

OXIDATION OF SUGARS BY CE (IV) IN AQUEOUS SULPHURIC ACID: KINETIC AND VISCOMETRIC APPROACH

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ABSTRACT

The kinetics of oxidation of sugars by cerium (IV) has been studied in aqueous sulfuric acid medium. The reaction is first order with respect to the accident. The plot of jobs against sugar concentration is linear for all the substrates. The kinetic data have been analyzed to correlate the viscosity and rate of oxidation of sugars in sulfuric acid.

The probable mechanism has been suggested with dependence of rate on the viscosity. The influence of viscosity on rate of reaction was observed. The linear relation was found between viscosity and reaction rate. The linearity coefficients were greater than 0.93 for all the sugars.

KEYWORDS: kinetics, Sugars, Ce (IV), Oxidation, sulfuric acid and Viscosity

INTRODUCTION

The viscosity data of aqueous concentrated hydrochloric acid have been utilized to investigate the influence of viscosity and viscosity parameters on the rate of hydrolysis of methyl acetate [1]. In a sulfuric acid water system strong ion solvent interactions have been proposed in the viscometric study [2]. The survey of literature has shown that considerable work has been done on the oxidation of various compounds by cerium (IV) in sulfate [3, 4, and 5], perchlorate [6, 7] and nitrate [8] acid medium. Kinetics of oxidation of D- fructose by cerium (IV) has been reported both in the absence and presence of surfactant in sulphuric acid medium [9]. The involvement of HSO_4^- ion with cerium (IV) has been considered in the mechanism proposed for the study.

The same author has reported the oxidation of L- sorbose [4], D- manose [10] and Arabians [3] by cerium (IV) in aqueous acidic medium. In the oxidation of arabinose it has been proposed that the pyramid form of monosaccharide and $\text{Ce}(\text{SO}_4)_3^{2-}$ are reactive species in the progress of the reaction.

In the present work, we have taken study with glucose, fructose and sucrose as substrates to determine the effect of viscosity in aqueous sulfuric acid on the rate of oxidation by Ce (IV) in the presence of sulfuric acid. The major constituents which contribute towards the viscosity of the reaction medium are sulfuric acid and sugars in aqueous solutions in this study. There are reports on viscosity studies of both these constituents in water and they have tremendous structure maker capacity [11, 12]. In the concentrated solutions (0.4 to 1.4 ml dm^{-3}) all features of the viscosity of reaction solutions have the same viscosity/ solvent effect on the rate of oxidation of sugars. We assume that there will be solvent particles, anions, cations and non ionic particles in such solutions which will contribute to the total viscosity of the medium and structure making characteristics.

EXPERIMENT

All the reagents used were of A.R. Grade chemicals and used without further purification. Double distilled water was used throughout this work. The strength of the acid of the each solution checked by titration against a standard solution of sodium hydroxide using phenolphthalein as an indicator.

The viscosity measurements were taken in a calibrated suspended-level Viscometer placed in a thermostated water bath for constant temperature. The solutions of sulfuric acid of knowing concentration was taken at Viscometer and flow time of the solution was measured. Each measurement was repeated thrice and average time of flow was used to calculate the viscosity. The Viscometer used in the study was purchased from Infusil India Pvt. Ltd. Having number BG43500 size 2 and BG43499 size 1. The densities of the solutions were measured with calibrated pycnometer and single pan electronic balance citizen make.

All kinetic measurements were performed under pseudo first order condition at a constant temperature at 298K unless stated otherwise. The reaction was initiated by mixing previously thermo stated solution of sugars and sulphuric and which also continue the required amount of Ce (IV) sulfate. The progress of the reaction was followed by measuring decrease in an observance of Ce (IV) at 353 NM as a function of time. The application of Beer's law to Ce (IV) at this wave length was verified. It was also verified that there is negligible interference from other regents at this wave length in aqueous sulfuric acid. In the presence of a crylonitrile, oxidant and substrate in aqueous sulfuric acid for all the sugars formation of turbidity were observed after several hours.

