Kinetics and Mechanistic Study of Platinum (II) Catalyzed Oxidation of Plant Derived D-(+) Galactoseby Cerium(IV) In Aqueous Sulphuric Acid Medium

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Abstract: The kinetics of the Platinum(II) catalyzed oxidation of plant derived $D_{-}(+)$ Galactose by cerium(IV) in sulphuric acid medium have been studied in the temperature range of (310-335)K. The order of the reaction found to be first order with respect to $D_{-}(+)$ Galactose in catalyzed reactions. The reaction proceed through the formation of an intermediate complex and the rate of the reaction decreases with increasing $[H_2SO_4]$. A1:2 stoichiometry is observed in the oxidation of $D_{-}(+)$ Galactose. The effect of temperature was studied and Arrhenius equation and various activation parameters have been calculated. Arabinose and formic acid have been identified as main oxidation products. A plausible mechanism was proposed and a rate law explaining the experimental results is derived.

Keywords: acid medium, catalyzed, kinetics, cerium, D(+) Galactose, oxidation, stoichiometry,

I. Introduction

The study and research on sugar chemistry is one of the necessary as well as interesting field in the modern analytical chemistry. It is well known that the basic metabolism of a cell is driven by the energy and these carbohydrates are the fuel of cell's energy. In our present work we have studied on D (+)-Galactose, which is monosaccharide containing six carbons and an aldehyde group, and is classified as an aldose and a hexose. It is found in dairy products, sugar beets, other gums and mucilages.D(+)- Galactose is commonly found in milk as part of the disaccharide lactose. In the human body, glucose is changed into D(+) Galactose via hexogenesis to enable the mammary glands to secrete lactose. However, most lactose in breast milk is synthesized from galactose taken up from the blood and only $35 \pm 6\%$ is made from galactose from De-novo synthesis [1]. In human body the main pathway of D(+)- Galactose metabolism is the Leloir pathway [2]. However, the Non-animal derived (NAD) D(+)- Galactose is a naturally occurring hexose sugar manufactured from wood-based or other biomass hydrolysates using an aqueous chromatographic separation process.

Platinum (II) is one of the noble metal having the ability to act as either reductant or catalyst. In aqueous acid medium the rate of the reaction increases as the PtCl₂gets dissociated i,e with increasing Cl⁻ ion concentration in the solution. The reaction proceed through different intermediate chloride complex formation of Platinum, as a result the mechanism of the reaction pathway is not only very complicated but also having several intermediate steps. It is quite difficult to identify the rate determining step (r.d.s) of the medium. The beauty of noble metals to use as catalyst because of their strong catalytic influences in both organic and inorganic chemistry leading to the applied field[3,4]. Any reaction mechanism have to obey certain parameters such as nature of both the oxidant and treating substrate as well as the transition state to enhance the activity of the reactant molecules to the activated by supplying activation energy (E_a)under certain experimental conditions. The kinetics oxidation of several carbohydrates by different inorganic, hybrid molecules even by organometallic compounds have been reported elsewhere [5,6,7,8,9,10,11].

Our works have both the theoretical and applied impact in the field of analytical chemistry. Here we first time report the kinetic study and plausible mechanism of plant derived D(+)- Galactose by Cerium (IV) in presence of Platinum (II) in aqueous H_2SO_4 medium at 310K. The primary results indicate that the reaction between D(+)- Galactose and Cerium(IV) in acidic medium is feasible in presence of catalytic amount of Platinum(II).

So the objectives of our study leads to

- i) To identify the products
- ii) Predict the probable pathway of the reaction
- iii) Deduce rate law
- iv) Activation parameters to be calculated

