CHAPTER-3

OXIDATION OF SUGARS

BY

VANADIUM (V)

IN AQUEOUS SULPHURIC ACID
The study of saccharides has special importance due to their multidimensional physical, biological and industrial relevance [1, 2, 3, 4]. The behaviour of electrolytes in aqueous carbohydrates and carbohydrates containing small quantity of ions which are present in body fluids has became subject of interest [5, 6, 7]. Simple saccharides have received attention due to their ability to protect biological macro molecules in addition to their importance to pharmaceutical and food [8].

The molecular interaction of sugars in solutions plays an important role in governing the mechanism of any system. The aqueous solutions of sugar have been used by many workers in studying the solute – solvent interaction in aqueous and mixed solvent system including studies related to viscosity of the medium [9, 10, 11, 12, 13, 14, 15]. The solvent – solvent interaction produced in solvent mixture can effect solute – solvent interaction and preferential solvation [16].

Solvent plays an important role in many chemical processes. Organic liquids are characterised by several properties that make them suitable for dissolving and providing reaction media for various type of solutes or reactant [17]. During recent past workers have shown considerable interest in explaining the role of solvent properties like preferential solvation on reaction rates [18, 19, 20, 21].

The study of the oxidation of organic compounds by vanadium (V) has an importance due to role of vanadium in relation to the insuline – mimetic act and catalytic activities [22, 23, 24]. The study of oxidation mechanism of compounds by vanadium (V) has also an importance in the studies concerning possible role of transient ions of chromium and manganese on certain oxidation reactions by both chromic acid and potassium permanganate [25]. The kinetics of oxidation of sugars have been carried out in both acidic and alkaline media using such oxidants as transition metal ions, inorganic acids, organometalic complexes and enzymes due to there biological importance [26].

Kinetics of oxidation of sugars by vanadium (V) in sulphuric acid, perchloric and hydrochloric acid solutions has been subject of research [27]. These studies are not related to the medium effect on rate of reaction. The present study is therefore undertaken to study the effect of medium mainly viscosity on rate of oxidation of sugars by vanadium (V) in sulphuric acid.
3.1 OXIDATION OF SUGARS BY VANADIUM (V)

Oxidation of carbohydrates by transition metal ions vanadium (V), chromium (VI), thallium (III), manganese (VII), cerium (IV) and colloidal MnO₂ are of especial interest due to there application in biological sciences [28]. The oxidation of sugars by vanadium (V) has special importance due to there biological relevance and application in oxidation reaction by chromium / potassium permanganate [25, 27]. In the higher acid concentration range (> 4.5 mol dm⁻³) the following active species and equilibrium have been reported.

\[
\text{VO}_2^+ + 2\text{H}^+ + 2\text{HSO}_4^- \rightleftharpoons [\text{V(OH)}_2(\text{HSO}_4)_2]^+ \quad \text{...(3.1)}
\]

The vanadium (V) is amphoteric [29] and at lower acid concentration (pH ≥ 1.0) exist in a form of pervannadyl ion \(\text{VO}_2^+\). The ion \(\text{VO}_2^+\) may be in hydrated form in lower concentration range.

\[
\text{VO}_3^- + 2\text{H}^+ \rightleftharpoons \text{VO}_2^+ \quad \text{H}_2\text{O} \quad \text{...(3.2)}
\]

The results of these studies have revealed that in some cases the mechanism was proposed on the basis of the formation of intermediate complex between substrate and the oxidant while in some cases the mechanism were proposed on the basis of formation of free radical in the oxidation process. All these studies have reported that the oxidation of sugars shows first order dependence on vanadium (V), \(\text{H}^+\) ion and \(\text{HSO}_4^-\) ion.

The effect of sulphuric acid concentration on rate of oxidation has both acid independent and dependant path, depending upon the concentration range. The plot between \(k_{\text{obs}}\) and [\(\text{H}_2\text{SO}_4\)] has non linear nature but the rate increases with the increase of sulphuric acid concentration. The various explanations have been proposed for the justification of the effect of acid concentration on rate of reaction.

3.2 EXPERIMENTAL

All the solutions were prepared using the chemical mentioned in the list of chemicals and by the methods described in the chapter 2. The studies were carried
out according to the experimental methods with the instrument mentioned in the chapter 2.

The rate constants were calculated by using the rate expression under pseudo first order condition.

