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Research Article

OXIDATION OF VANILLIN BY IODATE IN AQUEOUS ACETIC ACID MEDIUM: A KINETIC AND MECHANISTIC STUDY

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ABSTRACT

The kinetics and mechanism of the oxidation of vanillin by iodate in aqueous acetic acid medium is studied. The reaction exhibits first order in [Iodate], fractional order in [vanillin] and [acid]. Variation of ionic strength had no effect on the reaction rate. Increase in the reaction rate by a decrease in the dielectric constant of the medium is observed. The reaction was studied at four different temperatures and the related activation and thermodynamic parameters were calculated. The product of oxidation was confirmed as vanillic acid by spectral analysis. Based on the results a plausible mechanism has been proposed and the appropriate rate law has been derived.

Keywords: Vanillin, Iodate, Kinetics, Mechanism.

1. INTRODUCTION

Vanilla is arguably the world's most popular flavour and is derived from mature pods of the orchid *Vanilla planifolia*. It constitutes one of the most preferred flavours and fragrance ingredients in ice-creams, confectioneries, milk products, perfumes, pharmaceuticals, liqueur and other cordial industries, thereby forming a whopping multimillion-dollar market [1]. For centuries vanilla flavour remained classified for the rest of the world since it was ascribed as a flavour of nobility by Aztecs and pre-Columbian Mayas. It was in 1519 that vanilla was exposed to the world with the Spanish invasion of the Aztecs. It was transported to Europe and subsequent development of hand pollination techniques led to its expansion to other parts of the world [2]. Today, Madagascar is the largest producer of natural vanilla with 75% of world production followed by Indonesia, China, Mexico, and Papua New Guinea. Vanilla is a mixture of ~ 200 compounds; however, it's characteristic flavour and fragrance comes mainly from the molecule vanillin [1]. Vanillin is a specialized metabolite and the main ingredient of vanilla extract that occurs in concertation of 1.0-2.0% w/w in cured vanilla beans [3]. Vanillin has different functional groups, like aldehyde, hydroxyl and ether attached to an aromatic ring. The physicochemical properties of vanillin are described in Table 1. Vanillin is either isolated from vanilla extract or is chemically synthesized from guaiacol. Besides being known for flavour and fragrance, it has diverse bioactive properties, namely anticancer, neuroprotective, antibiotic potentiation, and anti-quorum sensing [4-6]. Moreover, the bioactivities of curcumin are now attributed to the constituent and stable degradation products, i.e. vanillin and ferulic acid [7]. Though recent studies on vanillin have eluded to its bioactive potential, in comparison to curcumin the level of research activity is very limited.

Recently, there has been increasing research in the field of natural foods, specifically with respect to the additives such as flavouring agents and preservatives. Amidst the variety of flavouring agents of natural origin being used today, vanilla encompasses a prominent place in the market. It has been extensively used for the preparation of cakes, soft drinks, ice creams, chocolates, liquors, perfumes, pharmaceuticals, and nutraceuticals [8]. Natural vanilla is a concoction of components extracted from the cured pods of different Vanilla species: *Vanillus planifolia* and *Vanillus tahitensis* [9]. However, due to its pod quality and yield *V. planifolia* is valued the most [10].

Vanillin (4-hydroxy-3-methoxybenzaldehyde), commercially called *p*-vanillin (Van) occurs [11] in nature as a glucoside, which hydrolyses to vanillin and sugar. It is the major flavour component of natural vanilla. Vanillin 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 vapour pressure of 0.01599 Pa at

298 K indicates Vanillin will exist solely as a vapour in the ambient atmosphere. Vanillin displays antioxidant and antimicrobial properties and it may be used as a food preservative [12] and is also useful in the synthesis of drugs like Aldomet, L-Dopa [13] and Trimethaprim. It is also used in the preparation of perfume, metal-plating industries and as a catalyst in the polymerization of methyl methacrylate [14]. 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. Vanillin shows up in all sorts of products-in foods and flavouring, obviously but also in fragrances, cosmetics and aromatherapy.

