)[12], in acid medium.

Sodium or potassium bromate is an inexpensive, innocuous, mild and selective oxidant. The chemistry of bromate is quite interesting because of its ability to act as an oxidizing and brominating reagent[13]. Bromate oxidations of organic and inorganic reactions usually involve complications such as an induction period[14], autocatalysis[15] and involvement of two reactions [16, 17]. Even bromate oxidations sometimes involve oscillation reactions [18–21]. The product of bromate oxidation is bromide ion, which can be safely recycled; making bromate oxidations environmentally benign compared to metal ion oxidations. Hence, the chemistry of bromate ion in an aqueous acid medium is of considerable interest, given its importance in mechanistic chemistry. We have been interested in the kinetics and mechanism of oxidation by bromate and a few reports have emanated from our laboratory [22, 23]. There seems to be no report on the mechanistic aspects of oxidation of vanillin by bromate. In this paper we report the kinetics of oxidation of vanillin by bromate in aqueous acetic acid as the solvent, with emphasis on the mechanism and thermodynamic aspects. Our interest in oxidation of vanillin is due to the fact that the vanillin can be treated as a model system of the individual unit of the lignin molecule[24].

In the present study we aim to investigate thoroughly the kinetics and mechanism of oxidation of vanillin by bromate in sulphuric acid medium containing mercury(II), to identify the active species of the substrate, oxidant and oxidation products and evaluate the related kinetic and thermodynamic parameters of the reaction.

## EXPERIMENTAL

The stock solution of vanillin (S. D. Fine) was prepared in glacial acetic acid. Acidic solution was used due to low solubility of vanillin in water. Purity of the substrates was checked by their melting points, UV, IR and NMR spectra. $KBrO_3$ (Reidal), $H_2SO_4$ and $Hg(OAc)_2$ (Merck) were of analytical reagent grade and were used as received. $D_2O$ (99.4% pure) was obtained from the Baba Atomic Research Centre, Mumbai, India. Acetic acid (BDH) was purified by refluxing with chromic acid and acetic anhydride for 6 h and then distilled. Other solutions were prepared with either double distilled water or purified acetic acid and were standardized by known methods. A Shimadzu multipurpose recording double beam UV-visible spectrophotometer equipped with a temperature controller was used for absorption studies. Separation and identification of organic intermediates in the reaction were performed using high performance liquid chromatography (HPLC). The experiments were performed with Shimadzu equipment using an ion-exchange column at 45º C and a UV detector working at 220 nm. The intermediates and the products were identified from their retention time ($t_r$).

### *2.1. Kinetic measurements*

All the kinetic measurements were carried out in black–coated vessels at constant temperature ( ± 0.1 º C ) and performed under pseudo-first-order conditions with [vanillin] >> [bromate]. The reaction was initiated by the rapid addition of known amounts of oxidant to reaction mixtures containing the required amounts of substrate, mercuric acetate, sulphuric acid, acetic acid and water in glass–stoppered Pyrex boiling tubes that were thermostated at the same temperature. The progress of the reaction was monitored by iodometric determination of unconsumed [bromate] in known aliquots of the reaction mixtures at different time intervals. However, before adopting iodometric method, it was ensured that the presence of vanillin in the quenching solution of potassium iodide did not change the bromate titre value. The course of the reaction was studied for at least two half–lives. The rate constants ( $k$, $s^{-1}$ ) were determined from the pseudo-first-order plots of log [oxidant] against time. The pseudo-first-order plots were linear ( $r^2 \geq 0.99$ ) for more than 80 % completion of the reaction and the rate constants ( $k$, $s^{-1}$ ) were reproducible within ± 5 % . Freshly prepared solution of vanillin in purified acetic acid was used to avoid any possible side reactions.

### 2.2. Stoichiometry and product analysis

Different reaction mixtures with different sets of reactants containing various amounts of bromate and vanillin at fixed concentration of acid, ionic strength and temperature were allowed to react for 24 h in an inert atmosphere. After completion of the reaction, the unreacted bromate was estimated iodometrically. The obtained results indicated that one mole of bromate consumed three moles of vanillin in the predominant reaction as represented in the following equation.