3.3 RESULTS

In the study, the kinetics of oxidation of glucose, fructose and sucrose by vanadium (V) in aqueous sulphuric acid medium has been studied. The experimental values of rate constant obtained under experimental conditions at different concentration of the reactant species are presented below.

3.3.1 Dependence of rate on initial [oxidant]

The effect of [Vanadium (V)] on the reaction rate was studied at constant concentration of sulphuric acid, sugars and temperature. The values of rate constant \( k_{\text{obs}} \) are summarized in Table 3.1 in the concentration range of vanadium (V) used in the study, the rate constant \( k_{\text{obs}} \) was independent of the [vanadium (V)]. These observation are in agreement with a first order dependence on [vanadium (V)]\(_T\) and the reaction follows a first order rate law given by equation 3.3.

\[
-\frac{d[\text{vanadium (V)}]}{dt} = k_{\text{obs}} [\text{vanadium (V)}]_T \quad \text{...(3.3)}
\]

Table 3.1 Variation of rate with initial [Vanadium (V)] at 298 K

[Sugars ] = 0.04 mol dm\(^{-3}\)

[H\(_2\)SO\(_4\) ] = 2.0 mol dm\(^{-3}\)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>[Oxidant] mol dm(^{-3})</th>
<th>(10^5 k_{\text{obs}}) ( sec(^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fructose</td>
<td>Sucrose</td>
</tr>
<tr>
<td>1</td>
<td>0.002</td>
<td>17.1</td>
</tr>
<tr>
<td>2</td>
<td>0.003</td>
<td>17.2</td>
</tr>
<tr>
<td>3</td>
<td>0.004</td>
<td>17.0</td>
</tr>
<tr>
<td>4</td>
<td>0.005</td>
<td>17.3</td>
</tr>
<tr>
<td>5</td>
<td>0.006</td>
<td>17.2</td>
</tr>
</tbody>
</table>
In the synopsis of the work three sugars namely glucose, fructose and sucrose were proposed for the kinetic study. During the study when the reaction was started under similar conditions of the concentration of sulphuric acid, concentration of substrate (fructose and sucrose) and temperature, it was notice that the rate of reaction for glucose was many times smaller than the rate of oxidation of other two sugars. Hence the kinetic study of the glucose in the context of all range of concentration were not possible under similar experimental condition used for other two sugars namely fructose and sucrose.

3.3.2 Dependence of rate on initial [Substrate]

The effect of initial [sugars] on rate of reaction was investigated in the concentration range 0.04 mol dm$^{-3}$ to 0.09 mol dm$^{-3}$. The values of rate constant for both the sugars are presented in Table 3.2.

Table 3.2 Variation of rate with initial [Substrate] at 298 K

[Vanadium (V)] = 0.004 mol dm$^{-3}$
[\(\text{H}_2\text{SO}_4\)] = 2.0 mol dm$^{-3}$

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[Substrate] mol dm$^{-3}$</th>
<th>(10^5 k_{\text{obs}} \text{ (sec}^{-1}\text{)})</th>
</tr>
</thead>
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<td></td>
<td></td>
<td>Fructose</td>
</tr>
<tr>
<td>1</td>
<td>0.04</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>2.1</td>
</tr>
<tr>
<td>3</td>
<td>0.06</td>
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<tr>
<td>4</td>
<td>0.07</td>
<td>2.9</td>
</tr>
<tr>
<td>5</td>
<td>0.08</td>
<td>3.2</td>
</tr>
<tr>
<td>6</td>
<td>0.09</td>
<td>3.7</td>
</tr>
</tbody>
</table>
3.3.3 Dependence of rate on initial [H₂SO₄]

In aqueous sulphuric acid concentration the rate constant were measured at different concentration of sulphuric acid at constant concentration of substrate and oxidant. The results are given in Table 3.3.

