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Oxidation of D(+) Fructose by Sodium Metaperiodate in Alkaline Medium using $[RhCl_3(H_2O)_2OH]^-$ Complex as a Homogeneous Catalyst

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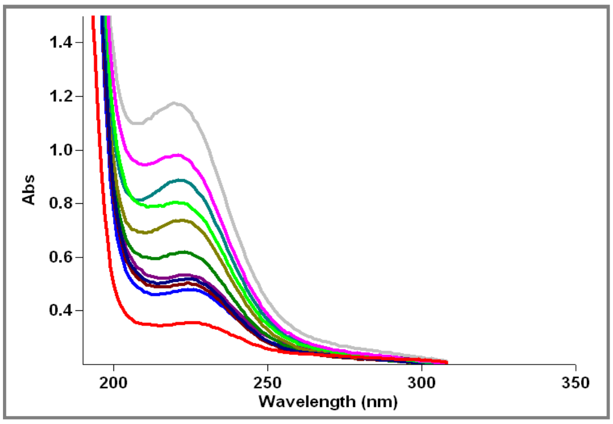
ABSTRACT

The present paper deals with the kinetics and mechanism of Rh(III)-catalyzed oxidation of D- fructose by sodium metaperiodate in alkaline medium at temperature $40^0C\pm0.1^0C$*. The reaction shows first-order kinetics with respect to* $[IO_4]^-$*, [Rh(III)] and [Fructose] throughout their variations. First-order kinetics in* $[OH^-]$ *at its low concentrations tends to zero-order at higher concentrations. Nil effect of* $[Cl^-]$ *on the rate of oxidation of fructose has been observed. There was no effects of ionic strength (μ) and dielectric constant (D) of the medium on the rate of the oxidation was observed. From the study of effect of temperature on the rate of reaction, various activation parameters such as energy of activation, enthalpy of activation along with entropy of activation were calculated.* $[RhCl_3(H_2O)_2OH]^-$ *and* $H_2IO_6^{3-}$ *were postulated as the main reactive species of Rh(III)-chloride and* IO_4^- *in alkaline medium, respectively. A most probable reaction mechanism has been proposed in the light of observed kinetic orders, activation parameters and spectrophotometric evidences collected for the existence of reactive species of oxidant and catalyst as well as for the formation of complexes during the course of reaction.*

Graphical Abstract



Spectra of solutions [1-11] recorded at room temperature.

Keywords: Oxidation, Rh(III), D-fructose, Alkaline medium, $NaIO_4$.

INTRODUCTION

A study of literature indicated many possible fields of application for the carbohydrates, most of which serve as energy stores, as the chief fuel of biological [1] system, and metabolic intermediate in biosynthesis. Oxidation of reducing sugars by different oxidizing agents is of special importance due to their industrial and biological significance. One of the products of oxidation of sugar, formic acid, is used in the production of pharmaceuticals, dyes, flavors and perfume ingredients, textiles, leather and rubber. Heavy metal complex compounds have been applied in treatment of the patients with various diseases, for instance, they proved effectiveness in the treatment of the patients with cancers, anaemia, arthritis, chronic inflammation, bacterial infections and alimentary tract disorders [2, 3]. Earlier kinetics and mechanism of Rh(III) catalyzed oxidation of some redox reactions have been reported [4-7]. Periodate has been used extensively as a diol cleaving reagent [8]. Oxidation of some industrially and biologically important sugars by periodate [9, 10], has been reported in literature. As far as our knowledge is concerned no report is available, where Rh(III) chloride is used as homogeneous catalyst in the kinetic oxidation of fructose by sodium meta periodate. In view of the importance of rhodium (III) complexes as antibacterial, antitumor [11], mutagenic agents [12], specific nutritional or physiological roles and therapeutic or pharmacological actions of sugars and also in view of biological and industrial activity of periodate, the present study in the form of Rh(III)-catalysed oxidation of D(+)fructose in alkaline medium created by $NaIO_4$ has been undertaken.

The main objectives of the present study are to ascertain, (i) The influence of the oxidant, substrate and the medium on the reaction kinetics (ii) Catalytic potential of rhodium in the oxidation of fructose. (iii)The possibility of formation of complex or complexes during the course of reaction, (iv) The plausible reaction mechanism and (v) The value of the activation parameters.

MATERIALS AND METHODS

Materials: All the solutions were prepared in doubly distilled water. The solution of rhodium(III) chloride (Loba) was prepared by dissolving 1g of sample in hydrochloric acid (HCl) of known strength and the strength of rhodium(III) chloride ($RhCl_3.3H_2O$) was found to be 3.80×10^{-3} M in which the strength of HCl was maintained at 3M. The solution of sodium metaperiodate (Sigma chemicals) was prepared by dissolving weighed amount of its in double distilled water. The strength of prepared sodium metaperiodate solution was checked by standardizing it against sodium thiosulphate solution iodometrically. Solution of fructose was always freshly prepared before use. An aqueous solution of perchloric acid, sodium perchlorate, potassium chloride, sodium hydroxide, sodium thiosulphate and potassium iodide (all of E.Merck) were prepared in double distilled water. KCl was required to fix the Cl^- ion concentration and $NaClO_4$ was employed to maintain the required ionic strength of the medium.

Kinetic measurements: The reaction mixture containing the desired volume of all reactants i.e. $NaIO_4$, OH^-, Rh(III) chloride and water except reducing sugar was taken in conical flask which kept in the thermostatic bath at constant temperature 40°C ± 0.1°C. The requisite volume of sugar solution was also placed within the same thermostatic bath at the same temperature. After 30 min, when the reaction mixture has attained the temperature of the bath, the required volume of sugar solution was sucked out by pipette and poured into reaction mixture to initiate the reaction. The actual progress of reaction was followed by estimating the amount of remaining $NaIO_4$ at regular time intervals iodometrically.