The above stoichiometric equation is consistent with the results of product analyses. The oxidation product of vanillin was identified as the corresponding carboxylic acid (vanillic acid) by both spectral and chemical analyses. Similar oxidation product of vanillin with different experimental condition was reported earlier[5–9, 26]. The formation of 4-hydroxy-3-methoxy benzoic acid was confirmed by I. R. Data. The major peaks of the product appear at 3429.05, 1651.88 and 2072.98 $cm^{-1}$. The yield was about 85%. The formation of vanillic acid was confirmed from the above spectral data. A free hydroxyl stretching vibration near 3429.05 $cm^{-1}$ was observed in the product as compared to that at 3177.52 $cm^{-1}$ in vanillin. The shift to higher frequency is probably due to association of water molecules with the product. A broad intense peak at 1651. 88 $cm^{-1}$ is retained in the product due to absorption of $–OCH_3$ group. A new sharp intense peak at 2072.98 $cm^{-1}$ appeared in the product which is probably due to C=O stretching vibration of –COOH group. It is inferred from different peaks and bands that the product is 4-hydroxy-3-methoxy benzoic acid. Bromide ion was identified by adding $AgNO_3$ solution, resulting in the formation of pale yellow AgBr precipitate.

## RESULTS AND DISCUSSION

### 3.1. Role of Mercuric Acetate

The presence of mercuric acetate (in excess of bromate concentration) simply means that $Br_2$ oxidation has been completely suppressed; $Br_2$ otherwise would have been formed by interaction of bromate and bromide (the reduction product of bromate) as:

$$BrO_3^- + 5\,Br^- + 6\,H^+ \rightleftharpoons 3\,Br_2 + 3\,H_2O \qquad (2)$$

It is necessary to make clear that, in the present study, no free radicals are present and the reaction rates are independent of [$Hg(OAc)_2$]. These considerations confirm only the complex forming ability of Hg(II) with bromide ions in these reactions. Thus, Hg (II) acts as a scavenger [17, 25] for any bromide ion formed ensuring that the oxidation takes place purely through bromate. The kinetic results remained the same over a wide concentration range (0.001 to 0.01 mol $dm^{-3}$) of mercuric acetate. In order to mask all the bromide ions formed, an optimum concentration (0.005 mol $dm^{-3}$) of mercuric acetate has been employed throughout the study. The reported rate constants and thermodynamic parameters therefore stand for pure bromate (unmixed with $Br_2$) oxidation.

### *3.2. Effect of Concentration and Kinetic runs*

At fixed concentration of other reactants and when [vanillin] is in 10–fold excess over [bromate], the disappearance rate of [bromate] followed first-order rate law as was observed from the log initial rate (with respect to concentration/time) versus log [bromate] ($R^2$> 0.998) for more than three half-lives of the reaction. Further, the pseudo–first-order rate constant ( $k$, $s^{-1}$ ), evaluated from the slopes of such plots remained unchanged **Table 1** with the variation of [bromate], confirming the first order dependence of the rate on [bromate]. Under the same experimental conditions, the rate of reaction increased with increase in [vanillin] **Table 1** and the plots of log $k$ versus log [vanillin] were linear **Fig. 1a** with slope values of less than unity (0.43). Further, dependence of $k$ ( $s^{-1}$ ) values on the [vanillin] was in accordance with the Lineweaver–Burk kinetics in each case **Fig. 1b**.

The effect of [$H^+$] on the reaction rate was studied in order to establish the active species of reactants present in the solution. At fixed concentrations of substrate, bromate, and other conditions remaining constant, the reaction rate increased linearly with increase in [$H_2SO_4$]

**Table 1** and the order with respect to [acid] was found to be fractional (1.43) and is evident from non-zero intercept in plot of 1/$k$ against 1/[$H_2SO_4$] **Fig. 2**.

The effect of ionic strength of the medium on the reaction rate was studied using $Na_2SO_4$, with other experimental conditions held constant. There was a significant effect of ionic strength on the reaction rate **Table 2** hence the ionic strength of the medium was not fixed at any constant value. The dielectric constant ( D ) of the medium was varied using different proportions of acetic acid and water. The D values were calculated from the equation $D = D_W V_W + D_A V_A$, where $D_W$ and $D_A$ are the dielectric constants of pure water and acetic acid respectively, and $V_W$ and $V_A$ are the volume fractions of components water and acetic acid respectively in the total mixture.The reaction rate

decreased with an increase in dielectric constant of the medium **Table 1**. Plots of log *k* versus 1 / D **Fig. 3** were found to be linear with positive slopes. Blank experiments performed showed that acetic acid was not oxidized significantly by bromate under prevailing conditions.

### *3.3. Test for Free Radicals*

The reactions were studied in the presence of added acrylonitrile to understand the intervention of free radicals. There was no effect of added acrylonitrile ( 0. 1–1.0 mol dm $^{-3}$ ) on the reaction rate, and also no precipitate due to polymerization of acrylonitrile was observed, suggesting the absence of any free radical formation in the reaction. To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm $^{-3}$ of 2, 6-di-*t*-butyl-4-methylphenol (butylated hydroxyl toluene or BHT). It was observed that the BHT was recovered unchanged, almost quantitatively.