Table 3.3 Variation of rate with initial [H₂SO₄] at 298 K

[Sugars ] = 0.04 mol dm⁻³
[ Vanadium(V)] = 0.004 mol dm⁻³

| S. No. | [H₂SO₄ | mol dm⁻³ | 10⁵ k_{obs} (sec⁻¹) |
|--------|----------|-----------------|
|        |          | Fructose       | Sucrose  |
| 1      | 1.0      | 9.1            | 2.2      |
| 2      | 1.5      | 17.1           | 3.7      |
| 3      | 2.0      | 25.4           | 5.5      |
| 4      | 2.5      | 33.5           | 7.3      |
| 5      | 3.0      | 42.2           | 9.2      |

3.4 DISCUSSION

The results shown in table 3.1 to 3.3 were used to analyse the effect of various reactant on rate of oxidation of sugars. The pseudo first order rate at constant [oxidant] and [H₂SO₄], increased with increasing [sugars]. The plot between [sugars] and k_{obs} is shown in Fig 3.1, for both the substrates. The plots are linear and the linearity coefficient is > 0.98. The rate constant is increased with increasing [H₂SO₄]. The plot between [H₂SO₄] and the rate constant were also linear for both the sugars. The representative plots are given in Fig 3.2.
\[ y = 40.571x + 0.0295 \]
\[ R^2 = 0.9956 \]

\[ y = 21.714x - 0.0114 \]
\[ R^2 = 0.9823 \]

Fig 3.1
$y = 16.52x - 7.58$
$R^2 = 0.9998$

$y = 3.52x - 1.46$
$R^2 = 0.9983$

Fig 3.2

$10^5 k_{obs}$ (sec$^{-1}$)

[H$_2$SO$_4$] mol dm$^{-3}$

A Fructose
B Sucrose
These results confirm that the order of reaction with respect to substrate is one in the sulphuric acid medium. The reaction rate was accelerated with the increase in the sulphuric acid concentrations. The very high concentrations of sulphuric acid were not used to avoid the undesirable solvent effect such as viscosity, dielectric constant etc in the kinetic measurement because we have proposed to study the effect of solvent related to the viscosity of the medium on rate of oxidation. The solvent effect related to the viscosity can be studied only at constant acid concentration to eliminate the catalytic effect of the acid. It results that the oxidation of glucose would not be carried out by changing the concentration of reactant according to experimental conditions.

The results of the study of the kinetics of the oxidation of two sugars reported above namely fructose and sucrose could be summarized as below-

(i) The reactions have a first order dependence on vanadium (V), confirmed by the experimental data which was independent of the initial vanadium (V) concentration.

(ii) The reactions are acid catalyzed and the catalytic effect increases with increasing concentration of sulphuric acid.

(iii) The reaction rates have linear dependence on concentration of sulphuric acid. The plot between concentration of sulphuric acid and rate constant indicates the order of the reaction nearly unity with respect to sulphuric acid concentration.

(iv) The order with respect to the substrate concentration is also one for both the sugars. The linear plot of rate constant against substrate concentration passing through the origin is an indication of second order kinetics, first order with respect to sugar and first order with respect to vanadium.

(v) The addition of substrate to the solution of vanadium results in a shift in the absorbance wave length measured in the spectrophotometric study, which is an indication of the intermediate complex formation between vanadium (V) and substrate. Similar shift was also noted on increasing the acid concentration which is indication of protonation equilibria between various vanadium (V) species in sulphuric acid.

(vi) The reaction mixture on partial oxidation polymerizes the acrylonitrile with in few minutes, indicating the presence of free radical in the progress of the reaction.

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(vii) It is well established by earlier worker that the [V(OH)$_3$HSO$_4$]$^+$ is kinetically active species of vanadium in aqueous sulphuric acid [30].

### 3.5 MECHANISM

On the basis of the above facts and experimental results the mechanism for the oxidation of sugars by vanadium(V) in aqueous sulphuric acid medium has been proposed by considering the complex ion and free radical formation as given in scheme I

\[
\begin{align*}
&\text{Intermediate complex} \\
&\text{slow} \\
&\text{fast} \\
\end{align*}
\]

According to scheme I the overall reaction rate is given by equation 3.8.

\[
\text{Rate} = k K_1 K_2 [R-OH]_T [H^+] [V(V)] [HSO}_4^-] 
\]

When the values of \( K_1 [H^+] [HSO}_4^-] \) is less than one rate equals to

\[
\text{Rate} = k K_1 K_2 [R-OH]_T [H^+] [V(V)] [HSO}_4^-] 
\]
The above mechanism is in agreement with the experimental results and mechanism proposed for oxidation of glucose [31].

