

Kinetics and Mechanism of Oxidation of Vanillin by Chromium(VI) in Sulfuric Acid Medium

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Abstract

The kinetics of oxidation of vanillin (VAN) by chromium(VI) in sulfuric acid medium was studied by a spectrophotometric technique. The reaction exhibited a first order dependence with respect to [Cr(VI)] and fractional-first orders with respect to [VAN] and [H⁺]. Varying ionic strength or dielectric constant of the reaction medium had no significant effect on the oxidation rate. The proposed mechanism includes an intermediate complex formation between vanillin and chromium(VI) before the rate-determining step. The final oxidation product of vanillin was identified by both spectral and chemical analysis as vanillic acid. The suitable rate law has been deduced. The reaction constants included in the various steps of the suggested mechanism have been evaluated. The activation parameters of the rate constant of the rate-determining step of the mechanism and the thermodynamic quantities of the equilibrium constant have been evaluated and discussed.

Keywords: Vanillin; Chromium(VI); Oxidation; Kinetics; Mechanism

Introduction

Vanillin is a phenolic aldehyde, which is an organic compound including aldehyde, hydroxyl and ether. It is the primary component of the extract of the vanilla bean. Vanillin is a significant flavoring reagent in the industry of food and is widely used in the production of drugs. It has been also used as a chemical intermediate in the preparation of pharmaceuticals and other fine chemicals. Furthermore, it is used in the synthesis of perfume and as a catalyst in various polymerization reactions. When the hydroxyl group in vanillin molecule is protected, vanillin is oxidized to vanillic acid [1]. Kinetics of oxidation of vanillin has been studied previously in alkaline solutions by different reagents, as hexacyanoferrate(III) [2], diperiodatoargentate(III) [3], bismuth(V) [4], diperiodatonickelate(IV) [5] and periodate catalyzed by ruthenium(III) [6], and in acid media by cerium(IV) [7].

Oxidation reactions are very important in nature and in organic synthesis. Among the most important oxidants is chromium(VI) which may play a significant role in the chemistry of vanillin in the environment due to the mutagenic and carcinogenic activity of chromium. Chromium exists in both trivalent, Cr(III), and hexavalent, Cr(VI), species in aqueous solutions and the two oxidation states are identified by various physical/chemical behavior and toxicity. Chromium(VI) compounds are very dangerous for biological systems, but those of chromium(III) are relatively non-toxic [8]. Chromium(VI) is employed for oxidation of organic compounds and it is reduced to lower oxidation states [9]. The chemistry of Cr(V) and Cr(IV) as intermediate species which may be formed during reduction of chromium(VI) were attracted many researchers because of their involvement in the mechanism of Cr-induced cancers [10].

A literature survey revealed that various literature are available on the kinetics of chromium(VI) oxidations of different inorganic [11-15] and organic [16-24] substrates, whereas there is no available reports on the oxidation of the vanillin by this oxidant. Owing to the above arguments, the title reaction has been studied. The objectives of the present investigation are to explore the selectivity of vanillin towards chromium(VI), to identify the oxidation products of vanillin and to suggest a suitable oxidation mechanism.

Experimental

Materials

All employed chemicals in the present work were Merck-Aldrich reagents and bidistilled water was used in the preparation of their solutions. Vanillin solution was prepared by dissolving the sample in bidistilled water. Required solution of Cr(VI) was freshly prepared by dissolving the requisite weight of potassium chromate sample in bidistilled water and standardized it spectrophotometrically.

Kinetic measurements

Kinetic runs were performed under pseudo-first order conditions (vanillin was presented in a large excess relative to Cr(VI) oxidant). The reaction was followed by monitoring the decay of Cr(VI) absorbance at $\lambda_{\max} = 350$ nm, its maximum absorption wavelength. Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer was used for all absorbance measurements with temperature controlling system.

First order plots were linear up to more than two half-lives of the reaction completion and the pseudo-first order rate constants (k_{obs}) have been calculated by the least-squares method using such plots. The kinetic runs were reproducible to within $\pm 2-3\%$. The reaction orders with respect to the reactants were calculated as the gradients of double logarithms plots between k_{obs} and concentration of vanillin substrate and sulfuric acid at fixed other conditions.