### *3.4. Effect of Temperature*

The oxidation of vanillin was studied in the temperature range of 298–323 K and the evaluated rate constants, $k(s^{-1})$ are $0.35\times10^{-4}$, $0.58\times10^{-4}$, $1.54\times10^{-4}$, $3.33\times10^{-4}$, $7.67\times10^{-4}$ and $18.12\times10^{-4}$ at 298, 303, 308, 313, 318 and 323 K respectively. The activation parameters evaluated from the slope of Arrhenius plot **Fig. 4** of log *k* versus 1/T are: Ea = 130.96 ± 1.5 kJ mole$^{-1}$ ; $\Delta H^{\neq}$ = 128.36 ± 1.5 kJ mole$^{-1}$ ; $\Delta S^{\neq}$ = –98.23 J K $^{-1}$ mole$^{-1}$ $\Delta G^{\neq}$ = 97.62 ± 1.2 k J mole$^{-1}$ at 313 K at concentrations of Bromate = 0.001 moldm$^{-3}$, Vanillin = 0.01 moldm$^{-3}$; $H_2SO_4$ = 0.25 mol.dm$^{-3}$ and $Hg(OAc)_2$ = 0.005 mol.dm$^{-3}$. Large negative value of entropy indicates that the complex is more ordered than the reactants.

### *3.5. Active Species of the Reactants*

In acid solutions, the reactive species of bromate are likely to be $BrO_3^-$ and protonated bromate. Hence, the oxidation may be a reaction involving one of the oxidant species. Based on the earlier propositions made in bromate oxidations (in acid medium) by Indelli *et. al* [27], Anbar and Guttmann[28], Wright and Barton[29], and Rabai *et. al*[30], the following equilibrium steps (Eqs. 3– 6) may be considered.

$$BrO_3^- + H^+ \rightleftharpoons HBrO_3 \quad (3)$$

$$HBrO_3 + H^+ \rightleftharpoons H_2BrO_3^+ \quad (4)$$

$$H_2BrO_3^+ \rightleftharpoons BrO_2^+ + H_2O \quad (5)$$

These authors [27-30] consider the $H^+$ attack to bromate forming intermediates $HBrO_3$ and $H_2BrO_3^+$. Increase in the rate of reaction with acid concentration indicates the direct involvement of proton in the rate equation. Protonation of bromate results in the formation of $HBrO_3$ species, a more powerful oxidant.As $HBrO_3$ is a very strong acid [31], the $H_2BrO_3^+$ species will not be formed at the acid concentrations used to study the bromate–vanillin reaction. Another point to be considered is the possibility of bromate, after two protonations, losing water and forming the $BrO_2^+$ species as considered by other authors [28, 32]. However, this possibility has been ruled out by the results [33, 34] on the rate of exchange of isotopic oxygen between the oxyanion $XO_3^-$ (X = Cl, Br) and water as these rates are significantly low. These results indicate that the active species of oxidant is $HBrO_3$ in the reaction.

The present reaction between vanillin and bromate in acid medium has a stoichiometry of 3:1 (Van : bromate) with a first order dependence on [bromate] and apparent order less than unit order in [Van]. The less than unit order with respect to vanillin concentration suggests formation of an intermediate complex between vanillin and bromate in a pre-equilibrium step. The kinetic evidence for complex formation is the plot of 1/*k*against 1/[Van] which was found to be linear with a positive intercept on 1/[Van] axis as shown in **Fig.1b**, similar to well known Lineweaver-Burk kinetics. The enhancement of reaction rate by changing the composition of acetic acid in the reaction mixture, while keeping the oxidant and substrate concentrations unchanged suggests that the dielectric constant of the medium play an important role. The linear plot of log *k* versus 1/D with a positive slope **Fig. 3** suggests that the reaction may be between an ion and a dipole or in between ions of opposite charge. However, the constancy in the obtained results of ionic strength effect **Table 2** suggests that the reaction is in between an ion and a dipole molecule.

## MECHANISM

Based on the aforementioned reasons and in accordance with experimental results, bromate ion is suggested to react with protonated form of vanillin in a fast pre-equilibrium step to give an intermediate complex ( C ). The decomposition of the complex ( C ) leads to the formation of vanillic acid and intermediate species of bromate which further reacts with another mole of vanillin to form vanillic acid and HOBr. This upon reaction with vanillin further results in the formation of vanillic acid and bromide ion, which is confirmed by pale yellow precipitate of AgBr, satisfying the observed stoichiometry. The proposed mechanism is illustrated in Scheme 1.