3.6 DEPENDENCE OF REACTION RATE ON VISCOSITY OF THE MEDIUM

The reaction rate obtained on the basis of viscosity approach can be compared with the increase in the rate with increase in concentration of the substrate. The comparison shows that the graph between viscosity of the medium and concentration of the substrate has a considerable importance. The graph between concentration and viscosity of the substrate in aqueous solutions at 298 K are given in Fig 3.3, 3.4 and 3.5.
$y = 0.7116x + 0.8858$
$R^2 = 0.9842$

Fig 3.3
\[ y = 4.645x - 1.0723 \]

\[ R^2 = 0.9893 \]
$y = 0.9337x + 0.774$

$R^2 = 0.9888$

Fig 3.5
In the measurement of the viscosity the effect of other reactant, oxidant and acid has not considered because the concentration of these reactants have constant magnitude. Thus the viscosity of the substrate in aqueous medium can be taken as the viscosity of the reaction media as an experimental purpose. This assumption has been used in order to asses the effect of viscosity on the rate of reaction of the medium.

A simple way of obtaining the relationship between viscosity of the medium and rate of reaction is careful study of rate of reaction with change of concentration of the substrate used in the determination of the viscosity of the medium.

The plots between viscosity and rate of reaction are shown in Fig. 3.6 and Fig. 3.7. It is seen that for both the substrates the cures are linear in nature. For both the substrate it has been found that the values of rate constant obtained experimentally are in reasonable agreement with the relation obtained between concentration and viscosity of the substrate.
\[ y = 0.0009x - 0.001 \]

\[ R^2 = 0.9655 \]

**Fig 3.6**

- **Viscosity poise**
- **Fructose**
- **T = 298 K**
\[ y = 7E^{-05}x - 9E^{-06} \]

\[ R^2 = 0.9668 \]

\[
\begin{array}{c|c|c|c|c|c|c|c}
0 & 0.00005 & 0.0001 & 0.00015 & 0.0002 & 0.00025 & 0.0003 & 0.00035 & 0.0004 \\
\hline
0 & 1 & 2 & 3 & 4 & 5 & 6 & & \\
\end{array}
\]

Viscosity poise
Sucrose
\( T = 298 \text{ K} \)

**Fig 3.7**
\[ y = 0.0007x - 0.0002 \]
\[ R^2 = 0.9739 \]

Fig 3.8
\[ y = 0.0003x - 8E-05 \]
\[ R^2 = 0.9809 \]

Fig 3.9
In acidic solutions the moment H$_3$O$^+$ ion loses its proton to a neighbouring water molecule it itself transforms into water molecule. However the time taken in the transfer process is about 10$^{-14}$ sec. While the time of H$_3$O$^+$ ion wait for its adjacent water molecules to reorient is about 2.4×10$^{-13}$ sec. [32]. The contribution towards viscosity by the H$^+$ ions can be considered negligible and the contribution of sugars mainly at higher concentration is responsible for the increase in viscosity in aqueous solutions.

Spectroscopic studies have shown that the hydration of saccharides depends upon the hydroxyl group, the hydrogen bonding sites and the relative position of the hydroxyl groups in the carbohydrate molecules [33]. In purely aqueous solutions mono and disaccharides have structure – maker character as observed from viscometric measurement [34].

In our study the following linear relations are applicable for fructose (Fig. 3.3 and Fig. 3.8)

\[ \eta = 0.7116 [S] + 0.8858 \quad \ldots (3.11) \]

\[ k_{obs} = 0.0007 [S] - 0.0002 \quad \ldots (3.12) \]

These equations can be rearranged and equation (3.11) can be divided by equation (3.12).

\[ \frac{0.7116 [S]}{0.0007 [S]} = \frac{\eta - 0.8858}{k_{obs} + 0.0002} \quad \ldots (3.13) \]

Where [S] = fructose

\[ k_{obs} = 0.0009 \eta - 0.0009 \]

or

\[ k_{obs} = 0.0009 (\eta - 1) \quad \ldots (3.14) \]

The eq (3.14) is in agreement with the linear relation obtained in the graph \( \eta \) versus \( k_{obs} \) given by equation (3.15)
\[ k_{\text{obs}} = 0.0009 \eta - 0.001 \quad \ldots(3.15) \]

The value of intercept 0.001 is nearly equal 0.0009.