Stoichiometry and product analysis: Several sets of reaction mixture containing different amounts of $[IO_4^-]$:[Fructose] at constant ionic strength were allowed to react for 72 h at 40°C in closed vessels under the condition of $[IO_4^-]>>$[Fructose]. The estimation of residual $[IO_4^-]$ was determined iodometrically and after accounting for the remaining oxidant concentration. It was found that each mole of fructose consumed 4 moles of periodate. Thus, the ratio of consumption of reductant to oxidant is 1:4. Accordingly, the following stoichiometric equation can be formulated

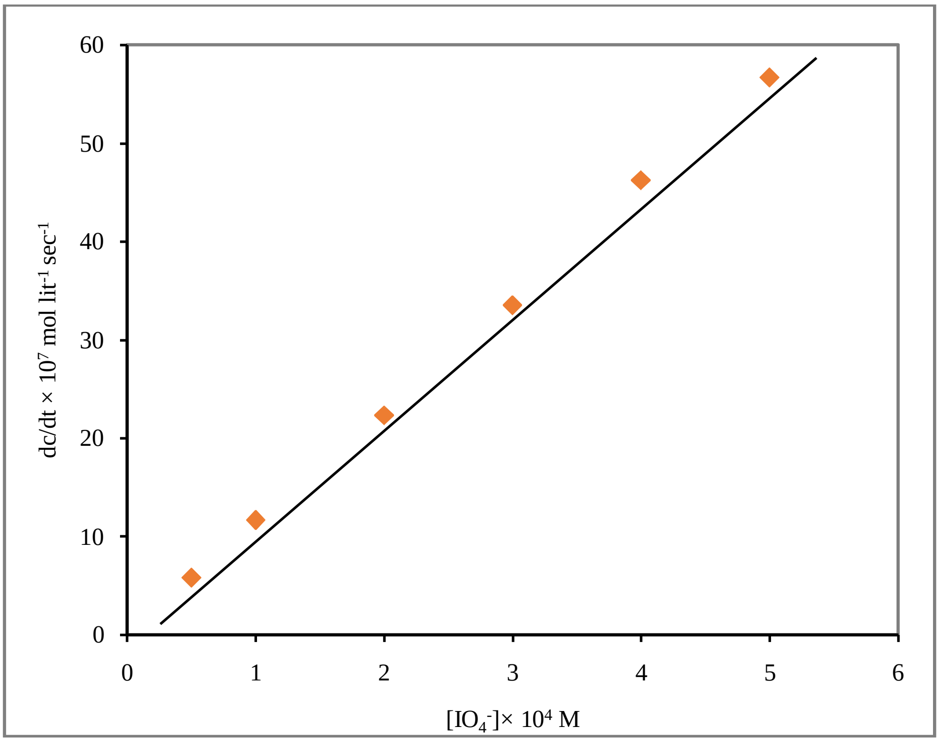
$$\underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Periodate}}{4IO_4^-} \xrightarrow{Rh(III)/OH^-} \underset{\text{Formic acid}}{HCOOH} + \underset{\text{Arabinoic acid}}{C_6H_{10}O_6} + 4IO_3^-$$

RESULTS AND DISCUSSION

Kinetic studies pertaining to Rh(III)-catalysed oxidation D(+) fructose by sodium metaperiodate in alkaline medium was made at several reactant concentrations at 40°C±0.1°C. For the determination of order of reaction, the help of Ostwald's Isolation method along with van't Hoff differential method has been taken. In the light of Ostwald's Isolation method, the concentration of IO_4^- was taken in a very small quantity as compared to the concentration of substrate throughout the study. The initial rate of reaction in each kinetic run was determined by the slope of the tangent of the plot drawn between unconsumed $IO_4^-$and time and pseudo first-order rate constant (k_1) was calculated by dividing the observed initial rate by the [$NaIO_4$] (Eq.1).

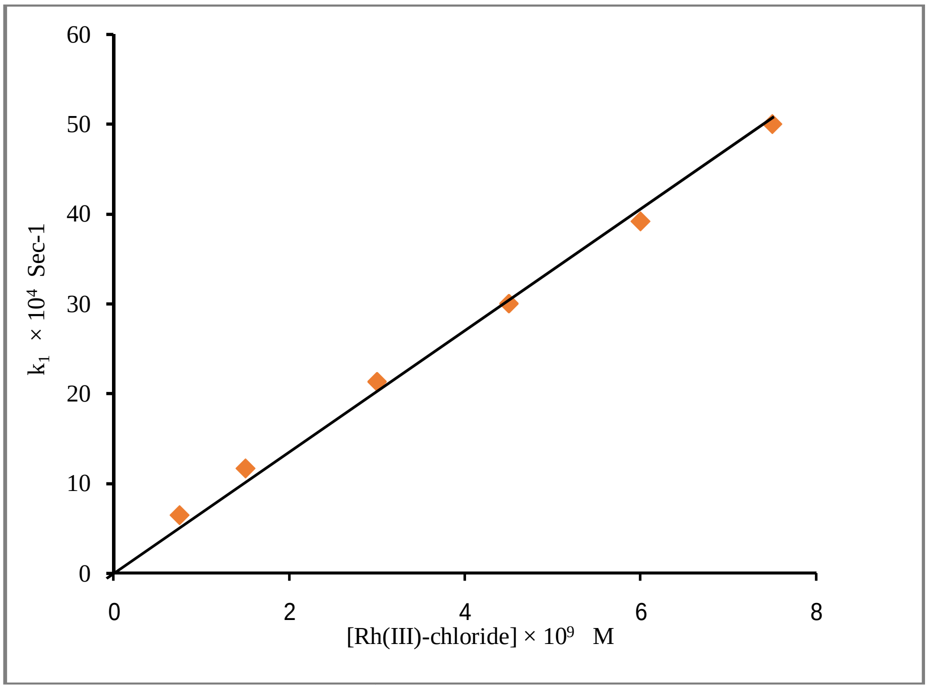
$$k_1 = -\frac{dc/dt}{[IO_4^-]} \qquad ...(1)$$