**Scheme 1**

## RATE LAW AND ITS VERIFICATION

On the basis of the reaction in Scheme 1, the rate in terms of decrease in concentration of bromate can be expressed as Eq. 5.

$$\text{Rate} = \frac{-\text{d}[\text{BrO}_3^-]}{\text{dt}} = kd[\text{Complex , C}] \cdots (6)$$

On the basis of the equilibrium step in Scheme 1,

$$[\text{Complex C}] = K_c Ke[\text{Vanillin}][\text{bromate}][\text{H}^+] \cdots (7)$$

In terms of total bromate concentration, rate can be represented as:

$$\text{Rate} = \frac{-\text{d}\,[\text{Br (V)}]_\text{T}}{\text{dt}} = kd[\text{Complex , C}]$$

$$\text{Rate} = \frac{-\text{d}\,[\text{Br (V)}]_\text{T}}{\text{dt}} = kdK_c Ke[\text{Vanillin}][\text{bromate}][\text{H}^+] \quad \cdots (8)$$

Since, bromate is present in complexed and uncomplexed forms, at any time the total concentration of bromate can be given as Eq. (9).

$$[\mathrm{Br(V)}]_T = [\mathrm{BrO_3^-}] + [\mathrm{Complex, C}] \cdots (9)$$

$$[\mathrm{Br(V)}]_T = [\mathrm{BrO_3^-}] + K_c Ke[\mathrm{Vanillin}][\mathrm{bromate}][\mathrm{H^+}] \cdots (10)$$

$$[\mathrm{Br(V)}]_T = [\mathrm{BrO_3^-}][1 + K_C Ke[\mathrm{Vanillin}][\mathrm{H^+}]] \cdots (11)$$

Therefore,

$$[\mathrm{BrO_3^-}] = \frac{[\mathrm{Br(V)}]_T}{1 + K_C Ke[\mathrm{Vanillin}][\mathrm{H^+}]} \qquad \cdots (12)$$

The rate law in terms of total bromate concentration can be given as

$$\mathrm{Rate} = \frac{-\mathrm{d}\,[\mathrm{BrO_3^-}]}{\mathrm{dt}} = \frac{kd\, K_C Ke[\mathrm{Vanillin}][\mathrm{H^+}][\mathrm{Br(V)}]_T}{1 + K_C Ke[\mathrm{Vanillin}][\mathrm{H^+}]} \qquad \cdots (13)$$

The rate law (Eq. 13) is in accordance with the observed experimental results, wherein a first-order dependence on [bromate], and fractional order each in [vanillin] and [$H_2SO_4$] was observed.

$$\frac{\mathrm{Rate}}{[\mathrm{Br(V)}]_T} = k = \frac{kd\, K_C Ke[\mathrm{Vanillin}][\mathrm{H^+}]}{1 + K_C Ke[\mathrm{Vanillin}][\mathrm{H^+}]} \qquad \cdots (14)$$

$$\frac{1}{k} = \frac{1}{kdK_C Ke[\mathrm{Vanillin}][\mathrm{H^+}]} + \frac{1}{kd} \cdots (15)$$

According to Eq. (15), other conditions being constant, 1/*k* versus 1 / [$H_2SO_4$] should be linear **Fig. 2b** with a definite intercept and the same was observed. Similarly, in line with Eq. (15), the plot of 1/*k* against 1/[Vanillin] (at constant [$H^+$] ) was linear with a definite intercept on the 1/*k* axis. Such an observation supports the validity of the rate law (Eq. 13) and hence the proposed reaction mechanism (Scheme 1). The proposed mechanism is further supported by the solvent influence on the reaction rate. The intermediate complex **C** is less polar than the reactants due to dispersal of charge and hence, decreasing polarity of the solvent media is expected to stabilize the complex **C** in preference to the reactants thereby enhancing the reaction rate. Such a solvent influence has actually been observed **Table 1**.

The Arrhenius plot of log *k* versus 1/T was a straight line. From the slope value of the straight line, the thermodynamic parameters of the reaction were calculated. The positive values of

free energy of activation $\Delta G^{\#}$ and enthalpy of activation, $\Delta H^{\#}$ in the present study indicated that transition state was highly solvated while negative value of entropy of activation, $\Delta S^{\#}$ suggested the formation of a rigid transition state with reduction of degree of freedom of molecules.