Oxidation of Vanillin has been studied previously by few reagents such as hexacyanoferrate(III) [15], diperiodato-argentate(III) [16], bismuth(V) [17], diperiodato nickelate(IV) [18], periodate catalyzed by ruthenium(III) [19] in alkaline medium and by cerium(IV)[20], peroxomonosulphate [21], ruthenium(III) catalysed hexachloroplatinate (IV) [22], in acid medium.

Sodium or Potassium iodate is an inexpensive, innocuous, mild and selective oxidant. The chemistry of Iodate is quite interesting because of its ability to act as an oxidizing and iodinating reagent [23]. Iodate oxidations of organic and inorganic reactions usually involve complications such as an induction period [24], autocatalysis [25] and involvement of two reactions [26, 27]. Even iodate oxidations sometimes involve oscillation reactions [28-31]. The product of iodate oxidation is Iodide ion, which can be safely recycled; making Iodate oxidations environmentally benign compared to metal ion oxidations. Hence, the chemistry of Iodate 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 of Vanillin and a report has emanated from our laboratory [32, 33]. There seems to be no report on the mechanistic aspects of oxidation of Vanillin by Iodate. In this paper we report the kinetics of oxidation of Vanillin by Iodate 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 [34]. In the present study we aim to investigate thoroughly the kinetics and mechanism of oxidation of Vanillin by Iodate in sulphuric acid medium containing mercury (II), and to identify the active species of the substrate, oxidant and the oxidation products. We have also evaluated the kinetic and thermodynamic parameters of the reaction.

2. EXPERIMENTAL

2.1. Material and Methods

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. KIO_3 (BDH, AR), H_2SO_4 and $Hg(OAc)_2$ (Merck) were of analytical reagent grade and were used as received. Acetic acid (BDH) was purified by refluxing with chromic acid and acetic anhydride for 6 h and then distilled. Standard solutions were prepared with either double distilled water or purified acetic acid. 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 45°C and a UV detector working at 220 nm. The intermediates and the products were identified from their retention time (t_r).

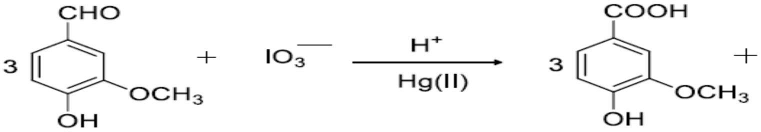
2.2. Kinetic measurements

All the kinetic measurements were carried out at constant temperature (±0.1°C) and performed under pseudo-first-order conditions with [Vanillin] >> [Iodate]. 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 [Iodate] 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 iodate 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.

2.3. Stoichiometry and product analysis

Different reaction mixtures with different sets of reactants containing various amounts of Iodate 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 Iodate was estimated iodometrically. The obtained results indicated that one mole of Iodate consumed three moles of Vanillin as represented by the equation 1.



(1)

The above stoichiometry is consistent with the results obtained by 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 [15-19, 32, 33]. The formation of 4-hydroxy-3-methoxy benzoic acid (Vanillic acid) was confirmed by its spot test and IR 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. Iodide ion was identified by adding $AgNO_3$ solution, resulting in the formation of yellow precipitate of silver iodide.

3. RESULTS AND DISCUSSION

3.1. Role of mercuric acetate

Mercury (II) acts as a homogeneous catalyst, co-catalyst and oxidant [24]. In the present study, mercury (II) acetate has been used as a scavenger for iodide ions (reduction product of KIO_3) which forms a complex, HgI_4^{2-} to prevent parallel oxidation of the substrate by the I_2, thus preventing complications in KIO_3 oxidation. The reaction has been carried out in the absence of KIO_3 and at constant concentration of all other reagents, the reaction did not occur thus ascertaining the non-involvement of mercuric acetate as an oxidant and confirming its role as scavenger of iodide ions. The added mercuric acetate over a wide concentration range (0.001-0.01 $mol.dm^{-3}$) had no effect on the rate of reaction. In order to keep back all the iodide ions formed, an optimum concentration (0.0025 $mol.dm^{-3}$) of mercuric acetate was employed.