For determining the order of reaction with respect to [IO_4^-], its concentration has been varied from 0.50×10^{-3}M to 5.00×10^{-3}M at constant concentration of all other reactants. It is clear from the data given in table1 that throughout the variation of periodate, the rate of the reaction increases in the same proportion in which the concentration of $NaIO_4$ is increased, which leads to the conclusion that the order of reaction with respect to $[IO_4]^-$ is unity throughout its ten-fold variation. This result is further verified by the straight lines passing through the origin in the plots of -dc/dt versus [IO_4^-] in the oxidation of fructose (Figure 1). A straight line passing through the origin obtained from the plot of k_1 vs [Rh(III)] (Figure 2), further confirms the first-order dependence of the reaction on [Rh(III)] throughout its ten-fold variation. The pseudo first-order rate constant (k_1) increases with increase in concentration of fructose (Figure 3), suggesting first order dependence of the reaction on [fructose]. At low concentrations the pseudo first-order rate constant (k_1) is found to be directly proportional to [OH^-], and at higher concentrations it becomes almost independent of [OH^-](Fig.4) in the oxidation of fructose. The role of KCl and $NaClO_4$ was just to fix the chloride ion concentration and the ionic strength of the medium. Slight positive effect of [Cl^-] on the rate of reaction was observed. First order rate constant remains unaffected by varying the ionic strength of the medium. Since reaction rate is independent of ionic strength concentration therefore it is concluded that there is absence of primary salt effect, indicating the participation of uncharged species of one of the reactant in rate determining step. For the effect of dielectric constant (D) of the medium on pseudo first-order rate constant (k_1) the experiments, by varying the concentration of ethanol from 5% to 20% were performed under uniform conditions. It is observed that change in dielectric constant has no effect on the rate of the reaction. Reactions have also been studied at four different temperatures 35°C, 40°C, 45°C and 50°C. The Arrhenius plots of log k vs. 1/T (T=absolute temperature) were found to be linear. The activation energy can be calculated from the slopes of the plots of log k vs. 1/T. From these values, the thermodynamic parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ were evaluated. The rate constants measured at these temperatures led to the values of Ea, $\Delta H^{\#}\Delta S^{\#}$ of the slow step in oxidation of fructose catalyzed by Rh(III) by alkaline periodate solution. The values of specific rate constant (kr), Arrhenius factor (A), energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were found at 40^0C in the oxidation of fructose as 6.79 mol^{-2} dm^6s^{-1}, 58.20 mol^{-2} dm^6s^{-1}, 65.86 kJ mol^{-1}, 66.57 kJ mol^{-1} and 28.50 JK^{-1} mol^{-1} respectively.



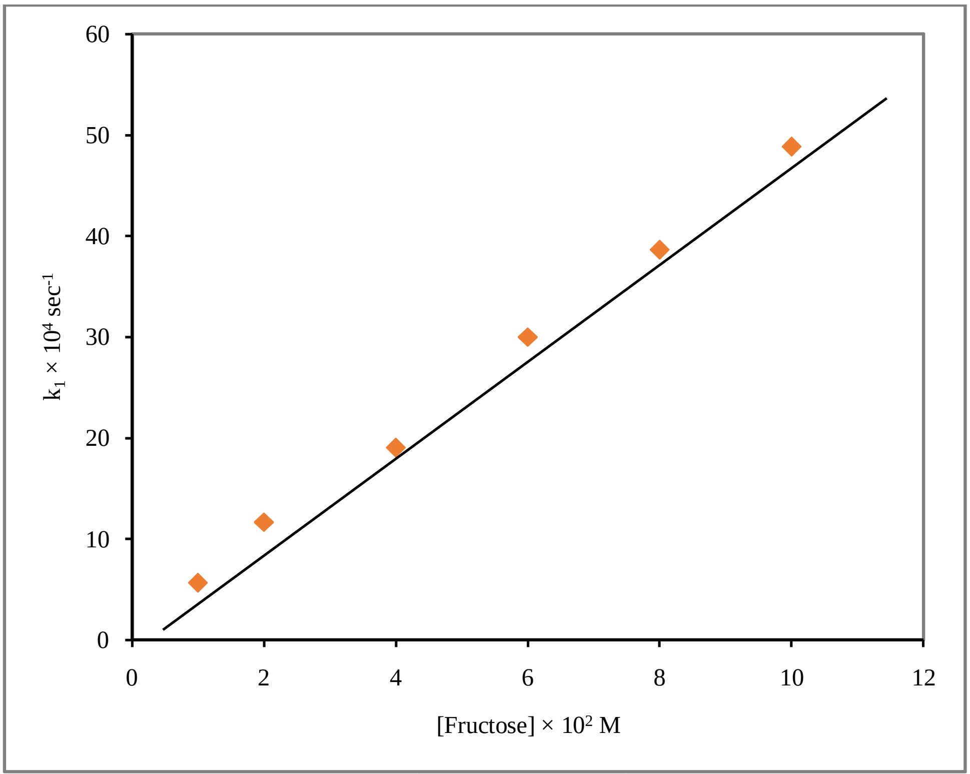
Solution conditions:[D-fructose] = 2.00× 10^{-2} M, [Rh(III)] = 1.50 ×10^{-9} M, [NaOH] = 30.00 × 10^{-2} M, KCl = 1.00 × 10^{-5}M, μ = 0.80M

Figure 1. Plot between –dc/dt and $[NaIO_4]$ at 40 ^{0}C±0.1 ^{0}C.



