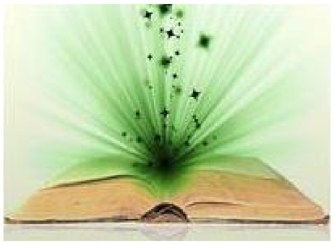
Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry, 2012, 1 (1): 79-96

(International Peer Reviewed Journal)



Kinetic Study of Oxidation of Milk Sugar by Ceric Ammonium Sulphate in Acidic Medium

Surendra K. Rajput[*1] **and Sonal Choubey**[*2]

1. Department of Chemistry, Govt. N.P.G. College Raipur-492010 (C.G), India
2. Department of Chemistry, Disha Institute of management and Technology

E-mail: sonalchoube@gmail.com

ABSTRACT

The kinetics of uncatalysed and catalysed oxidation of D-galactose by Cerium(IV) has been studied in acidic medium in the temperature range 303-338 K. The reaction has been found to be first order with respect to [D-galactose]. The rates follow first order kinetics in [Ir(III)] catalysed oxidation reaction. The effect of [HSO_4^-] has also been observed. The increase in ionic strength of the medium decreases the rate of uncatalysed reaction while increases catalysed reaction. A1:2 stoichiometry is observed in the oxidation. From the effect of temperature on the reaction rate, the Arrhenius and activation parameters were calculated. A suitable mechanism was proposed and a rate law explaining the experimental results is derived.

Keywords: Cerric Ammonium Sulphate (CAS), Oxidation of milk sugar (D-Galactose,), Kinetics, Mechanism in Ir (III) catalyst.

INTRODUCTION

The oxidation of aldoses by chlorine and bromine have been reported in alkaline media [1,2]. The use of periodate in the non-catalyzed oxidation of carbohydrates and Ru (III) and the ruthenate ion-catalyzed oxidation of reducing sugars in an alkaline medium are available[3]. From the previous work on cerium oxidation it has been seen that cerium is a strong oxidizing agent and it can oxidize various organic and inorganic substances such as amino acids[4], antimony(III)[5], 4-piperidones[6], formic acid[7], phenethyl alcohols[8], glycols[9], dialkylsulphoxides[10], tellurium(IV)[11], toluene, benzene (Ru catalyzed)[12], cyclic alcohol[13] and cyclic ketones (Ru catalysed)[14] etc.

MATERIALS AND METHODS

The progress of the reaction between Ce(IV) and D-galactose in aqueous sulfuric acid medium is studied .Ceric ammonium sulphate (0.5M) acidified with sulfuric acid in presence of $IrCl_3$ catalyst, $KHSO_4$(salt) and sodium thiosulfate (reductant) solution of same concentration, taken separately in 250 ml iodine flasks and placed in a thermostat for an hour to attain the temperature of the bath. The rates could be measured in daylight [19]. Afterwards, the requisite volume of the carbohydrate solution (2%-8% of reaction mixture) was poured into a reaction flask. A stop watch is started when approximately half of carbohydrate solution drained out of the pipette into the reaction vessel [15-17]. An aliquot of 10ml of reaction mixture is withdrawn quickly at known intervals of time and poured into another iodine flask containing a drop of 0.05M potassium iodide solution to arrest the reaction. Hypo solution of known concentration was then titrated back against cerric ammonium sulphate solution of the same strength. A micro burette is used for this purpose. From the titre value, the amount of cerric ammonium sulphate present in the aliquot was determined.

Product identification: Completion of the reaction was marked by the complete fading of the yellow color due to Ce(IV). The product of oxidation of D-galactose was detected and estimated. The generation of free radicals during the course of the oxidation is confirmed by using acrylonitrile monomer [18,19]. To a reaction mixture containing [Ce (IV)] =4.0×10^{-3} M, [D-galactose]=5.0×10^{-2} and [H_2SO_4] = 0.5 M ,20%,v/v acrylonitrile was added. Formation of a polymer (white precipitate) appeared slowly, indicating that the reaction system can initiate polymerization of acrylonitrile and also prove the generation of radicals in the reaction [20].

Qualitative analysis of the oxidized reaction mixture with the excess Carbohydrate over Ce(IV) (the kinetic condition) in presence of H_2SO_4 is performed. After the kinetic experiment is completed, a part of the oxidized reaction mixture was treated with alkaline hydroxylamine solution, and the presence of lactones in the reaction mixture is tested by $FeCl_3.HCl$ blue test [21].

To the other part of the reaction mixture, barium carbonate was added to make the solution neutral[22]. $FeCl_3$ solution that has been colored violet with phenol when added to this reaction mixture gave a bright yellow coloration[28], indicating the presence of aldonic acid. It was concluded that lactone, formed in the rate-determining step, was hydrolyzed to aldonic acid in neutral medium in a fast step. Formic acid and corresponding acid are confirmed by the help of spot tests [35], chemical equivalence and kinetic studies. The identification of aldonic acid were made by comparative paper chromatography and by properties of its diethyldithioacetal derivative.

Qualitative identification of reaction products from cerium(IV) oxidations of various reductants are made by comparative descending paper chromatography. These chromatograms are run on Whatman No. 1 paper exclusively.

RESULTS AND DISCUSSION

Under the condition [S]>>[Ce(IV)]>>[Ir(III)], the reaction was studied at different concentration of D-galactose at fixed concentrations of other reactants. The order of reaction with respect to substrate D-galactose is determined at fixed concentration of cerium(IV) for different concentrations of D-galactose. The results are given in (Table-1,2).

Table-1 Effect of variation of [D-galactose]; on the uncatalysed reaction rate
10^3x[Cerium(IV)] = 4.0 M; 10x[H_2SO_4] = 5.0 M; Temp. = 303 K

Run No.	10^2x[D-galactose] M	k_1 x10^4 min^{-1}
1	**5.00**	**19.1**
2	4.00	14.5
3	3.00	12.8
4	2.00	10.1
5	1.50	8.6
6	1.00	6.7
7	0.50	4.7

Table -2 Effect of variation of [D-galactose]; on the catalysed reaction rate
10^3x[Ce(IV)] = 4.0M; 10x[H_2SO_4] = 5.0M; 10^6x[Ir(III)] = 2.4 M; Temp.=303K

Run No.	10^2x [D-galactose] M	k_1 x10^3 min^{-1}
1	1.3	11.0
2	2.5	17.0
3	3.8	25.0
4	**5.0**	**35.0**
5	9.6	68.0
6	34.0	234.1

The results show that the rate constant is directly proportional to the concentration of D-galactose for both uncatalysed and catalysed system. The plot of 1/k_1 v/s 1/[D-galactose] (Figure-1a,2a) and plot of log k_1 v/s log[D-galactose] (Figure-1b,2b) are linear.

