



KINETICS AND MECHANISM OF SUCROSE Y V(V) IN AQUEOUS SULPHURIC ACID MEDIUM

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ABSTRACT

Kinetics of oxidation of sucrose by vanadium(V) in aqueous sulphuric acid medium have been investigated at 298K. The kinetic result indicated the first order dependence on V(V). The reaction rate increases with the increase in the concentration of the sucrose. The rate equation has been drawn on the basis of the experimental results.

Keyword : Oxidation, Vanadium(V), Sulphuric acid, Oxidation kinetics.

I. INTRODUCTION

The study of the oxidation of organic compounds by vanadium (V) has an importance due to role of vanadium in relation to the catalytic activity [1]. The study of oxidation mechanism of compounds by vanadium (V) has also an importance in the studies concerning possible role of transient ions oxidation reactions [2,3,4]. The kinetics of oxidation of D-glucopyranose-6-phosphate has been carried out in acidic media using such oxidants as V(V) [5].

Kinetics of oxidation of sucrose by vanadium (V) in sulphuric acid, perchloric and hydrochloric acid solutions has been subject of research [6]. 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 sucrose by vanadium (V) in sulphuric acid.

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_{obs} and $[H_2SO_4]$ 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 [7].

II. EXPERIMENT

The sulphuric acid was purchased from E. Merck and used without further purification. Double distilled water was used to prepare all concentrations of the acid. The strength of the acid of the each solution checked by titration against a standard solution of sodium hydroxide using phenolphthalein as an indicator. Progress of the reaction was monitored in the term of concentration of V(V) at 343nm with the help of spectrophotometer.

III. RESULT AND DISCUSSION

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.

Table 1: Effect of [Reactant] on the reaction rate k_{obs} at 298K

S.No.	[Sucrose] mole dm^{-3}	H_2SO_4 mole dm^{-3}	[V(V)] mole dm^{-3}	Value of 10^5 k_{obs} (sec^{-1})
1	0.4	2.0	0.002	9.0
2	0.4	2.0	0.003	9.1
3	0.4	2.0	0.004	9.2
4	0.4	2.0	0.005	9.1
5	0.4	2.0	0.006	9.2
6	0.04	2.0	0.004	0.8
7	0.05	2.0	0.004	1.1
8	0.06	2.0	0.004	1.3
9	0.07	2.0	0.004	1.6
10	0.08	2.0	0.004	1.7
11	0.09	2.0	0.004	1.9
12	0.04	1.0	0.004	2.2
13	0.04	1.5	0.004	3.7
14	0.04	2.0	0.004	5.5
15	0.04	2.5	0.004	7.3
16	0.04	3.0	0.004	9.2

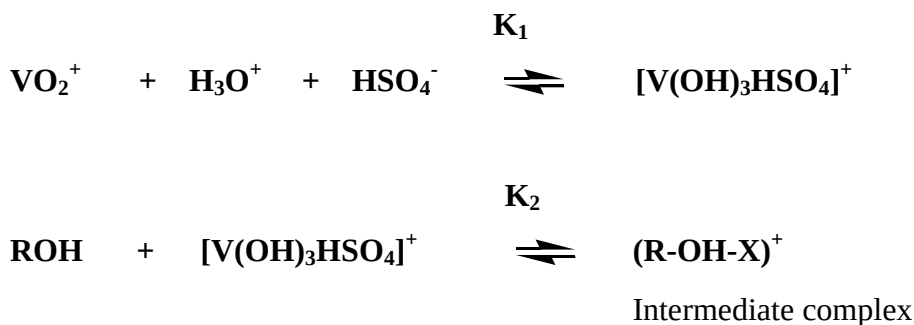
The results of the study of the kinetics of the oxidation of sucrose could be summarized as below-

The reactions have a first order dependence on vanadium (V), confirmed by the experimental data which was independent of the initial vanadium (V) concentration. The reactions are acid catalyzed and the catalytic effect increases with increasing concentration of sulphuric acid.

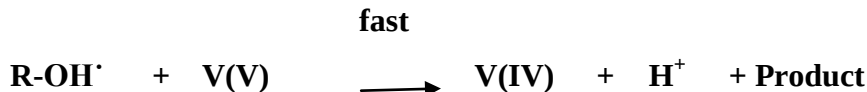
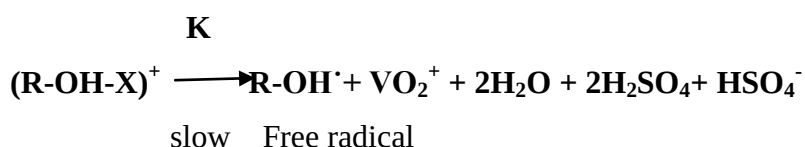
The reaction rates have linear dependence on concentration of sulphuric acid. The plot between concentration of sulphuric acid and rate constant indicates the order of the reaction nearly unity with respect to sulphuric acid concentration. The order with respect to the substrate concentration is also one for sucrose. 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 sucrose and first order with respect to vanadium. 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. 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. It is well established by earlier worker that the $[\text{V}(\text{OH})_3\text{HSO}_4]^+$ is kinetically active species of vanadium in aqueous sulphuric acid.

IV. MECHANISM

On the basis of the above facts and experimental results the mechanism for the oxidation of sucrose 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



Where X represent the species $[\text{V}(\text{OH})_3\text{HSO}_4]^+$



Scheme I

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

$$\begin{aligned} \text{Rate} &= k K_1 K_2 [\text{R-OH}]_T [\text{H}^+] [\text{V(V)}] [\text{HSO}_4^-] \\ &= \frac{k K_1 K_2 [\text{R-OH}]_T [\text{H}^+] [\text{V(V)}]_T [\text{HSO}_4^-]}{[1 + K_1 \text{H}^+] [\text{HSO}_4^-]} \end{aligned}$$

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

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

V. CONCLUSION

The rate expression proposed in the study is in good agreement with experimental result and previous studies related to the oxidant behavior (8).

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