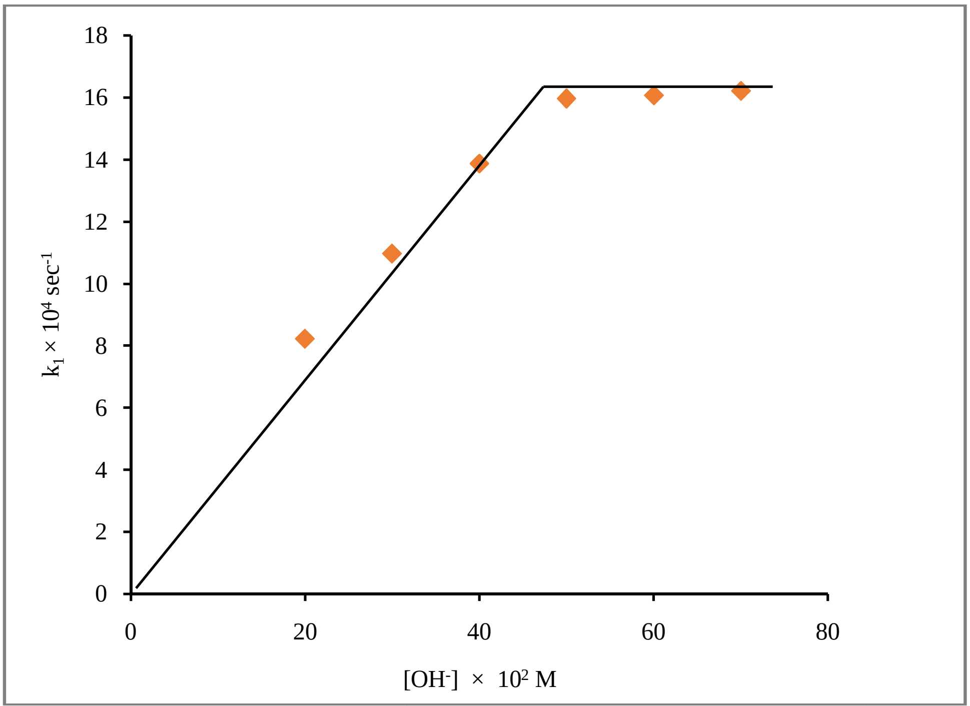
Solution conditions:$[IO_4^-]$ = 1.00 ×10^{-3}M, [D-fructose] = 2.00 × 10^{-2} M, [NaOH] = 30.00 × 10^{-2} M, KCl = 1.00 × 10^{-5}M, μ = 0.80M.

Figure 2. Plot between $k_1$and [Rh(III)]at 40^{0}C±0.1^{0}C.



Solution conditions: $[IO_4^-] = 1.00 \times 10^{-3}$M,$[Rh(III)] = 1.50 \times 10^{-9}$ M, $[NaOH] = 30.00 \times 10^{-2}$ M, $KCl = 1.00\ X10^{-5}$M, $\mu = 0.80$M

Figure 3. Plot between k_1 and [Fructose] at 40 ^{0}C±0.1 ^{0}C.



Solution conditions: $[IO_4^-] = 1.00 \times 10^{-3}$M,[D-fructose] = 2.00×10^{-2} M, $[Rh(III)] = 1.50 \times 10^{-9}$ M, $KCl = 1.00 \times 10^{-5}$M, $\mu = 0.80$M

Figure 4. Plot between k_1 and [NaOH] at 40^{0}C±0.1^{0}C.

Reactive species of periodate in alkaline medium: Crouthamel and co-workers [13] detected the following equilibria in aqueous solution of periodate which are pH controlled.

$$H_5IO_6 \rightleftharpoons H_4IO_6^{-} + H^{+}$$

$$H_4IO_6^{-} \rightleftharpoons IO_4^{-} + 2H_2$$

$$H_4IO_6^{-} \rightleftharpoons H_3IO_6^{2-} + H^{+}$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^{+}$$

The concentration of H_5IO_6, IO_4^{-1} and $H_3IO_6^{2-}$ in periodate solution were determined by absorption intensities and the extinction coefficient reported by Crouthamel *et. al* [14] on 222.5μm. It is reported [15] that at pH 10.2, 100% of periodate is $H_3IO_6^{2-}$ and at pH 13.6, 100% of periodate is $H_2IO_6^{3-}$. In Rh(III) ion catalyzed oxidation of D-fructose, since the pH of the system is varied between 13.30 to 13.85, hence it is reasonable to assume that there exists an equilibrium between two types of species i.e $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. It is clear that increase in the concentration of [OH^-] the equilibrium will shift to the right side with more and more formation of $H_2IO_6^{3-}$. On the basis of the observed fractional order in [OH^-] it is assumed that $H_2IO_6^{3-}$ is the main reactive species of IO_4^-.

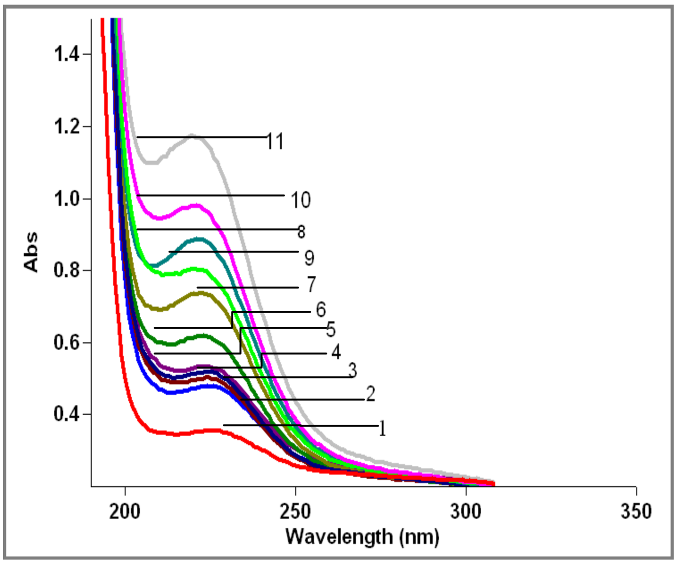
Reactive species of Rh(III)-chloride in alkaline medium: W.C. Wolsey *et.al.*, [16] have reported that various complex species i.e.$RhCl^{2+}$, $RhCl_2^{+}$, $RhCl_3$, $RhCl_4^{-}$, $RhCl_5^{2-}$, and $RhCl_6^{3-}$ formed between rhodium(III) and chloride ion with the change in concentration of hydrochloric acid from 0.01M to 2.00 M. According to James and Rempel [17], in aqueous acidic solution only anionic complexes $[RhCl_6]^{3-}$, $[Rh(H_2O)Cl_5]^{2-}$ and $[Rh(H_2O)Cl_4]^{-}$ will activate molecular hydrogen for the homogeneous reduction of ferric ion and catalytic activities of these complexes increase with increasing number of chloride ligands present. They have also proposed that when Rh(III)-chloride is prepared in 3-5 M HCl solutions, the 5:1 chloro species persists over this range of HCl concentration. Whereas Harrord and Halpern [18] reported that $[RhCl_6]^{3-}$ is predominates species of $RhCl_3$ in 3.0M-5.0M HCl solution. Later on James and Rempel [19] reported that the activity of the $[Rh(H_2O)Cl_5]^{2-}$ species in 0.20 M HCl-5.80 M $HClO_4$ is about twice that in the 3M HCl media. They have also proposed that cationic species show no reactivity while neutral species $[RhCl_3(H_2O)_3]$ show reactivity in the hydration of acetylenes catalysed by Rh(III) chloride complexes and this activity increases to maximum for a solution containing mainly the 5:1 chloro species. It is also reported [20] that on boiling aqueous solutions of the rhodium trichloride, $[Rh(H_2O)_6]^{3+}$ is formed and with excess HCl the rose pink $[RhCl_6]^{3-}$ is obtained. Between these two species there are clearly several intermediates. On aquation $[RhCl_6]^{3-}$ produces $[RhCl_5(H_2O)]^{2-}$, cis $[RhCl_4(H_2O)_2]^{-}$ and fac-$RhCl_3(H_2O)_3$.