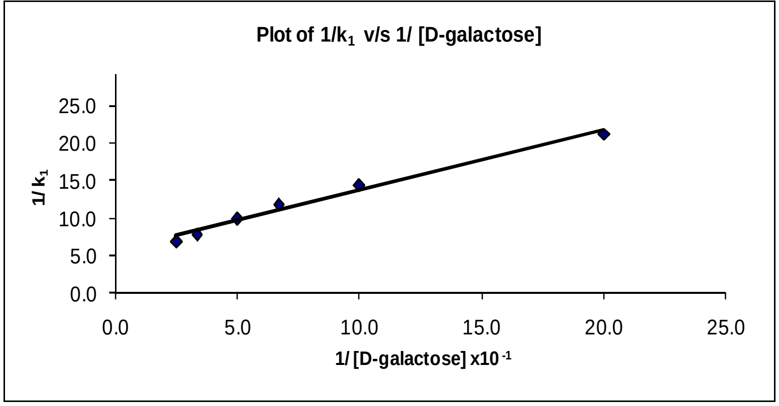
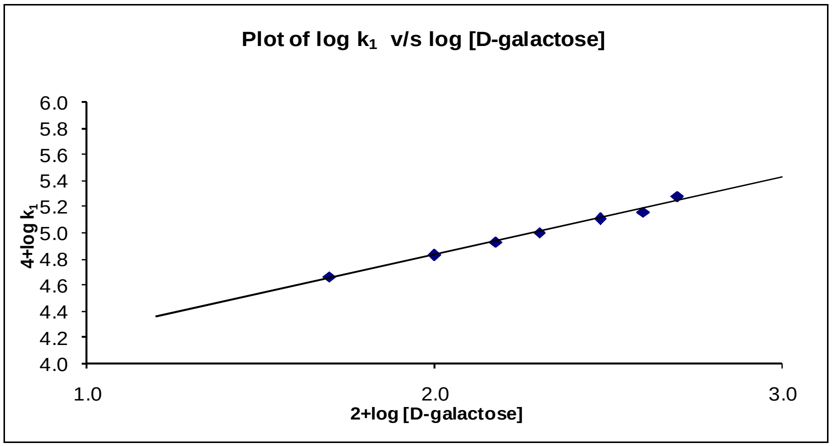


Figure 1. 1a Effect of variation of [D-galactose]; on the uncatalysed reaction rate
10^3 x[Cerium(IV)] = 4.0 M; 10x[H_2SO_4] = 5.0 M; Temp. = 303 K



1.b

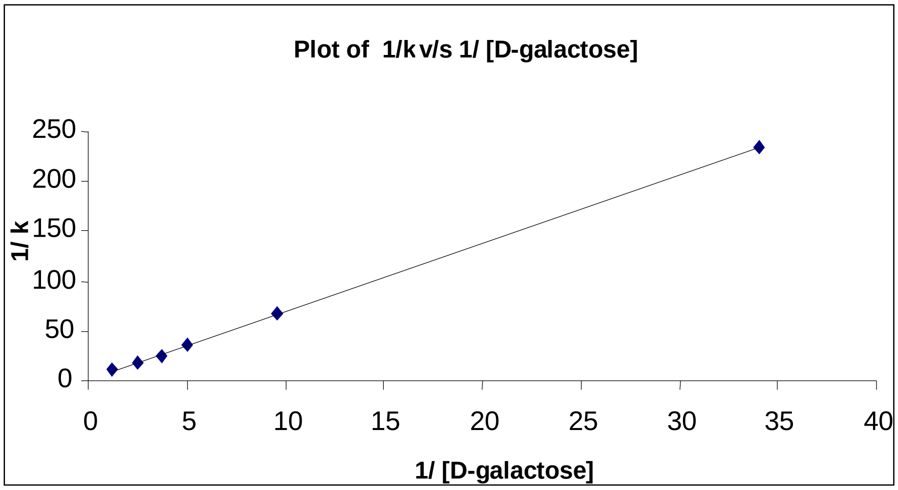
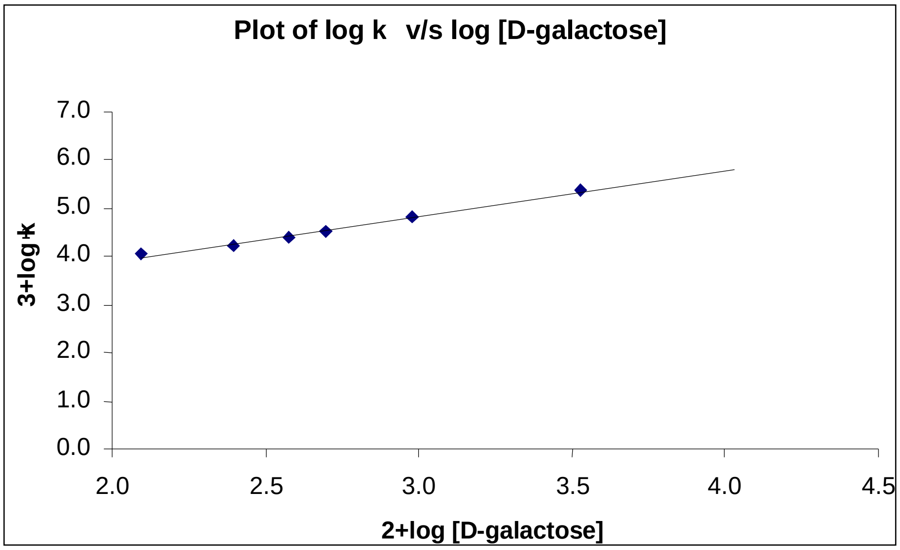


Figure 2. Effect of variation of [D-galactose]; on the catalysed reaction rate

10^3x[Ce(IV)] = 4.0M; 10x[H_2SO_4] = 5.0M; 10^6x[Ir(III)] = 2.4 M; Temp.=303K

2.a



2.b

Table – 7 Effect of variation of [Catalyst]; on the reaction rate
10^3x[Ce(IV)]=4.0 M;10^2x[D-galactose]=5.0 M;10x[H_2SO_4]=5.0 M;Temp.=303K;

Run No.	10^6 x [Ir(III)]M	10^2 x k_1 min^{-1}
1	**2.4**	**3.5**
2	4.0	5.9
3	8.0	7.8
4	12.0	12.0
5	16.0	18.7
6	20.0	24.5

The data (Table-7) indicates that the rate is dependent on the catalyst concentration. When a graph is plotted between $IrCl_3$ concentration and the rate constant, a linear curve is obtained indicating that the rate is linearly related to $IrCl_3$ concentration. The reaction rate increases with increase in [Ir(III)] and the plot of log k_1 v/s log [Ir(III)] is linear.(Figure-6)

