Kinetics of oxidation of D-arabinose and D-xylose by vanadium (V) in the presence of manganese II as homogeneous catalyst

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**ABSTRACT:** Kinetics of oxidation of D-arabinose and D-xylose by acidic solution of vanadium (V) ions in the presence of manganese (II) has been reported. First-order dependence of the reaction rate was observed on [sugars] and [H\textsuperscript{+}] at low concentrations throughout the oxidation reaction and a zero-order dependence on [sugar] and [H\textsuperscript{+}] was observed at high concentrations. First-order kinetics with respect to [Mn (II)] was also observed throughout the oxidation for both sugars. The results indicate the effect of Cl\textsuperscript{−} concentration is negligible. The reaction rates increase with the ionic strength of the medium. Various activation parameters were evaluated and provide further support to the proposed mechanism. Formic acid was reported as one of the oxidation products of these sugars.

**Keywords:** kinetics; vanadium (V); oxidation; arabinose; xylose; manganese (II) chloride catalysis; perchloric acid

**Introduction**

The biological and economic importance of carbohydrates has been largely responsible for the interest in the study of their biochemical and physiochemical properties along with their reactivity. Studies have been carried out on the structural elucidation, chemical degradation, and oxidation reactions. The catalytic oxidation of sugars has been carried out both in acidic and alkaline media, using such oxidants as transition metal ions, inorganic acids, organometallic complexes, and enzymes \[1-10\]. Recently Mn (II) was reported to catalyze the oxidation of arabinose and xylose by

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chromium VI [10]. In view of the biological importance of carbohydrate and the limited research carried out using Mn (II) as catalyst, this study seeks to report the catalytic importance of Mn (II) in the oxidation of arabinose and xylose using vanadium V as oxidant.

The aim of this study is to determine the kinetic orders with respect to each reactant of the reactions, as well as to present a suitable reaction mechanism for the oxidation of the reducing sugars under investigation.

**Material and Methods**

All chemicals were of analytical reagent grade and were used as received. Vanadium (V) (BDH) was prepared by dissolving 3 g of NH₄VO₃ in 40 cm³ of 2 M NaOH and 80 cm³ of 1M H₂SO₄ were added to the mixture. A yellow solution indicates Vanadium (V) [11].

In preparation of the required concentration a dilution factor was employed and its concentration was checked iodometrically. A solution of MnCl₂ (Uchem limited) was prepared by dissolving the sample in known strength of very dilute hydrochloric acid (0.001 M). The standard solutions of arabinose and xylose (A. R. grade) were freshly prepared with double-distilled water. The standard solution of HClO₄ (E. Merck) was used to maintain the required acidity. KCl (Analar) was prepared by dissolving its required amount in doubly distilled water to fix the Cl⁻ ion concentration; and NaClO₄ (Analar) was used to maintain the required ionic strength of the medium.

**Kinetic Measurements**

Appropriate quantities of the solutions of V (V), HClO₄, MnCl₂, KCl, and NaClO₄ were placed in separate glass vessels and kept for at least one hour in a thermostated water bath after reaching the temperature of 40 °C; then, the calculated amount of each reaction mixture was added together into a particular glass vessel, followed by the required amount of double-distilled water mixed together. The reaction mixture was then placed in a thermostated water bath maintained at a constant temperature of 40 °C (±0.5 °C) and the reaction was initiated by adding the required amount of oxidant solution placed separately in the same bath. The reaction progress was followed by estimating the decrease in the absorbance of V (V) spectrophotometrically at 525 nm in regular time intervals.

**Polymerization Test**

To test for the presence of free radicals in the reaction a 20% acrylamide solution was added to reaction mixtures containing the substrate and the vanadium (V) solution and then placed in an inert atmosphere for 24 hours. When the reaction mixture was
diluted with methanol, a precipitate was formed in the reaction mixture. This confirms the formation of free radicals in the redox reactions under investigation.