In the present investigation, the solution of Rh(III)chloride was prepared in 3M HCl solution and its concentration was determined as 3.79×10^{-3} M. This original solution was further diluted with the help of double distilled water and the concentration of the catalyst Rh(III)-chloride in each kinetic run was fixed in the order of 10^{-9}. In view of the literature reported earlier and also in view of the conditions under which the experiments were performed for the effect of [IO_4^-], [reducing sugar], [OH^-] and [Rh(III)-chloride] on the rate of oxidation, it can safely be assumed that the starting species of Rh(III)-chloride in the reactions is the neutral species i.e. $[RhCl_3(H_2O)_3]$. This assumption finds support from the report [20] where it has been assumed that $[RhCl_3(H_2O)_3]$ is the reactive species of Rh(III)-chloride in the oxidation of styrene, stilbene and phenylacetylene by acid periodate.

Since the present study for Rh(III)-catalysed oxidation of D-fructose by periodate has been made in alkaline medium, a decision about the reactive species of Rh(III)-chloride can be taken only after considering the effect of OH^- concentration on the rate of oxidation. When concentration of OH^- has been varied at constant concentrations of all other reactants and at constant temperature, it was found that the order of reaction with respect to [OH^-] is fractional positive throughout its variation. On the basis of observed kinetic order with respect to OH^- concentration and also on the basis of spectra observed for $[RhCl_3(H_2O)_3]$ solution alone and for $[RhCl_3(H_2O)_3]$ solutions with two different concentrations of OH^- where an increase in absorbance from 0.61 to 0.91 and 1.02 was noted, it can be assumed that the following equilibrium exists in the reaction under investigation (Figure 5(1), (2) and (3)).

$$RhCl_3(H_2O)_3 + OH^- \rightleftharpoons [RhCl_3(H_2O)_2(OH)]^- + H_2O$$

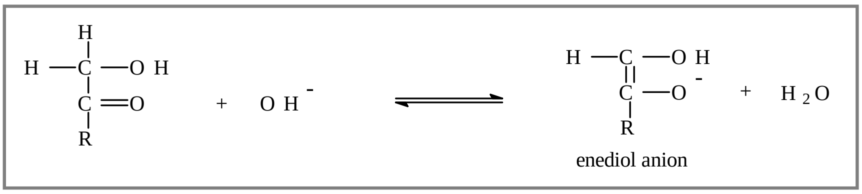
Out of the two species $[RhCl_3(H_2O)_3]$ and $[RhCl_3(H_2O)_2(OH)]^-$, the species $[RhCl_3(H_2O)_2(OH)]^-$ can be considered as the reactive species of Rh(III) chloride in alkaline medium because only with this reactive species the fractional positive order in $[OH^-]$ can very well be explained and a suitable rate law can be derived.

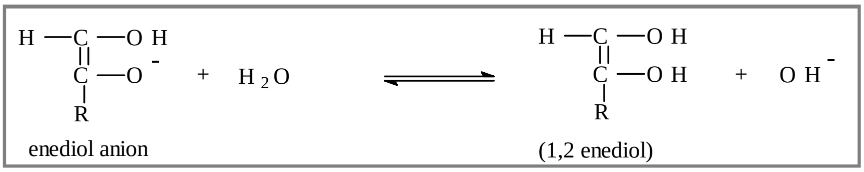


Solution conditions : (1) [Rh(III)] = 3.79×10^{-6} M, (2) [Rh(III)] = 7.58×10^{-6} M, (3) [Rh(III)] = 7.58×10^{-6} M, $[OH^-] = 2.0 \times 10^{-3}$ M. (4) [Rh(III)] = 7.58×10^{-6} M, $[OH^-] = 4.0 \times 10^{-3}$ M, (5) [Rh(III)] = 7.58×10^{-6} M, $[OH^-] = 8.0 \times 10^{-3}$ M, (6) [Rh(III)] = 7.58×10^{-6} M, $[OH^-] = 4.0 \times 10^{-2}$ M,$[IO_4^-] = 1.00 \times 10^{-4}$ M, (7) [Rh(III)] = 7.58×10^{-6} M, $[OH^-] = 4.0 \times 10^{-2}$ M,$[IO_4^-] = 2.00 \times 10^{-4}$ M, (8) [Rh(III)] = 7.58×10^{-6} M, $[OH^-] = 4.0 \times 10^{-2}$ M,$[IO_4^-] = 4.00 \times 10^{-4}$ M, (9) [Rh(III)] = 7.58×10^{-6} M, $[OH^-] = 4.0 \times 10^{-2}$ M,$[IO_4^-] = 2.00 \times 10^{-3}$ M,[D-fructose] = 0.1 M, (10)[Rh(III)] = 7.58×10^{-6} M, $[OH^-] = 4.0 \times 10^{-2}$ M,$[IO_4^-] = 2.00 \times 10^{-3}$ M,[D-fructose] = 0.2 M, (11)[Rh(III)] = 7.58×10^{-6} M, $[OH^-] = 4.0 \times 10^{-2}$ M,$[IO_4^-] = 2.00 \times 10^{-3}$ M,[D-fructose] = 0.4 M

Figure 5. Spectra of solutions [1-11] recorded at room temperature.