Results

Spectral changes

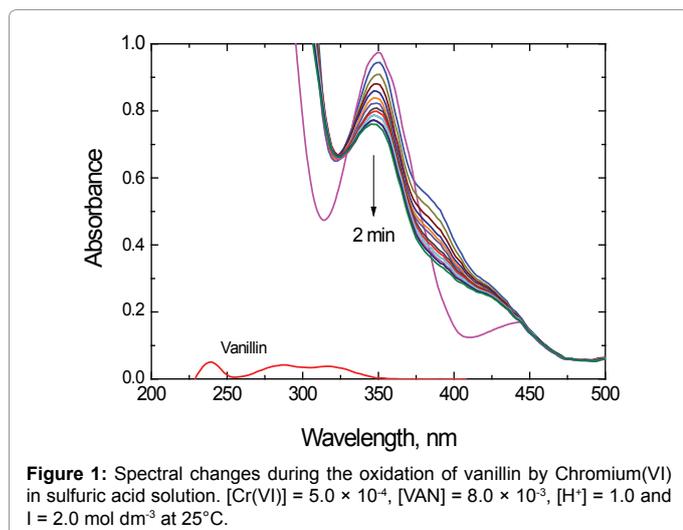
The spectral changes throughout the oxidation of vanillin by Cr(VI) in sulfuric acid medium are illustrated in Figure 1. The main

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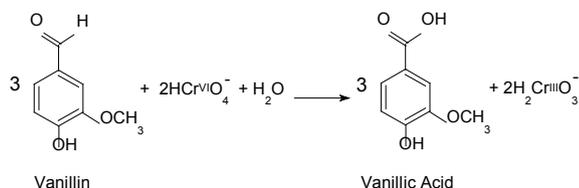
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characteristic feature in the scanned spectra was the gradual decay of Cr(VI) band with time at $\lambda = 350$ nm. Also, there was a change in the shape of spectra with appearance of an absorption band in the region of 370–400 nm.

Reaction stoichiometry

To determine the reaction stoichiometry, various reaction mixtures containing different ratios of Cr(VI) to the vanillin substrate were mixed at constant acidity, ionic strength and temperature then were kept for 12 hours in a dark place. The stoichiometry which was determined spectrophotometrically indicated consuming two moles of Cr(VI) for three mole of vanillin substrate to yield the oxidation products as shown in the following equation,



The oxidation product of vanillin was identified as the corresponding carboxylic acid (vanillic acid) by both spectral and chemical analyses as reported [25,26]. Similar oxidation product of vanillin has been also reported earlier [2,3].

Dependence of the oxidation rate on [chromium(VI)]

The effect of chromium(VI) concentration on the rate of reaction was studied by varying its concentration in the range of $(2.0\text{--}10.0) \times 10^{-4}$ mol dm⁻³ at fixed [VAN], [H⁺] and ionic strength. The obtained first order plots were found to be linear for more than two half-lives of the reaction completion. Also, the value of k_{obs} was independent of the initial [Cr(VI)] as listed in Table 1. The results indicated that the order of reaction with respect to [Cr(VI)] is confirmed to be one.

Dependence of the oxidation rate on [vanillin]

The value of k_{obs} was measured at various concentrations of the vanillin substrate at constant [Cr(VI)], [H⁺], ionic strength and temperature. The results showed that increasing vanillin concentration increased the oxidation rate. A plot of k_{obs} versus [VAN] was linear with a non-zero intercept (Figure 2) confirming that the reaction order with respect to [VAN] was less than unity.

Dependence of the oxidation rate on [acid]

The effect of [H⁺] on the oxidation rate was examined by carrying out the kinetic runs at various hydrogen ion concentration in the range $(0.4\text{--}1.9$ mol dm⁻³) while other variables were kept constant. Increasing acid concentration was found to increase the oxidation rate (Table 1). A plot of $\log k_{\text{obs}}$ versus $\log [\text{H}^+]$ was linear with a slope of 0.68 (Figure 3) confirming the fractional-first order dependence of the reaction with respect to [H⁺].