II. Experimental Work

The chemical reaction between Cerium(IV) and plant derived D(+)- Galactose (Sigma Aldrich) in aqueous acidic medium was carried out in the following way. First of all a fresh solution of Cerium(IV) and D(+)- Galctose was prepared by dissolving calculated amount in deionised water. The measured solution was standardised iodometrically by using standard sodium thiosulphate (Sigma Aldrich) solution, in presence of starch indicator. The solution of Platinum(II) chloride (Sigma Aldrich) was prepared by dissolving the PtCl₂ in H₂SO₄ of measured strength and a known strength of KHSO₄ (salt) solution taken in a 250 ml iodine flask. The solutions were kept in a thermostat for an hour to maintain the desired experimental temperature. The rates could be measured in daylight due to the higher stability of Cerium (IV) in acidic medium[12]. Thereafter, the requisite volume of the carbohydrates solution (5-8% of reaction mixture)was poured into reaction flask. A stop watch is started when approximately half of carbohydrate solution drained out of the pipette into the reaction mixture [13-15]. An aliquot of 10 ml of reaction mixture is withdrawn quickly at known intervals of time and poured into another iodine flask containing a drop of known strength [5% KI (Sigma Aldrich)] solution to arrest the reaction. The liberated iodine was titrated against standard sodium thiosulphate solution. A micro burette is used for this purpose. From the titre value, the amount of cerium(IV) present in the aliquot could be easily determined.

III. Analysis of Product

Completion of the reaction identified by the complete fading of the yellow colour due to the presence of Ce(IV). The generation of free radicals during the course of the oxidation is confirmed by using acronitrile monomer [12,16]. Certain amount of acronitrile was added to the reaction mixture slowly and after the addition of acronitrile a white precipitate appears slowly which proved that the reaction system can initiate the polymerization of acronitrile through the radical formation[17-18]. $C_6H_{12}O_6 + 2Ce^{+4}$ \longrightarrow $C_5H_{10}O_5 + HCOOH + 2Ce^{+3} + 2H^+$

After the completion of the above experiment the reaction mixture was treated with alkaline hydroxyl amine solution which intend to form lactone. The presence of lactones was tested by FeCl₃.HCl blue test [19-20]. To confirm the formic acid formation and concerned arabinose was confirmed by the help of spot test [21] paper chromatography and High Performance Liquid Chromatography (HPLC) method, chemical equivalence and kinetic study. The carbon centred chiral centre leading to the arabinose free were confirmed by EPR spin method [22].

IV. Result and Discussion

Under the conditions [substrate] >> [Ce(IV)] >> [Pt(II)] the reaction is studied at different concentration of D(+)-Galactose at fixed concentrations of other reactants. The order of reaction with respect to oxidant cerium(IV) is determined at constant concentration of substrate D(+)-Galactose for different concentration of cerium(IV). The results are given in (Table 1). The results show that the rate constant is inversely proportional to the concentration of cerium(IV) for catalysed system. In presence of Platium(II) the plot log (a-x) V/S Time was found to be linear (Fig.1), which indicates the first order kinetics with respect to oxidant. The order of reaction with respect to substrate D(+)-Galactose is determined at fixed concentration of other reactants for different concentration of D(+)-Galactose. The observations are given in Table 2. The results shows that the plot of logk₁v/s D(+)- Galactose concentration is found to be a straight line for catalysed system (Fig. 2), which indicates that the rate of the reaction is directly proportional to the substrate concentration.

In order to see the effect of $[H^+]$ ion concentration on the reaction kinetics, the reaction has been carried out at different concentration of H_2SO_4 , keeping other reactants concentration constant. From the kinetics study it has been observed that the rate of reaction decreases with increase of sulphuric acid concentration in Platinum(II) catalysed oxidation. The reason of decrease of reaction rate due to the removal of reactive species of cerium(IV). The results indicate the involvement of Ce(IV)- sulphato species.

To see the effect of Platinum(II) catalyst on the reaction rate the reaction has been carried out at different initial concentration of Platinum(II) chloride, while keeping all other reactant concentration constant. The plotted graph between Platinum(II) concentration and the rate constant showed a linear curve which indicate that the rate is linearly related to Platinum(II) concentration. The plot of $\log_{l_1} v/s \log[Pt(II)]$ is given in Fig.6. The rate of reaction increases with increase in Pt(II) concentration clearly suggest that the rate is directly proportional to the catalyst [Pt(II)]. The rate of reactions were also studied at different concentration of salt [KHSO₄], while the concentrations of other reactants are constant. From the plotted data it is evident that the rate of the reaction is inversely proportional to the HSO₄⁻ ion concentration. The concentration of [HSO₄⁻] electrolyte increase as a result of the salting-out effect the concentration of cerium(IV) at the reaction site decreases. Thus the [HSO₄⁻] dependence can be represented as equation (i)