## CONCLUSION

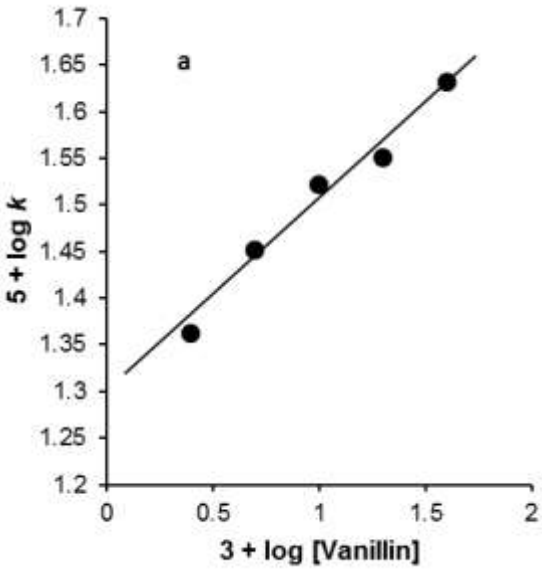
The kinetics of oxidation of vanillin by bromate has been investigated in sulphuric acid medium. The oxidation product was identified as vanillic acid by spectral and chemical analyses. The reaction was carried out at four different temperatures and the activation and thermodynamic parameters were evaluated. A plausible mechanism has been proposed to explain the experimental observations.

**Table -1 Dependence of rate on the factors influencing the oxidation of vanillin by bromate in acidic medium at 313 K**

| [Bromate] × $10^{-3}$ (mol $dm^{-3}$) | [Vanillin] × $10^{-2}$ (mol $dm^{-3}$) | [$H^+$] (mol $dm^{-3}$) | ($AcOH-H_2O$) (% v/v) | $k$× $10^4$ ($s^{-1}$) |
|---|---|---|---|---|
| **0.25** | 1.00 | 0.25 | 50-50 | 0.80 |
| **0.50** | 1.00 | 0.25 | 50-50 | 1.27 |
| **1.00** | 1.00 | 0.25 | 50-50 | 3.33 |
| **1.50** | 1.00 | 0.25 | 50-50 | 4.31 |
| **2.00** | 1.00 | 0.25 | 50-50 | 5.18 |
| **3.00** | 1.00 | 0.25 | 50-50 | 6.04 |
| 1.00 | **0.25** | 0.25 | 50-50 | 2.30 |
| 1.00 | **0.50** | 0.25 | 50-50 | 2.98 |
| 1.00 | **1.00** | 0.25 | 50-50 | 3.33 |
| 1.00 | **2.00** | 0.25 | 50-50 | 3.55 |
| 1.00 | **4.00** | 0.25 | 50-50 | 4.29 |
| 1.00 | 1.00 | **0.125** | 50-50 | 0.65 |
| 1.00 | 1.00 | **0.25** | 50-50 | 3.33 |
| 1.00 | 1.00 | **0.50** | 50-50 | 11.55 |
| 1.00 | 1.00 | **0.75** | 50-50 | 13.81 |
| 1.00 | 1.00 | **1.00** | 50-50 | 15.35 |
| 1.00 | 1.00 | **1.50** | 50-50 | 33.39 |
| 1.00 | 1.00 | 0.25 | 50-50 | 1.97 |
| 1.00 | 1.00 | 0.25 | 50-50 | 3.33 |
| 1.00 | 1.00 | 0.25 | 50-50 | 4.03 |
| 1.00 | 1.00 | 0.25 | 50-50 | 4.22 |
| 1.00 | 1.00 | 0.25 | **20-80** | 0.29 |
| 1.00 | 1.00 | 0.25 | **30-70** | 0.53 |
| 1.00 | 1.00 | 0.25 | **40-60** | 1.13 |
| 1.00 | 1.00 | 0.25 | **50-50** | 3.33 |
| 1.00 | 1.00 | 0.25 | **60-40** | 6.90 |

**Table -2 Effect of varying ionic strength in the oxidation of Vanillin by bromate in acidic medium at 313 K**

| $Na_2SO_4$ (mol $dm^{-3}$) | $k \times 10^4$ ($s^{-1}$) |
|---|---|
| $2.5\times10^{-2}$ | $1.35\times10^{-4}$ |
| $5.0\times10^{-2}$ | $1.38\times10^{-4}$ |
| $7.5\times10^{-2}$ | $1.38\times10^{-4}$ |
| $10.0\times10^{-2}$ | $1.34\times10^{-4}$ |
| $15.0\times10^{-2}$ | $1.32\times10^{-4}$ |
| [Bromate] = $1\times10^{-3}$ (mol $dm^{-3}$); [Vanillin] = $1\times 10^{-2}$ (mol $dm^{-3}$); [$H_2SO_4$] = 0.25 (mol $dm^{-3}$); [$Hg(OAc)_2$] = $5.0\times10^{-3}$ (mol $dm^{-3}$); [AcOH-$H_2O$] = 50-50( % v/v); Temp = 313 ±0.1 K . | |