**Stoichiometry and product analysis**

Reaction mixtures, in which the concentration of V (V) presented a large excess of the reducing sugars, were kept in the presence of appropriate quantities of KCl, NaClO₄, MnCl₂, and HClO₄ at room temperature for 72 hours. Estimation of the unreacted V (V) showed that 1 mol of each sugar consumes 1 mol of V (V) for oxidation to take place, on the assumption that all the sugars are consumed under this condition. Formic acid was confirmed as one of the oxidation products of these two sugars using spot test [12].

\[
V_2O_5 + H_2O + C_5H_{10}O_5 \xrightarrow{Mn(II) / H^+} HCOOH + RCOOH + V_2O_4 + H_2 \ g
\]

where, \( R = C_3H_7O_3 \)

**Results and Discussion**

The progress of the reaction was followed by measuring the decrease in absorbance of the vanadium (V) ions at regular time interval, using a UNISPEC SM7504UV spectrophotometer. The pseudo first-order rate constants (\( k_{obs} \)) were determined from the linear portion of the plots of log (absorbance) versus time [16].

**Table 1.** Effect of variation of [sugars] and [HClO₄] of the medium on pseudo first-order rate constant \( k_{obs} \) in the oxidation of arabinose and xylose at 40°C.

<table>
<thead>
<tr>
<th>[HClO₄] M</th>
<th>[Sugar] M</th>
<th>( k_{obs} \times 10^5 s^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>0.01</td>
<td>0.17</td>
</tr>
<tr>
<td>0.15</td>
<td>0.01</td>
<td>0.68</td>
</tr>
<tr>
<td>0.21</td>
<td>0.01</td>
<td>0.98</td>
</tr>
<tr>
<td>0.27</td>
<td>0.01</td>
<td>1.12</td>
</tr>
<tr>
<td>0.33</td>
<td>0.01</td>
<td>1.32</td>
</tr>
<tr>
<td>0.39</td>
<td>0.01</td>
<td>1.47</td>
</tr>
<tr>
<td>0.45</td>
<td>0.01</td>
<td>1.53</td>
</tr>
<tr>
<td>0.51</td>
<td>0.01</td>
<td>1.55</td>
</tr>
<tr>
<td>0.57</td>
<td>0.01</td>
<td>1.59</td>
</tr>
<tr>
<td>0.15</td>
<td>0.002</td>
<td>1.21</td>
</tr>
<tr>
<td>0.15</td>
<td>0.008</td>
<td>1.63</td>
</tr>
<tr>
<td>0.15</td>
<td>0.010</td>
<td>2.15</td>
</tr>
<tr>
<td>0.15</td>
<td>0.012</td>
<td>2.72</td>
</tr>
<tr>
<td>0.15</td>
<td>0.014</td>
<td>3.19</td>
</tr>
<tr>
<td>0.15</td>
<td>0.016</td>
<td>3.55</td>
</tr>
<tr>
<td>0.15</td>
<td>0.018</td>
<td>3.87</td>
</tr>
<tr>
<td>0.15</td>
<td>0.020</td>
<td>3.92</td>
</tr>
<tr>
<td>0.15</td>
<td>0.022</td>
<td>3.97</td>
</tr>
</tbody>
</table>

Solution conditions: \( [V (V)] = 1 \times 10^{-3} M; [MnCl₂] = 6 \times 10^{-4} M; [KCl] = 5 \times 10^{-4} M; [NaClO₄] = 0.1 M. \)

From the observation of Table 1 one may conclude that the concentrations of [sugars] and [HClO₄] varied; this table indicates the rate of oxidation increases as the
[sugar] and [HClO₄] increases. It suggests the reaction is acid-dependent concerning [HClO₄] [10].

Table 2. Effect of the variation of [NaClO₄] and [MnCl₂] of the medium on pseudo first-order rate constant kₐₒₛ in the oxidation of arabinose and xylose at 40°C