Reactive form of fructose in alkaline medium: It is well known [21-22] that the reducing sugars undergo a tautomeric change in presence of alkali and exists as the enediol anion and enediol



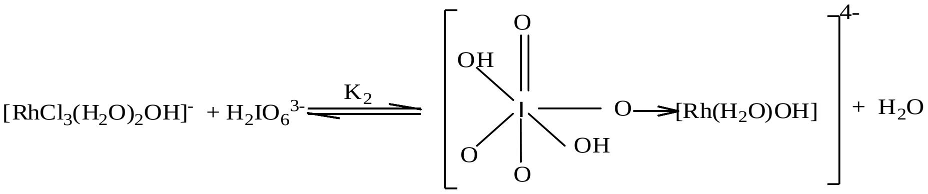


Taking into account the base catalyzed formation of enediol anion and enediol and also the positive effect of $[OH^-]$ on the rate of oxidation, it can very easily be concluded that it is the enediol form of sugar which participates as reductant in the reactions under investigation.

Spectrophotometric evidence for the formation of various complexes during the course of reaction: To ascertain the formation of possible complex or complexes during the course of reaction, spectra were obtained by using Varian Carry 300 Bio UV-VIS Spectrophotometer. When spectra for the solutions of Rh(III)alone and for the solutions of Rh(III) with three different concentrations of OH^- were collected, it was found that there is substantial increase in absorbance from 0.478 to 0.53 with the increase in $[OH^-]$ (Fig.5(1),(2),(3),(4)). This increase in $[OH^-]$ can be assumed as due to more and more formation of $RhCl_3(H_2O)_2OH]^-$ according to the following equilibria.

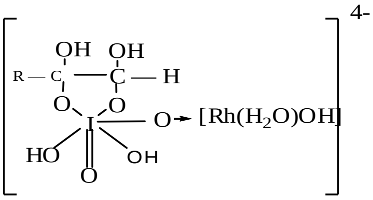
$$RhCl_3(H_2O)_3] + OH^- \rightleftharpoons RhCl_3(H_2O)_2OH]^- + H_2O \qquad (2)$$

Above equilibrium with positive effect of $[OH^-]$ on the rate of oxidation clearly shows that $RhCl_3(H_2O)_2OH]^-$ is the reactive species of Rh(III) in alkaline medium. In order to ascertain the possibility of formation of complex between reactive species of IO_4^- i.e. $[H_2IO_6]^{3-}$ and reactive species of Rh(III) chloride i.e. $[RhCl_3(H_2O)_2OH]^-$ in alkaline medium, spectra for the solutions of Rh(III) chloride and OH^- with varying concentration of IO_4^- were collected. It was found that there was an increase in absorbance from 0.61 to 0.80 at wavelength 222nm, with an increase in concentration of sodium metaperiodate (Fig.5 (5),(6) and(7)). This result can be made to make a basis for the existence of the following equilibria in our reaction under investigation.

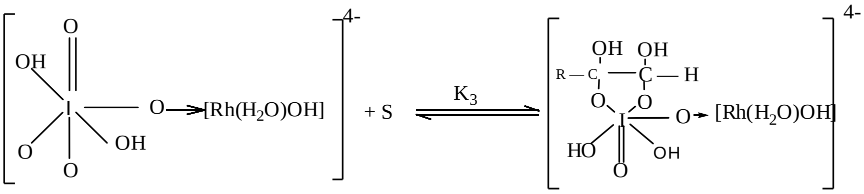


(II)

It is reported [23, 24] in the literature that transition metal ions form a complex with sugar molecule. In order to verify the formation of a complex between the complex indicated above on the right hand side and a sugar molecule, spectra for solutions of Rh(III) chloride, OH^-, and IO_4^- with three different concentrations of reducing sugar were collected.From the persusal of the spectra shown in figure 5 ((8), (9) and (10)), it is clear that there is an increase in absorbance of the solution with the increase in reducing sugar concentration. This increase in absorbance with the increase in reducing sugar concentration might be assumed as due to more and more formation of the complex,