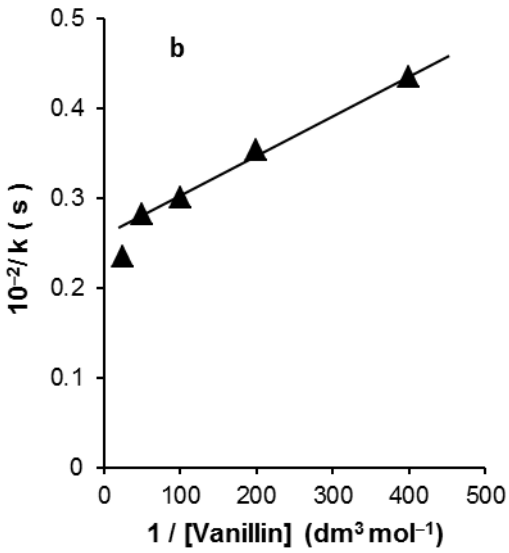
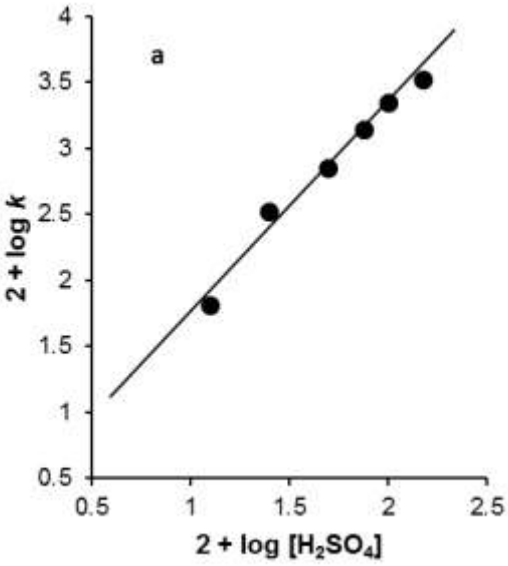




