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Kinetic and Mechanistic Interpretation of the Sucrose Oxidation by Cerium(IV) in Aqueous H_2SO_4

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Abstract: Ce(IV) oxidation of sucrose in aqueous H_2SO_4 was studied by monitoring the loss of oxidant iodometrically. The rate increased linearly with both [Ce(IV)] and [sucrose], giving first-order dependence on each. The reaction slowed as the concentrations of H^+ and added sulphate rose, and it was also lowered by increasing ionic strength The activation energy, obtained from rate measurements at different temperatures, was 26.6 ± 0.2 kcal mol^{-1}. Formic acid was the principal product, and about 24 moles of Ce(IV) were consumed per mole of sucrose. A mechanism involving Ce(IV)-sulphate species is proposed that accounts for these observations.

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

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I. INTRODUCTION

This work investigates the kinetics of sucrose oxidation by Ce(IV) in aqueous sulphuric acid. Although cerium chemistry is well documented, few studies have examined in detail how Ce(IV) reacts with sucrose [1][2]. Tetravalent cerium is widely valued as an oxidant in many chemical processes, and this paper seeks to fill the gap with a thorough kinetic treatment of the Ce(IV)-sucrose reaction.

Cerium, a lanthanide, has an electronic structure and redox behaviour that have been studied at length [3]. In the +4 state it forms strongly oxidising compounds that drive many organic transformations [4], including the conversion of alcohols to aldehydes and ketones [5], the breaking of carbon-carbon bonds [6], and the installation of new functional groups [7]. Ce(IV) salts are useful in synthesis because cerium readily cycles between Ce^{3+} and Ce^{4+} [8][9]. This reversible change in oxidation state improves both the efficiency and selectivity of reactions, making Ce(IV) a valuable reagent for building complex molecules. Even so, the kinetic pathways and mechanism by which Ce(IV) oxidises sucrose remain poorly characterised, which motivates the present study.

Knowing the kinetic parameters and mechanism of this reaction helps clarify the wider uses of cerium chemistry [10]. With the electronic configuration [Xe] $4f^1$ $5d^1$ $6s^2$, cerium needs very little energy to alter the occupancy of its electronic levels, because the 4f and outer valence orbitals lie close in energy. This feature, unusual among the lanthanides, underlies cerium's usefulness across many reactions and applications [2][11]. By examining how the reaction rate responds to variables such as temperature and the concentrations of the reactants, acid, and sulphate, we aim to build a detailed kinetic profile of the reaction. These data are relevant both to fundamental understanding and to industrial processes that rely on Ce(IV) oxidation [12][13].

The main goal is therefore a systematic kinetic study of sucrose oxidation by Ce(IV) in aqueous sulphuric acid, measuring rates under a range of conditions to develop a kinetic model [14]. Establishing the rate law and activation energy will give a clearer view of the oxidation mechanism [1]. Cerium's accessible dual oxidation states add further interest, since they strongly affect how Ce(IV) behaves as an organic oxidant [15]. Through this research, we aim to enhance the understanding of Ce(IV) chemistry and its role in organic synthesis. The results may inform both the theory of chemical kinetics and the design of more efficient catalytic processes [16][17]. By clarifying how Ce(IV) behaves in this reaction, the study contributes to the academic literature and offers practical guidance for industries that use cerium-based oxidants [18][17].

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II. EXPERIMENTAL

All materials utilized in the experiment were of reagent grade, ensuring their high purity and suitability for precise analytical purposes. Additionally, a standard stock solution of sodium thiosulphate was meticulously prepared [15]. Ceric ammonium sulphate was dissolved in 2 N H_2SO_4, and its concentration was fixed by iodometric standardisation. To follow the reaction, 5 mL samples were withdrawn from the reacting mixture at suitable time intervals, and each was quenched in 10 mL of 5% aqueous KI. The iodine liberated in this step is equivalent to the Ce(IV) that had not yet reacted, so it was titrated against standard sodium thiosulphate to obtain the residual Ce(IV) concentration. Published work on Ce(IV) oxidations in sulphuric acid indicates that Ce(IV) binds sulphate ions to form complexes, and a number of distinct Ce(IV) species have been proposed for this medium [17]. The rate data in Tables 1–4 are consistent with the mechanism below:

$$Ce(SO_4)_2 + \text{Sucrose} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} complex\ [X] \quad (1)$$

$$[X] \xrightarrow[slow]{k_2} Ce^{3+} + \text{Radical} \quad (2)$$

Ce(IV) is used up as the reaction proceeds, the rate can be defined in terms of its concentration decrease, leading to the expression in Equation (3).