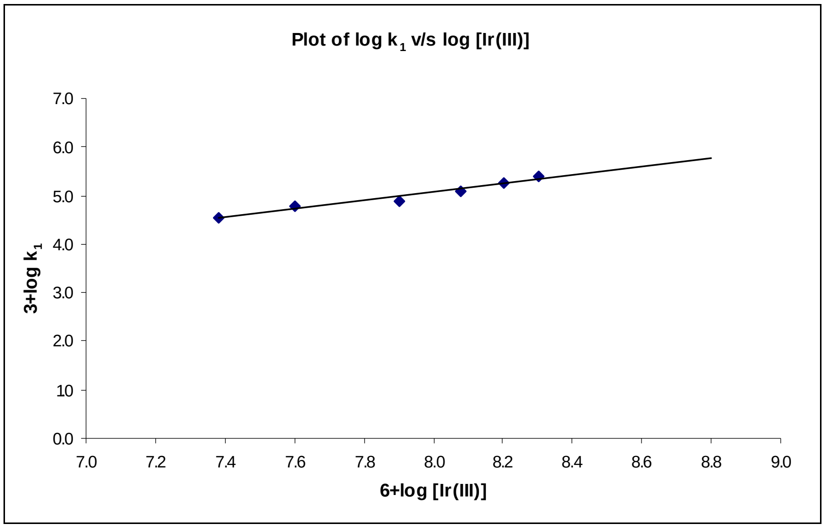


Figure – 6 Effect of variation of [Catalyst]; on the reaction rate **10^3x[Ce(IV)] = 4.0 M;10^2x[D-galactose]=5.0M; 10x[H_2SO_4]= 5.0M; Temp.=303K**

In order to see the effect of H^+ ion concentration on the reaction rate, it was found that the reaction rate decreases with increase of sulphuric acid concentration in uncatalysed oxidation while increases in Ir(III) catalysed oxidation. The reaction has been carried out at various initial concentration of H_2SO_4 acid. [H^+] was varied over the range of 0.5-2.0 M while other reactants are constant. The results are given in (Table-3,4).

Table-3 Effect of variation of $[H^+]$; on the uncatalysed reaction rate
10^3x[Cerium(IV)] = 4.0 M; 10^2x[D-galactose] = 5.0 M; Temp. = 303 K;

Run No.	10x $[H_2SO_4]$ M	k_1 x10^4 min^{-1}
1	**5**	**19.0**
2	7	11.5
3	11	8.4
4	13	7.7
5	17	6.5
6	21	5.3

Table – 4 Effect of variation of $[H^+]$; on the catalysed reaction rate
10^3x[Ce(IV)]=4.0M;10^2x[D-galactose]=5.0M; 10^6x[Ir(III)]= 2.4M; Temp.=303K;

Run No.	10x$[H_2SO_4]$ M	10^2 xk_1 min^{-1}
1	**5.0**	**3.5**
2	7.0	6.8
3	9.0	15.8
4	11.0	28.8
5	13.0	55.5
6	15.0	88.0

Because of the involvement of large number 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). The results indicate the involvement of cerium(IV)-sulphato species.(Table-3) The uncatalyzed reaction rate decreases with increase in $[H^+]$ and the plot of log k_1 v/s log $[H^+]$ is linear with negative slope.(Figure-3).

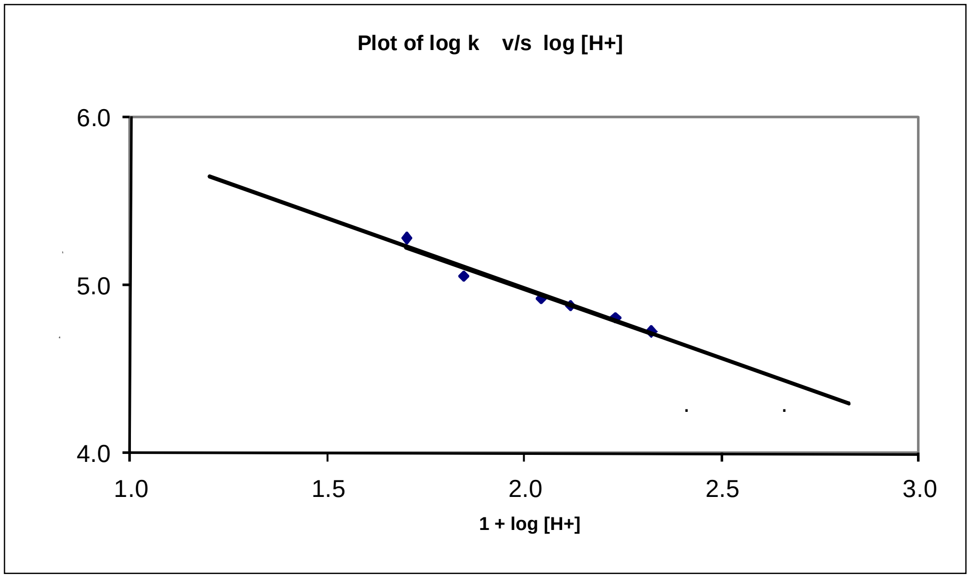


Figure-3 Effect of variation of [H^+]; on the uncatalysed reaction rate
10^3x[Cerium(IV)] = 4.0 M; 10^2x[D-galactose] = 5.0 M; Temp. = 303 K;

[H^+] is varied over the range 0.5-2.0M at fixed [Ce(IV)], [S] and [Ir(III)]. [H^+] is calculated ignoring the dissociation of [HSO_4^-] and assuming [H^+] ≈ [H_2SO_4]. Here k_{obs} increases obviously with the increase of [H^+].The plot of $1/k_{obs}$ against $1/[H^+]$ at 298K is found to be linear with a positive intercept and slope.(Figure-4)

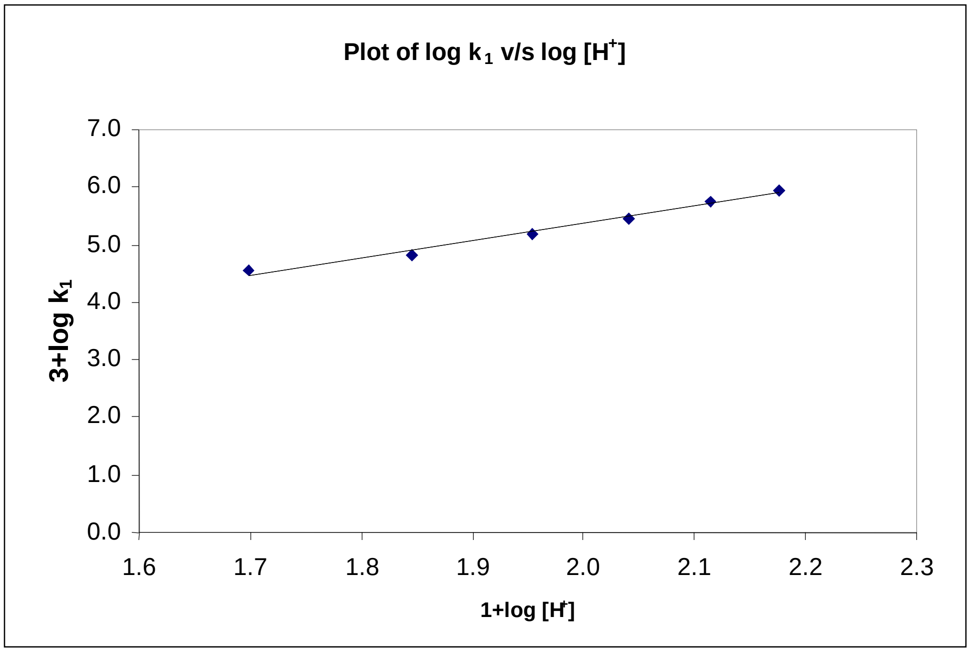


Figure – 4 Effect of variation of [H^+]; on the catalysed reaction rate
10^3x[Ce(IV)]=4.0 M;10^2x[D-galactose]=5.0 M;10^6x[Ir(III)]=2.4M; Temp.=303 K;

The reactions were studied in the range of 0.4-5.0x10^{-2} M of potassium hydrogen sulphate, while keeping all other reactants constant [H^+]([H^+]=0.5M), [Ce(IV)], [S], Ir(III)and□.