10^4 [Cr(VI)] (mol dm ⁻³)	10^3 [VAN] (mol dm ⁻³)	[H ⁺] (mol dm ⁻³)	I (mol dm ⁻³)	$10^5 k_{\text{obs}}$ (s ⁻¹)
2.0	8.0	1.0	2.0	14.7
3.0	8.0	1.0	2.0	15.1
4.0	8.0	1.0	2.0	16.0
5.0	8.0	1.0	2.0	15.2
6.0	8.0	1.0	2.0	14.8
8.0	8.0	1.0	2.0	15.6
10.0	8.0	1.0	2.0	14.9
5.0	2.0	1.0	2.0	4.9
5.0	4.0	1.0	2.0	8.8
5.0	6.0	1.0	2.0	12.2
5.0	8.0	1.0	2.0	15.2
5.0	10.0	1.0	2.0	19.0
5.0	12.0	1.0	2.0	20.9
5.0	14.0	1.0	2.0	24.3
5.0	8.0	0.4	2.0	8.1
5.0	8.0	0.6	2.0	11.0
5.0	8.0	0.8	2.0	13.2
5.0	8.0	1.0	2.0	15.2
5.0	8.0	1.3	2.0	18.1
5.0	8.0	1.6	2.0	21.2
5.0	8.0	1.9	2.0	23.6
5.0	8.0	1.0	2.0	15.2
5.0	8.0	1.0	2.3	15.7
5.0	8.0	1.0	2.6	16.4
5.0	8.0	1.0	3.0	15.9
5.0	8.0	1.0	3.3	16.2
5.0	8.0	1.0	3.6	17.1
5.0	8.0	1.0	4.0	16.4

Experimental error $\pm 3\%$

Table 1: Effect of variation of [Cr(VI)], [VAN], [H⁺] and ionic strength (I) on the observed first order rate constant k_{obs} in the oxidation of vanillin by chromium(VI) in sulfuric acid solution at 25°C.

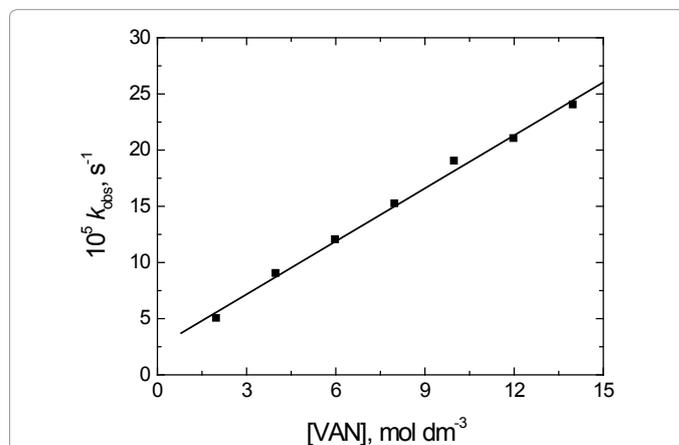
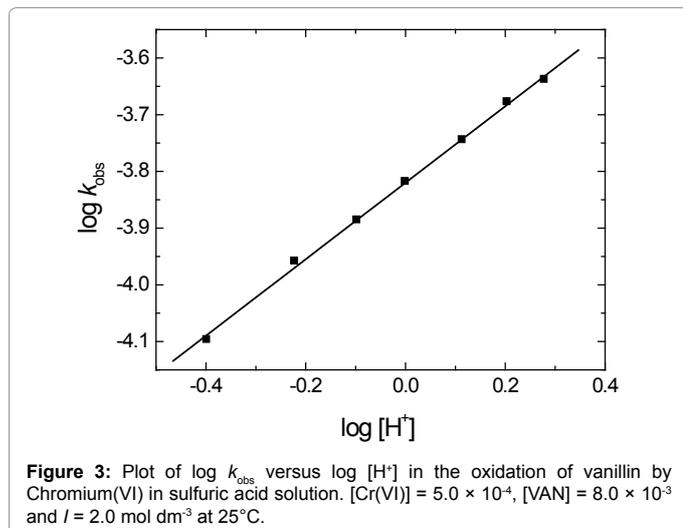


Figure 2: Effect of variation of [VAN] on the observed first order rate constant k_{obs} in the oxidation of vanillin by Chromium(VI) in sulfuric acid solution. [Cr(VI)] = 5.0×10^{-4} , [H⁺] = 1.0 and I = 2.0 mol dm⁻³ at 25°C.



Dependence of the oxidation rate on the ionic strength and dielectric constant

The ionic strength was varied from 2.0 to 4.0 mol dm^{-3} using sodium sulfate at constant $[VAN]$, $[Cr(VI)]$ and $[H^+]$. Increasing the ionic strength had a negligible effect on the reaction rate (Table 1). The effect of the dielectric constant (D) of the reaction medium on the oxidation rate has been investigated at different solvent compositions of acetic acid and water in the reaction medium. As for ionic strength, changing dielectric constant of the medium did not affect the reaction rate.

