Uncatalysed Oxidation of D-(+) Galactose by Cerium (IV) in Aqueous Acidic Medium-A Kinetic and Mechanistic Approach

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Authors' contributions

This work was carried out in collaboration between all authors. This experimental work was carried out by author MKG. Author SKR supervised the work. Author MKG collected the data form practical work and write down the whole manuscript. All authors read and approved the final manuscript.

| Research Article |

ABSTRACT

The Kinetics investigation of uncatalysed oxidation of D-(+) galactose by cerium (IV) have been studied in an acidic medium in the temperature range 308-328K. The reaction has been found to be first order with respect to D-(+) galactose in an uncatalysed reaction. The effect of $[HSO_4^-]$ has also been observed. The rate of reaction decreased with increasing the ionic strength of the medium. A 1:2 stoichiometry is observed in the oxidation reaction. From the effect of temperature on the reaction rate, various activation parameters have been computed. The various thermodynamic parameters were calculated form rate measurements at 308, 313, 318, 323 and 328 K respectively. A suitable mechanism has been proposed and a rate law explaining the experimental observations.

Keywords: Oxidation; uncatalysed; D-(+) galactose; cerium (IV); acidic medium and kinetics.

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1. INTRODUCTION

Carbohydrates are the fuel of life, being the main energy source for living organisms and the central pathway of energy storage and supply for most cells. The study of carbohydrates, many researchers have investigated the oxidative degradation of monosaccharides and their derivatives. Kinetic studies have been used as a tool to know the mechanism of a reaction [1-2]. Chemistry of cerium is a very broad area which has received considerable attention through the years, resulting in substantial advance both in the synthetic [3-4] and mechanistic categories. Cerium (IV) is a well known oxidant in acidic media [5-7] having reduction potential [8-9] of the couple Ce(IV)/Ce(III) 1.70V and is stable only in high acid concentration. In sulphuric acid and sulphate media, several sulphate complexes [10-12] of cerium (IV) form, but their role has not received much attention so far. Kinetic provides the most important indirect evidence in the mechanism. The metal ion oxidants have been widely employed in the synthetic chemistry [13-15] including carbohydrates chemistry [16-18]. These are stable, in expensive and can readily be stored and handled. The kinetic method of analysis have been widely developed and accepted in chemical analysis of different samples [19] and kinetic study of Ru(III) catalysed oxidation of sucrose by sodium periodate in acidic medium have been studied by various scientists [21-22].Some reports are also available on, micelle catalyzed oxidation of D-mannose by cerium(IV) in sulfuric acid [28] and the oxidation of amino acids by colloidal MnO_2 in the absence and presence of surfactants [29].

A review of literature shows that there is no information available on the kinetics and oxidation of D-(+) galactose in absence of catalyst by cerium (IV) oxidant from the mechanistic view point. There was a need for understanding the mechanism of oxidation of D-(+) galactose. This study may throw some light on the metabolic conversions in the biological system. Hence in the present communication, the kinetics and mechanistic aspects of the oxidation of D-(+) galactose by cerium (IV) in acidic medium at different temperatures has been investigated.

2. MATERIAL AND METHODS

2.1 Chemicals

Chemicals of absolute pure quality were used without further purification. Stock solution of D-(+) galactose and potassium bisulphate is prepared in double distilled water. Ce (IV) stock solution were prepared by dissolving ceric ammonium sulphate in aqueous sulphuric acid. sodium thiosulphate solution was standardized with standard iodine solution. All chemicals were purchased from E. Merck.
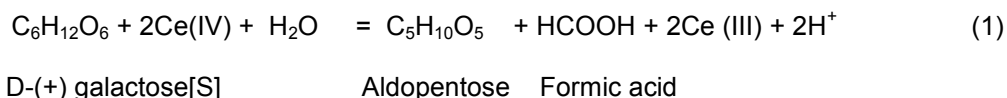
2.2 Kinetic Procedure