Here [HSO_4^-] ≈ [$KHSO_4$]+[H_2SO_4] ignoring the dissociation of [HSO_4^-] in the strongly acidic solution. The observations are given in (Table-5, 6).

Table- 5 Effect of variation of [$KHSO_4$]; on the uncatalysed reaction rate

10^3x[Ce(IV)] =4.0 M; 10^2 x D-galactose=5.0M; 10x[H_2SO_4] = 5.0 M; Temp.= 303K

Run No.	10^3 x[$KHSO_4$] M	k_1 x 10^4 min^{-1}
1		**19.0**
2	5	15.5
3	10	11.5
4	20	9.4
5	30	9.3
6	50	8.9

Table – 6 Effect of variation of [$KHSO_4$]; on the catalyzed reaction rate

10^3x[Ce(IV)] = 4.0 M;10^2x[D-galactose]=5.0 M;10x[H_2SO_4]=5.0 M; 10^6x[Ir(III)]=2.4M; Temp.=303K

Run No.	10^3 x[$KHSO_4$]M	10^2 x k_1 min^{-1}
1	**0.0**	**3.5**
2	19.3	8.3
3	20.0	12.9
4	24.0	140
5	33.7	16.3
6	50.0	19.5

The graphical plot for the log k_1 v/s log [HSO_4^-] is found to be a straight line (Figure-5),

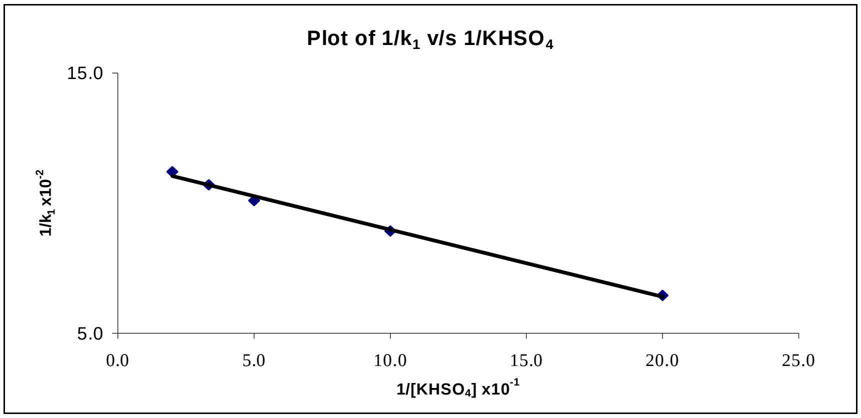


Figure- 5 Effect of variation of uncatalysed [KHSO4];
10^3x[Ce(IV)]=4.0M;10^2xD-galactose=5.0M;10x[H2SO4]=5.0M; Temp.=303K

This indicate that the rate of the reaction is inversely proportional to the -HSO_4^- ion concentration. As the concentration of this electrolyte increases, the concentration of cerium(IV) at the reaction site decreases due to salting-out effect of the salts. Thus, exclusion effect seems to be responsible for rate decrease in presence of inorganic electrolytes. Thus the hydrogen sulfate dependence can be represented as Eq. (1)

$$k_{obs} = \frac{a}{b + c\,[HSO_4^-]} \qquad \text{........ (1)}$$

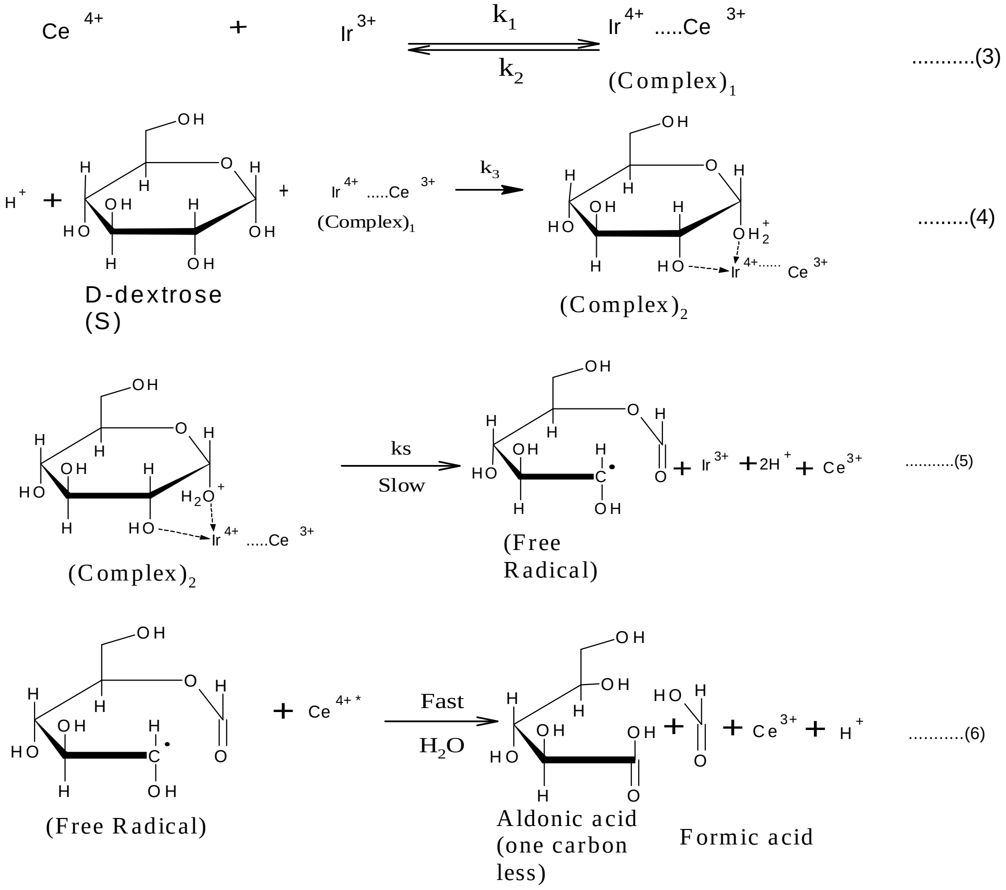
Where a, b and c are constants under the experimental conditions.