<table>
<thead>
<tr>
<th>[NaClO₄] M</th>
<th>[V (V)] x 10⁻³ M</th>
<th>[MnCl₂] x 10⁻⁴ M</th>
<th>kₐₒₛ x 10⁵ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.0</td>
<td>6.0</td>
<td>0.65</td>
</tr>
<tr>
<td>0.08</td>
<td>1.0</td>
<td>6.0</td>
<td>0.73</td>
</tr>
<tr>
<td>0.13</td>
<td>1.0</td>
<td>6.0</td>
<td>0.86</td>
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<tr>
<td>0.15</td>
<td>1.0</td>
<td>6.0</td>
<td>1.23</td>
</tr>
<tr>
<td>0.16</td>
<td>1.0</td>
<td>6.0</td>
<td>1.36</td>
</tr>
<tr>
<td>0.20</td>
<td>1.0</td>
<td>6.0</td>
<td>1.46</td>
</tr>
<tr>
<td>0.25</td>
<td>1.0</td>
<td>6.0</td>
<td>1.58</td>
</tr>
<tr>
<td>0.1</td>
<td>1.0</td>
<td>1.0</td>
<td>0.38</td>
</tr>
<tr>
<td>0.1</td>
<td>1.0</td>
<td>3.0</td>
<td>1.15</td>
</tr>
<tr>
<td>0.1</td>
<td>1.0</td>
<td>5.0</td>
<td>1.85</td>
</tr>
<tr>
<td>0.1</td>
<td>1.0</td>
<td>7.0</td>
<td>2.70</td>
</tr>
<tr>
<td>0.1</td>
<td>1.0</td>
<td>9.0</td>
<td>3.45</td>
</tr>
<tr>
<td>0.1</td>
<td>1.0</td>
<td>11.0</td>
<td>3.98</td>
</tr>
</tbody>
</table>

D-arabinose

D-xylose

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.67</td>
<td>150.48</td>
<td>89.65</td>
</tr>
<tr>
<td>0.38</td>
<td>0.91</td>
<td>154.63</td>
<td>90.32</td>
</tr>
<tr>
<td>1.15</td>
<td>0.91</td>
<td>86.65</td>
<td>90.32</td>
</tr>
<tr>
<td>1.85</td>
<td>1.41</td>
<td>150.48</td>
<td>89.65</td>
</tr>
<tr>
<td>2.70</td>
<td>1.90</td>
<td>154.63</td>
<td>90.32</td>
</tr>
<tr>
<td>3.45</td>
<td>2.80</td>
<td>150.48</td>
<td>89.65</td>
</tr>
<tr>
<td>3.98</td>
<td>3.20</td>
<td>154.63</td>
<td>90.32</td>
</tr>
</tbody>
</table>

Solution conditions: [sugar] = 1.00 x 10⁻² M, [HClO₄] = 0.15 M, [KCl] = 5 x 10⁻⁴ M.

Table 2 displays the effect of varying the concentrations of [NaClO₄] and the catalyst [MnCl₂]. This table indicates the reaction rate increases as the sodium perchlorate concentration increases, indicating that reactions take place between ions of similar charges [18]. The rate of reaction also increases as the catalyst concentration increases, indicating that the reaction is catalyst-dependent [10].

The reactions were also studied at four different temperatures: 40, 50, 60, and 70 °C and the observed values of pseudo first-order rate constant, kₐₒₛ, were used to calculate the activation parameters of the various sugars, including their entropy of activation reported in Tables 3a and b. The Arrhenius activation energies, Eₐ, for the uncatalyzed path were 98.83 and 99.90 kJmol⁻¹ for xylose and arabinose, respectively, while the Arrhenius activation energies for the catalyzed path were 45.16 and 44.52 kJmol⁻¹ for arabinose and xylose, respectively. The difference in the Arrhenius activation energies for the uncatalyzed and catalyzed reactions concerning the different sugars indicates the reaction is catalyzed.

Table 3. Energy of activation and other activation parameters observed for the oxidation of D-arabinose and D-xylose at 40°C.

(a) For the catalyzed path

<table>
<thead>
<tr>
<th>SUGARS</th>
<th>Eₐ  (kJmol⁻¹)</th>
<th>ΔH#  (kJmol⁻¹)</th>
<th>ΔS#  (Jmol⁻¹K⁻¹)</th>
<th>ΔG#  (kJmol⁻¹)</th>
<th>Kₐₒₛ (s⁻¹) x 10⁵</th>
<th>A (mol⁻²dm⁶s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylose</td>
<td>44.52</td>
<td>41.92</td>
<td>-154.63</td>
<td>90.32</td>
<td>1.33</td>
<td>5.42 x 10⁴</td>
</tr>
<tr>
<td>Arabinose</td>
<td>45.16</td>
<td>42.55</td>
<td>-150.48</td>
<td>89.63</td>
<td>2.15</td>
<td>8.93 x 10⁷</td>
</tr>
</tbody>
</table>

(b) For the uncatalyzed path
Average linear regression coefficients, $r \geq 0.89$, were observed for all activation parameters.