In the same way the relation for sucrose obtained in the study can be taken as actual relation between viscosity and \( k_{\text{obs}} \).

\[ k_{\text{obs}} = 0.00007 (\eta - 0.12) \quad \ldots(3.16) \]

### 3.7 CONCLUSION

From the above discussion and analysis of the kinetic data it is concluded that the value of rate constant for the solutes having structure maker character in aqueous solutions is directly proportional to the viscosity of the solutions used in the kinetic study. Further investigations in the light of influence of viscosity / medium effect on rate of reaction are expected to be an important example as a model.
<table>
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<tr>
<th>Reference</th>
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<th>Journal</th>
<th>Volume</th>
<th>Year</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Radha Rani Gupta and Mukhtar Singh</td>
<td>J. Indian Chem. Soc.</td>
<td>85</td>
<td>2008</td>
<td>176</td>
</tr>
<tr>
<td>4</td>
<td>R. N. Goldberg and Y. B. Tewari</td>
<td>J. Biol. Chem.</td>
<td>264</td>
<td>1989</td>
<td>9897</td>
</tr>
<tr>
<td>5</td>
<td>S. K. Lomesh, Neelam Sharma, and Sushil Kumar</td>
<td>J. Indian Chem. Soc.</td>
<td>81</td>
<td>2004</td>
<td>881</td>
</tr>
<tr>
<td>6</td>
<td>Shashi Kant, Pankaj Dogra, and Sushil Kumar</td>
<td>Indian J. Chem. Soc., SecA</td>
<td>43</td>
<td>2004</td>
<td>2555</td>
</tr>
<tr>
<td>7</td>
<td>S. K. Lomesh, Pawan Jamwal, and Rakesh Kumar</td>
<td>J. Indian Chem. Soc.</td>
<td>83</td>
<td>2006</td>
<td>156</td>
</tr>
<tr>
<td>8</td>
<td>D. P. Miller</td>
<td>J. Phys. Chem. (B)</td>
<td>104</td>
<td>2000</td>
<td></td>
</tr>
</tbody>
</table>
and J. J. Depablo

9 R. Mathpal, Monathshetefur Chem., 137
S. Joshi
and
N. D. Kandpal

and
C. Rakkppan

11 P. C. Dey, Monathshetefur Chemie., 134(6)
M. A. Motin,
T. K. Biswas
and
E. M. Haque

and
E. R. Patnaik

B. R. Arbad,
M. P. Lokhande
and
S. C. Mehrotra

D. K. Choudhary
and
K. S. Birdi

B. Sahu,
S. Pradhan
and

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<table>
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<tr>
<th></th>
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<tr>
<td></td>
<td>H. R. Khan</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>T. A. Turney</td>
<td>Oxidation Mechanism,</td>
</tr>
</tbody>
</table>
26 (i) L. F. Sala, A. F. Cirelli and R. M. de Lederkren

(ii) M. Gupta, S. K. Saha and P. J. Banerjee

(iii) J. Barek, A. Berka and A. Pokorna- Hladikova

(iv) S. Signorella, L. Ciullo, R. Lafarga and L. F. Sala

(v) K. K. Gupta and S. N. Basu

(vi) E. O. Odebummi and R. Marufu

(vii) S. Gregory- Neyhart and R. R. Thorp

(viii) K. Michael and J. Harold


27(i) A. Kumar and R. N. Mehrotra

(ii) K. K. Sen Gupta, S. Sen Gupta and S. K. Mandal

(iii) P. O. I. Virtanen, S. Kurkisuo, H. Nevala and S. Pohjola

(iv) P. O. I. Virtanen and R. Lindroos-Heinanen

(v) Z. Khan and Kabir- Ud- Din

(vi) Z. Khan, P.S. S. Babu and Kabir- Ud- Din

28(i) S. Signorella, M. Rizotto, V. Daier, C. Frascaroli, D. Pdopoli, D. Martino, A. Bousseksou
and
L. F. Sala

(ii) Z. Khan,
P. Kumar and
Kabir- ud- Din

(iii) P. Kumar and
Z. Khan

29 S. Yamada,
S. Funahashi and
M. Tanaka

30 K. K. Sen Gupta,
B. A. Begum and
B. B. Pal

31 Bidyut Saha,
Sucharita Sarkar and
Kiran M. Chowdhury

32 John O’ M Bockris and
Amulya K. N. Reddy

33(i) R. K. Schmidt,
M. Karplus and
J. W. Brady

(ii) M. J. Tait,
A. Suggett, F. Frank, and
S. Abbett


Modern Electrochemistry vol(1) (1977) 487.


and
P. A. Quickenden

(iii) A. Suggett,
S. Abbett
and
P. J. Lillford

(iv) M. D. Danford


34 T. C. Bai,
C. C. Huang,
W. W. Yao
and
C. W. Zhu