(Arabinose)

 $k_{obs} = \frac{a}{b + c [HSO_4]}$ (i)

Where a,b,c are constants under experimental conditions. Here the value of k_{Obs} increases with the increase of [H⁺]. The plot of $1/k_{obs}$ v/s $1/[H^+]$ at 310K is found to be linear with a positive intercept and slop. To observe the effect of temperature on the reaction rate, the reaction kinetics was studied at different temperature from 310K to 335K, keeping all other reactants constant shown in Table4.

The experiment shows that the velocity of reaction increases with rise in temperature. The validity of Arrhenius equation showed in Fig. 4. The plot obtained by plotting $logk_1 v/s 1/T$ is linear for the catalysed oxidation.

4.1 Energy and Entropy of ActivationThe energy of activation (Ea) was found to be 45.56 KJ/mole for Pt(II) catalysed oxidation. The value of frequency factor at 320K is 7.85 min⁻¹ and entropy of activation at 320K is - 102.85 J/mole and free energy of activation (ΔG^*) is 71.68 KJ/mole but the value of enthalpy of activation (ΔH^*) is 41.88 KJ/mole. The value of entropy of activation is found to be negative. The high value of negative ΔS^* suggests the formation of more order activated complex, whereas the high positive value of the free energy of activation (ΔG^*) and enthalpy of activation (ΔH^*) indicate that the transition state is highly solvated. Energy of activation, free energy of activation and entropy parameters suggest that Pt(II) forms the activated complex more easily compared to the other noble metals.

4.2 Reaction mechanism and Derivation of rate lawAfter the detailed kinetic study, the kinetic data obtained are quite interesting. The reaction pathway follow the Michaelis-Menten model, suggesting that 1:1 type complex of substrate D(+)- Galactose and Pt(II) catalysed is formed in the first equilibrium step. The kinetic study came into fact that the D(+)- Galactose, cerium(IV) and catalyst Pt(II) interact with each other in two equilibrium steps to form an intermediate complex [23-25]. It is assumed that the intermediate complex disproportionate to form a free radical and reduced to Ce⁺³ ion. It is to be said approximately the involvement of C₁ and C₂ hydrolysis [26] in a complex. Here substrate i,eGalactose is easily protonised in acid media in presence of catalyst Pt(II), which indicate the involvement of H⁺ in the pre equilibrium step. Cerium (IV) has been found kinetically active in this study with generation of free radicals in the reaction. A proposed kinetic scheme is given below:-

Scheme 1:





4.3 Rate law The proposed mechanism leading to the formation of complex [Ce(IV)-S] is formed and this is the rate determining step followed by a slow redox decomposition giving rise to aldoxide radical which oxidised by Ce(IV) rapidly. The oxidation of D(+)- Galactose was studied at different temperature for 310 to 330 K. It has been observed that the disappearance of cerium(IV) in this reaction increases sharply with increasing of concentration of D(+)- Galactose.

 $[S] + 2 Ce^{+4}$ _____ Arabinose + HCOOH + 2 Ce^{+3} + 2 H^+(ii)

Here 1 mole of Substrate [S] = D-(+) Galactose is oxidised by two mole of cerium(IV). So, the rate law of disappearance of Ce(IV) is,

 $-d[Ce(IV)]/dt = 2 k_s [Complex]$ (iii) Based on the above proposed mechanism, the rate law can be deduced as follows:-

 $-d[complex]/dt = k_1 [Ce(IV)] [Pt(II)] - k_2 [Complex] - k_3 [Complex] [S] \dots (iv)$

at steady state

-d[complex]/dt = 0(v)

 $k_1[Ce(IV][Pt(II] = k_2[Complex] + k_3[Complex][S] \dots(vi)$

so, therefore the concentration of complex becomes,

k₁[Ce(IV)][Pt(II)]