**Mechanism: Reaction Scheme**

In our study comparing the oxidation of xylose and arabinose by V (V) in the presence of Mn (II) chloride as homogeneous catalyst, the entropy of activation was negative; this suggests the reaction proceeds through a hydride transfer process for complex formation. Thus, when vanadate is acidified by a perchloric acid the yellow pervanadyl ion, $\text{VO}_2^+$, is formed as the initial species [14].

$$\text{VO}^3^- + 2\text{H}^+ \rightarrow \text{VO}_2^+ + \text{H}_2\text{O} \quad (1)$$

This may exist in hydrated form $\text{V} \text{(OH)}_4^+$ [15]. In a stronger perchloric acid ($\text{H}^+ > 2$ M) the species becomes protonated to form $\text{VO} \text{(OH)}^{2+}$ [13].

A reaction mechanism based on the observed kinetic results and the spectral information collected for the formation of complex presents itself as proposed in the reaction scheme below [17]:

$$
\begin{align*}
\text{C}_3\text{H}_7\text{O}_3 + \text{H}^+ & \rightarrow \text{K}_1 \\
\text{C}_3\text{H}_7\text{O}_3 & \text{Mn}^2+ \\
\text{C}_3\text{H}_7\text{O}_3 + \text{K}_2 & \rightarrow \text{(SH)}^+ \\
\text{C}_3\text{H}_7\text{O}_3 & \text{Mn}^2+ \\
\text{C}_3\text{H}_7\text{O}_3 & \text{K}_3
\end{align*}
$$

(2)

Where $\text{SH}^+$ represents the protonated form of the sugars.

The protonated sugar then reacts with the catalyst Mn (II), according to the equation (3) below to give the first complex labelled $\text{C}_1$.

(3)

The positively charged complex then reacts further with the protonated vanadium
in the slow and rate determining step.

\[
\begin{array}{c}
\text{H} \quad \text{C} \quad \text{O} \quad \cdot \quad \text{Mn(II)} \quad \text{H} \\
\text{H} \quad \text{C} \quad \text{OH} \\
\text{R} \\
\end{array}
\]

\[\text{C}_1\]

\[+ \quad \text{VO}_2^+ \quad \xrightarrow{k_3} \quad \text{VO}_2^+ \quad \text{SH}^+ \quad \text{Mn(II)} \quad \text{complex C}\]

Equation (4) is supported by the positive effect of the addition of sodium perchlorate to the rate of the reactions; it indicates that reactions take place between ions of similar charges [18]. The lower aldose undergoes further oxidation with the protonated chromic acid to yield the erythronic acid.

\[
\text{Complex } \xrightarrow{\text{fast}} \quad \text{VO}^2+ \quad \text{Mn(II)} \quad \text{HCOOH} \quad \text{formic acid} \quad \text{R} - \text{C} - \text{H} \\
\text{OH} \\
\]

\[\text{R} - \text{C} - \text{H} + \quad \text{V(V)} \quad \xrightarrow{\text{Mn(II)}/\text{H}^+} \quad \text{R} - \text{C} = \text{O} \quad \text{OH} \quad + \quad \text{V(IV)} \quad \text{H}^+ \quad (4/5)
\]

From the proposed mechanism, the rate of the reaction in terms of decrease in the concentration of \text{V (V)} was derived as:

\[
- \frac{\text{d}[\text{VO}_2^+]}{\text{dt}} = k_3 [C] [\text{VO}_2^+]
\]

6) From the reaction mechanism the total \text{Mn (II)}, i.e., \text{Mn (II)}_T, is given below:

\[
\text{Mn(II)}_T = \text{Mn(II)} + C
\]

where \( \text{Mn(II)} = \text{Mn(II)}_T - C \)

\[
K_1 [S] [H^+] = [\text{SH}^+]
\]

7) Substituting equation 7 into the equation below:

\[
K_2 = \frac{C}{[\text{SH}^+] [\text{Mn(II)}]}
\]

\[
K_2 = \frac{C}{K_1 [S] [H^+] [\text{Mn(II)}]}
\]