**Fig: 1a**: Plot of log *k* against log[Vanillin]

**Fig: 1b**: Plot of 1/*k* against 1/[Vanillin]



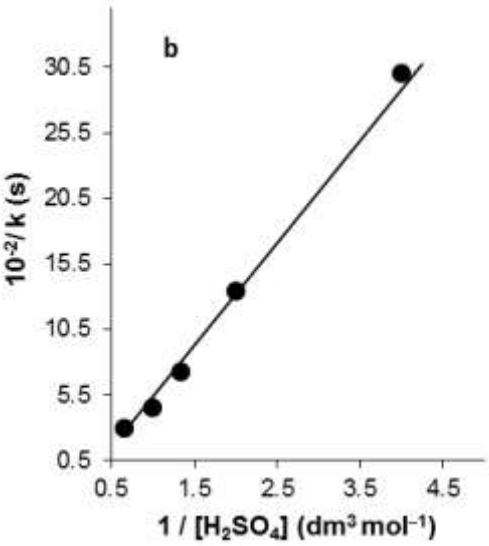




**Fig: 2a**: Plot of log *k* against log [$H_2SO_4$]

**Fig: 2b**: Plot of 1/*k* against 1/ [$H_2SO_4$]

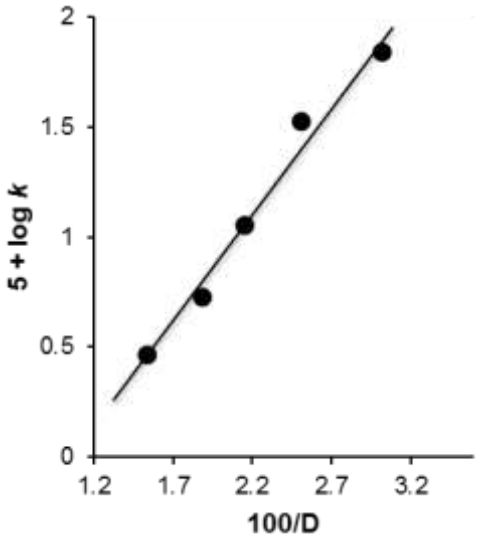



**Fig: 3**: Plot of log *k* against 1/D

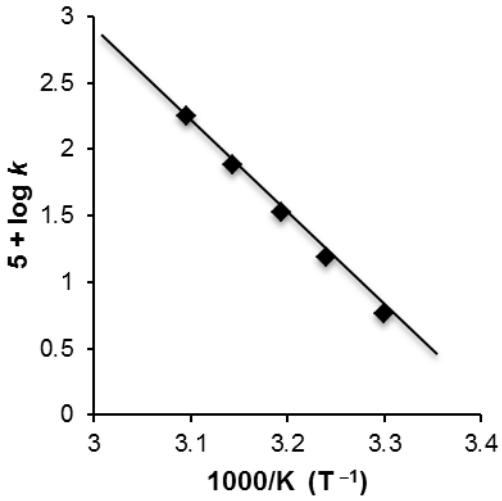



**Fig: 4**: Plot of log *k* versus 1/T

## ACKNOWLEDGEMENTS

The authors are thankful to the University Grants Commission, New Delhi, India, for the financial support in the form of Research Fellowship award (T. Sathish)

## REFERENCES

1. Janson, T., "In vitro studies of biological effects of cigarette smoking condensate. II. Introduction of sister-chromatid exchanges in human lymphocytes by weakly acidic semivolatile constituents ". Mutat. Res. 1986; 169: 129–139.
2. Davidson, P.M., Naidu, A.S., in: Naidu AS (Ed.), Phyto-phenols, Natural food antimicrobial Systems, CRC Press, USA, 2000. P. 265.
3. Makurub, M.I., "Toxicity of Vanillin" . Gig. Sanit. 1980; 6: 78–80.
4. Imoto, M., Maeda, T., Ouchi, T., "Studies of vinyl polymerization part 372 polymerization of methyl methacrylate initiated with vanillin". Chem. Lett. 1978; 2: 153–156.
5. Timy, P.J., Nandibewoor, S.T., Tuwar, S.M.,"Kinetics and Mechanism of the Oxidation of Vanillin by Hexacyanoferrate(III) in Aqueous Alkaline Medium".J. Solution Chem. 2006; 35:51–62.
6. Deepak, S.M., Chimatadar, S.A., Nandibewoor, S.T.,"Oxidation of vanillin by a new oxidant diperiodatoargentate(III) in aqueous alkaline medium". Ind. Eng. Chem. Res. 2007; 46: 1459–1464.
7. Mishra, P., "Kinetics and mechanism of oxidation of 4-hydroxy-3-methoxy benzaldehyde (Vanillin) by Bi(V) in aqueous alkaline medium". Int. J. Pharma. Tech. Res. 2009; 1: 1234–1240.

8. Kathari, C., Pol, P., Nandibewoor, S.T., "The kinetics and mechanism of oxidation of vanillin by diperiodatonickelate (IV) in aqueous alkaline medium". Turk. J. Chem. 2002; 26: 229–236.
9. Patil, D.G., Magdum, P.A., Nandibewoor, S.T.,"Mechanistic investigations of uncatalyzed and ruthenium(III) catalyzed oxidation of vanillin by periodate in aqueous alkaline medium".J. Solution Chem. 2015; 44: 1205–1223.
10. Satapathy, P.K., Baral, D.K., Aswar, A.S., Mohanty, P., "Kinetics and mechanism of oxidation of vanillin by Cerium(IV) in aqueous perchlorate medium. Indian J. Chem. Tech. 2013; 20: 271–275.
11. Kutti Rani, S., Nirmal Kumar, S., Crystal, Y. Wilson., Gopi, A., Easwaramoorthy, D., "Oxidation of vanillin by peroxomonosulphate thermodynamic and kinetic investigation". J. Ind. Eng. Chem. 2009; 15, 898–901.
12. Ahmed Fawzy, Ishaq, A., Zaafarny, Khalid, S. Khairou., Lalya, S. Almazroai, Badraiah, A., Al-jahdali, Tahani M. Bawazeer.,"Ruthenium(III)-Catalyzed Oxidation of Vanillin by Anticancer Hexachloroplatinate(IV) Complex in Perchloric Acid Solutions: A Kinetic Study". Am. J. Phys. Chem. 2016; 5(3): 56–64.
13. Furniss, B.S., Hannaford, A.J., Smith, P. W. G., Tatchell,A. R., Vogel's Text book of Practical Organic Chemistry. Fifth ed. LPE, Pearson Education: 2004.
14. Jonnalagadda, S.B., Chinake, C., Simoyi, R. H., "Kinetics and mechanism of the reaction between Thymol Blue and bromate in acidic medium". J. Chem. Soc. Faraday. Trans. 1995; 9: 1635–1640.
15. Desai, S. M., Hallligudi, N. N., Nandibewoor, S.T.,"Kinetics and mechanism of ruthenium(III)-catalysed oxidation of allyl alcohol by acid bromate-autocatalysis in catalysis". Transition Met. Chem.2002; 27(2): 207–212.
16. Sanjeeva Reddy, Ch., Sundaram, E.V., "Mechanism of acid bromate oxidation of trans mono-substituted cinnamic acids: structure reactivity correlation - a non-linear Hammett's plot". Tetrahedron.1989; 45: 2109– 2126.
17. Sanjeeva Reddy,Ch., Vijayakumar, T.,"Aquachlororuthenium(III) complex catalysis in the oxidation of malonic and methylmalonic acids by bromate in perchloric acid medium. Study of induction period and evaluation of individual kinetic parameters". Transition Met. Chem. 2007; 32: 246–256.
18. Ruoff, P., Varga, M., Koros, E., "How Bromate Oscillators Are Controlled". Acc. Chem. Res. 1988; 21: 326–332.