[Complex] = _____ (vii)

$$\{k_2+k_3[S]\}$$

at steady state condition, the rate of disappearance of Ce(IV) can be given as

 $-d[Ce(IV)]/dt = 2k_{s} [Complex]_{1} \dots (viii)$

putting the value of [Complex], we have

$$-d[Ce(IV)/dt = \frac{2 k_{S}k_{1}k_{3}[S] [Ce(IV)][Pt(II)]}{\{k_{2} + k_{3}[S]\}}$$
(ix)

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Now the total Cerium(IV) may be considered as

 $[Ce(IV)]_{T} = [Ce(IV)]_{e} + [Complex] \qquad \dots \qquad (x)$

Putting the value of [Complex] we have $k_1[Ce(IV)][Pt(II)] \qquad(xi)$ $[Ce(IV)]_T = [Ce(IV)]_e^+ \frac{k_1[Ce(IV)][Pt(II)]}{\{k_2+k_3[S]\}}$

$$[Ce(IV)]e \{k_2 \! + \! k_3[S]\} + [k_1[Ce(IV][Pt(II)]$$

or, $[Ce(IV)]_T =$

..... (xii)

$\{k_2 + k_3[S] \ \}$

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

 $\{k_2\!\!+k_3\![S]\}+\{k_1\![Pt(II)]\}$

From equation (x) & (xiii) the final rate law can be written as

$$\frac{-d [Ce(IV)]}{dt} = \frac{2k_{S}k_{1}k_{3}[S][Pt(II)]}{\{k_{2} + k_{3}[S]\}} \times \frac{[Ce(IV)]_{T}\{k_{2} + k_{3}[S]\}}{\{k_{2} + k_{3}[S]\} + \{k_{1}[Pt(II)]\}} \dots (xiv)$$
or $\frac{-d [Ce(IV)]}{dt} = \frac{2k_{S}k_{1}k_{3}[S][Pt(II)][Ce(IV)]_{T}}{\{k_{2} + k_{3}[S]\} + \{k_{1}[Pt(II)]\}} \dots (xv)$
Under the present experimental condition, we may assume that
 $\{k_{2} + k_{3}[S]\} >> \{k_{1}[Pt(II)]\} \dots (xvi)$
So, the equation (xvii) becomes as
$$\frac{-d[Ce(IV)]}{dt} = \frac{2k_{S}k_{1}k_{3}[S][Pt(II)][Ce(IV)]_{T}}{k_{2} + k_{3}[S]} \dots (xvi)$$

$$\frac{-d[Ce(IV)]}{dt} = \frac{2k_{S}k_{1}k_{3}[S][Pt(II)][Ce(IV)]_{T}}{k_{2} + k_{3}[S]} \dots (xvii)$$

$$\frac{-d[Ce(IV)]}{dt} = \frac{2k_{S}k_{1}k_{3}[S][Pt(II)][Ce(IV)]_{T}}{k_{2} + k_{3}[S]} \dots (xvii)$$

$$\frac{Or, 1/k_{obs}}{dt} = \frac{1}{2k_{S}k_{1}[Pt(II)]} + \frac{k_{2}}{2k_{S}k_{1}k_{3}[S][Pt(II)]} \dots (xix)$$

From the plot $1/k_{Obs}$ V/S 1/[S] from which the constants $1/k_sk_1$ and $k_2/k_sk_1k_3$ are determined from the slope and intercept respectively. According to the above equation, when plots are made between $1/k_{Obs}$ V/S 1/[S], a positive intercept would be observed which confirms the validity of the mechanism and also the rate law. Equation (xviii) also suggests that the plot of $1/k_{Obs}$ V/S 1/[Pt(II) at constant [S] and $[H^+]$ should yield good linear plots through the origin.

The values of $k_s k_1 k_3$ and k_2 for [S] can also be calculated from the double reciprocal plots, as shown in the graphs.

V. Kinetically Active Ce(IV) Species

Here under the experimental condition (as described) in aqueous sulphuric acid medium the important Ce(IV) sulfato complexes are Ce(SO₄)⁺², Ce(SO₄)₂, HCe(SO₄)₃, and the relevant equilibrium constant are [27-30] Ce⁺⁴ + HSO₄⁻ \approx Ce(SO₄)⁺² + H⁺ β_1 = 3500(xx)

The equilibrium constants β_1,β_2 and β_3 are reported to be 3500, 200 and 3.4 at 25° c respectively.

