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Mechanistic Studies of Ru(III) Chloride Catalyzed Oxidation of Lactose by Sodium Metaperiodate in Alkaline Medium

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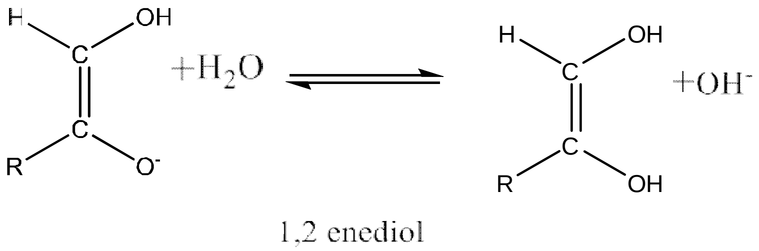
ABSTRACT

Kinetics of oxidation of lactose by sodium metaperiodate in the presence of Ruthenium(III) chloride as homogeneous catalyst in alkaline medium has been carried out at 40^{0}C. Reaction follows first order kinetics in the lower concentration range of sodium metaperiodate, lactose and OH$^-$ ion while the order shifts from first to zero at their higher concentrations range. The reaction follows first-order kinetics in Ru(III) chloride concentration. Negligible effect of chloride ions was observed. Change in the ionic strength of the medium did not bring about any appreciable change in the rate of oxidation of lactose. The reaction rate enhanced significantly on increasing the temperature. HIO_5^{2-} and $HRuO_5^-$ have been postulated as the reactive species of sodium metaperiodate and Ru(III) respectively in alkaline medium.

Graphical Abstract



Keywords: Alkaline medium, Lactose, Mechanism, Ru(III)chloride, Sodium metaperiodate.

INTRODUCTION

Periodate has been used extensively in oxidation of organic as well as inorganic compounds. The periodate oxidation is undoubtedly one of the most widely used reactions in organic chemistry [1-10]. $NaIO_4$ has been successfully explored as a versatile oxidant for a variety of fundamental organic transformations such as C–H activation, oxidative functionalization of alkenes and other interesting oxidative transformations and its application in the synthesis of bioactive natural products. The reaction has found its greatest application in the field of carbohydrate chemistry. Sodium metaperiodate is a mild oxidant that is routinely used for the conversion of cis-glycol groups in carbohydrates to reactive aldehyde groups. Sodium periodate can be used alone or with transition metals for oxidation reactions. Ruthenium (III) acts as an efficient catalyst [11-15] both in acidic and alkaline medium which is used in present investigation. Ru(III) ions are found to catalyze many periodate oxidations. The kinetics of oxidation of sugars by a variety of oxidants has been reported [16-18] in both acidic and alkaline media. Studies involving the oxidation of the sugars by metal ions or their complexes in an alkaline medium are limited [19-20].These biological and economic importance of the carbohydrates and especially the disaccharides have been largely responsible for the interest in the study of their bio and physiochemical properties and reactivity. In view of the facts regarding importance and utility of $NaIO_4$, lactose and Ru(III) the present study has been undertaken.

MATERIALS AND METHODS

All the reagents used were of highest purity percentage available. All the solutions used were prepared in double distilled water to prevent any foreign ion interference. An aqueous solution of sodium metaperiodate (E. Merck) was prepared by accurately weighing and dissolving it in double distilled water. The prepared solution of $NaIO_4$ was standardized against standard solution of sodiumthiosulphate (Qualigens Chemicals) iodometrically. Standard solution of lactose (Loba) was freshly prepared by exactly weighing and dissolving the weighed amount in double distilled water. A solution of Ru(III) chloride (Unichem Limited) was prepared in HCl of known strength (10.00×10^{-2}M) and its concentration was maintained at 6.69×10^{-3}M. A weighed amount of sodium hydroxide (E.Merck) was dissolved in double distilled water. Each kinetic run was performed at a constant temperature of 40ºC with an accuracy of ±0.1°C. In a conical flask all the reactants except reducing sugar were mixed in required quantity and hanged in thermostatic water bath maintained at 40ºC. Freshly prepared solution of lactose was also kept in separate conical flask within the same thermostatic water bath at the same temperature. When both the solutions have acquired the temperature of the bath, measured amount of the sugar solution was pipetted out and was mixed in the conical containing reaction mixture. As soon as the sugar solution was mixed with the reaction mixture the reaction gets initiated. To know the actual progress of the reaction, 5 mL of the reaction mixture were taken out and poured in a conical containing 5 mL of KI (4%) solution and 5 mL of $HClO_4$ solution and the liberated iodine equivalent to unconsumed periodate was titrated against hypo solution using starch as an indicator. The initial rates (–dc/dt) were obtained from the slopes of concentration of remaining periodate versus time graphs in the initial stages of the reactions by plane mirror method.

