Kinetics and mechanism of oxidation of vanillin by Cerium(IV) in aqueous perchlorate medium

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The oxidation reaction of vanillin with cerium (IV) in perchloric acid medium has been studied spectrophotometrically over the range \(5.0 \leq [\text{Vanillin}]_T \leq 25.0\); \(0.3 \leq [\text{H}^+]_T \leq 0.8\); \(I = 1.0 \text{ mol dm}^{-3} (\text{NaClO}_4)\) and \(293 \leq T \leq 308\text{K}\). The rate of the reaction has been found to increase with the increase in \([\text{H}^+]_T\) and \([\text{Vanillin}]_T\). The reaction follows first order kinetics with respect to each \([\text{Ce(IV)}]_T\), \([\text{Vanillin}]_T\) and fractional order with respect to \([\text{H}^+]_T\). The reaction proceeds in two paths and the values of \(k_1\) and \(k_2\) have been calculated using a suitable rate law. The \(\Delta H^\# \text{(kJ mol}^{-1}\)) for \(k_1\) and \(k_2\) paths are \(3.45 \pm 0.24\) & \(43.61 \pm 2.49\) and \(\Delta S^\# \text{(JK}^{-1} \text{mol}^{-1})\) for \(k_1\) and \(k_2\) paths are \(-247.81 \pm 0.81\) & \(-141.23 \pm 8.26\) respectively. High negative value of activation entropy is indicative of ordered transition state for the reaction. The product of the reaction has been found to be 4-hydroxy-3-methoxybenzoic acid.

Keywords: Cerium(IV), Kinetic study, Oxidation reaction, Perchlorate medium, Vanillin

Cerium(IV) is an unusually strong one electron oxidant in perchlorate medium. Ceric salts in various acidic solutions have been widely utilized for the oxidation of organic as well as inorganic compounds\(^1-8\). In some cases, the mechanistic approach has been based on the intermediate complex formation, while in others the results have been interpreted by free radical mechanism. Sometimes, the anionic species present in the reaction have been considered responsible for deciding the cationic species of cerium(IV). The mechanisms suggested by various authors are not uniform, indicating that wide varieties of mechanism are possible depending upon the nature of cationic oxidant species as well as the various conditions for the reaction.

Vanillin is a very popular flavoring reagent in the food industry and widely used in the synthesis of drugs; 40% of vanillin is consumed in manufacturing drugs like L-Dopa, Aldomet and Trimethaprin. It is also used in the preparation of perfume and as a catalyst to polymerise methacrylate. It has both phenolic and aldehyde groups and is capable of undergoing oxidation differently. 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\(^9\). It is known that the oxidation reactions are complicated and that the vanillin is oxidized to various products depending on the nature of oxidant.

When vanillin was oxidized using HClO\(_2\)\(^{10}\) or ClO\(_2\)\(^{11}\), the product of the reaction was 4-formyl-5-methoxycarbonylpenta-2,4-dienoic acid; with H\(_2\)O\(_2\) as oxidants\(^{12-14}\), the product was 2-methoxy quinine; with BaMnO\(_4\)\(^{15}\), or DPN\(^{16}\), the product was 4-hydroxy-3-methoxy benzoic acid; and with Fe(CN)\(_6\)\(^3-\) or FeCl\(_3\)\(^{17}\), the product was dimeric vanillin.

In order to explore the mechanistic aspects of Ce(IV) oxidation in perchlorate medium with vanillin as a substrate the current study has been carried out. The purpose of the study is to investigate the redox chemistry of Ce(IV) in the perchloric acid medium to provide further information on the redox properties of the model related to lignin as well as on the mechanism of reaction.

Experimental Procedure

Materials

The stock solution of cerium(IV) in HClO\(_4\) was prepared by dissolving ceric ammonium nitrate (B.D.H) in aqueous perchlorate acid (70%). The acid strength of the stock solution was determined by Mc Auley’s method\(^{18}\). The stock solution of vanillin (Aldrich) was prepared by dissolving vanillin in glacial acetic acid medium (1:1). Acidic solution was used due to the low...
solubility of vanillin in water. The solution remains stable over a few weeks when stored in the dark at low temperature. All laboratory chemicals were of analytical grade and used without purification. The hydrogen ion concentration of the solution was adjusted by adding HClO. Double distilled water was used throughout the reaction. During kinetic investigation, a constant ionic strength ($I = 1.0$ mol dm$^{-3}$ NaClO$_4$) was maintained. [H$^+$)$_r$ was maintained by the addition of HClO$_4$ and its amount present with Ce(IV). Absorbance was recorded with a Cecil CE-7200 UV-Visible spectrophotometer equipped with CE 2024 thermostatic controller. Ten-millimeter quartz suprasil cuvettes were used. IR spectra were recorded in a FTIR-2000-104 FTIR ABB Bomen (Canada) spectrophotometer.