Dependence of the oxidation rate on [manganese(II)]

To explore the involvement of chromium(IV) as an intermediate species of chromium in the oxidation reaction, various concentrations of Mn(II) ion have been added to the reaction medium. The results showed that the oxidation rate decreased with increasing $[Mn(II)]$ as illustrated in Figure 4.

Dependence of the oxidation rate on temperature

The oxidation rate was measured at five temperatures, namely, 293, 298, 303, 308 and 313 K with varying both $[VAN]$ and $[H^+]$. The oxidation rate increased with raising temperature. The activation parameters of the rate constant of the rate-determining step (k_1) and the thermodynamic quantities of the equilibrium constants involved in the oxidation mechanism (K_1 and K_2) were calculated and listed in Tables 2 and 3.

Polymerization test for free radical intermediate

Intervention of free radicals during the oxidation reaction was examined by the polymerization test where a known quantity of acrylonitrile was added to the partially oxidized reaction mixture and kept for about 4 h in an inert atmosphere. On diluting the reaction mixture with methanol, no white precipitate was formed thus confirming the absence of free radical in the oxidation reaction.

Discussion

It has been reported [27] that, in redox reactions including Cr(VI) oxidant in acid media, there are two suggested reaction mechanisms for electron transfer, the first one was proposed to involve a successive one-electron transfer in two steps. The second suggested one was a simultaneous two-electron transfer in a single step. Both mechanisms may be considered during reduction of Cr(VI) to form either Cr(V) or

Cr(IV) species, respectively [28-30]. In the present investigation, the negative result of free radical intervention excluded formation of Cr(V) species. On the other hand, the involvement of Cr(IV) species in the reaction can be proved by decreasing the oxidation rate upon addition of manganese(II) to the reaction medium. This is because Mn(II) has been recognized as a frequently tool for trapping Cr(IV) intermediate species [31]. Therefore, if Cr(IV) species was involved, addition of Mn(II) to the reaction will remove it from the reaction resulting in a decrease in the oxidation rate according to the equation, $Cr(IV) + Mn(II) = Cr(III) + Mn(III)$. The observed decrease in the oxidation rate upon addition of Mn(II) (Figure 4) is considered as a good evidence to the contribution of Cr(IV). The inhibition effect occurs due to the competition existing between the substrate and Mn(II) to react with Cr(IV).

On the other hand, chromium(VI) was suggested [32,33] to exist in aqueous acid media mainly as acid chromate, H_2CrO_4 , as represented by the first step in Scheme 1. Increasing the oxidation rate upon increasing $[H^+]$ suggested the protolytic process of the chromate ion, i.e., the protonated species of the chromate oxidant (H_2CrO_4) may be considered as the kinetically reactive species which play the main role in the oxidation kinetics.

Rate Constant (s^{-1})	Temperature (K)					Activation parameters			
	288	293	298	303	308	ΔS^\ddagger ($Jmol^{-1}K^{-1}$)	ΔH^\ddagger ($kJ mol^{-1}$)	ΔG^\ddagger_{298} ($kJ mol^{-1}$)	E_a^\ddagger ($kJ mol^{-1}$)
$10^4 k_1$	4.61	5.82	7.50	9.82	12.19	-106.71	33.98	65.78	35.57