3.2. Effect of concentration and kinetic runs

At fixed concentration of other reactants and when [vanillin] is in 10-fold excess over [Iodate], the effect of [Iodate] on the reaction rate was studied in the concentration range of 0.0005-0.002 mol dm^{-3}. The reaction follows first order with respect to [Iodate] as is evident from log [Iodate]t versus time plots and the pseudo-first order rate constants are found to be independent of initial iodate concentration (Table 1).

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 (0.52). 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, Iodate, and other conditions remaining constant, the reaction rate increased linearly with increase in $[H_2SO_4]$ and the order with respect to [acid] was found to be fractional (Table 1).

The effect of ionic strength of the medium on the reaction rate was studied using Na_2SO_4, with other experimental conditions held constant. The concentration of Na_2SO_4 at 0.025-0.150 mol dm^{-3} and the obtained rate constant values were constant suggesting no significant effect of ionic strength on the reaction rate; hence the ionic strength of the medium was not fixed at any constant value.

Table 1: Dependence of rate on the factors influencing the oxidation of Vanillin by Iodate in acidic medium at 313 K

[Iodate] ×10^{-4} (mol.dm^{-3})	**[Van] ×10^{-3}** (mol.dm^{-3})	**[H^+]** (mol.dm^{-3})	**Ac-OH: H_2O** (% v/v)	***k*** **×10^{-4}** (s^{-1})
5	10	0.25	50:50	1.06
7.5	10	0.25	50:50	1.05
10	10	0.25	50:50	1.05
15	10	0.25	50:50	1.06
20	10	0.25	50:50	1.05
10	**5**	0.25	50:50	0.71
10	**7.5**	0.25	50:50	0.96
10	**10**	0.25	50:50	1.05
10	**20**	0.25	50:50	1.45
10	**40**	0.25	50:50	2.63
10	**60**	0.25	50:50	2.90
10	**80**	0.25	50:50	3.32
10	10	**0.25**	50:50	1.05
10	10	**0.5**	50:50	1.89
10	10	**1**	50:50	2.14
10	10	**1.5**	50:50	3.05
10	10	**2**	50:50	4.33
10	10	0.25	**30:70**	0.53
10	10	0.25	**40:60**	0.81
10	10	0.25	**50:50**	1.05
10	10	0.25	**60:40**	6.9

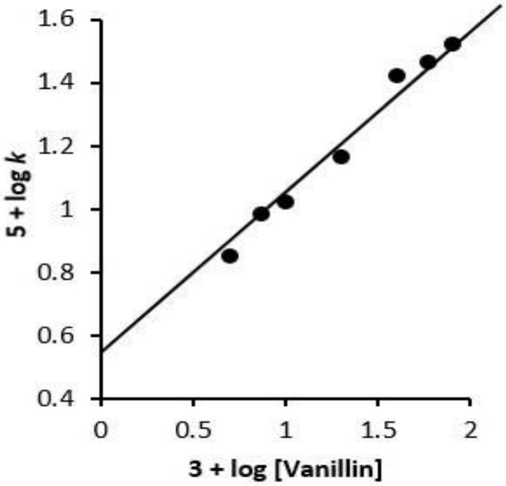


Fig. 1a: Plot of log *k* against log [Vanillin]

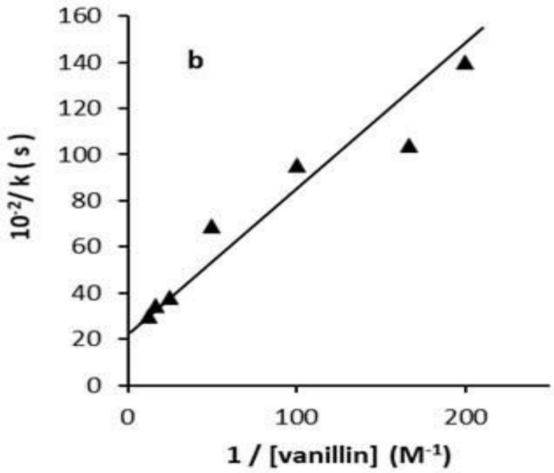


Fig. 1b: Plot of 1/*k* against 1/[Vanillin]