RESULTS AND DISCUSSIONS

Dependence of Rate on Initial [Oxidant]

The effect of [Cerium (IV)] on the reaction rate was studied at a constant concentration of sulfuric acid, sugars at constant temperature. The values of rate constant jobs in the concentration range 2.0 to 6.0×10^{-4} Mol dm⁻³ of cerium (IV) are summarized in Table 1. The rate constant jobs were independent of the initial [cerium (IV)]. These observations are in agreement with a first order dependence on [cerium (IV)]_T and the reaction follows a first order rate law given by the equation.

$$-d [\text{cerium (IV)}] / dt = k_{\text{obs}} [\text{cerium (IV)}]_{\text{T}}$$

Dependence of Rate on Initial [Substrate]

The pseudo first order rate constant k_{obs} were calculated at constant [Ce (IV)] and sulphuric acid but at different substrate concentrations in the range 0.4 to 1.4 mol dm⁻³. The plots of k_{obs} against [Sugars] are linear in all the cases. These plots give a straight line with a negative slope and positive slope depending upon the nature of sugar. The values of rate constant are given in Table 1. The detailed study related to variations of the reactant has not been carried out in the studio, but we have tried to correlate the viscosity and reaction rate in these oxidations of sugars by Ce (IV) in sulfuric acid. The plot between [sugars] and k_{obs} are linear with linearity coefficient 0.9626 for fructose and 0.9051 for glucose.

Table 1: Effect of [Reactants] on the Reaction Rate K_{obs} At 298K

S. No	[Substrate] mole dm^{-3}	[H ₂ SO ₄] mole dm^{-3}	[Ce(IV)] mole dm^{-3}	Value of $10^4 k_{obs}$ (sec ⁻¹)		
				Glucose	Fructose	Sucrose
1	0.02	2.0	0.0002	0.72	1.05	0.5
2	0.02	2.0	0.0003	0.70	0.99	0.52
3	0.02	2.0	0.0004	0.73	1.01	0.56
4	0.02	2.0	0.0005	0.69	1.04	0.51
5	0.02	2.0	0.0006	0.71	1.04	0.51
6	0.4	2.0	0.0002	4.08	19	3.09
7	0.6	2.0	0.0002	5.4	27.9	6.09
8	0.8	2.0	0.0002	6.2	33.2	7.39
9	1.0	2.0	0.0002	14.2	34.6	8.85
10	1.2	2.0	0.0002	21.3	43.4	13.2
11	1.4	2.0	0.0002	30.3	45.8	21.0
12	0.02	1.0	0.0002	1.89	2.05	2.00
13	0.02	1.5	0.0002	1.78	1.57	1.95
14	0.02	2.0	0.0002	1.92	1.34	1.92
15	0.02	2.5	0.0002	1.61	1.14	0.73
16	0.02	3.0	0.0002	1.49	1.04	0.53

Dependence of Rate on Initial [H₂SO₄]

The concentration range 1.0 to 3.0 mol dm^{-3} was used for the variations in [H₂SO₄] in the study. The concentrations of oxidant and substrate were taken constant. The observed dependence of the rate on the concentration of sulphuric acid in case of all the substrates shows that the rate decreases slightly with increase in concentration of sulphuric acid. The reaction rates are represented in Table 1.

Various proton dependent equilibria exist between the reactants [13]. The quantitative interpretation of the [H₂SO₄] dependence is very much complicated and uncertain. Hence due to this complexity no attempt was made to explain the observed [H₂SO₄] dependence in the mechanism proposed. However, the qualitative observation is in agreement with the fact that Ce (IV) oxidation of sugars in aqueous sulphuric media is retarded by an increasing [H₂SO₄]. The retardation in the rate with increasing H₂SO₄ suggests the removal of reactive species of Ce (IV) [10].

MECHANISM AND DISCUSSIONS

A reducing sugar can exist in different form in aqueous solutions [14]. It has been established that the rate of oxidation of sugars is the sum of rate contributed by the α - and β - anomers, together with the free aldehydic / ketonic forms [15, 16]. In the aqueous H₂SO₄ media complexation of sugars / organic substrate with Ce (IV) - sulphato species is a rare possibility [17]. The various species of cerium (IV) Ce(OH)³⁺, CeSO₄²⁺, Ce(SO₄)₂, HCe(SO₄)₃⁻, H₃Ce(SO₄)₄⁻ and Ce(SO₄)₃²⁻ are known to be present in H₂SO₄ media [18, 19]. The decrease in the rate of oxidation with increasing concentration of sulphuric acid confirms the presence of Ce- sulphato species with cerium (IV) ions in equilibrium with solvent or substrate molecules. The following steps given in scheme I are quite reasonable in which complex formed with Ce (IV) ion disproportionate in the rate determining step to give Ce (III) and a free radical. The presence of free radical has been confirmed in the oxidation process.