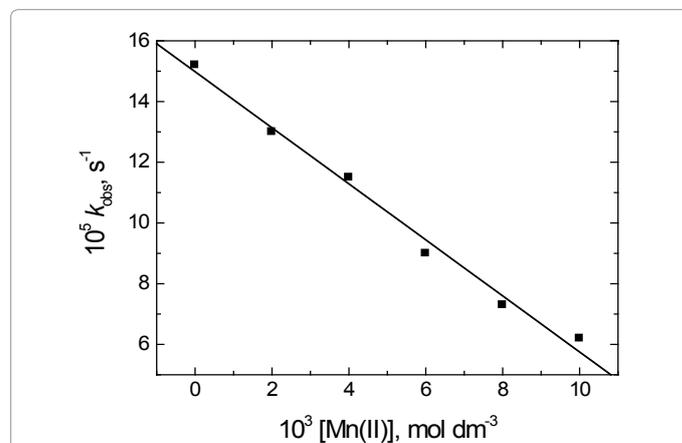
Experimental error $\pm 4\%$

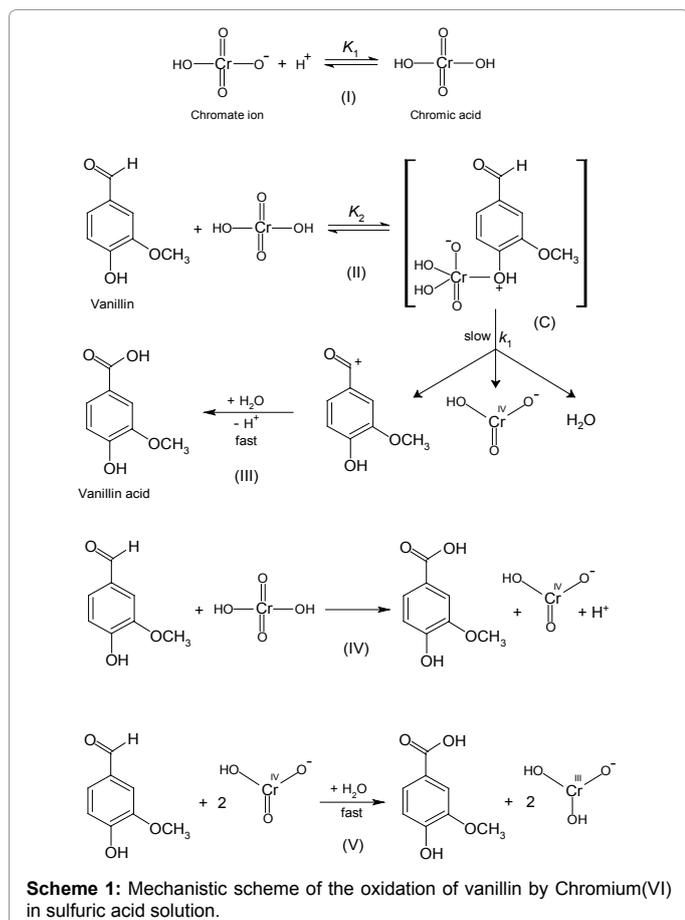
Table 2: Values of the rate constant of the slow step (k_1) at different temperatures and its associated activation parameters in the oxidation of vanillin by Chromium(VI) in sulfuric acid solution.

Equilibrium constant ($dm^3 mol^{-1}$)	Temperature (K)					Thermodynamic parameters		
	293	298	303	308	313	ΔH° ($kJ mol^{-1}$)	ΔG°_{298} ($kJ mol^{-1}$)	ΔS° ($Jmol^{-1}K^{-1}$)
$10^2 K_1$	8.37	10.77	12.72	16.41	21.09	35.51	5.69	-100.38
$10^2 K_2$	6.53	5.46	4.73	3.35	2.84	-33.42	-15.61	-59.77

Experimental error $\pm 3\%$

Table 3: Values of the equilibrium constants (K_1 and K_2) at different temperatures and their thermodynamic quantities in the oxidation of vanillin by Chromium(VI) in sulfuric acid solution.





The present reaction between chromium(VI) and vanillin in H_2SO_4 solution showed a stoichiometry of 3:2 (VAN : Cr(VI)) with a first order dependence with respect to [Cr(VI)] and a less than unit order dependence with respect to [VAN]. The less than unit order dependence on vanillin concentration can be attributed to complex formation between vanillin and chromium(VI) in a pre-equilibrium step. The formation of the complex was also proved kinetically [34] by a non-zero intercept of the plot of $1/k_{obs}$ versus $1/[VAN]$ as shown in Figure 5. Further evidence for complex formation was obtained from the UV-Vis spectra as shown in Figure 1. The complex formation between chromium(VI) and different organic compounds in acid media was also reported [16-19,35,36]. Furthermore, the negligible effects of both ionic strength and dielectric constant of the medium were consistent with a reaction occurs between two neutral molecules [37-39] i.e., between vanillin and H_2CrO_4 .

Based on the forgoing aspects, the most reasonable reaction mechanism which may be suggested (Scheme 1), involves a fast complexation between the vanillin substrate and the kinetically active chromium(VI) species (H_2CrO_4), step (II), to give an intermediate complex (C). The latter was slowly decomposed in the rate-determining step followed by subsequent fast steps, (III) - (V), to give rise to the final oxidation products.