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

The rate expression derived from this scheme is given in Eq. (4).

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

In Ce (IV) oxidations, it has been proposed that the inhibitory action is due to HSO_4^- ion. The inhibitory action of HSO_4- ion is explained as due to conversion of the reactive form of Ce(IV), $Ce(SO_4)_2$ to the unreactive species $Ce(SO_4)_4^{4-}$ according to the equilibrium (a) and (b).

$$Ce(SO_4)_2 + HSO_4^- \overset{k'}{\rightleftharpoons} Ce(SO_4)_3^{2-} + H^+ \quad \text{----------(a)}$$

$$Ce(SO_4)_2 + HSO_4^- \overset{k''}{\rightleftharpoons} Ce(SO_4)_4^{4-} + H^+ \quad \text{----------(b)}$$

Similarly, with the increase in sulphuric acid concentration, the reaction velocity would also decrease.

III. RESULTS AND DISCUSSIONS

The dependence on Ce(IV) was examined first. The data in Table 1 show first-order behaviour with respect to the oxidant. This was confirmed in Fig. 1, where the rate (-dc/dt) is plotted against the concentration of ceric ammonium sulphate. Table 2 likewise shows that the reaction is first order in sucrose, and the plot of (-dc/dt) against [sucrose] in Fig. 2 supports this.

The effect of ionic strength is given in Table 3, with the corresponding (-dc/dt) values plotted against ionic strength in Fig. 3. Table 4 lists the rates at different sulphuric acid concentrations. A plot of (-dc/dt) against [H_2SO_4] (Fig. 4) gave a straight line, showing that the rate falls as the acid concentration rises.

The activation energy for the oxidation of sucrose was calculated to be 26.6 ± 0.2 kcal mol^{-1}. To determine the stoichiometry, several runs were carried out with different [Ce(IV)] to [sucrose] ratios. Analysis of the unconsumed Ce(IV) showed that one mole of sucrose consumes 24 moles of Ce(IV). Formic acid was identified by thin-layer chromatography as the oxidation product in every case.

➢ *Effect of [Ce(IV)] on the Rate of Oxidation of Sucrose in Sulphuric Acid Medium*

Table-1 Temperature = 40°C [Sucrose] = 12.5 x 10^{-3} M [H_2SO_4] = 5.0 x 10^{-1} M μ= 1.68

[Ce(IV)] x 10^3M	$-\frac{dc}{dt}$ **x 10^3 mole $lit.^{-1}$ min^{-1}**
10.00	9.486
8.00	7.324
6.00	4.960
4.00	3.273
2.00	1.587

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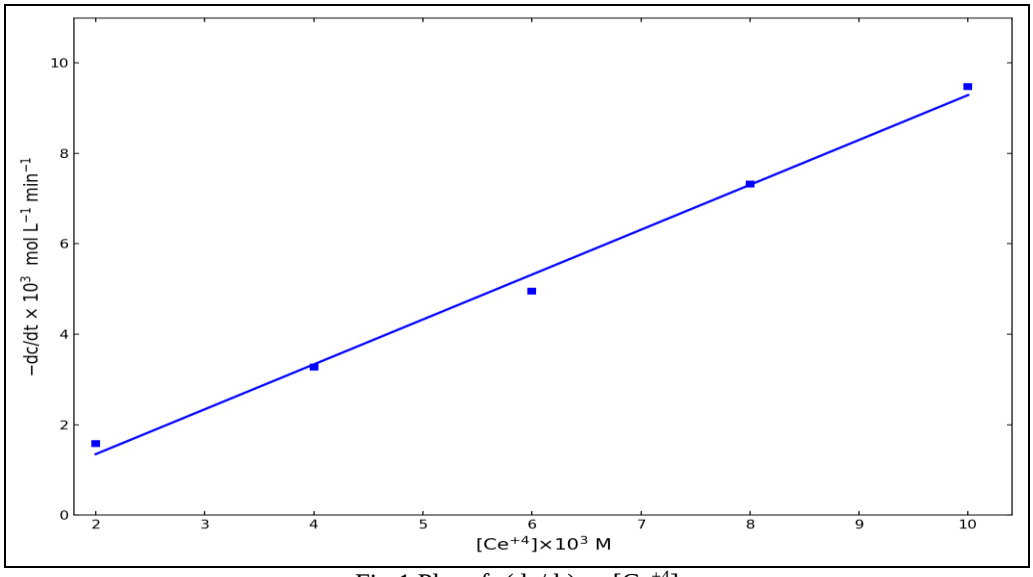