Table 2

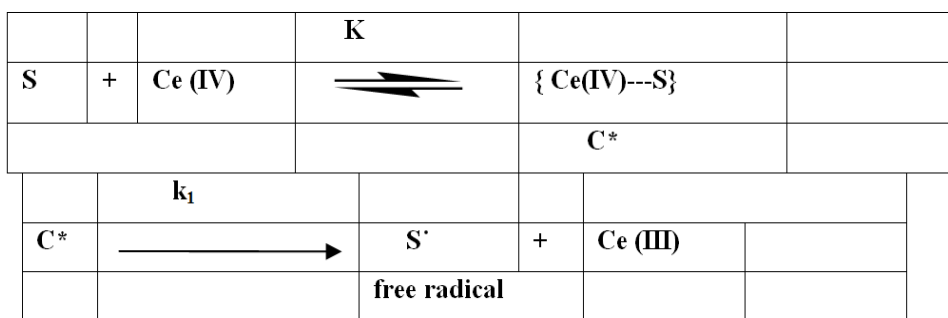
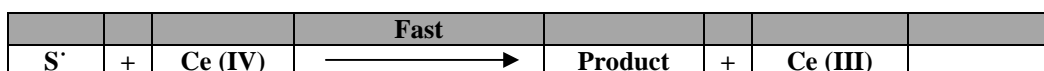


Table 3



Where S is Sugar.

Scheme I

The derived rate law for scheme I can be given by the equation

Table 4

$-\frac{d[\text{Ce(IV)}}{dt}$	=	$k_1 K [\text{S}] [\text{Ce(IV)}]$
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The above proposed mechanism is in accordance with the observations of first order dependence both in Ce (IV) and sugars and is also in agreement with the proposed mechanism [12, 20].

DEPENDENCE OF REACTION RATE ON VISCOSITY OF THE MEDIUM

In the previous section, we have proposed the linear relation between viscosity and k_{obs} of the substrate, on the basis of experimental results obtained in the oxidation of glucose, sucrose and fructose by vanadium (V) in aqueous sulphuric acid. In this chapter we analyze the experimental data of rate constant again in the light of viscosity effect as we have analyzed the results in the earlier chapter. In this study the experimental conditions, substrates, reaction media are similar as used in the previous study but only in place of vanadium (V) a different oxidant cerium (IV) has been used. Keeping in view the absorbance of the metal ion, the concentration of the oxidant Ce (IV) is taken twenty times less than the concentration of the vanadium (V). In both the studies, the reaction was first order with respect to the oxidant. The obtained values of the rate constants for the variation of viscosity have been used from Table 1. The plot between viscosity and k_{obs} values are given in Fig 1, 2 and 3. These plots were found to be linear having linearity coefficient > 0.92 , showing the dependence of rate on the viscosity of the reaction medium.