Kinetic runs were performed in stopper glass vessels in a controlled temperature ± 0.1ºC on water bath. Requisite volume ($90cm^3$) of all reagents, including substrate, were introduced into a reaction vessel and thermally equilibrated to 35ºC. A measured volume ($10cm^3$) of cerium solution, also at 35ºC was rapidly poured into the reaction vessel. The kinetics of the reaction was studied under the conditions [Substrate]>>[Oxidant] in the case of Ce(IV).The kinetics were followed by estimating aliquots of the reaction mixture for cerium(IV) iodometrically, using starch indicator. Doubly recrystallised milk sugar (E.Merck) were used for kinetic studies. Cerium solution was always made up and stored in black coated flask to

prevent photochemical reaction. The solution was then standarised with sodium thiosulphate solution using starch indicator. Aqueous solution of D-(+) galactose were prepared fresh each day. Kinetics of redox reactions between D-(+) galactose and cerium (IV) in sulphuric acid medium was followed under pseudo first order reaction at constant temperature.

2.3 Stochiometry and Product Analysis

Qualitative analysis of the oxidized reaction mixture with excess of carbohydrate with cerium (IV) in presence of H_2SO_4 was performed. After completion of kinetic experiment, a part of oxidized reaction mixture was treated with alkaline hydroxylamine solution and the presence of lactones in the reaction mixture was tested by $FeCl_3.HCl$ blue test [25].Formic acid formation and respective aldopentose were confirmed by spot test[23] and also by paper chromatography and high performance liquid chromatographic method. Formation of intermediate carbon centered aldopentose free radicals were confirmed by induced polymerization reaction with acrylonitrile and EPR spin trapping method [24].

The observed [20] stoichiometry of the reaction corresponds to the reaction can be represented by the equation. (1)

$$C_6H_{12}O_6 + 2Ce(IV) + H_2O = C_5H_{10}O_5 + HCOOH + 2Ce (III) + 2H^+ \qquad (1)$$

D-(+) galactose[S] Aldopentose Formic acid

In this reaction one mole of substrate oxidized by two mole of cerium (IV).

3. RESULT AND DISCUSSION

Experimental results indicate that the oxidation of D-(+) galactose by cerium (IV) in absence of catalyst is very sluggish. The order of reaction with respect to [Oxidant] was determined in (Table 1). Result shows that the rate constant is inversely proportional to the concentration of cerium (IV). This indicates the first order kinetics with respect to oxidant.

The order of reaction was determined at different concentration of D-(+) galactose and at fixed concentrations of other reactants in (Table 2). Plot of k_1 v/s D-(+) galactose concentration is found to be a straight line (Fig. 1a), which indicates that rate of reaction is directly proportional to the substrate concentration. The plot of log k_1 v/s log [D-(+) galactose] are linear. This indicates that the order with respect to D-(+) galactose is one (Fig. 1b).

The effect of H^+ ion concentration, on the reaction rate, the reaction has been carried out at various initial concentration of sulphuric acid tabulated in (Table 3). It has been observed that with increasing the concentration of $[H^+]$, the value of reaction rate decreased. This showed negative effect of $[H^+]$on the rate of reaction of D-(+)galactose. The involvement of proton dependent equilibria in the cerium (IV), the exact computation on $[H^+]$ is not possible. The inhibition of reaction rate by the addition of H_2SO_4 may be due to the removal of reactive species of cerium (IV). Thus results indicate that the involvement of cerium (IV)-sulphato species. The plot of k_1 v/s $1/[H^+]$ and log k_1 v/s log $[H^+]$ was linear [Fig. 2(a) and 2(b)].The result indicates that the order with respect to $[H^+]$ is inverse first.

The reactions were studied at different concentration of $KHSO_4$, while the other reactants are constant. The observations are given in (Table 4). Which indicates, the rate of reaction is

inversely proportional to HSO_4^- ion concentration. Thus the addition of salts viz. $KHSO_4$ did not have much effect on the rate of reaction.

To observe the effect of temperature on the reaction rate, the reaction was studied at different temperatures, while keeping all other reactants are constant in (Table 5). The kinetic data shows that the velocity of reaction increases with rise in temperature, showing the validity of the Arrhenius equation (Fig. 3). So an attempt has been made to correlate the various activation parameters on the reaction mechanism.

**Table 1. Effect of variation of [Cerium (IV)] on the reaction rate at 308K**

Run no.	10^3x[Ce(IV)] mol dm^{-3}	k_1x10^4(s^{-1})
1	1.00	1.24
2	2.00	1.16
3	3.00	1.18
4	4.00	1.13
5	5.00	1.00
6	7.00	0.99

10^2[D-(+) galactose]=5.00 mol dm^{-3}; 10^2[H$_2$SO$_4$]=3.00 mol dm^{-3}, 10^3[KHSO$_4$]= 5.00 mol dm^{-3}.