Mechanism of the reaction: The kinetic data (i.e. 1/k_{obs} versus 1/[S]) fits well with the Michaelis-Menten model, suggesting that 1:1 type complex of Substrate and Ir(III) is formed in the first equilibrium step.

Substrate is easily protonised in acid media in presence of catalyst, indicating involvement of H^+ in the reaction in the preequilibrium step. $Ce(SO_4)_2$ has been found kinetically active in this study with generation of free radicals in the reaction. Thus a mechanism consistent with the above kinetics is proposed. (Scheme-1)

$$d\,Ce(IV)/dt = 2\,k_s\,[Complex]_1 \qquad \text{................(2)}$$

Eq.(2) indicates that 1 mole of substrate is oxidized by 2 moles of Ce(IV). The above equation (1) can also be written as shown in equation (2) from the scheme-1.



[Scheme-1]

Mechanism of Oxidation of D-galactose in presence of Ir(III) catalyst.

In equation (6), $Ce^{*}(IV)$ represents any species of Ce(IV). Step(5) is the rate determining step. According to the present mechanism, applying the steady-state condition to the free radicals[24].

$$k_{obs} = \frac{2fk_s\, k_1 k_3 [\mathrm{Ir(III)}]_T\, [S]\, [H^+]}{k_3\, [S]\, [H^+] + k_2} \quad ....(7)$$

Here, *f* denotes the fraction of kinetically active species to the total cerium(IV) and subscript T stands for total concentration. Based on the above mechanism, the **rate law** can be established as follows:-

$$\frac{-d\,[\mathrm{Complex}]_1}{dt} = k_1\,[\mathrm{Ir(III)}]_T\,[\mathrm{Ce(IV)}] - k_2[\mathrm{Complex}]_1 - k_3\,[\mathrm{Complex}]_1[\mathrm{S}][\mathrm{H}^+] \ldots(8)$$

Applying steady state hypothesis

$-d[\mathrm{Complex}]_1/dt = 0$

hence $k_1\,[\mathrm{Ir(III)}]_T\,[\mathrm{Ce(IV)}] = k_2[\mathrm{complex}]_1 + k_3[\mathrm{complex}]_1[\mathrm{S}][\mathrm{H}^+]$ ....(9)

Therefore, the concentration of the complex becomes

$$[\mathrm{complex}]_1 = \frac{k_1[\mathrm{Ir(III)}]_T\,[\mathrm{Ce(IV)}]}{\{k_2+k_3[\mathrm{S}][\mathrm{H}^+]\}} \qquad \ldots\ldots\ldots(10)$$

At steady state condition , the rate of disappearance of [Ce(IV)] as given as equ.

$$\frac{-d[\mathrm{Ce(IV)}]}{dt} = 2\,ks\,[\mathrm{complex}]_2 \ldots\ldots \qquad (2)$$

or:

$$\frac{-d[\mathrm{Ce(IV)}]}{dt} = 2\,k_s\,k_3\,[\mathrm{S}][\mathrm{H}^+][\mathrm{complex}]_1 \qquad \ldots\ldots\ldots(11)$$

Putting the value of $[\mathrm{complex}]_1$

$$\frac{-d[\mathrm{Ce(IV)}]}{dt} = \frac{2\,k_s\,k_1\,k_3[\mathrm{S}][\mathrm{H}^+][[\mathrm{Ir(III)}]_T\,[\mathrm{Ce(IV)}]}{\{k_2+k_3[\mathrm{S}][\mathrm{H}^+]\}} \qquad \ldots\ldots\ldots(12)$$

Now, the total [Ce(IV)] may be considered as:

$$[\mathrm{Ce(IV)}]_T = [\mathrm{Ce(IV)}]_e + [\mathrm{complex}]_1 \qquad \ldots\ldots\ldots(13)$$

Putting the value of $[\mathrm{complex}]_1$

$$[\mathrm{Ce(IV)}]_T = [\mathrm{Ce(IV)}]_e + \frac{[k_1[\mathrm{Ir(III)}]_T\,[\mathrm{Ce(IV)}]}{\{k_2+k_3[\mathrm{S}][\mathrm{H}^+]\}} \qquad \ldots\ldots\ldots(14)$$

$$[\mathrm{Ce(IV)}]_T = \frac{[\mathrm{Ce(IV)}]_e\{k_2+k_3[\mathrm{S}][\mathrm{H}^+]\} + [k_1[\mathrm{Ir(III)}]_T\,[\mathrm{Ce(IV)}]}{\{k_2+k_3[\mathrm{S}][\mathrm{H}^+]\}} \qquad \ldots\ldots\ldots(15)$$

The value of $[\mathrm{Ce(IV)}]_T$ comes out to be:

$$[\mathrm{Ce(IV)}] = \frac{[\mathrm{Ce(IV)}]_T\,\{k_2+k_3[\mathrm{S}][\mathrm{H}^+]\}}{\{k_2+k_3[\mathrm{S}][\mathrm{H}^+]\}+\{k_1[\mathrm{Ir(III)}]_T\}} \qquad \ldots\ldots\ldots(16)$$

From equation 7 and 11, the final rate law comes out to be:

$$\frac{-d[\mathrm{Ce(IV)}]}{dt} = \frac{2\,k_s\,k_1k_3\,[\mathrm{S}][\mathrm{H}^+]\,[\mathrm{Ir(III)}]_T}{\{k_2+k_3[\mathrm{S}][\mathrm{H}^+]\}} \times \frac{[\mathrm{Ce(IV)}]_T\,\{k_2+k_3[\mathrm{S}][\mathrm{H}^+]\}}{\{k_2+k_3[\mathrm{S}][\mathrm{H}^+]\}+[k_1[\mathrm{Ir(III)}]_T} \qquad \ldots\ldots\ldots(17)$$

$$\frac{-d[\mathrm{Ce(IV)}]}{dt} = \frac{2.k_s\,k_1k_3\,[\mathrm{S}][\mathrm{H}^+]\,[\mathrm{Ir(III)}]_T\,[\mathrm{Ce(IV)}]_T}{\{k_2+k_3[\mathrm{S}][\mathrm{H}^+]\}+[k_1[\mathrm{Ir(III)}]_T} \qquad \ldots\ldots\ldots(18)$$

Under the present experimental condition, one might assume the following inequality:

$$\{k_2+k_3[S][H^+]\} >> \{k_1[Ir(III)]_T\} \qquad \text{...(19)}$$

And hence, Equation (11) reduces to:

$$\frac{-d[Ce(IV)]}{dt} = \frac{2\ k_s k_1 k_3\ [S][H^+]\ [Ir(III)]_T[Ce(IV)]_T}{k_2 + k_3\ [S][H^+]} \qquad \text{...(20)}$$

$$k_{obs} = \frac{\dfrac{-d[Ce(IV)]}{dt}}{[Ce(IV)]_T} = \frac{2\ k_s k_1 k_3\ [S][H^+]\ [Ir(III)]_T}{k_2 + k_3\ [S][H^+]} \qquad \text{..(21)}$$

$$\frac{1}{k_{obs}} = \frac{1}{2\ k_s k_1\ [Ir(III)]_T} + \frac{k_2}{2k_s k_1 k_3[S][H^+][Ir(III)]_T} \qquad \text{.......(22)}$$

From the plot 1/k_{obs} against 1/[S] is made 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 equations; when plots are made 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. Equation (22) also suggests that the plot of 1/k_{obs} versus 1/[H^+] at constant $[Ir(III)]_T$ and [S] should also be linear. 1/k_{obs} versus 1/[Ir(III)] at constant [S] and [H^+] should yield good linear plots through the origin.