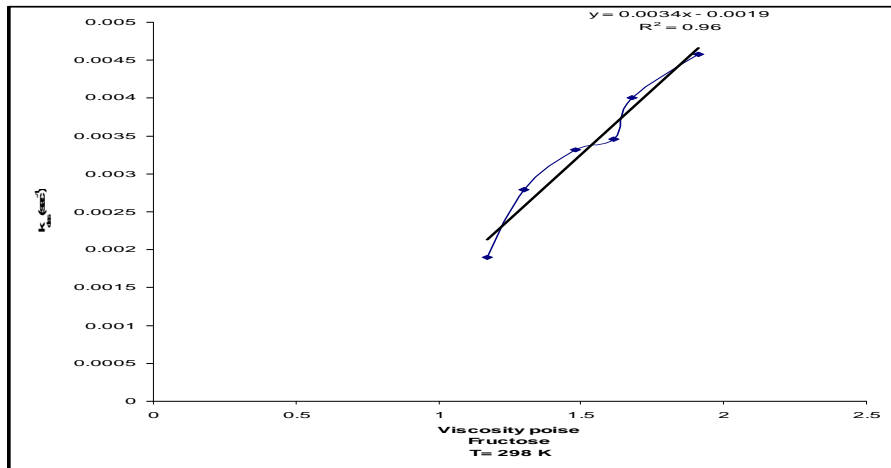


Figure 1

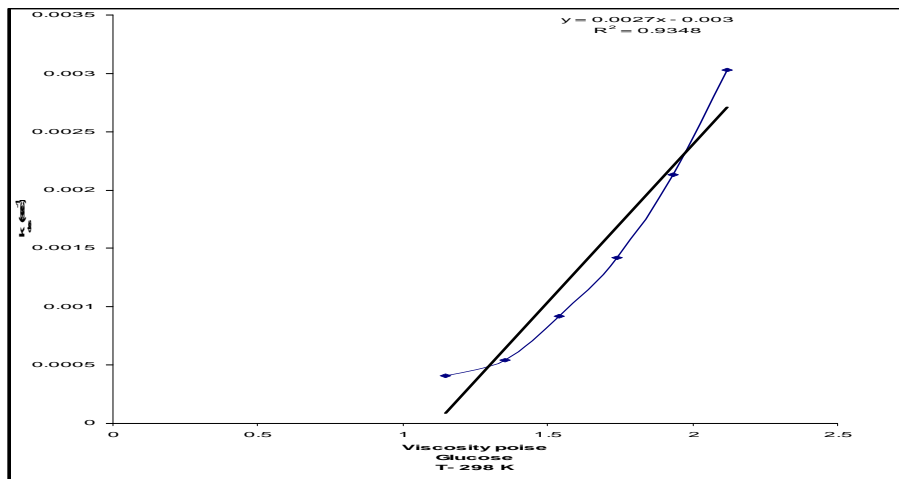


Figure 2

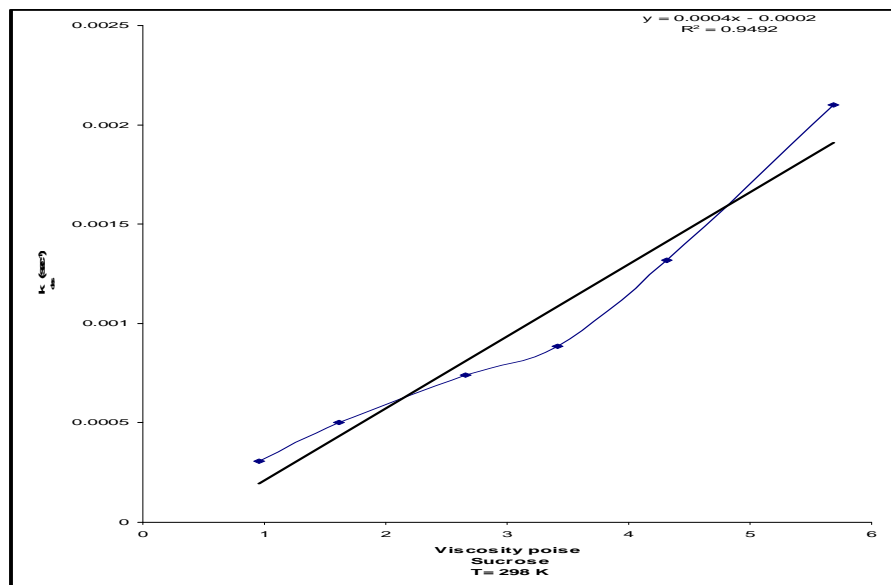


Figure 3

A comparison of the effect of viscosity on rate of oxidation of sugars in the study shows the order as follows-

Fructose > Glucose > Sucrose

On the other hand, the linear relations between viscosities are presented by equations 4.8, 4.9 and 4.10 for each substrate.

Table 5

K_{obs}	=	0.0034 H - 0.0019		Fructose
K_{obs}	=	0.0027 H - 0.003		Glucose
K_{obs}	=	0.0004 H - 0.0002		Sucrose

It is clear that k_{obs} is directly proportional to viscosity.

CONCLUSIONS

The results of the present investigation have strengthened our earlier conclusion that, the viscosity of the reaction medium has an influence on rate of reaction. It has been further established that this effect is measurable by monitoring the reacting species having structure maker property in aqueous solution.

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