Table 2. Effect of variation of [D-(+) galactose] on the reaction rate at 308K

Run no.	10^2x[D-(+)galactose]mol dm^{-3}	k_1x10^4(sec^{-1})
1	0.50	0.42
2	1.00	0.71
3	2.00	1.09
4	3.00	1.32
5	4.00	1.77
6	5.00	2.15
7	6.00	2.71

10^3[Ce(IV)]=3.00 mol dm^{-3};10^2[H$_2$SO$_4$]=3.00 mol dm^{-3};10^3[KHSO$_4$]= 5.00 mol dm^{-3}.
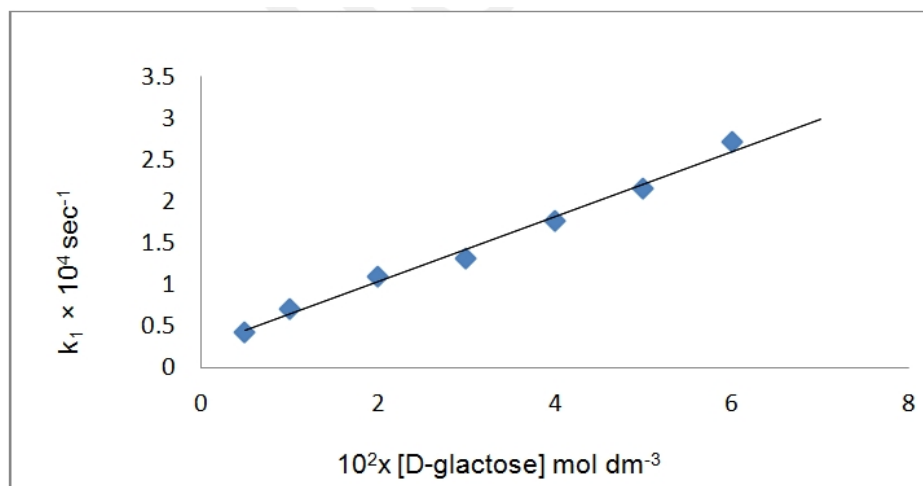
Fig. 1(a). Plot of k_1 v/s [D-(+) galactose]

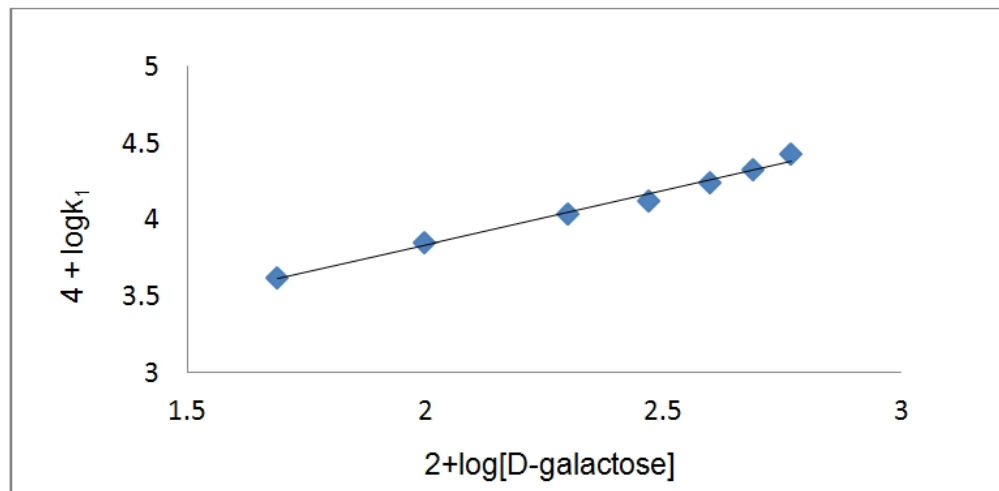**Fig. 1(b). Plot of logk$_1$ V/s log [D-(+) galactose]**