Among the different sulfato species the kinetically active species should be inferred on the basis of kinetic data, but not according to the magnitude of concentration [28].

From the relationship between HSO_4^- and $K_{Obs}Ce(SO_4)_2$ has been found as the kinetically active species in the present study. The concentration of $Ce(SO_4)_2$ can be approximately obtained. As we know from the mass balance equation (xxiii) is obtained.

From equation (xx) - (xxii), the following equation can be derived $\begin{bmatrix} Ce(SO_{4})_{2} \end{bmatrix} \begin{bmatrix} H^{+} \end{bmatrix}^{2}$

$$[Ce^{+4}] = \frac{\beta_1 \beta_2 [HSO_4^-]^2}{[Ce(SO_4)_2] [H^+]} = \frac{\beta_1 \beta_2 [HSO_4^-]^2}{\beta_2 [HSO_4^-]}$$

 $[Ce(SO_4)_2] = -$

$$\frac{[\text{HCe}(\text{SO}_4)_3]}{\beta_3[\text{HSO}_4]}$$

 $[\mathsf{HCe}(\mathsf{SO}_4)_3] = \beta_3 [\mathsf{Ce}(\mathsf{SO}_4)_2] [\mathsf{HSO}_4]$

Substituting the above equation into equation (xxiv)

$$[Ce(IV)]_{T} = \frac{[Ce(SO_{4})_{2}][H^{+}]^{2}}{\beta_{1}\beta_{2}[HSO_{4}^{-}]^{2}} + \frac{[Ce(SO_{4})_{2}][H^{+}]}{\beta_{2}[HSO_{4}^{-}]} + [Ce(SO_{4})_{2}] + \beta_{3}[Ce(SO_{4})_{2}][HSO_{4}^{-}]$$
(xxiv)

By considering the relative magnitudes of the successive formation equilibrium constants which are in the order $\beta_1 >> \beta_2 >> \beta_3$, the value of $[Ce(SO_4)_2] [H^+]^2$ $[Ce(SO_4)_2] [H^+]$

$$\beta_1 \beta_2 [\text{HSO}_4^-]^2$$
 and

 $\beta_2[\text{HSO}_4^-]$

are much less than the latter two terms. Therefore we get equation (xxiv) from equation (xxiii)

Or,
$$[Ce(IV)]_{T} = [Ce(SO_{4})_{2}] (1 + \beta_{3}[HSO_{4}^{-}])$$

So, $[Ce(SO_{4})_{2}] = \frac{[Ce(IV)]_{T}}{1 + \beta_{3}[HSO_{4}^{-}]} = f[Ce(IV)]_{T}$
Or, $f = \frac{1}{1 + \beta_{3}[HSO_{4}^{-}]}$ (xxvi)

Where f denotes the fraction of kinetically active species to the total cerium (IV) Now applying the steady-state condition to the free radicals [27,31]

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Where T stands for total concentration

m

Substituting equation (xxvii) into equation (xxviii) we get,

$$k_{Obs} = \frac{2 k_{S} k_{1} k_{3} [Pt(II)]_{T} [S] [H^{+}]}{k_{3} [S] [H^{+}] + k_{2} \{1 + \beta_{3} [HSO_{4}^{-}]\}}$$
Assuming that
$$m = \frac{2 k_{S} k_{1} k_{3} [Pt(II)]_{T} [S] [H^{+}]}{k_{3} [S] [H^{+}] + k_{2}}$$
So, equation (xxviii) may be written as
$$K_{Obs} = \frac{m}{1 + \beta_{3} [HSO_{4}^{-}]}$$

$$\frac{1}{1 + \beta_{3} [HSO_{4}^{-}]} = \frac{1}{1 + \beta_{3} [HSO_{4}^{-}]} = (xxix)$$

Equation (xxix) is same as equation (i) from which we can able to explain the negative number order dependence on $[HSO_4^-]$. Equation (xviii) suggests that $1/k_{Obs}v/s$ $[HSO_4^-]$ should be linear and matches with the experimental data. Accordingly to thethe principle of salt effect, there must be a neutral molecule in rate determining step, which confirms Ce(SO₄)₂ as the kinetically active species in the present study.