19. Zhabotinsky, A.M., "A history of chemical oscillations and waves". Chaos. 1991; 1: 379–386.
20. Onel, L., Bourceanu, G., Bitter, I.,Wittmann, M., Noszticzius, Z.,"Uncatalyzed reactions in the classical Belosov-Zhabotinsky System.2. The Malonic Acid-Bromate Reaciton in acidic media". J. Phys. Chem. A. 2006; 110(3):990– 996.
21. Nath, M.A., Rastogi, R.P., Perzada, G.M.,"Oscillatory behaviour of isomers of hydroxybenzoic acid with and without catalyst". J. Braz. Chem. Soc. 2009; 20:1–4.
22. Sanjeeva Reddy, Ch., Sunitha Manjari, P., "Homogeneous catalysis of Oxovanadium(IV) in the oxidation of substituted 4-oxoacids by bromate in acid medium: A mechanistic study". J. Mol. Catal A.2010; 328: 76–87.
23. Sanjeeva Reddy, Ch., Sunitha Manjari, P., "Mechanistic investigations on the manganese(II) catalyzed oxidation of substituted 4–oxo acids by bromate in aqueous sulphuric acid medium : Study of linear free–energy and isokinetic relationships".Trans. Met.Chem.2011; 36: 707–719.
24. Kennedy, J. F., Phillips G. O., P. A. Williams, P. A."Lignocellulosics Science, Technology, Development and Use". Ellis Horwood: New York; 1994: 635.
25. Bailar, J.C., "The chemistry of coordination compounds". Reinhold: New York; 1956: 14.
26. Kalyani, P., Ravi Teja, P., Sunitha Manjari, P., "Mechanistic Investigations of Oxidation of Vanillin by N-Bromosuccinimide-A Kinetic Approach". Der Pharma Chemica. 2018; 10(2): 128–133.
27. Indelli, A., Nolan Jr, G., Amis, E.S.," Salt effects in the reaction between bromate and iodide ions". J. Am. Chem. Soc. 1960; 82: 3233– 3236.
28. Anbar, M., Guttmann, S., "The catalytic effect of chloride ions on the isotopic oxygen exchange of nitric and bromic acids with water". J. Am. Chem. Soc. 1961; 83 (23) 4741–4745.
29. Wright, C. A., Barton, A. F. M., "Kinetics of bromate-iodide reaction:catalysis by acetate and other carboxylate ions". J. Chem. Soc. (A). 1968; 1747– 1750.
30. Rabai, Gy., Bazsa, Gy., Beck, M. T., "Kinetic investigation of the bromate-ascorbic acid-malonic acid system". Int. J. Chem. Kinet. 1981; 13 (12): 1277– 1288.
31. Alves, W. A., Tellez, C. A., Sala, S. O., Santos, P. S., Raria, R. B., " Dissociation and rate of proton transfer of $HXO_3$ (X=Cl, Br) in aqueous solution determined by Raman Spectroscopy". J. Raman Spectrosc. 2001; 32: 1032–1036.
32. Sigalla, J., "Reduction of bromate by halides and the mechanism of oxidation-reduction reactions". J. Chim. Phys. 1958; 55: 758– 767.

33. Hoering, T. C., Butler, R. C., Mc Donald, H. O., "The Oxygen exchange between Oxy-anions and water; Bromate and iodate ions". J. Am. Chem. Soc. 1956; 78 (19) : 4829– 4831.
34. Hoering, T. C., Ishimori, F. T., Mc Donald, H. O., "The Oxygen exchange between Oxy-anions and water. II. Chlorite, Chlorate and Perchlorate ions". J. Am. Chem. Soc. 1958; 80 (15): 3876– 3879.