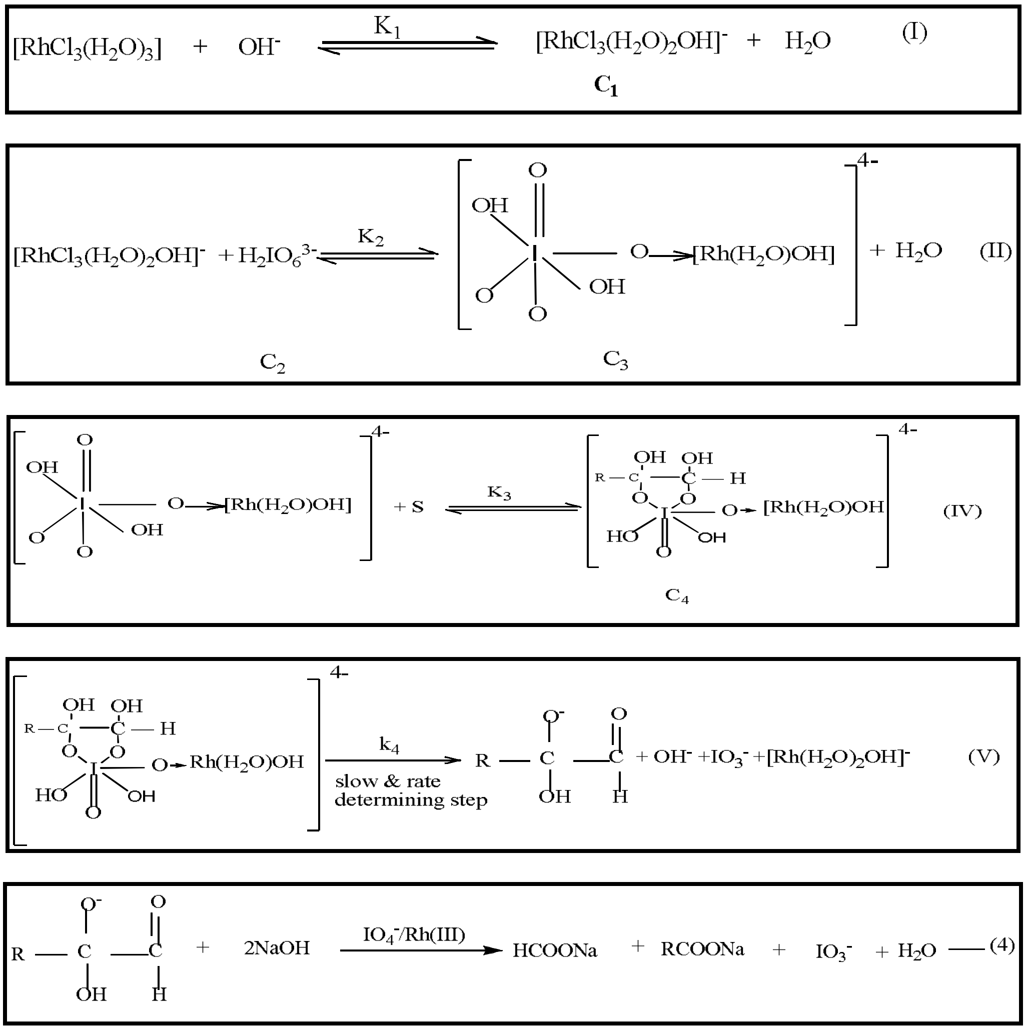


According to the following equilibrium.



Where, S represents the reactive species of sugar molecule in alkaline solution.

Reaction path for the oxidation of D-fructose by alkaline solution of sodium metaperiodate in presence of chloro-complex of Rh(III): On the basis of observed kinetic orders with respect to IO_4^-, OH^-, Rh(III) and fructose concentration and also on the basis of spectral information collected for the formation of different complexes during the course of reaction together with the entropy of activation, a probable reaction path in the form of reaction scheme.



Reaction Scheme

Considering stoichiometric data, the rate of the reaction in terms of formation of product or in terms of decreasing concentration of IO_4^- is given by equation

$$\text{rate} = -\frac{d[IO_4^-]}{dt} = 4k_4[C_4] \qquad (3)$$

Upon applying the law of chemical equilibrium to steps(I), (II) and (III) of the mechanism, we have

$$[C_1] = K_1[\text{Rh(III)}]\,[OH^-] \qquad (4)$$

$$[C_3] = K_1\,K_2[C_2][\text{Rh(III)}]\,[OH^-] \qquad (5)$$

$$[C_4] = K_1 K_2 K_3 [C_2][\mathrm{Rh(III)}][\mathrm{OH}^-][S] \qquad (6)$$

On substituting the value of $[C_4]$ from equation (6) to rate equation (3), we get

$$\text{rate} = -\frac{d[\mathrm{IO}_4^-]}{dt} = 4K_1 K_2 K_3 k_4 [C_2][\mathrm{Rh(III)}][\mathrm{OH}^-][S] \qquad (7)$$

According to the mechanism, the total concentration of Rh(III) can be written as equation (8)

$$[\mathrm{Rh(III)}]_T = [\mathrm{Rh(III)}] + [C_1] \qquad (8)$$

$$[\mathrm{Rh(III)}]_T = [\mathrm{Rh(III)}] + K_1[\mathrm{Rh(III)}][\mathrm{OH}^-] \qquad (9)$$

$$[\mathrm{Rh(III)}] = \frac{[\mathrm{Rh(III)}]_T}{1 + K_1[\mathrm{OH}^-]} \qquad (10)$$

Now equations (7) and (10) will give

$$\text{rate} = -\frac{d[\mathrm{IO}_4^-]}{dt} = \frac{4K_1 K_2 K_3 k_4 [C_2][\mathrm{Rh(III)}]_T[\mathrm{OH}^-][S]}{1 + K_1[\mathrm{OH}^-]} \qquad (11)$$

The rate law (11) is in complete agreement with our observed kinetic data. Equation (11) can also be written as

$$\frac{[\mathrm{IO}_4^-][\mathrm{Rh(III)}]_T[S]}{\text{rate}} = \frac{1}{4K_1 K_2 K_3 k_4} \cdot \frac{1}{[\mathrm{OH}^-]} + \frac{1}{4K_2 K_3 k_4} \qquad (12)$$

Where, C_2 representing $[H_2IO_6]^{3-}$ has been replaced by $[IO_4^-]$

Eq. (12), indicates that if a plot is made between $\frac{[\mathrm{IO}_4^-][\mathrm{Rh(III)}]_T[S]}{\text{rate}}$ and $\frac{1}{[\mathrm{OH}^-]}$, a straight line with positive intercept on *y*-axis will be obtained. Straight lines with positive intercepts on *y*-axis obtained by the plots of $\frac{[\mathrm{IO}_4^-][\mathrm{Rh(III)}]_T[S]}{\text{rate}}$ versus $\frac{1}{[\mathrm{OH}^-]}$ on one hand proves the validity of the rate law (11) and on the other hand the proposed reaction scheme, on the basis of which the rate law (11)has been derived. From the values of the intercepts and slopes of the plots, the values of K_1 and $K_2K_3k_4$ have been calculated and found as 1.6212 mol^{-1} lit and 0.568 x10^8 mol^{-2} lit^2 sec^{-1}, respectively, for the oxidation of fructose. Utilizing these values of the constants, the reaction rates were calculated for the variations of [Rh(III)], $[\mathrm{OH}^-]$,and are presented in Table-1 along with the experimental rates. Almost the same values of two rates ,i.e. the calculated and observed, further proves the validity of the rate law (11) and hence the proposed reaction scheme.

