

Kinetic and Mechanistic Investigation of Fructose with Ceric Ammonium Sulphate in Aqueous H₂SO₄

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Abstract: A kinetic investigation of the oxidation of fructose by Cerium(IV) in an aqueous sulphuric acid medium reveals that the reaction obeys first-order kinetics in both Ce(IV) and fructose. Increasing hydrogen ion concentration [H⁺] was found to lower the rate of reaction, and hydrogen sulphate ions likewise exert an inhibitory effect. The activation energy for the process has been determined, and a plausible mechanism is proposed in which Ce(IV) and fructose first combine to give an intermediate complex, whose slow decomposition constitutes the rate-determining step leading to the final products.

Keywords: Kinetics, Oxidation, Ce(IV), Fructose, Sulphuric Acid.

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I. INTRODUCTION

Chemical kinetics deals with how fast chemical reactions proceed, what factors govern their speed, and the step-by-step pathways through which reactants are transformed into products [1]. The field can be traced back to Willhelmy's investigation of cane-sugar inversion, which first introduced the rate constant and demonstrated the influence of temperature on reaction speed [2]. Since a rate law mirrors the underlying sequence of elementary steps, measuring reaction rates continues to be one of the most reliable ways of probing reaction mechanisms.

Temperature dependence was placed on a quantitative footing by Arrhenius in 1889, who showed that reaction rates rise sharply with temperature. For many reactions in solution the rate roughly doubles for every 10 °C rise, an empirical observation known as the Q10 rule [3]. The Arrhenius relation connects this behaviour to the activation energy, which is evaluated here for the oxidation of fructose.

Oxidation and reduction reactions in aqueous solutions have been widely studied because they are fundamental to many chemical processes. These reactions involve the transfer of electrons between different species in the solution, leading to changes in their oxidation states. Oxidation-reduction (redox) reactions involve the transfer of electrons

between two chemical species. In these reactions, a reducing agent loses electrons, meaning it undergoes oxidation. Meanwhile, an oxidizing agent gains those electrons, meaning it undergoes reduction. Redox reactions are key to understanding how substances interact by exchanging electrons, driving many chemical changes in nature and industry [4].

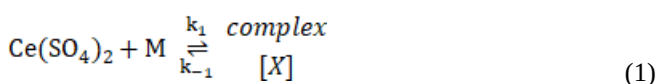
The present work reports a kinetic study of the Ce(IV)-mediated oxidation of fructose carried out in aqueous sulphuric acid. Ce(IV) is widely used as an oxidising agent across many branches of chemistry [5]-[9], and cerium(IV) salts, in which cerium is present in its +4 state, find application in numerous organic transformations [10] — reactions that may create or cleave chemical bonds, install new functional groups, or otherwise alter organic substrates. What sets cerium apart from the other lanthanides is its electronic structure, with a configuration of [Xe]4f¹5d¹6s². Because the energy of its inner 4f electrons lies so close to that of its valence electrons [11, 12], comparatively little energy is needed to shift electrons between these levels. This is what allows cerium to display the so-called “dual valence states” of +3 and +4 [13, 14] — a flexibility not typically seen in other lanthanides, which usually settle into a single dominant oxidation state [15, 16]. It is this distinctive behaviour that makes cerium so valuable across a range of chemical reactions and applications [17].

II. MATERIALS AND METHODS

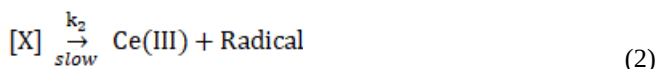
➤ Experimental

All chemicals employed were of analytical reagent grade. A standard sodium thiosulphate solution was first prepared [18], after which a ceric ammonium sulphate solution made up in 2N H₂SO₄ was standardised against it iodometrically, using starch as the indicator. To monitor the progress of the reaction, 5 ml aliquots were withdrawn from the reaction mixture at fixed time intervals; each aliquot was immediately quenched by adding 10 ml of 5% aqueous KI (potassium iodide) solution. The iodine liberated, which corresponds stoichiometrically to the unreacted Ce(IV) remaining, was then estimated by titrating against the standardised sodium thiosulphate solution.