Table 3. Effect of variation of [H$^+$] on the reaction rate at 308K

Run no.	10^2x[H$_2$SO$_4$] mol dm^{-3}	k$_1$x10^4(sec^{-1})
1	0.50	2.76
2	1.00	1.72
3	2.00	1.10
4	3.00	0.85
5	4.00	0.75
6	6.00	0.60

10^3[Ce(IV)]=3.00 mol dm^{-3};10^2[D-(+)galactose]=5.00mol dm^{-3},10^3[KHSO$_4$]=5.00 mol dm^{-3}.
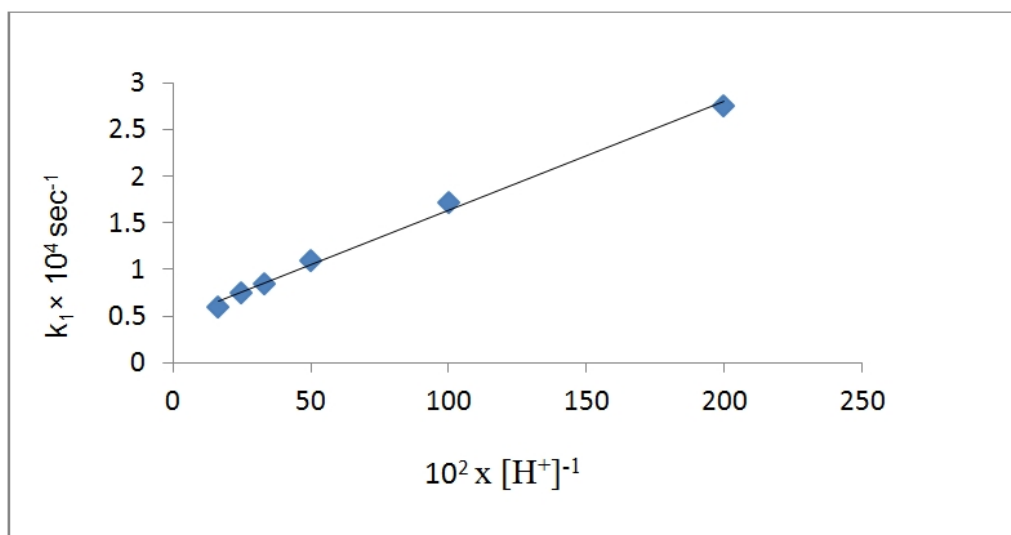

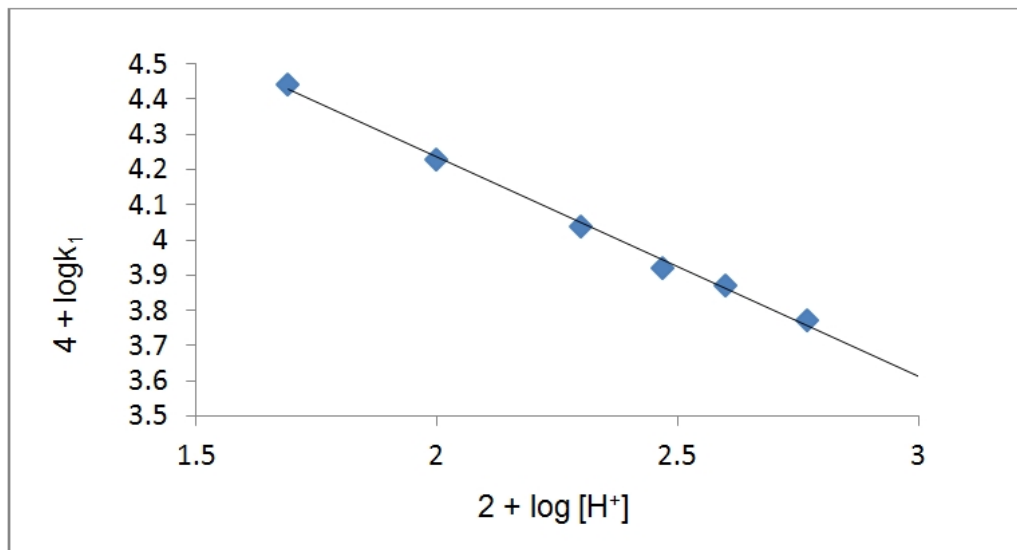**Fig. 2(a). Plot of k$_1$ v/s [H$^+$]$^{-1}$**

Fig. 2(b). Plot of log k$_1$ v/s log[H$^+$]

Table 4. Effect of variation of [KHSO$_4$] on the reaction rate at 308K

Run No.	10^3 x [KHSO$_4$] mol dm^{-3}	k$_1$x10^4(sec^{-1})
1	0.50	2.76
2	1.00	2.45
3	2.00	1.85
4	3.00	1.30
5	4.00	0.71
6	5.00	0.16

10^3[Ce(IV)]=3.00 mol dm^{-3}; 10^2[D-(+)galactose]=5.00 mol dm^{-3}, 10^2[H$_2$SO$_4$]= 3.00 mol dm^{-3}.