**Kinetic studies**

For the kinetic experiments, the ionic strength was maintained with NaClO$_4$ solution. The solution of vanillin at the desired [H$^+$] was thermally equilibrated at a given temperature. Then the required amount of thermally equilibrated cerium(IV) solution was added to the vanillin solution at 303K and the change in absorbance was monitored at 370 nm. Pseudo-first-order conditions were maintained throughout these experiments by using a large excess of vanillin. [Cerium(IV)] : [Vanillin] used was 1:5, 1:10, 1:15, 1:20 and 1:25. The rate constants ($k_{obs}$) values were obtained from the slopes of –ln($A_t - A_e$) versus time plots, as shown below:

$$-\ln(A_t - A_e) = k_{obs}t + C \quad \ldots \ldots (1)$$

where $A_t$ and $A_e$ are the absorbance of the reaction mixture at time ‘t’ and at equilibrium respectively. The reported rate data are an average of duplicate runs and are reproducible to within ± 3%. The correlation coefficient of plots used to determine $k_{obs}$ is found to be 0.99 in most of the cases.

**Stoichiometry**

The oxidation of vanillin was found to proceed by the 1:2 stoichiometry, as shown below:

\[
\begin{align*}
\text{4-hydroxy-3-methoxy benzaldehyde} & \quad + 2\text{Ce}^{4+} + \text{H}_2\text{O} & \rightarrow & \quad \text{4-hydroxy-3-methoxy benzoic acid} + 2\text{Ce}^{3+} + 2\text{H}^+ \\
\end{align*}
\]

$$\ldots \ldots (2)$$

The formation of 4-hydroxy-3-methoxy benzoic acid was confirmed by IR. data. The major peaks of the product appear at 3429.05, 1651.88 and 2072.98 cm$^{-1}$. The yield was about 80%. The formation of Ce(III) can be followed using UV spectroscopy by studying the decrease of absorbance at 370 nm ($\lambda_{max}$ of Ce$^{4+}$) in an experiment with slight excess of vanillin.

**Product characterization**

In order to get the reaction product, cerium(IV) and vanillin were mixed in 1:10 molar ratio at [H$^+$] = 0.3 mol dm$^{-3}$. The solution was heated in a water bath for about 1h. Then the solution was left for evaporation at room temperature in vacuum desiccator for few days. Fine green colored crystals appeared which were washed with ethanol to remove the excess of vanillin and finally dried in a desiccator.

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.

**Results and Discussion**

**Effect of [Cerium(IV)] on the rate**

In the first set of kinetic experiments, [Ce(IV)]$_r$ was varied from $9.84 \times 10^{-4}$ to $29.52 \times 10^{-4}$ mol dm$^{-3}$ at fixed excess concentration of vanillin (20.0 $\times$ 10$^{-3}$ mol dm$^{-3}$), [H$^+$] = 0.3 mol dm$^{-3}$, $T$ = 303K and ionic strength; $I$ = 1.0 mol dm$^{-3}$ (NaClO$_4$). The pseudo-first-order plots are found to be linear ($r^2 = 0.99$) in each case giving $k_{obs} \times 10^4$ (s$^{-1}$) = 2.76 ± 0.06. The independence of $k_{obs}$ at 303K under the condition [Vanillin]$_r$ = 20 $\times$ 10$^{-3}$ mol dm$^{-3}$, [H$^+$] = 0.3 mol dm$^{-3}$, $I$ = 1.0 mol dm$^{-3}$ (NaClO$_4$) over the [Ce(IV)] range from $9.84 \times 10^{-4}$ to $29.52 \times 10^{-4}$ mol dm$^{-3}$ is in agreement with first order dependence in [Ce(IV)]$_r$. As the order of the reaction is one with respect to [Ce(IV)]$_r$, the rate law is given by the following equation:

$$\text{Rate} = k_{obs} [\text{Ce(IV)}]_r \quad \ldots \ldots (3)$$

**Effect of variation of [H$^+$] on rate**

The electron transfer reaction has been carried out in [H$^+$] range 0.3-0.8 mol dm$^{-3}$. Hydrogen ion concentration was varied employing perchloric acid at different concentrations of vanillin, i.e. $5 \times 10^{-3}$, $10 \times 10^{-3}$,
15 × 10⁻³, 20 × 10⁻³, 25 × 10⁻³ mol dm⁻³ at [Ce(IV)] = 9.84 × 10⁻⁴ mol dm⁻³ and I = 1.0 mol dm⁻³. With the increase in [H⁺] from 0.3 mol dm⁻³ to 0.8 mol dm⁻³, 
\( k_{obs} \times 10^4 \) (298K) changes from 1.05 s⁻¹ to 2.03 s⁻¹, when [Ce(IV)] = 9.84 × 10⁻⁴ mol dm⁻³, [Vanillin] = 5 × 10⁻³ mol dm⁻³, and I = 1.0 mol dm⁻³. The \( k_{obs} \) data relating to [H⁺] variation are given in Table 1. The plots of \( k_{obs} \) versus [H⁺] at different [Vanillin] and at 298K are shown in Fig. 1.

### Table 1 — Observed rate constant \( (k_{obs}) \) for the reaction of Ce(IV) and vanillin at different hydrogen ion concentrations and temperatures

<table>
<thead>
<tr>
<th>T, K</th>
<th>[Vanillin] × 10⁻³ mol dm⁻³</th>
<th>( k_{obs} \times 10^4 ), s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>5.0</td>
<td>0.3  0.4  0.5  0.6  0.8</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>1.13 1.35 1.70 2.00 2.48</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>1.48 1.84 2.07 2.37 3.16</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>2.02 2.34 2.66 2.86 3.54</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>2.50 2.82 3.05 3.26 3.91</td>
</tr>
<tr>
<td>298</td>
<td>5.0</td>
<td>1.05 1.20 1.35 1.58 2.03</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>1.40 1.57 1.94 2.23 2.71</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>1.80 2.08 2.32 2.62 3.43</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>2.37 2.60 2.93 3.15 3.84</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>2.85 3.15 3.42 3.67 4.31</td>
</tr>
<tr>
<td>303</td>
<td>5.0</td>
<td>1.23 1.37 1.53 1.77 2.23</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>1.63 1.78 2.17 2.45 2.93</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>2.10 2.27 2.55 2.85 3.68</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>2.70 2.85 3.18 3.42 4.13</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>3.18 3.47 3.77 4.07 4.70</td>
</tr>
<tr>
<td>308</td>
<td>5.0</td>
<td>1.47 1.57 1.73 1.98 2.45</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>1.93 2.02 2.45 2.70 3.22</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>2.45 2.50 2.82 3.13 3.97</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>3.05 3.15 3.48 3.75 4.46</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>3.57 3.82 4.15 4.52 5.15</td>
</tr>
</tbody>
</table>

\( \text{a [H⁺], mol dm}⁻³ \).

Effect of variation of [Vanillin] and temperature on reaction rate

At a fixed [Ce(IV)] = (9.84 × 10⁻⁴ mol dm⁻³) and I = 1.0 mol dm⁻³ (NaClO₄), the effect of [Vanillin] on the rate was studied in the 5.0 - 25.0 × 10⁻³ mol dm⁻³ range at 293, 298, 303 and 308K. The results are shown in Table 1. The rate of the reaction is found to increase with increase in temperature and increase in [Vanillin]. The plots of \( k_{obs} \) versus [Vanillin] at different [H⁺] and at 298K are shown in Fig. 2.

Effect of ionic strength

The effect of ionic strength on the rate of the reaction was also studied employing NaClO₄ at fixed [Ce(IV)] = 9.84 × 10⁻⁴, [Vanillin] = 10 × 10⁻³ & [H⁺] = 0.3 mol dm⁻³ at T = 303K. The rate of the reaction slowly increases with the increase in ionic strength of the medium. \( k_{obs} \times 10^4 \) changes from 1.07 - 1.63 when ionic strength of the medium is changed from 0.4 - 1.0 mol dm⁻³ (Table 2).

Since there is marginal increase in rate constant, there is reaction between positively charged

![Fig. 1 — Plots of \( k_{obs} \times 10^4 \) versus [H⁺] at different [Vanillin] and \([\text{Ce(IV)}]\) at 298K. [Vanillin] was varied from 5.0 × 10⁻³ mol dm⁻³ to 25 × 10⁻³ mol dm⁻³ and [H⁺] was varied from 0.3 mol dm⁻³ to 0.8 mol dm⁻³.](Image)

![Fig. 2 — Plot of \( k_{obs} \times 10^4 \) versus [Vanillin] at different [H⁺] at 298K. [H⁺] was varied from 0.3 - 0.8 mol dm⁻³.](Image)
Table 3—Rate constants $k_1$ and $k_2$ for the oxidation of vanillin by Ce(IV) at different temperatures

<table>
<thead>
<tr>
<th>T, K</th>
<th>$k_1$, mol$^{-1}$ dm$^3$ s$^{-1}$</th>
<th>$k_2 \times 10^3$, mol$^{-1}$ dm$^3$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>0.1698</td>
<td>4.25</td>
</tr>
<tr>
<td>298</td>
<td>0.1771</td>
<td>6.40</td>
</tr>
<tr>
<td>303</td>
<td>0.1844</td>
<td>7.66</td>
</tr>
<tr>
<td>308</td>
<td>0.1918</td>
<td>10.59</td>
</tr>
</tbody>
</table>

$\Delta H^\circ = 3.45 \pm 0.24$ kJ mol$^{-1}$.