A perusal of literature regarding Ce(IV) oxidation in sulphuric acid shows the complex formation of Ce(IV) with sulphate ions [19, 20]. Earlier workers have also described various species [21, 22] of Ce(IV) in sulphuric acid medium. The kinetic results recorded in Table 1 are in good agreement with the following mechanism:



Where M stands for Fructose



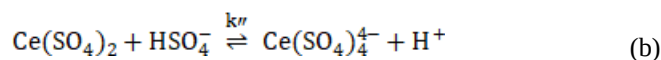
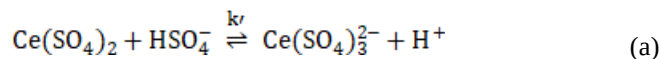
Reaction rate can be defined in terms of the decrease in Ce(IV) concentration over time. Hence rate is expressed as equation (1).

$$-\frac{d[\text{Ce(IV)}]}{dt} = k_2[\text{X}] \quad (3)$$

The proposed mechanism accounts for the observed rate law. (2)

$$-\frac{d[\text{Ce(IV)}]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [\text{Ce(IV)}] [\text{M}] \quad (4)$$

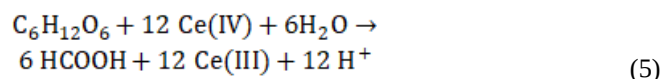
In Ce(IV) oxidations, it has been proposed that the inhibitory action is due to HSO₄⁻ ion [23, 24]. The inhibition caused by HSO₄⁻ ions [25] arises because the active Ce(IV) species, Ce(SO₄)₂, is converted into the inactive Ce(SO₄)₄⁴⁻ complex via the equilibria given in (a) and (b).



Likewise, an increase in sulphuric acid concentration leads to a corresponding decrease in reaction velocity.

III. RESULTS AND DISCUSSION

The reaction exhibited first-order dependence on both Ce(IV) concentration (Figure 1) and fructose concentration (Figure 2). Increasing the H₂SO₄ concentration was found to lower the reaction velocity (Figure 4), while the data in Figure 3 similarly indicate a decline in -dc/dt values as the ionic strength of the medium increases. The activation energy (ΔE) for fructose oxidation was determined to be 21 ± 0.2 kcal/mole. A series of experiments was also carried out using varying ratios of [Ce(IV)] to [fructose]. Analysis of the excess Ce(IV) revealed a stoichiometry of about 12.9 moles of Ce(IV) consumed for every mole of fructose oxidized. This value is close to the 12 equivalents expected for the conversion of fructose to six molecules of formic acid according to equation (3), in agreement with the one-electron oxidizing character of Ce(IV).



The slight excess over 12 may be due to experimental uncertainty in the estimation of unreacted Ce(IV). The oxidation product in each case was found to be formic acid. Formic acid was identified by the Thin Layer Chromatography (TLC) technique.

Table 1 Experimental Uncertainty in Estimation of Unreacted

[Ce(IV)] x10 ³ M	[Fructose] x10 ³ M	[H ₂ SO ₄] M	Ionic strength (μ)	Temperature (°C)	[HSO ₄ ⁻] x10 M	-dc/dt x10 ⁴ mole.lit. ⁻¹ min. ⁻¹
3.60	4.00	0.50	1.57	45	-	3.30
3.20	4.00	0.50	1.57	45	-	2.75
2.80	4.00	0.50	1.57	45	-	2.37
2.40	4.00	0.50	1.57	45	-	2.00
2.00	4.00	0.50	1.57	45	-	1.65
1.60	4.00	0.50	1.57	45	-	1.35
2.00	3.50	0.50	1.54	45	-	1.53
2.00	3.00	0.50	1.54	45	-	1.33
2.00	2.80	0.50	1.54	45	-	1.30
2.00	2.60	0.50	1.50	45	-	1.25
2.00	2.20	0.50	1.54	45	-	0.96
2.00	4.00	0.50	1.91	45	-	0.93
2.00	4.00	0.50	1.84	45	-	1.03

2.00	4.00	0.50	1.76	45	-	1.20
2.00	4.00	0.50	1.69	45	-	1.37
2.00	4.00	0.50	1.61	45	-	1.75
2.00	4.00	0.50	1.54	45	-	2.03
2.00	4.00	1.50	-	45	-	0.83
2.00	4.00	1.30	-	45	-	1.03
2.00	4.00	1.10	-	45	-	1.20
2.00	4.00	0.90	-	45	-	1.31
2.00	4.00	0.70	-	45	-	1.60
2.00	4.00	0.50	-	45	-	2.02
1.67	2.50	0.50	1.53	50	-	1.89
1.67	2.50	0.50	1.53	45	-	1.19
1.67	2.50	0.50	1.53	40	-	0.74
1.67	2.50	0.50	1.53	35	-	0.45
2.50	10.00	0.50	2.00	40	5.00	0.55
2.50	10.00	0.50	2.00	40	4.00	0.69
2.50	10.00	0.50	2.00	40	3.00	0.77
2.50	10.00	0.50	2.00	40	2.00	0.86
2.50	10.00	0.50	2.00	40	1.00	1.03