Table 5. Effect of variation of Temperature, on the reaction rate

Temperature in K	1/T x10^{-3}	k$_1$x10^4 sec^{-1}
308	3.24	2.76
313	3.19	4.88
318	3.14	7.00
323	3.09	9.10
328	3.04	11.20

Kinetic and thermodynamic activation parameters for uncatalysed reaction	
Parameter	**D-(+)galactose**
E$_a$* (kJ mol^{-1})	58.8
ΔH* (kJ mol^{-1})	56.2
ΔS* (J mol^{-1})	-44.4
ΔG* (kJ mol^{-1})	70.3
log A	10.5

10^3[Ce(IV)]=3.00 mol dm^{-3};10^2[D-(+)galactose]=5.00 mol dm^{-3};10^2[H$_2$SO$_4$]=3.00 mol dm^{-3}; 10^3[KHSO$_4$]=5.00 mol dm^{-3}
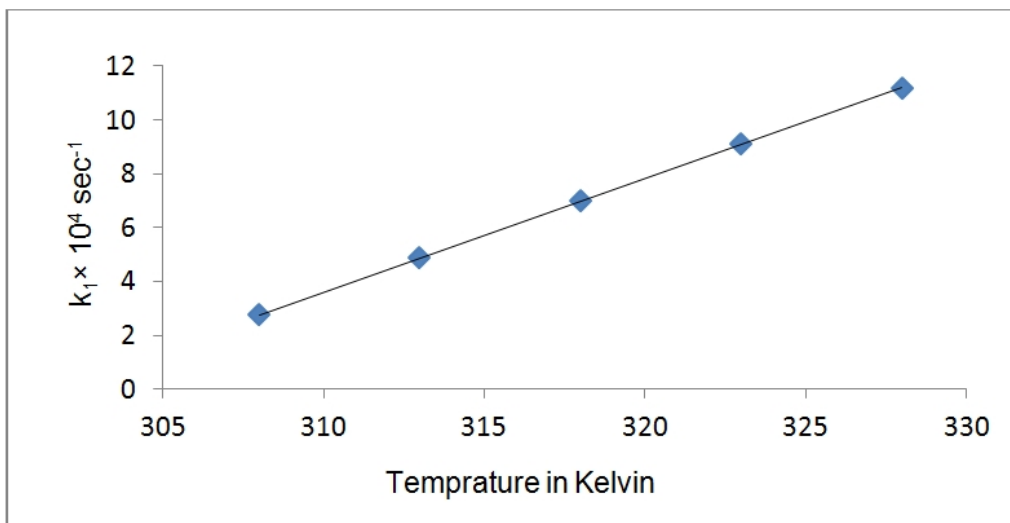
Fig. 3. Plot of k_1 v/s T

3.1 Energy and Entropy of Activation

The result shows that the average value of activation energy (E_a) was found to be 58.8 kJmol^{-1}.The value of enthalpy of activation (ΔH^*) at 318k is 56.2 kJmol^{-1},entropy of activation (ΔS^*) at 318k is -44.4Jmol^{-1},frequency factor (A) at 318 k is10.5 and Gibb's free energy of activation (ΔG^*) 70.3 kJmol^{-1}.In order to seen that the high positive value of change in free energy(ΔG^*) indicates reaction is highly solvated transition state, while negative value of change in entropy (ΔS^*) suggested, the formation of an activated complex with reduction in the degree of freedom of molecules.