Making the complex ‘C” subject of the formulae:
\[
C = K_2 K_1 [S] [H^+] \text{ [Mn(II) ]}
\]
\[
C = K_2 K_1 [S] [H^+] \text{ [Mn(II) ]}_T - C
\]
\[
C = K_2 K_1 [S] [H^+] \text{ [Mn(II) ]}_T - K_2 K_1 [S] [H^+] C
\]
\[
C = \frac{K_2 K_1 [S] [H^+] \text{ [Mn(II) ]}_T}{1 + K_2 K_1 [S] [H^+]}
\]
\[
(8)
\]

Substituting eq. 8 into eq. 6 gives:
\[
\frac{\text{Rate}}{-d[VO_2^+]} dt = \frac{k_3 K_2 K_1 [S] [H^+] [VO_2^+] \text{ [Mn(II) ]}_T}{1 + K_2 K_1 [S] [H^+]}
\]
\[
(9)
\]

The inverse reaction gives:
\[
\frac{\text{Mn(II)}_T}{\text{Rate}} = \frac{1}{k_3 K_2 K_1 [S] [H^+] [VO_2^+]} + \frac{1}{k_3 [VO_2^+]}
\]
\[
(10)
\]

From the double reciprocal plot of the graph Mn (II)/rate against 1/[S] and Mn (II)/rate against 1/ [H^+] the values of \(k_3 K_2 K_1\) and \(k_3\) were obtained as the slope and intercept respectively. From the respective plots of the data a straight line was obtained with a positive intercept, which confirms the validity of equation (10).

For xylose the values presented in figures 1 and 3, obtained from the plots of Mn (II)/rate against 1/[S] and Mn (II)/rate against 1/ [H^+] were, respectively, 2.123 moldm\(^{-3}\)s\(^{-1}\) and 0.0483 moldm\(^{-3}\)s\(^{-1}\); the value \(k_3\) obtained from the intercepts of the above plots are 0.308 s\(^{-1}\) and 0.033 s\(^{-1}\), respectively.

A similar plot was also made for arabinose, and it also supports the validity of the equation (figures 5 and 7) and the values of the plot were found to be 0.416 moldm\(^{-3}\)s\(^{-1}\) and 0.092 moldm\(^{-3}\)s\(^{-1}\) and the value of \(k_3\) obtained from the intercepts of the above plots are 0.280 s\(^{-1}\) and 0.072 s\(^{-1}\).

At low concentration of [S] and [H\(^+\)] the whole 1 >> \(K_2 K_1 [S][H^+]\) will be valid, so the rate = \(k_3 K_2 K_1 [S][H^+][VO_2^+]\).

The graph of rate/Mn (II) vs. [S] and a graph of rate/Mn (II) vs. [H\(^+\)] were plotted; the values of \(k_3 K_2 K_1\) obtained for xylose (figures 2 and 4) are 2.045 moldm\(^{-3}\).s and 0.040 moldm\(^{-3}\).s respectively.
Figure 1. Plot of Mn (II)\textsubscript{obs}/k\textsubscript{obs} against 1/[xylose] at 40\degree C. [V (V)] = 1 \times 10^{-3} M, [MnCl\textsubscript{2}] = 6 \times 10^{-4} M; [KCl] = 5 \times 10^{-4} M; [NaClO\textsubscript{4}] = 0.1 M, [HClO\textsubscript{4}] = 0.15 M.

Figure 2: Plot of rate/Mn (II)\textsubscript{T} against [xylose] at 40\degree C. [V (V)] = 1 \times 10^{-3} M, [MnCl\textsubscript{2}] = 6 \times 10^{-4} M; [KCl] = 5 \times 10^{-4} M; [NaClO\textsubscript{4}] = 0.1 M, [HClO\textsubscript{4}] = 0.15 M.
**Figure 3**: Plots of Mn (II)$_T$/K$_{obs}$ against 1/[H$^+$] for xylose at 40°C: [xylose] = 0.01 M [V (V)] = 1 × 10$^{-3}$ M, [MnCl$_2$] = 6 × 10$^{-4}$ M; [KCl] = 5 × 10$^{-4}$ M; [NaClO$_4$] = 0.1 M.