VI. Figures and Tables Captions:

Fig. 1: Plot of log(a-x) v/s time Fig 2: Plot of log k_1 v/s log [D-(+) galactose Fig 3:Plot of log k_1 v/s log[KHSO₄] Fig.4: Plot of log k_1 v/s log[H⁺] Fig.5: Plot of log k_1 v/s log[Pt(II)] Table1: Effect of variation of [Cerium(IV] on the reaction rate at 310K Table 2: Effect of variation of [D-(+) Galactose] on the reaction rate at 310K Table 3: Effect of variation of [KHSO₄] on the reaction rate at 310K Table 4: Effect of variation of temperature on the reaction rate Table 5: Effect of variation of [H⁺] on the reaction rate at 310K. Table 6: Effect of variation of [catalyst] on the reaction rate at 310K.

m

k_{Obs}







Teble: 1

Run No.	10^3 x[Ce(IV)] mol-dm ⁻³	$K_1 x 10^4 \text{ sec}^{-1}$
1	1.00	7.24
2	2.00	6.67
3	3.00	5.95
4	4.00	5.25
5	5.00	4.87
6	6.00	4.17

Table 1: Effect of variation of [Cerium(IV] on the reaction rate at 310K.

Table : 2		
Run No.	10 ² x[D-(+) Galactose]	$K_1 x 10^4 \text{ sec}^{-1}$
1	1.00	2.57
2	3.00	3.855
3	5.00	5.18
4	7.00	8.72
5	10.00	12.57
6	12.00	15.084

Table 2: Effect of variation of [D-(+) Galactose] on the reaction rate at 310 K.

Table 3		
Run No.	10 ³ x[KHSO ₄] mol-dm ⁻³	$K_1 x 10^4 \text{ sec}^{-1}$
1	1	6.43
2	2	7.91
3	4	10.4
4	5	11.1
5	7	12.3
6	8	13.08
7	10	13.97

Table 3: Effect of variation of [KHSO₄] on the reaction rate at 310 K.

Table 4		
Temperature (K)	1/T x10 ⁻³	$K_1 X 10^4 \text{ sec}^{-1}$
310	3.48	6.1
315	3.42	7.79
320	3.38	9.1
325	3.33	11.49
330	3.29	16.7
335	3.24	19.2

Table 4: Effect of variation of temperature on the reaction rate.

Table	5
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Run No.	10^{2} x[H ₂ SO ₄] mol-dm ⁻³	$K_1 x 10^4 \text{ sec}^{-1}$
1	2	6.5
2	4	5.8
3	6	5.05
4	8	4.7
5	10	4.2
6	12	3.65
7	14	3.35

Table 5: Effect of variation of [H⁺] on the reaction rate at 310 K.

Table 6

Tuble 0		
Run No.	10^5 x[Pt(II)] mol-dm ⁻³	$K_1 x 10^4 \text{ sec}^{-1}$
1	6	6.53
2	8	7.34
3	10	8.15
4	12	9.1
5	14	9.87
6	16	10.65

 Table 6: Effect of variation of [catalyst] on the reaction rate at 310 K.

VII. Conclusions

The oxidation of plant derived D(+)-Galactose is an unique process in acid medium. This

Chemical reaction proceed slowly but the rate of the reaction increased in presence of Pt(II) catalyst. The reaction proceed through the measurable velocity in presence of small amount $(10^{-5} \text{mol dm}^{-3})$ of platinum. The main active species of cerium(IV) is considered to be $Ce(SO_4)_3$, although other species might be active to a much lesser extent. The beauty of the study of the reaction rate involves the estimation of the activation energy and equilibrium constant involves in the mechanism. The observed results were explained by plausible mechanism. The rate laws were also deduced by the help of kinetic study. It is to be said that plant derived galactose which was unique in the kinetic study research, and Pt(II) shows efficient catalytic behaviours in the reaction medium.

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