Fig 1 Plot of -(dc/dt) vs [Ce^{+4}]

➢ *Effect of [Sucrose] on the Rate of Oxidation of Sucrose by Ce(IV) in Sulphuric Acid Medium*

Table-2 Temperature = 40°C [Ce^{+4}] = 2.381 x 10^{-3} M [H_2SO_4] = 5.0 x 10^{-1} M μ= 1.542858

[Sucrose] x 10^3 M	$-\frac{dc}{dt}$ **x 10^3 mole lit.$^{-1}$ min^{-1}**
12.5	0.2205
6.25	0.1434
5.0	0.1286
2.5	0.0815

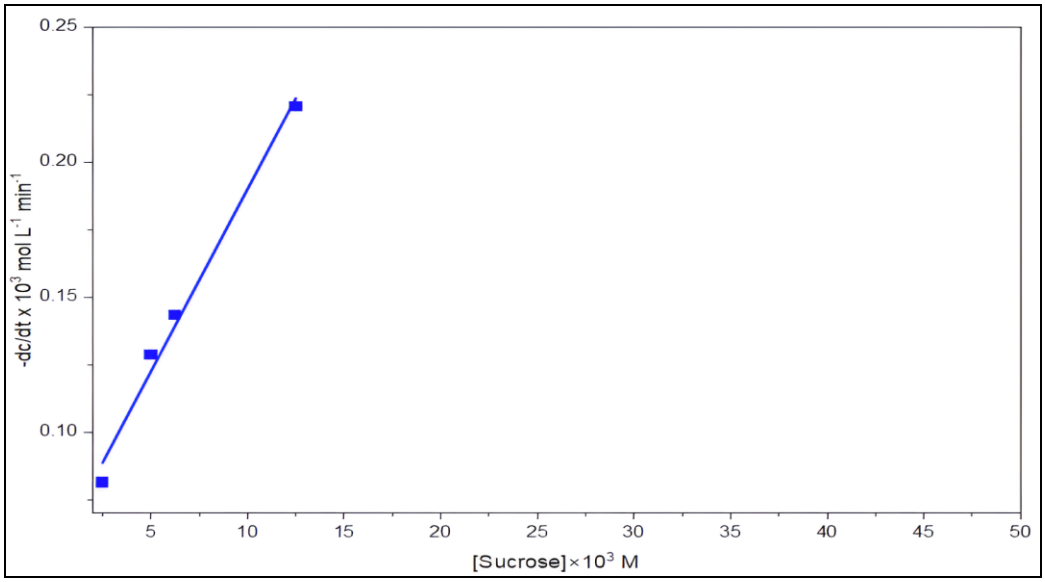


Fig 2 Plot of -(dc/dt) vs [Sucrose]

➢ *Effect of Ionic Strength (μ) on the Rate of Oxidation of Sucrose by Ce(IV) in Sulphuric Acid Medium*

Table-3 Temperature = 40°C [Sucrose] = 25.0x10^{-3}M [Ce(IV)] = 2.38 x 10^{-3} M [H_2SO_4] = 5.0 x 10^{-1} M

Ionic Strength(μ)	$-\frac{dc}{dt}$ **x 10^3 mole lit.$^{-1}$ min^{-1}**
1.542858	0.2885
1.692858	0.2307
1.842858	0.1884
2.142858	0.1108
2.292858	0.0911