3.2 Reaction Mechanism

The kinetics of the forgoing reactions were studied and showed that substrates and oxidant interact in an equilibrium step to form an intermediate complex which is assumed to disproportionate forming a free radical and reduced Ce(IV). It is believed that involvement of both $C_1$and C_2 hydroxyls in a complex formation. On the basis of above statement and observed first order dependence on [oxidant] as well as [substrate] a probable mechanism is proposed for the oxidation of D-(+)galactose such complex formation between the oxidant and substrate was observed in earlier studies[26-27]. Thus a mechanism consistent with the above kinetics is proposed (Scheme-I).
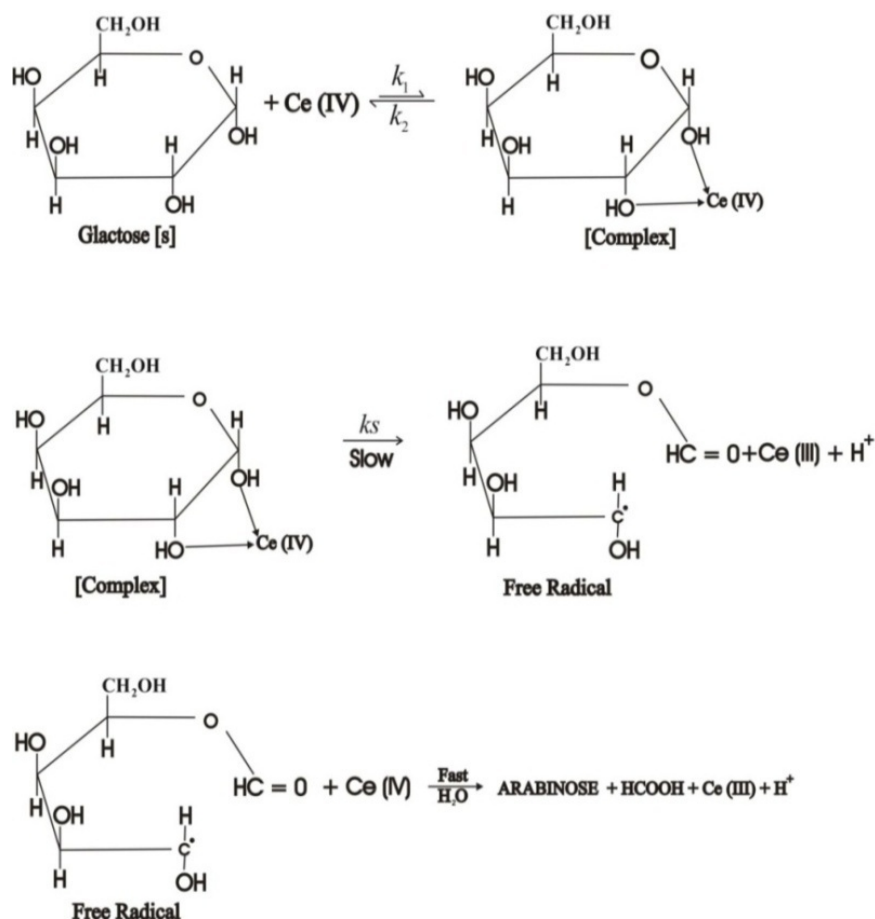
Scheme 1. The oxidation mechanism of D-(+) galactose

3.3 Rate Law

The proposed mechanism involves the formation of complex in a reversible manner which reach with the substrate at rate determining steps to form [Ce(IV)-S] complex followed by a slow redox decomposition giving rise to aldoxide radical which oxidized by Ce(IV) rapidly. The oxidation of D-(+) galactose at different temperatures from 308K to 328K was studied. The rate of disappearance of cerium (IV) in this reactions increases sharply with increasing concentration of D-(+) galactose.

Thus the rate of consumption of Ce(IV) from equation (1) is,

$$\frac{-d\left[Ce(IV)\right]}{dt} = 2k_s[complex]$$

(2)