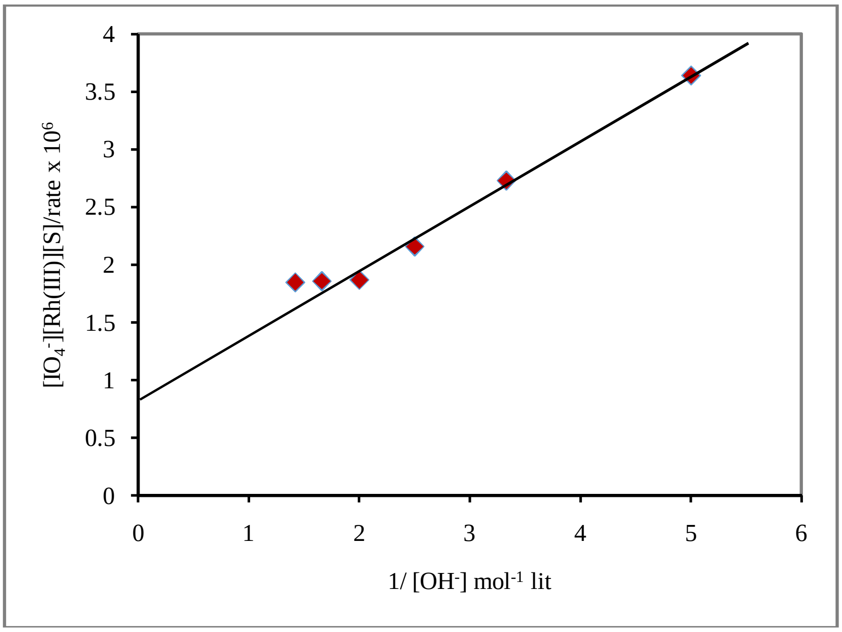


Fig. 6: Plot between $\frac{[IO_4^-][Rh(III)]_T[S]}{rate}$ and $\frac{1}{[OH^-]}$

Table1. Experimental and Calculated values of the rate for the variations of $[OH^-]$ in the Rh(III)-catalysed oxidation of fructose by periodate at 40^0C

$[OH^-] \times 10^2$ (M)	$dc/dt \times 10^7$ ($Msec^{-1}$)	
	Experimental rate	Rate Calculated on the basis of rate law (equation(11))
20.00	8.22	8.30
30.00	10.96	11.15
40.00	13.86	13.41
50.00	15.96	15.26
60.00	16.02	16.81
70.00	16.20	18.12

It was reported [25] that when reaction occurs between two oppositely charged species, the transition state becomes less polar than the initial state. In the present investigation, observed positive entropy of activation in the oxidation of fructose clearly supports the interaction between charged species, C_3, and endiol form of fructose leading to the formation of a less polar activated complex, C_4, which ultimately converts into products via several fast steps. This is also supported by the spectroscopic evidence collected for the formation of complex, C_4, in the step (IV) of the proposed reaction scheme.

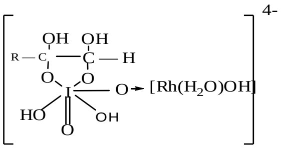
Comparative study: Efforts have also been made to compare the findings of this paper with the results reported, for the Ru(III)-catalyzed [26] oxidation of lactose by sodium meta periodate and the Rh(III)-catalyzed [27]oxidation of D(+) ribose by sodium iodate in alkaline medium. When the present study has been made for the effect of $[IO_4^-]$ on the rate of oxidation, it is found that the rate is directly proportional to $[IO_4^-]$. Contrary to this, the first to zero order kinetics in $[IO_4^-]$ and $[IO_3^-]$ were observed for both Ru(III) [26] and Rh(III)-catalyzed [27] oxidation, respectively. The present paper on the one hand shows similarity with Rh(III)-catalyzed [27] oxidation of reducing sugar being first order with respect to [ribose] throughout the variation, and on the other hand it differs in order with respect to [lactose], indicating first to zero order kinetics in [lactose] in the Ru(III)-catalyzed [26] oxidation. The present study, being very similar in kinetic order with respect to [catalyst] and [OH^-], where first order with respect to [catalyst] and first to zero order in [OH^-] was observed. On the basis of observed kinetic data and spectroscopic evidence, it has been assumed that the species $[RhCl_3(H_2O)_2OH]^-$ is the reactive species of Rh(III)-chloride in the present study as well as in Rh(III)-catalyzed [27] oxidation of ribose, whereas$HRuO_5$is found as reactive species of Ru(III)-chloride[26] in the oxidation of lactose. On the basis of observed kinetic data and spectroscopic evidence, it has been assumed that the species $[H_2IO_6]^{3-}$ is the reactive species of sodium meta periodate in the present study as well as in Ru(III)-catalyzed [26] oxidation of lactose, whereas $[IO_3]^-$ is found as reactive species of the potassium iodate in Rh(III) catalyzed [27] oxidation of ribose. In view of the facts mentioned above, it can be said that the present study is different in many respects from the other two studies reported earlier.

APPLICATION

The kinetic data collected by experimental observations will be utilized for elucidating oxidation path i.e. reaction mechanism of the above-mentioned redox processes.

CONCLUSION

Making basis to the observed kinetic data and spectrophotometric information, the following conclusions for the oxidation of D(+)fructose by IO_4^- using Rh(III) as catalyst in alkaline medium were derived-

1. $[H_2IO_6]^{3-}$, enediol form of reducing sugar and $[RhCl_3(H_2O)_2OH]^-$ have been assumed as the reactive species of periodate, reducing sugar and Rh(III)-chloride in alkaline medium, respectively.
2. The reaction shows first-order kinetics with respect to [IO_4^-] and [D-fructose] and fractional positive order kinetics in [OH^-].
3. The complex, , has been proposed as the most reactive activated complex in the Rh(III)-catalysed oxidation of D-fructose by sodium metaperiodate in alkaline medium.
4. In step (III) of reaction scheme, where an interaction between a charged species and a neutral substrate molecule is shown, is well supported by the observed positive entropy of activation.

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