The dielectric constant (D) of the medium was varied using different proportions of acetic acid and water. The reaction rate decreased with an increase in dielectric constant of the medium (Table 1). Plots of log *k* versus 1/D was found to be linear with positive slope and log *k* against D-1/2D+1 (Fig. 2) was found to be linear. Blank experiments performed showed that acetic acid was not oxidized significantly by bromate under prevailing conditions.

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 0.05mol 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.

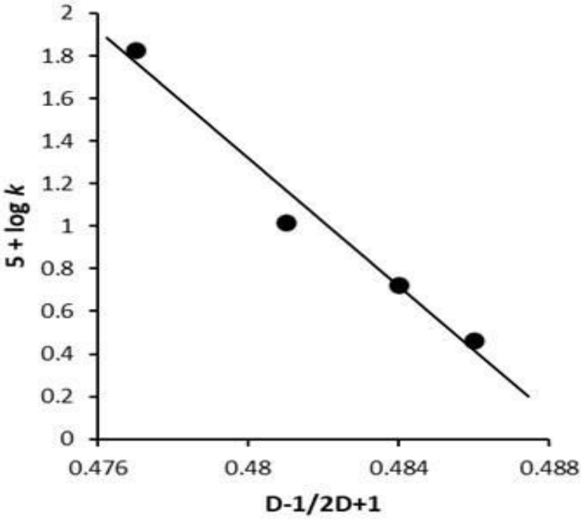


Fig. 2: Plot of log *k* against D-1/2D+1

The oxidation of vanillin was studied in the temperature range of 303-323 K and the evaluated rate constants, *k* (s^{-1}) are 0.25×10^{-4}, 0.77×10^{-4}, 1.05×10^{-4}, 1.54×10^{-4} and 3.12×10^{-4} at 303, 308, 313, 318 and 323 K respectively. The activation parameters evaluated from the slope of Arrhenius plot of log *k* versus 1/T (Fig. 3; $R^2 \geq 0.998$) are: Ea=61.27±1.5 kJ $mole^{-1}$,$\Delta H^{\ddagger}$= 58.66 ± 1.5 kJ $mole^{-1}$, $\Delta S^{\ddagger}$ = -61.27 J K^{-1} $mole^{-1}$, $\Delta G^{\ddagger}$ = 79.01 ± 1.2 k J $mole^{-1}$ at 313 K and at concentrations of [Iodate]=10×10^{-4}($mol.dm^{-3}$), [Vanillin] =10×10^{-3}($mol.dm^{-3}$), [H_2SO_4]=0.25($mol.dm^{-3}$), [Hg $(OAc)_2$]=2.5×10^{-4}($mol.dm^{-3}$) and [AcOH-H_2O]=50-50(% v/v).

Iodate exist as HIO_3 in the acidic medium [35] and the protonation of iodate ion, giving HIO_3 is known to be facile with a dissociation constant of 0.17 [36]. The present reaction between vanillin and Iodate in acid medium has a stoichiometry of 3:1 (Van: Iodate) with apparent order less than unity order in [Van] and first order in [Iodate]. As there is no influence of added salt on the reaction rate and a positive slope in the plot between log *k* and 1/D it suggests that the reaction is in between a positive ion and a dipole molecule or in between two dipole molecules. From the linear plot of log *k* versus D-1/2D+1, it is confirmed that the reaction is in between two dipole or neutral molecules and the negative slope of this plot suggests that the transition state is less polar than the reactants [37].