Based on mechanism as mentioned in the above, the rate law can be deduced as follows,

$$\frac{-d[Complex]}{dt} = k_1[Ce(IV)][S] - k_2[complex] \tag{3}$$

At steady state condition,

$$\frac{-d[Complex]}{dt} = 0 \tag{4}$$

Hence,

$$k_1[S][Ce(IV)] = k_2[complex] \tag{5}$$

Therefore, the concentration of the complex becomes,

$$[Complex] = \frac{k_1[S][Ce(IV)]}{k_2} \tag{6}$$

At steady state condition, the rate of disappearance of [Ce(IV)] as given as in equation (2)

$$\frac{-d[Ce(IV)]}{dt} = 2k_s[complex] $$

Putting the value of [Complex] form eq.(6) we have,

$$\frac{-d[Ce(IV)]}{dt} = \frac{2k_sk_1[S][Ce(IV)]}{k_2} \tag{7}$$

Now, the total Cerium (IV) may be considered as,

$$[Ce(IV)]_T = [Ce(IV)]_e + [complex] \tag{8}$$

Putting the value of [Complex] we have,

$$[Ce(IV)]_T = [Ce(IV)]_e + \frac{k_1[S][Ce(IV)]}{k_2} \tag{9}$$

$$[Ce(IV)]_T = \frac{[Ce(IV)]_ek_2 + [k_1[S][Ce(IV)]]}{k_2} \tag{10}$$

The value of $[Ce(IV)]_T$ becomes as, since $[Ce(IV)]_e \approx [Ce(IV)]$

$$[Ce(IV)] = \frac{[Ce(IV)]_Tk_2}{k_2 + k_1[S]} \tag{11}$$

From the equation (7) and (11), rate law becomes as,

$$\frac{-d\left[Ce(IV)\right]}{dt} = \frac{2k_s k_1[S]}{k_2} x \frac{[Ce(IV)]_T k_2}{k_2 + k_1[S]} \tag{12}$$

$$\frac{-d\left[Ce(IV)\right]}{dt} = \frac{2k_s k_1[S][Ce(IV)]_T}{k_2 + k_1[S]} \tag{13}$$

$$k_{obs} = \frac{-d\left[Ce(IV)\right]/dt}{[Ce(IV)]_T} = \frac{2k_s k_1[S]}{k_2 + k_1[S]} \tag{14}$$

$$\frac{1}{k_{obs}} = \frac{1}{2k_s} + \frac{k_2}{2k_s k_1[S]} \tag{15}$$

On the plot of $1/k_{obs}$ against $1/[S]$ is made from which the constants $1/k_s$ and $k_2/k_s k_1$ are determined form the slop and intercept respectively. According to the equation mentioned in the above, when plot between $1/k_{obs}$ and $1/[S]$, a positive intercept would be observed which confirms the validity of the mechanism and also the rate law.

4. CONCLUSIONS

The oxidation of D-(+) galactose by cerium (IV) in sulfuric acid medium is to take place between the positively charged species of cerium (IV) and pyranose form of the monosaccharide. The reaction occurs through the formation of an intermediate complex, which slowly undergoes uni-molecular decomposition to yield a free radical. The free radical then reacts with cerium (IV) species to form the product. The high negative value of ΔS^* suggests the formation of more activated complex, whereas, the positive value of free energy of activation (ΔG^*) and enthalpy of activation (ΔH^*) indicates that the transition state is highly solvated. Energy of activation, free energy of activation and entropy parameters suggest that it forms the activated complex. Mechanism consistent with observed rate laws has been suggested in this study.

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COMPETING INTERESTS

Authors do not have any competing interests with the publication of this work.

REFERENCES

1. Ghosh MK, Rajput SK. Uncatalysed Oxidation of Dextrose by cerium (IV) in aqueous acidic medium-A kinetic and mechanistic study. Res. J. Chem. Sciences. 2012;2(11):55-60.