**Figure 4**: Plot of rate/Mn (II)$_T$ against [H$^+$] for xylose at 40°C. [xylose] = 0.01 M, [V (V)] = 1 × 10$^{-3}$ M, [MnCl$_2$] = 6 × 10$^{-4}$ M; [KCl] = 5 × 10$^{-4}$ M; [NaClO$_4$] = 0.1 M.
Figure 5. Plot of Mn (II)$_T$/rate against 1/[arabinose]: [V (V)] = 1 $\times$ 10$^{-3}$ M, [MnCl$_2$] = 6 $\times$ 10$^{-4}$ M; [KCl] = 5 $\times$ 10$^{-4}$ M; [NaClO$_4$] = 0.1 M, [HClO$_4$] = 0.15 M.

Figure 6. Plot of rate/Mn (II)$_T$ against 1/[arabinose] at 40°C [V (V)] = 1 $\times$ 10$^{-3}$ M, [MnCl$_2$] = 6 $\times$ 10$^{-4}$ M; [KCl] = 5 $\times$ 10$^{-4}$ M; [NaClO$_4$] = 0.1 M, [HClO$_4$] = 0.15 M.
Figure 7. Plots of Mn (II) / rate against 1/[H+] for arabinose at 40°C, [arabinose] = 0.01 M, [V (V)] = 1 × 10^{-3} M, [MnCl2] = 6 × 10^{-4} M; [KCl] = 5 × 10^{-4} M; [NaClO4] = 0.1 M.

Figure 8: Plots of rate/Mn (II) against [H+] for arabinose at 40°C: [arabinose] = 0.01 M, [V (V)] = 1 × 10^{-3} M, [MnCl2] = 6 × 10^{-4} M; [KCl] = 5 × 10^{-4} M; [NaClO4] = 0.1 M.
A similar plot for arabinose gives the values of \( k_3 K_2 K_1 \) to be 0.342 moldm\(^{-3}\)·s and 0.064 moldm\(^{-3}\)·s respectively. The table 4a and 4b below gives the value of \( k_3 K_2 K_1 \) and \( k_3 \) obtained from the various plots above.

**Table 4a. Values of \( k_3 K_2 K_1 \) obtained from the various plots.**

<table>
<thead>
<tr>
<th>Sugars</th>
<th>Mn (II)/rate vs. 1/[S]</th>
<th>Mn (II)/rate vs. 1/[H(^+)]</th>
<th>Rate/Mn (II) vs.[S]</th>
<th>Rate/Mn (II) vs. [H(^+)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylose</td>
<td>2.123</td>
<td>0.0483</td>
<td>2.045</td>
<td>0.040</td>
</tr>
<tr>
<td>Arabinose</td>
<td>0.416</td>
<td>0.092</td>
<td>0.342</td>
<td>0.064</td>
</tr>
</tbody>
</table>

Average linear regression coefficients, \( r \geq 0.9 \), were observed for the parameters.

**Table 4b. Values of \( k_3 \) were obtained from the plots of Mn (II)/rate versus 1/[S] and Mn (II)/rate.**

<table>
<thead>
<tr>
<th>Sugars</th>
<th>Mn (II)/rate vs. 1/[S]</th>
<th>Mn (II)/rate vs. 1/[H(^+)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylose</td>
<td>0.308</td>
<td>0.033</td>
</tr>
<tr>
<td>Arabinose</td>
<td>0.280</td>
<td>0.072</td>
</tr>
</tbody>
</table>

Average linear regression coefficients, \( r \geq 0.9 \), were observed for the parameters.

The plots based on the two equations reveal that the values of \( k_3 K_2 K_1 \) and \( k_3 \) are in good agreement with one another. These results support the validity of the rate law equation.

\[
\text{Rate} = \frac{1}{k_3 K_2 K_1 [S] [H^+] [\text{VO}_2^{2+}]} + \frac{1}{k_3 [\text{VO}_2^{2+}]}.
\]

**Conclusion**

Vanadium, like other transition metals, has catalytic properties due to its participation in the rate determining step (slow step); the vanadium V catalyst works by providing an alternative reaction pathway to the reaction product. The rate of the reaction is increased as this alternative route has lower activation energy than the reaction route not mediated by the catalyst. Our conclusions are based on the spectral information and the observed kinetic data.

i. The observed negative entropy of activation for the oxidation of both sugars supports the fact that a complex is formed between the [sugar], [V (V)] and Mn (II).

ii. The value of activation energy (Ea) of the catalyzed and the uncatalysed paths is consistent with the accepted view that a slow reaction would require a higher energy of activation and also that the reactions are catalysed by Mn (II) under the reaction conditions.
References and Notes


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