The suggested mechanistic Scheme 1 leads to the following rate law expression (Appendix A),

$$\text{Rate} = \frac{k_1 K_1 K_2 [HCrO_4^-] [VAN] [H^+]}{1 + K_1 [H^+] + K_1 K_2 [VAN] [H^+]} \quad (1)$$

Under pseudo-first order condition,

$$\text{Rate} = \frac{-d[HCrO_4^-]}{dt} = k_{obs} [HCrO_4^-] \quad (2)$$

Comparison of Eq. (1) and (2) gives,

$$k_{obs} = \frac{k_1 K_1 K_2 [VAN] [H^+]}{1 + K_1 [H^+] + K_1 K_2 [VAN] [H^+]} \quad (3)$$

and with rearrangement of Eq. (3) leads to the following equations,

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1 [H^+]}{k_1 K_1 K_2 [H^+]} \right) \frac{1}{[VAN]} + \frac{1}{k_1} \quad (4)$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1 K_1 K_2 [VAN]} \right) \frac{1}{[H^+]} + \left(\frac{1}{k_1 K_2 [VAN]} + \frac{1}{k_1} \right) \quad (5)$$

According to Eq. (4) and (5), the plots of $1/k_{obs}$ versus $1/[VAN]$ at constant $[H^+]$ and $1/k_{obs}$ versus $1/[H^+]$ at constant $[VAN]$ should give straight lines with positive intercepts on the $1/k_{obs}$ axes, as were experimentally observed (Figures 5 and 6 respectively). Values of the rate constant of the slow step (k_1) along with the equilibrium constants K_1 and K_2 at different temperatures were calculated from the slopes and

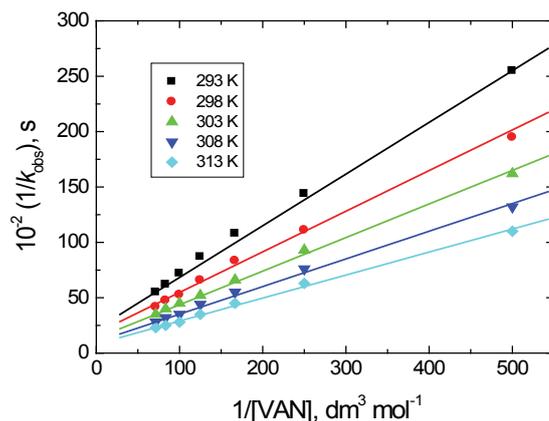


Figure 5: Plots of $1/k_{obs}$ versus $1/[VAN]$ at different temperatures in the oxidation of vanillin by Chromium(VI) in sulfuric acid solution. $[Cr(VI)] = 5.0 \times 10^{-4}$, $[H^+] = 1.0$ and $I = 2.0$ mol dm^{-3} .

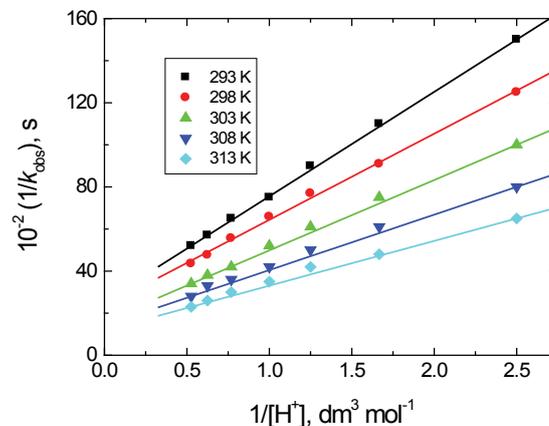


Figure 6: Plots of $1/k_{obs}$ versus $1/[H^+]$ at different temperatures in the oxidation of vanillin by Chromium(VI) in sulfuric acid solutions. $[Cr(VI)] = 5.0 \times 10^{-4}$, $[VAN] = 8.0 \times 10^{-3}$ and $I = 2.0$ mol dm^{-3} .

intercepts of such plots and were listed in Tables 2 and 3, respectively. The obtained values of the protonation constant of mono hydrogen chromate (K_1) are in agreement with those reported in the literature [40,41].

The activation parameters of the rate constants of the rate-determining step (k_1) are calculated using Arrhenius and Eyring plots, and were listed in Table 2. Also, the thermodynamic quantities of the equilibrium constants were determined using van't Hoff plots and were listed in Table 3.