The values of $k_sk_1k_3$ and k_2 for [S] can also be calculated from the double reciprocal plots .

Since Ir(III) is inert [25] in the proposed mechanism, it may bond to [Ce^{+4}] to form an outer-sphere complex (Ir^{+4}…Ce^{+3}), which is rapidly reduced into an inner sphere complex by D-galactose. As Ir^{+4} is unstable, the free radicals can be generated through an inner-sphere electron transfer process between Ir^{+4} and D-galactose. Meanwhile, Ir^{+3} and the partially oxidized product can be obtained. Thus, the oxidation of D-galactose occurs through the Ir^{+3}/Ir^{+4} catalytic cycle.

Kinetically active Ce(IV) species

Under the experimental conditions in aqueous sulfuric acid medium, the important cerium(IV) sulfato complexes are $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$ and $HCe(SO_4)_3^-$ and the relevant equilibrium are [23]

$$Ce^{4+} + HSO_4^- \longleftrightarrow Ce(SO_4)^{2+} + H^+ \qquad B_1 = 3500 \qquad (23)$$

$$Ce(SO_4)^{2+} + HSO_4^- \longleftrightarrow Ce(SO_4)_2 + H^+ \qquad B_2 = 200 \quad (24)$$

$$Ce(SO_4)_2 + HSO_4^- \longleftrightarrow HCe(SO_4)_3^- \qquad B_3 = 3\text{-}4 \quad (25)$$

Among the different sulfato species, the kinetically active species should be inferred on the basis of kinetic data, not according to the magnitude of concentration[26].

From the relationship between hydrogen sulphate 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. According to the mass balance Eq (26) is obtained.

$$[Ce(IV)]_T = [Ce^{4+}] + [Ce(SO_4)^{2+}] + [Ce(SO_4)_2] + [HCe(SO_4)^{3-}] \quad ......(26)$$

From Eq (23-25), the following equations can be derived

$$[Ce^{4+}] = \frac{[Ce(SO_4)_2]\,[H^+]^2}{B_1 B_2\,[HSO_4^-]^2}$$

$$[Ce(SO_4)^{2+}] = \frac{[Ce(SO_4)_2]\,[H^+]}{B_2[HSO_4^-]}$$

$$Ce(SO_4)_2 = \frac{H\,Ce\,(SO_4)_3^-}{HSO_4^-\,B_3}$$

$$H\,Ce(SO_4)_3^- = B_3[Ce(SO_4)_2]\,[HSO_4^-]$$

Substituting the above equation into Eq.(1) we get

$$[Ce(IV)]_T = \frac{[Ce(SO_4)_2]\,[H^+]^2}{B_1B_2[HSO_4^-]^2} + \frac{[H^+]\,[Ce(SO_4)_2]}{B_2[HSO_4^-]} + [Ce(SO_4)_2] + B_3[Ce(SO_4)_2\,[HSO_4^-] \quad (27)$$

By considering the relative magnitudes of successive formation equilibrium constants which are in the order $B_1 >> B_2 >> B_3$ the value of

$$\frac{[Ce(SO_4)_2]\,[H^+]^2}{B_1B_2[HSO_4^-]^2} \text{ and } \frac{[H^+][Ce(SO_4)_2]}{B_2[HSO_4^-]}$$

are much less than the latter two terms. Therefore, we get Eq(28) from Eq(27).

$$[Ce(IV)_T] \approx [Ce(SO_4)_2] + B_3[Ce(SO_4)_2]\,[HSO_4^-] \quad (28)$$

So, $[Ce(SO_4)_2] = \dfrac{[Ce(IV)]_T}{1 + B_3[HSO_4^-]} = f\,[Ce(IV)]_T$

$$f = \frac{1}{1 + B_3[HSO_4^-]} \quad (29)$$

Substituting Eq(29) into Eq(7), we get

$$k_{obs} = \frac{2k_s k_1 k_3\,[Ir(III)]_T\,[S]\,[H^+]}{(k_3[S]\,[H^+] + k_2)\,(1 + B_3[HSO_4^-]} \quad (30)$$

Assuming $m = \dfrac{2k_s\,k_1\,k_3[Ir(III)_T\,[S]\,[H^+]}{k_3\,[S]\,[H^+] + k_2}$

Eq. (30) may be written as

$$k_{obs} = \frac{m}{1 + B_3[HSO_4^-]} \quad (31)$$

Or

$$\frac{1}{k_{obs}} = \frac{1}{m} + \frac{B_3\,[HSO_4^-]}{m} \quad (32)$$

$$k_{obs} = \frac{a}{b + c\,[HSO_4^-]} \quad (1)$$

Equation (31) is the same as Eq. (1) which can explain well the negative number order dependence on $[HSO_4^-]$, Equation(32) suggests that $1/k_{obs}$ versus $[HSO_4^-]$ should be linear and agrees with the observed experimental data. From the slope (B_3/m) and intercept (1/m) obtained by the linear regression of $1/k_{obs}$ versus $[HSO_4^-]_n$ the ratio of slope to intercept is calculated i.e. B_3 is estimated to be same according to Eq. (32), which is in good agreement with previously reported value[23,27]. All the above results show that $Ce(SO_4)_2$ is the kinetically active species. Furthermore, the ionic strength has little effect on k_{obs}. According to the principle of salt effect, there must be a neutral molecule in rate determining step, which confirms $Ce(SO_4)_2$ as the kinetically active species in the present study.

In considering the result of kinetic studies the complex, forming ability of the acid anion with cerium (IV) must be considered. Thus, cerium (IV) oxidations in sulfuric acid, where the sulphate anion forms a stable complex with cerium(IV).

However, recent studies of cerium(IV) oxidation of aldose [28] and oxalate[29] in sulphuric acid report evidence for complex formation. It appears that detection of cerium(IV)-sugar complexes is dependent on the stability of the cerium(IV) inorganic species present. Increasing the stability of the cerium(IV) acid anion complex decreases the probability of detecting cerium(IV) sugar complexes. It can be detected whether the effect of increasing cerium(IV) acid anion complex stability actually affects a change in mechanism with a change in acid. The kinetics of this reaction are studied and showed that D-galactose[30] and cerium(IV) interact in an equilibrium step to form an intermediate complex which is assumed to disproportionate forming a free radical and reduced cerium(III).