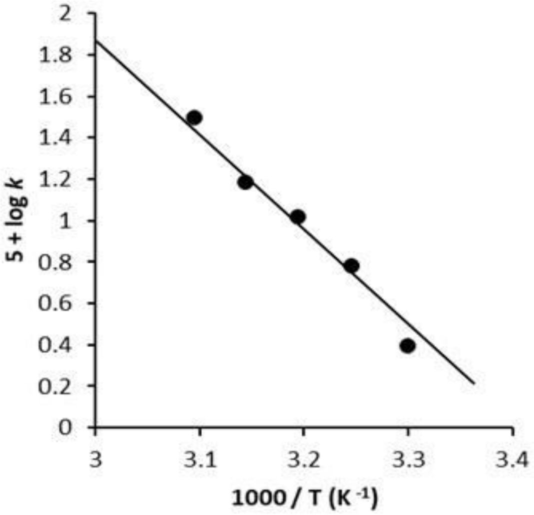
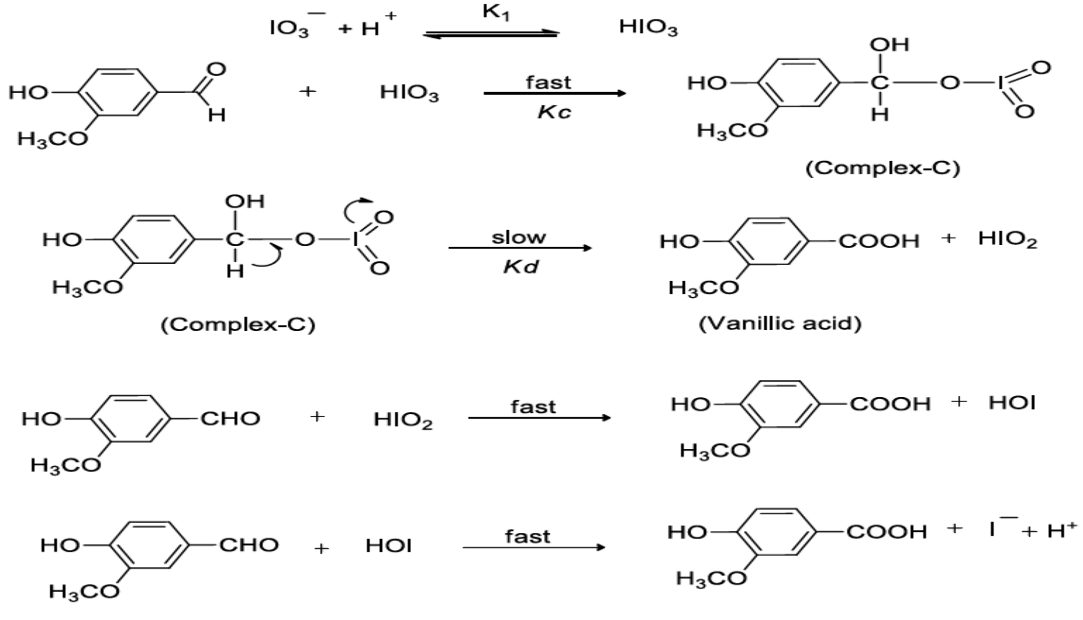


Fig. 3: Plot of log *k* versus 1/T



Scheme - 1

A definite intercept in the 1/*k* versus 1/[substrate] plot (Fig. 1b) suggests a complex formation between the substrate and the oxidant, prior to the rate determining step, thus confirming the Michaelis-Menten type kinetics. Based on the observed stoichiometry of the reaction and on the obtained experimental results, a plausible mechanism (Scheme 1) has been proposed which involves the reaction between the active species of iodate in acid medium, HIO_3 and vanillin in a fast pre-equilibrium step to give an intermediate complex (C). The decomposition of the complex (C) is the rate determining step resulting in the formation of Vanillic acid and Iodous acid (HIO_2) which subsequently reacts with vanillin and forms vanillic acid and Iodide ion (I^-). The formation of yellow precipitate of AgI (silver iodide) upon addition of silver nitrate confirms the formation of iodide ion, in accordance with the observed stoichiometry.