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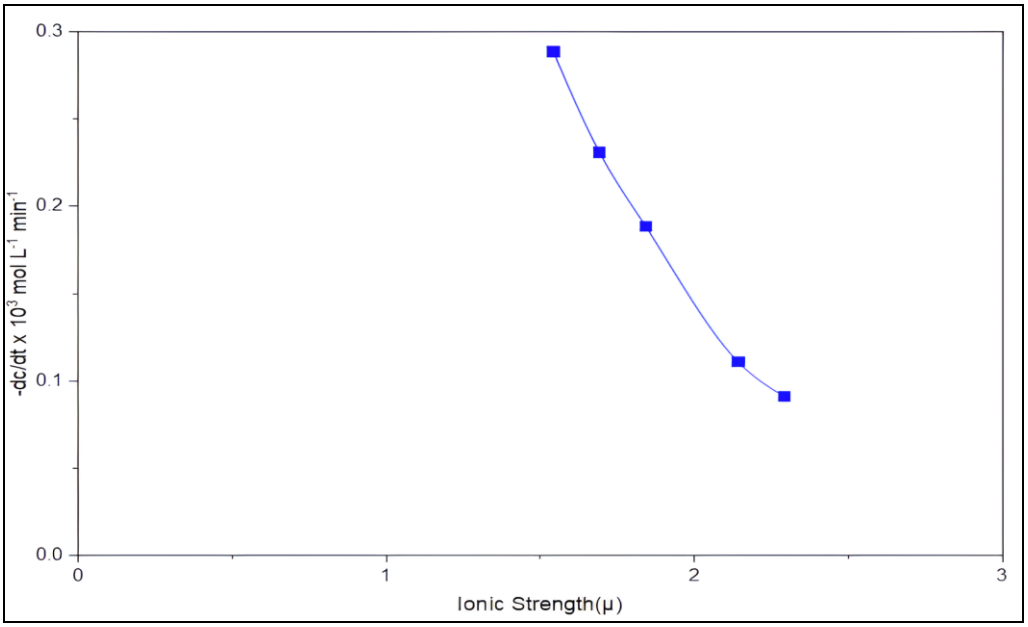


Fig 3 Plot of -(dc/dt) vs μ (Ionic Strength)

➢ *Effect of [H_2SO_4] on the Rate of Oxidation of Sucrose by Ce(IV)*

Table 4 Temperature = 40°C [Sucrose] = 25.0 x10^{-3}M [Ce(IV)] = 2.381 x 10^{-3} M

[H_2SO_4] x 10 M	$-\frac{dc}{dt}$ **x 10^3 mole lit.$^{-1}$ min^{-1}**
45.0	0.0918
37.0	0.1350
25.0	0.1943
13.0	0.255

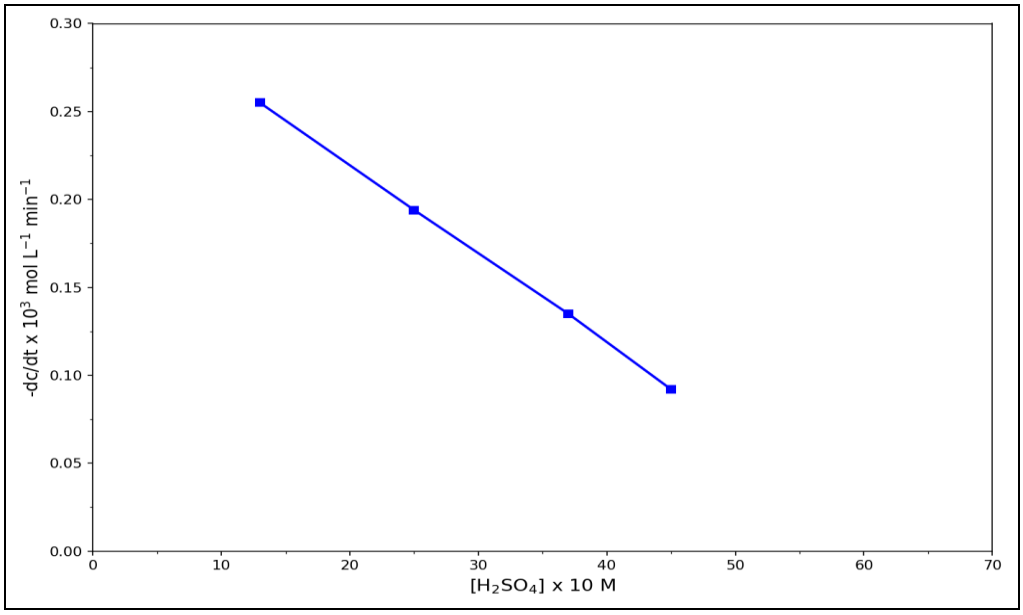


Fig 4 Plot of -(dc/dt) vs [H_2SO_4]

IV. CONCLUSION

The rate of sucrose oxidation by Ce(IV) is first order in each reactant, so it rises in direct proportion to both [Ce(IV)] and [sucrose]. Increasing the ionic strength of the solution lowered the rate. Added sulphate ions also retarded the reaction, most likely because they bind Ce(IV) into sulphato-complexes, which decreases the amount of free, more reactive Ce(IV) available to attack the substrate. From the temperature dependence of the rate, the activation energy (Ea) was calculated as 26.6 ± 0.2 kcal mol^{-1}, which corresponds to the energy barrier for the process. Formic acid was identified as the principal oxidation product by thin-layer chromatography.

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