The kinetics of this reaction were studied and showed that D-galactose[31] , Cerium (IV) and Ir(III) interact in two equilibrium steps to form an intermediate complex which is assumed to disproportionate forming a free radical and reduced to cerium(III). It is believed to involve both C_1 and C_2 hydroxyls in a complex. In (scheme-1), the reaction mechanism described above is depicted, which explains the products and kinetics of D-galactose[30-32] oxidation by cerium (IV).

Such mechanism[33] is possible, involving the free aldehydic form of the reducing sugar. In (scheme-1), the mechanism is depicted in two ways since it is not known whether the location of the free radical is determined by factors affecting radical stability or whether the position of the radical is simply the result of chance.

Since the rate of reactions catalyzed by iridium ions are very much dependent on the reductant concentrations, it has been suggested[34] that these reactions have a common step.

$$Ir^{3+} + Ce^{4+} \longrightarrow Ir^{4+}\text{-}Ce^{3+}$$

Then in rate determining step Ir^{4+} formed reacts with D-galactose in presence of H^+.

$$\text{D-galactose} + Ir^{4+}\text{-}Ce^{3+} + H^+ \longrightarrow \text{Free radical} + Ce^{3+} + Ir^{3+} + 2H^+$$

$$\text{Free radical} + Ce^{4+\,*} + H_2O \longrightarrow \text{Aldonic acid} + \text{Formic acid} + Ce^{3+} + H^+$$

The presence of formic acid in the reaction mixture after completion of the reaction has been confirmed by the spot test method[35].

Where Ir^{4+} gives the total Ir $^{(III)}$ concentration. The proposed mechanism involves the formation of $Ir^{(III)}$-cerium$^{(IV)}$ complex in a reversible manner which reach with the substrate at the rate determining step to form $[Ir^{(IV)}\text{-}Ce^{(III)}$ – D-galactose-$H^+]$ complex followed by a slow redox decomposition giving rise to the catalyst and aldoxide radical which is oxidized by cerium$^{(IV)*}$ rapidly. The mechanism is consistent with the existence of the complexes $(Ir^{4+\text{-}}Ce^{3+})$ and $(Ir^{4+}\text{-}Ce^{3+}$-D-galactose-$H^+)$.

Oxidation of the sugars at different temperatures from 303 to 338K is studied. The plots of log k_1 against 1/T are linear for both the catalyzed and un-catalyzed oxidation. The Arrhenius activation energy Ea for the uncatalyzed oxidation of D-galactose is 73.3 kJmol^{-1} while the catalyzed oxidation Arrhenius activation energy is 70.0 kJmol^{-1}. The value of the uncatalyzed Ea is greater than the Ea of the catalyzed reaction, which suggests that catalysis takes place. The negative entropy of activation $S^{\neq}$ for the catalyzed reaction indicates that the reaction proceed through hybrid transfer between the sugar molecules and $Ce^{(IV)}$ in Ir $^{(III)}$[36,37]. This trend is also a characteristic of oxidation of alcohols and aldehydes in $Ce^{(IV),}$ which is also supported by Mohammed Ilyas,[16] et al gives the Arrhenius plot for the catalyzed oxidation of the sugar. Interestingly enough, the value of k_1 for the reaction with D-galactose 16.2 min^{-1} closely resembles that expected from the combined, parallel reactions of $Ce^{(IV)}$ with the four alcoholic groups (1 primary and 3 secondary) present in the reductant molecule[38]. The molecule of D-galactose participates in the reaction in its cyclic form rather than in its free aldehyde, linear form. This is consistent with the findings reported for the degradative oxidation of monosaccharides by Ce^{4+} .

The kinetic data shows the increasing rate of reaction on increasing temperature in both catalyzed and uncatalysed oxidation. The results obtained by study of temperature variation are utilized to calculate various kinetic and activation parameters. The plot of log k_1 v/s 1/T is linear. The reaction velocities are measured at six different temperatures. All the six experiments are performed at the identical concentration of the reactants. The values of temperature coefficient calculated are given in (Table-8,9).

Table –8 Effect of variation of Temperature; on the uncatalysed reaction rate
10^3x[Cerium(IV)] = 4.0 M; 10x[H_2SO_4] = 5.0 M; 10^2x[D-galactose]= 5.0M;

Temperature K	1/T x 10^3	k_1 x 10^4 min^{-1}
303	**3.30**	**1.91**
313	3.19	4.29
323	3.09	11.62
333	3.00	20.21

Activation parameters for acidic Ce(IV) oxidation of D-galactose

Parameter	D-galactose
E_a (kJ mol$^{-1)}$	73.3
$\Delta H^{\neq}$ (k J mol^{-1})	70.7
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	-74.7
$\Delta G^{\neq}$(k J mol^{-1})	97.5
ln A	20.6

Table- 9 Effect of variation of Temperature; on the catalysed reaction rate
10^3[Ce(IV)] = 4.0 M; 10^2[D-galactose]=5.0M; 10x[H_2SO_4]=5.0 M; 10^6[Ir(III)]=2.4M;

Temperature K	1/T x 10^3	k_1 x 10^3 min^{-1}
303	**3.30**	**35.1**
318	3.145	61.5
323	3.096	73.98
328	3.049	98.6
333	3.003	116.0
338	2.959	154.0

Activation parameters for acidic Ce(IV) oxidation of D-galactose

Parameter	D-galactose
E_a (kJ mol^{-1})	70.0
$\Delta H^{\neq}$(k J mol^{-1})	67.3
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	-42.4
$\Delta G^{\neq}$(k J mol^{-1})	83.7
ln A	24.4

Energy and Entropy of Activation:.

The entropy of activation is found to be negative in both cases. The fairly high value of negative $\Delta S^{\neq}$ suggests the formation of more ordered activated complex, whereas, the high positive value of the free energy of the activation ($\Delta G^{\neq}$) and enthalpy of activation ($\Delta H^{\neq}$) indicate that the transition state is highly solvated. Energy of activation, free energy of activation and entropy parameters suggest that Ir(III) forms the activated complex more easily compared to the others. Mechanism consistent with observed rate laws have been suggested.

APPLICATIONS

The complex formed between cerium(IV) and the organic substrate in first equilibrium step gives another complex in the presence of catalyst which ultimately gives rise to products of oxidation. The reaction follows first order kinetics. Rate of the reaction follows direct proportionality with respect to catalyst concentrations.