2.   Ghosh MK, Rajput S K. Kinetics and Mechanism of Uncatalysed Oxidation of D-ribose by cerium (IV) in Aqueous Acidic Medium. Asian J. Research Chem. 2012;5(8):1047-1052.
3.   Mathew B, Narayana NV, Sreekumar, vipin. A new reagent for the spectrophotometric determination of cerium (IV).Microchim Acta. 2005;144:291-298.
4.   Kolitsch V, Shwendtner K. A new chromate of tetravalent cerium. Acta. Cryst. 2004;C60:89-90.
5.   Pol PD, Katharic CP, Nandibewoor ST. Kinetics of oxidative degradation of pantothenic acid by cerium (IV) in aqueous perchloric acid. Transition met. Chem. 2002;27:807-812.
6.   Thabaj KA, Chimatadar SA, Nandibewoor T. Mechanistic Study of Oxidation of palladium (II) by Cerium (IV) in Aqueous Acid. Transition met. Chem.2006;31:186-193.
7.   Chimatadar SA, Madawale SV, Nandibewoor ST. Mechanistic study of iodide catalysed oxidation of 1-glutamic acid by cerium(IV) in aqueous sulphuric acid medium. Transition met. Chem. 2007;32:634-641.
8.   Day MC, Selbin J. Theoritical Inorg. Chemistry. Reinhold Pub. Corp.:New York; 1964.
9.   Vogel AI. A text Book of quantitative Inorganic analysis.3rd Ed. Longmans: London; 1961.
10. Pottenger CR, Johnson DC. Mechanism of cerium (IV) oxidation of glucose and cellulose. J. of Polymer Science part A-1: Polymer Chem. 2003;8(2):301-318.
11. Patil RK, Chimatadar SA, Nandibewoor T. Mechanistic study of cerium (IV) oxidation of antimony (III) in aqueous sulphuric acid in the presence of micro amounts of manganese (II) by stopped flow technique. Transition Met. Chem. 2008;33:625-628.
12. Kharzeoua SE, Serebrennikou V. Study of Sulphato Complexes of Cerium (IV) by Infrared Absoption Spectra. Russ. J. Inorg. Chem. 1967;12:1601-1605.
13. Chinn LJ, Selection of oxidants in synthesis, oxid. at carbon atoms. :Marcel Dekker New York; 1971.
14. Augustin RL. Oxidation I & II, Marcel Dekker; New York; 1969.
15. Evans WL, Oxidation of Carbohydrate with alkaline permanganatc silver oxide and copper acetate. Chem. Rev. 1929;6:281-284.
16. Butterworth RF, Haneesian S. selected method of oxidation in carbohydrate chemistry. Sythesis. 1971;70-78.
17. Heyns K, Paulsen H. The mechanism of carbohydrate oxidation. Adv. crabohydr.Chem. 1962;17:169-176.
18. Manhas M, Singh M, Kumar P, Hashmi AA, Khan Z. Influence of cerium(IV) and manganese(II) on the oxidation of D-galactose by chromium(VI) in the presence of HClO4. Kinetics and Catalysis. 2009;50(1):82-87.
19. Laidler KJ. Chemical Kinetics. Tata-McGraw Hill: New Delhi; 1965.
20. Singh RB, Siddhartha SP. Kinetic Estimation of Dextrose from the Rate Data by pseudo-first order reaction. Asian J. Exp. bio. Sci. 2010;1(1):204-207.
21. Narendra K, Singh SK, Singh SS, Singh S. Kinetic study of Ru (III) catalysed oxidation of sucrose by sodium periodate in acidic medium. J. Chemtracs. 2009;11(1):289-292.
22. Singh AK, Chopra D, Rashmani S, Singh B. Kinetics and mechanism of Pd(II) catalyzed oxidation of D-arabinose, D-xylose and D-galactose by N-bromosuc-cinimide in acidic solution. Carbohydrate Research. 1998;314:157-159.
23. Feigle F. Spot Test in Organic Analysis, Elsevier publishing Company, New York, p.208,1956.
24. Muller H. Catalytic methods of analysis: Characterization, classification and methodology, Pure Applied Chemistry. 1995;67(4):601-613.
25. Kumar A,Mehrotra RN. Kinetics of oxidation of Aldo Sugars by quinquevalent vanadium ion in acid medium. Journal of Organic Chemistry. 1975;40(9):1248-1252.

26. Horton D. 60th ed. Advances in Carbohydrate Chemistry and Biochemisry. 2006;60.
27. Rajput SK, Chaubey S. Kinetic Study of Oxidation of Milk Sugar by Ceric Ammonium Sulphate in Acidic Medium. J. Applicable Chemistry. 2012;1(1):79-96.
28. Kabir-ud-Din, Ali Mohd. Sajid, Khan Z. Micelle catalyzed oxidation of D-mannose by cerium(IV) in sulfuric acid. Acta Physico-Chimica Sinica. 2008;24(5):810-816.
29. Mohd. Akram, Mohd. Altaf, Kabir-ud-Din. Kinetics and mechanism of the reduction of colloidal MnO_2 by glycyl-leucine in the absence and presence of Surfactants. 2012;16(3):217-225.

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