The obtained large negative values of ΔS^\ddagger are consistent with the formation of compacted intermediate complex of inner-sphere nature [42,43]. The experimental values of ΔH^\ddagger and ΔS^\ddagger were both favorable for electron-transfer process [44]. Again, the positive values of ΔH^\ddagger and ΔG^\ddagger indicate endothermic formation of the intermediate and its non-spontaneity, respectively.

Conclusions

The kinetics of oxidation of vanillin by chromium(VI) has been investigated in sulfuric acid solutions. H_2CrO_4 is suggested to be the kinetically active species of the oxidant which takes part in the oxidation reaction. The final oxidation product of vanillin was identified as vanillic acid. The rate and equilibrium constants involved in the different steps of the proposed mechanism along with their activation and thermodynamic parameters were evaluated and discussed.

Appendix A

Derivation of the rate law expression:

According to the suggested mechanistic Scheme 1,

$$K_1 = \frac{[H_2CrO_4]}{[HCrO_4^-][H^+]}, [H_2CrO_4] = K_1[HCrO_4^-][H^+] \quad (A.1)$$

$$\text{and } K_2 = \frac{[C]}{[VAN][H_2CrO_4]},$$

$$[C] = K_2[VAN][H_2CrO_4] = K_1K_2[VAN][HCrO_4^-][H^+] \quad (A.2)$$

From step (III) in Scheme 1, the rate law expression can be expressed by Eq. (A.3),

$$\text{Rate} = \frac{-d[HCrO_4^-]}{dt} = k_1[C] \quad (A.3)$$

Substituting Eq. (A.2) into Eq. (A.3) leads to,

$$\text{Rate} = k_1K_1K_2[VAN][HCrO_4^-][H^+] \quad (A.4)$$

The total concentration of $HCrO_4^-$ is given by,

$$[HCrO_4^-]_T = [HCrO_4^-]_F + [H_2CrO_4] + [C] \quad (A.5)$$

Where 'T' and 'F' stand for total and free.

Substituting Eq. (A.1) into Eq. (A.5) gives,

$$[HCrO_4^-]_T = [HCrO_4^-]_F + K_1[HCrO_4^-][H^+] + K_1K_2[VAN][HCrO_4^-][H^+] \quad (A.6)$$

$$[HCrO_4^-]_T = [HCrO_4^-]_F(1 + K_1[H^+] + K_1K_2[VAN][H^+]) \quad (A.7)$$

Therefore,

$$[HCrO_4^-]_F = \frac{[HCrO_4^-]_T}{1 + K_1[H^+] + K_1K_2[VAN][H^+]} \quad (A.8)$$

Also, the total concentration of vanillin is given by,

$$[VAN]_T = [VAN]_F + [C] = [VAN]_F + K_1K_2[VAN][HCrO_4^-][H^+] \quad (A.9)$$

Therefore,

$$[VAN]_F = \frac{[VAN]_T}{1 + K_1K_2[HCrO_4^-][H^+]} \quad (A.10)$$

Because of low concentration of $HCrO_4^-$ used, the term $K_1K_2[HCrO_4^-][H^+]$ in the denominator can be neglected. Hence,

$$[VAN]_F = [VAN]_T \quad (A.11)$$

In view of the high concentrations of $[H^+]$ we can write,

$$[H^+]_F = [H^+]_T \quad (A.12)$$

Substituting Eq. (A.8), (A.11) and (A.12) into Eq. (A.4) (and omitting 'T' and 'F' subscripts) gives,

$$\text{Rate} = \frac{k_1K_1K_2[HCrO_4^-][VAN][H^+]}{1 + K_1[H^+] + K_1K_2[VAN][H^+]} \quad (A.13)$$

Under pseudo-first order condition,

$$\text{Rate} = \frac{-d[HCrO_4^-]}{dt} = k_{obs}[HCrO_4^-] \quad (A.14)$$

Comparing Eqs. (A.13) and (A.14), the following relationship is obtained,

$$k_{obs} = \frac{k_1K_1K_2[VAN][H^+]}{1 + K_1[H^+] + K_1K_2[VAN][H^+]} \quad (A.15)$$

and with rearrangement, the following equations are obtained,

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1[H^+]}{k_1K_1K_2[H^+]} \right) \frac{1}{[VAN]} + \frac{1}{k_1} \quad (A.16)$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1K_1K_2[VAN]} \right) \frac{1}{[H^+]} + \frac{1}{k_1K_2[VAN]} + \frac{1}{k_1} \quad (A.17)$$

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