$\Delta S^\circ = -247.81 \pm 0.81$ JK$^{-1}$ mol$^{-1}$.

$\Delta H_{298}^\circ = 43.61 \pm 2.49$ kJ mol$^{-1}$.

$\Delta S_{298}^\circ = -141.23 \pm 8.26$ JK$^{-1}$ mol$^{-1}$.

Ce(IV) and neutral vanillin. The reaction mechanism is given below:

$$
\text{Ce}^{4+} + \text{H}_2\text{O} \quad \xrightarrow{K} \quad \text{CeOH}^{3+} + \text{H}^+
$$

$$
\text{Ce}^{4+} + \text{Vanillin} \quad \xrightarrow{k_1} \quad \text{Products}
$$

$$
\text{CeOH}^{3+} + \text{Vanillin} \quad \xrightarrow{k_2} \quad \text{Products}
$$

Rate = $k_1$ [Vanillin] [Ce$^{4+}$] + $k_2$ [Vanillin] [CeOH$^{3+}$]

$$
[k_1[H^+] + k_2K]/[H^+] + K)
$$

$$
[k_1[H^+] + k_2K]/[H^+] + K)
$$

$$
[k_1[H^+] + k_2K]/[H^+] + K)
$$

$$
[k_1[H^+] + k_2K]/[H^+] + K)
$$

The value of $K$ is known to be 6.4 (ref. 19). The $k_2$ (av) was calculated for each [H$^+$] value. Then the value of $K$ was gradually changed in such a manner that the plot of $k_2$ (av)([H$^+$] + K) versus [H$^+$] has maximum correlation coefficient value. With the best fitting, the slope and intercept were calculated. The $k_1$ (slope) and $k_2$ (intercept/K) were calculated at four different temperatures. $\Delta H^\circ$ (kJ mol$^{-1}$) and $\Delta S^\circ$ (JK$^{-1}$ mol$^{-1}$) were determined from the temperature variation data of $k_1$ and $k_2$ using Eyring equation. The values of $k_1$ and $k_2$ along with the corresponding activation parameters are shown in Table 3.

For the redox reaction of Ce(IV) in perchlorate medium with glycin$^{20}$, alanine$^{21}$ ethanol$^{22}$, malic acid$^{23}$, isopropyl alcohol$^{24}$, acetone$^{25}$, butan-2-ol$^{26}$ and DMSO$^{26}$ the $\Delta H^\circ$ (kJ mol$^{-1}$) values are 15.1, 18.9, 35.0, 20.6, 28.1, 16.9, 43.0 and 64.0 respectively. The corresponding $\Delta S^\circ$ (JK$^{-1}$ mol$^{-1}$) values are -18.26, 10.90, -181.0, 9.5, 13.0, -11.0, 54.0 and -98.0 respectively. For the redox reactions of Ce(IV) with vanillin used in this work, $\Delta H^\circ$ (kJ mol$^{-1}$) for $k_1$ and $k_2$ paths are 3.45 ± 0.24 and 43.63 ± 2.49 and the corresponding $\Delta S^\circ$ (JK$^{-1}$ mol$^{-1}$) are -247.81 ± 0.81 and -141.23 ± 8.26 respectively.

The values of $k_1$ are found to be higher than those of $k_2$ at all temperatures which is indicative of the fact that Ce$^{4+}$ reacts faster than CeOH$^{3+}$ with vanillin.

**Conclusion**

Vanillin, a popular flavoring reagent gets oxidized by Ce(IV) in perchlorate medium producing 4-hydroxy-3-methoxybenzoic acid. IR spectra support the formation of the above product. The reaction proceeds through Ce$^{4+}$ dependent path ($k_1$) and CeOH$^{3+}$ dependent path ($k_2$). The $k_1$ path is faster than $k_2$ path, indicating the fact that Ce$^{4+}$ is reacting faster than CeOH$^{3+}$. The electron transfer reactions for both $k_1$ and $k_2$ path pass through an ordered transition state.

**References**