CONCLUSION

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 intermediate complex undergoes a slow unimolecular decomposition to yield a free radical. The free radical then reacts with Ce(IV) species to form the product. It has also been observed that the rate of reaction increases with increase in the concentration of D-galactose. Increase in the rate might be due to the $(complex)_2$ formation between $(Complex)_1$ and D-galactose. If this is the case, then a part of the Ir(III) will be used to form complex compound and thus the concentration of Ir(III) will be reduced in the reaction mixture. Since the rate is linearly related to the catalyst concentration, a increase in the rate constant is observed with increasing concentration of D-galactose. Uncatalysed and Ir(III) catalysed oxidation of D-galactose by cerium(IV) has been investigated in sulphuric acid medium. It is proposed that the complex formed between cerium(IV) and the organic substrate in first equilibrium step gives another complex in the presence of catalyst which ultimately gives rise to products of oxidation. The reaction follows first order kinetics. Rate of the reaction follows direct proportionality with respect to catalyst concentrations.

The entropy of activation is found to be negative in both cases. The fairly high value of negative $\square S^{\neq}$ suggests the formation of more ordered activated complex, whereas, the high positive value of the free energy of the activation ($\square G^{\neq}$) and enthalpy of activation ($\square\square^{\neq}$) indicate that the transition state is highly solvated. Formic acid and a aldonic acid with one carbon atom less, were identified in the oxidation of D-(+)galactose by cerium ammonium sulphate(IV). Energy of activation, free energy of activation and entropy parameters suggest that Ir(III) forms the activated complex more easily compared to the others. Mechanism consistent with observed rate laws have been suggested.

ACKOWLEDGEMENT

The authors are grateful to Department of Chemistry, Govt. Nagarjuna P.G. College of Science, Raipur and Disha Institute of Engineering & Technology, Raipur for providing apparatus and other facilities.

REFERENCES

[1] Bhathacharya, N. and Gupta. M.L.S. Indian J. Chem, (**1967**), 5, pp. 554-556.
[2] Shilov, E.A. and Yasnikov, A.A., Khim. Ukr.Zh.,(**1952**), pp. 595-610.
[3] Singh, K., Chaurasia, N., Rehmani, S., Srivastava, J.and Singh, B., J. Chem. Res.,(**2005**), pp. 304-310.
[4] R. P. Rastogi and P. Chand, Ind. J. Chem., (**2003**), 42A, 1027 .
[5] a. V.Devra, J.Ind. Chem. Soc.,(**2005**), 82,290;
    a. b. D.C.Bilehal, R.M.Kulkarni and S. T.Nandibewoor, J. Ind. Chem. Soc., (**2003**), 83, 91.
[6] D.S.Munawalli, K.A.Thabaj, S.A.Chimatadar and S.T. Nandiwoor, Transition met. Chem.,(**2007**), 32,902
[7] D.S.Munawalli, K.A.Thabaj, S.A.Chimatadar and S.T. Nandiwoor, (**2007**), Transition met. Chem.,32,902 .
[8] A.K.Das,M.Das, Ind.J.Chem., (**1995**), 34A,866 .
[9] V.B.Rao and M.A.Rao. Ind.J.Chem.,(**2005**), 44A,80.
[10] . B.Singh,M.Singh and D.Kessarwani, Ind.J.Chem., (**2002**), 41A, 547.
[11] S.S.Mohanty,K.K Sahu and D.Bhatta, J.Ind.Chem.Soc., (**1996**), 73,351
[12] L.S.Dikshitulu, V.H. Rao, and S.N. Dindi, Ind. Jou Chem.,(**1981**), 20A, 784
[13] Praveen K. Tondon, Manish Srivastava, Santosh Kumar and Satpal Singh ,J.of Mol. Cat. A. Chem, (**2009**), 304, 101-106.

[14] Praveen K. Tandon, Alok K. Singh, Sunita Sahgal and Santosh Kumar J.of Mol. Cat. A. Chem,(**2008**), 282,136-143.

[15] L.F. Sala,M.A. Rizzotto, S.R. Signoerella. M.I. Frascaroli and S. Acebal, Oxid. Commun., (**1991**), 14, 56.

[16] a.Muhammad, S. S., and Rao, K. V., Bull. Chem. Soc., Japan,(**1963**), 36:949,

    i. C.A. 59:12601g.
    ii. b.Vogel, I. Longman-green, London,**1958**, p.73.

[17] Signorella, S.; Rizzotto, M.; dair, V.; Frascaroli, M.I.; Palopoli, C.; Martino, D.; Bousseksou A.; Sala, L.F.J. Chem. Soc., Dalton Trans.,(**1996**): 1607

[18] Singh, A.K., J. Srivastava, and S. Rahmani.(**2007**).Journal of Molecular Catalysis A: Chemical. 271: 151–160

[19] Kabir-ud-din; Ali Mohd. Sajid; Khan Zaheer., Acta Phys. – Chim. Sin., (**2008**), 24 (5) :810-816.

[20] [a] Sengupta, K.K.; Begum, B.A.; Pal, B.B. carbohydr. Res.,(**1998**), 309: 303

    i. [b] Abde Akher, M.; Smith, F.J.Am. Chem. Soc.,(**1951**), 73: 5859.

[21] Kumar, A,; Mahrotra, R.N.J.Org.Chem.,(**1975**), 40: 1248

[22] Sengupta, K.K.; Begum, B.A.; Pal, B.B. carbohydr. Res.,(**1999**), 315: 7

[23] Mishra S K & Gupta Y K, J Chem Soc A, (**1970**), 2918.

[24] Wang A Z & Shi T S, Acta ChimSin, 46 (**1988**), 207-211.

[25] Wilkins R G, *The study of Kinetics and Mechanism of Reaction of Transition Metal Complexas,* (Allyn & Bacon, Boston) (**1974**), p.518.

[26] Song W Y, Liz H & Wang A Z, Chem J Chinese Univ, 18, (**1997**), 1842.

[27] Mondal S.K.Kar D, Das M & Das A.K., *Indian J.Chem*, 37A, (**1998**), 765.

[28] Mehrotra, R. N., Z. Phys. Chem. ,(**1965**), 230:221

[29] El-Tantawy, Y. A., and Rechnitz, G. A., Anal. Chem., (**1964**). 36, 1774.

[30] Advances in Carbohydrate Chemistry and Biochemisry volume 60 by Derek Horton – (**2006**)

[31] Sci. Topics Research summaries by experts oxidation bonding electronics, Dr. Sun Chang Qing 27 June, (**2008**).

[32] Advances in Carbohydrate Chemistry and Biochemistry volume 60 by Derek Horton, (**2006**).

[33] Krishna, B. and Sinha, B.P., Z. phys. Chem.,(**1959**), 212, 149.

[34] D.A. House, Chem. Rev., (**1962**), 62, 185.

[35] Feigle, “Spot Test in Organic Analysis,” Elsevier Publishing Company, New York, (**1956**), p.208.

[36] Ashok, K.S., N. Chaurasia, R. Shahla., S. Jaya, and S. Bharat., Journal of Molecular Catalysis.(**2004**), 95(3-4):135-141.

[37] Muzart, J. (**2003**) Tetrahedron.59:5781-5816

[38] Maqsood, M.A., Z.A. Syed Misbah, and K. Zaheer. (**2007**). Research Letters in Physical Chemistry. Article ID 82901.