3.3. Rate law and its verification

On the basis of the reaction in Scheme-1, the rate in terms of decrease in concentration of Iodate can be expressed as in equation 5.

$$rate = -\frac{d[IO_3^-]}{dt} = \mathrm{k_d}[\mathrm{Complex, C}] \quad \dots(5)$$

On the basis of the equilibrium step in Scheme 1,

$$[Complex, C] = K_1 K_e [Van][IO_3^-][H^+] \quad \dots(6)$$

$$rate = -\frac{d[IO_3^-]}{dt} = k_d K_c K_1 [Van][IO_3^-][H^+]$$

In terms of total Iodate concentration given as

$$rate = -\frac{d[IO_3^-]_T}{dt} = k_d K_c K_1 [Van][IO_3^-][H^+] \quad \dots(7)$$

Since Iodate is present in complex and uncomplexed forms. Therefore, the total concentration of Iodate given as

$$[IO_3^-]_T = [IO_3^-] + [Complex, C]$$

$$[IO_3^-]_T = [IO_3^-] + K_c K_1 [Van][IO_3^-][H^+]$$

$$[IO_3^-]_T = [IO_3^-][1 + K_c K_1 [Van][H^+]]$$

$$[IO_3^-] = \frac{[IO_3^-]_T}{1 + K_c K_1 [Van][H^+]} \quad \dots(8)$$

The rate law in terms of total Iodate concentration can be given as equation (8) in equation (7)

$$rate = -\frac{d[IO_3^-]_T}{dt} = \frac{k_d K_c K_1 [Van][H^+][IO_3^-]_T}{1 + K_c K_1 [Van][H^+]} \quad \dots(9)$$

The rate law (in equation-9) is in accordance with the observed experimental results, wherein first order dependence on [Iodate] and fractional order dependence on both [Vanillin] and [acid] was observed. The rate law may be rearranged to equation 10 and 11 which are suitable for verification

$$\frac{rate}{[IO_3^-]_T} = k = \frac{k_d K_c K_1 [H^+][Van]}{1 + K_c K_1 [H^+][Van]} \quad \dots(10)$$

$$\frac{1}{k} = \frac{1}{k_d K_c K_1 [Van][H^+]} + \frac{1}{k_d} \quad \dots(11)$$

According to equation (11), the plot of 1/*k* versus 1/[H$^+$] (Fig. 4) (at constant [Van]) and the plot of 1/*k* against 1/[Vanillin] (at constant [H$^+$]) should be linear with a definite intercept on the 1/*k* axis. Such an observation supports the validity of the rate law (equation-9) and 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 fractional order (<1) dependence on [Vanillin] and a definite intercept in the 1/*k* versus 1/[Vanillin] plot (Fig. 1b) indicates that the substrate is involved in the complex formation with the oxidant.

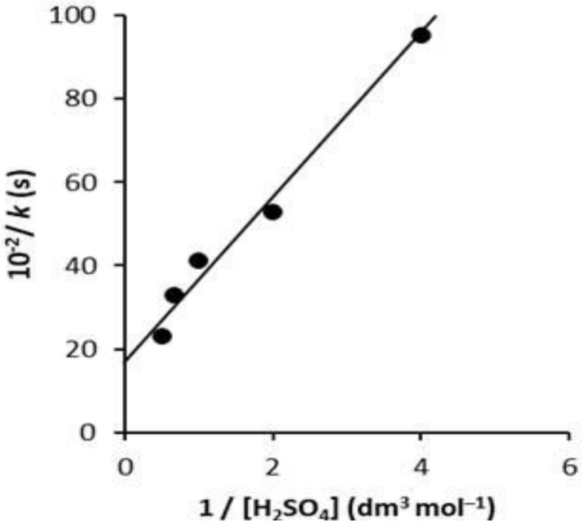


Fig. 4: Plot of 1/*k* against 1/ [H_2SO_4]

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

4. CONCLUSION

The kinetics of oxidation of Vanillin by Iodate 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.

5. ACKNOWLEDGEMENTS

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Conflict of interest

None declared

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