➤ Graphs

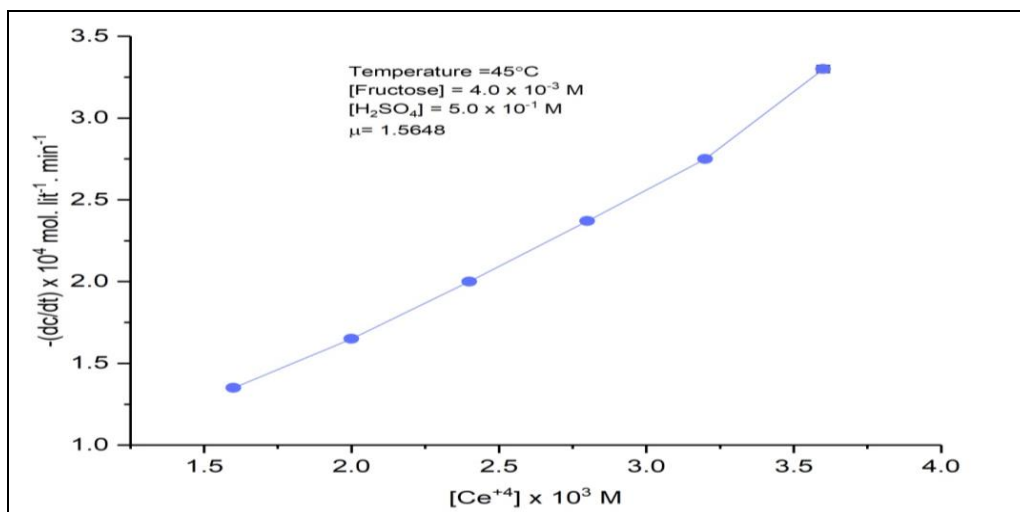
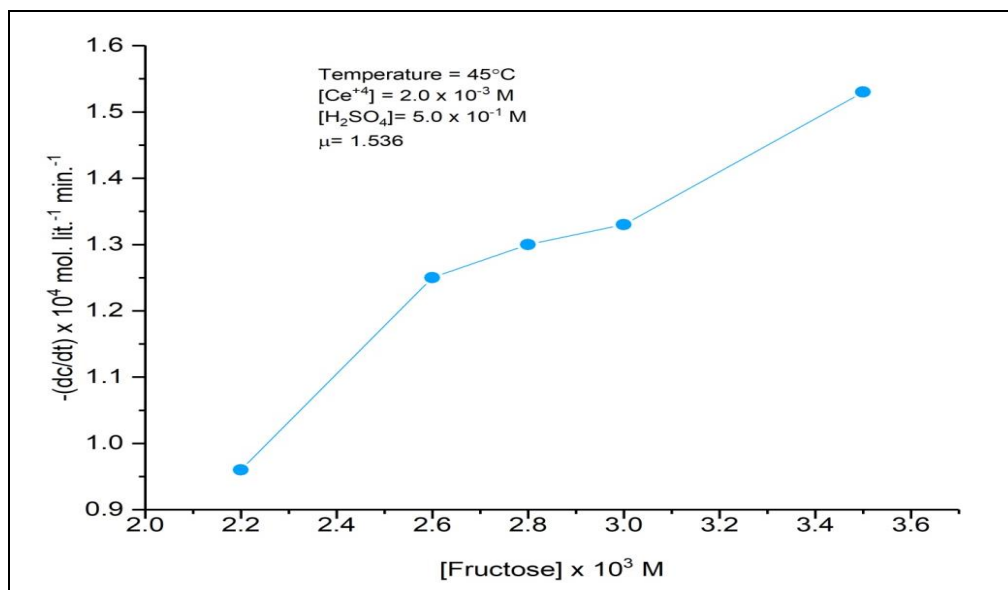
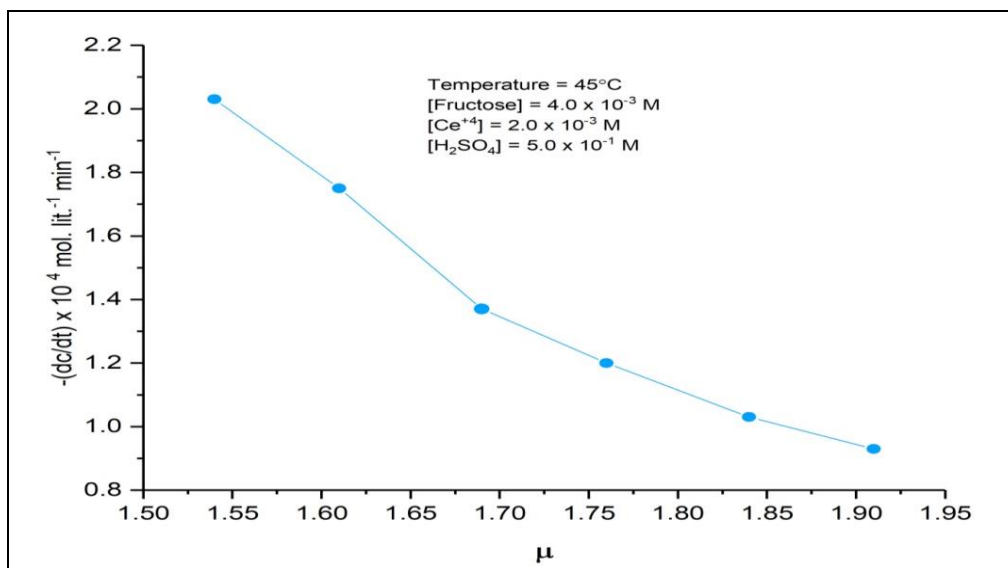
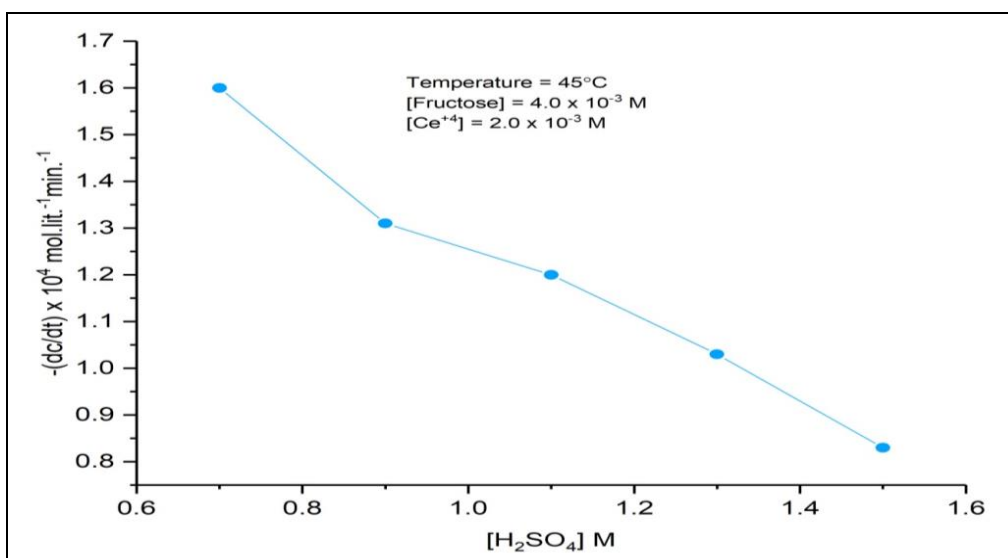
Fig 1 Plot of [Ce⁴⁺] Vs -(dc/dt)

Fig 2 Plot of [Fructose] Vs -(dc/dt)

Fig 3 Plot of μ (ionic strength) Vs $-(dc/dt)$ Fig 4 Plot of $[\text{H}_2\text{SO}_4]$ Vs $-(dc/dt)$

IV. CONCLUSION

The oxidation of fructose by Ce(IV) is first-order with respect to both Ce(IV) and fructose, which means that the reaction rate is directly proportional to the concentrations of these reactants. Consequently, a first-order dependence on the concentration of fructose was observed. The reaction velocity decreases with an increase in the ionic strength of the medium. Sulphate ions specifically retard the reaction, likely due to complex formation with Ce(IV) that reduces the availability of free Ce(IV) for the oxidation process. The activation energy (ΔE_a) for the oxidation of fructose was determined to be $21 \pm 0.2 \text{ kcal/mol}$, reflecting the energy barrier for the reaction. The main oxidation product was identified as formic acid, which was confirmed using TLC.

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