Stoichiometry and reaction products: Various sets of experiments having different [$NaIO_4$]: [Lactose] ratios were carried out. Determination of remaining concentration of $NaIO_4$ indicated that 4-moles of periodate ions were required to oxidize one mole of lactose in the presence of alkaline solution of ruthenium (III)-chloride and accordingly, following stoichiometric equation represented as-

$$C_{12}H_{22}O_{11} + 4IO_4^- + H_2O \longrightarrow 2HCOOH + 2C_4H_9O_4COOH + 4IO_3^-$$

Lactose Arabinonic acid

RESULTS AND DISCUSSION

The kinetics of Ru(III)-catalyzed oxidation of lactose by $NaIO_4$ in alkaline medium has been studied at 40^0C. To know the effect of $NaIO_4$ on the rate of reaction, a number of kinetic experiments were performed by varying $NaIO_4$ concentration and keeping the concentration of all other reactants constant at constant temperature of 40ºC and at constant ionic strength of the medium. Oxidation of lactose follows first order kinetics in the lower concentration range of sodium metaperiodate while order shifts from first to zero at its higher concentration range (Fig.1). During the variation of Ru(III)-chloride from 9.64 x 10^{-6} M to 96.40 x 10^{-6} M, the concentration of all other reactants were kept constant. The reaction follows first order kinetics with respect to Ru(III)-chloride throughout its variation (Fig.2). For the determination of effect of reducing sugar on the rate of oxidation, the concentration of lactose was varied from 0.50×10^{-2} M to 12.00 $\times10^{-2}$ M at constant concentration of all other reactants and at constant temperature 40°C. Fig.3 shows a plot between the values of first-order rate constant, $k_1$and [Lactose]. This plot clearly shows first-order kinetics in the lower concentration range of lactose whereas order shifts from first to zero order at its higher concentration range throughout its ten-fold variation. First order kinetics was observed at low concentration of OH^- while at higher concentration of OH^- the order was found to be zero in the variation of [OH^-] at constant concentration of all other reactants and at constant temperature 40^0C (Fig.4). The rate of the reaction remains unaffected by the change in [Cl^-] and ionic strength of the medium. To determine the effect of temperature on the rate in oxidation of lactose by $NaIO_4$ using Ru(III) as catalyst, experiments were performed under identical conditions at four different temperatures, viz. 35^0C, 40^0C, 45^0C and 50°C. By the observed values of first order rate constant, k_1, the values of activation parameters like $\Delta S^{\#}$, $\Delta G^{\#}$, $\Delta H^{\#}$, E_a and A for Ru(III)-catalyzed oxidation were calculated and found as -1.6193 e.u,14.784 kcal, 12.845kcal mol^{-1}, 13.47 kcal mol^{-1} and 7.846×10^{12} mol^{-2} lit^2 sec^{-1}, respectively.

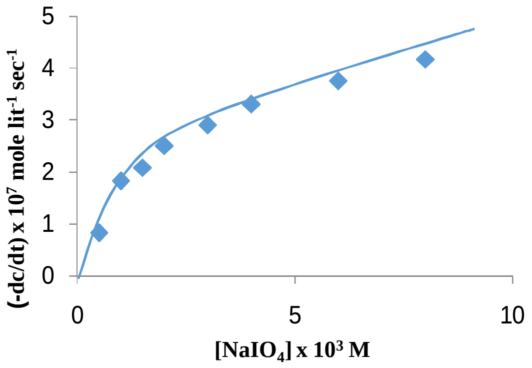


Figure 1. Plot between (-dc/dt) and [$NaIO_4$] at 40^0 C
Solution conditions: [Lactose] = 10.00 x 10^{-2} M, [NaOH] = 2.00 x 10^{-2} M, [$RuCl_3$] = 28.92 x 10^{-6} M

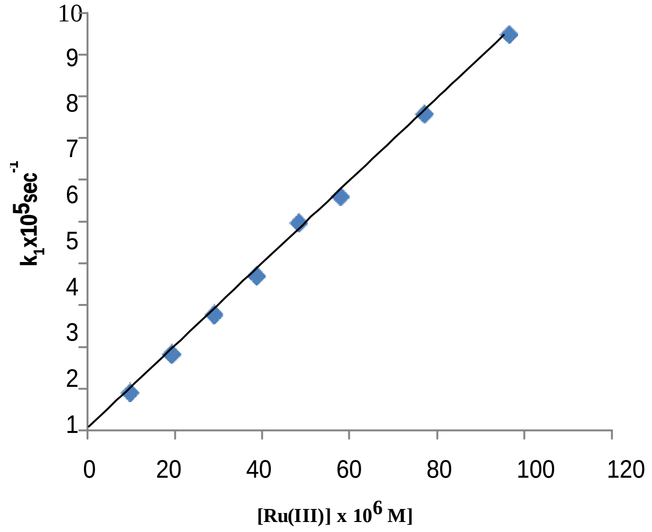


Figure 2. Plot between (k_1) and [$RuCl_3$] at 40^0 C
Solution conditions: [$NaIO_4$] = 1.00 x 10^{-3}, [Lactose]= 10.00 x 10^{-2} M, [NaOH] = 2.00 x 10^{-2}M

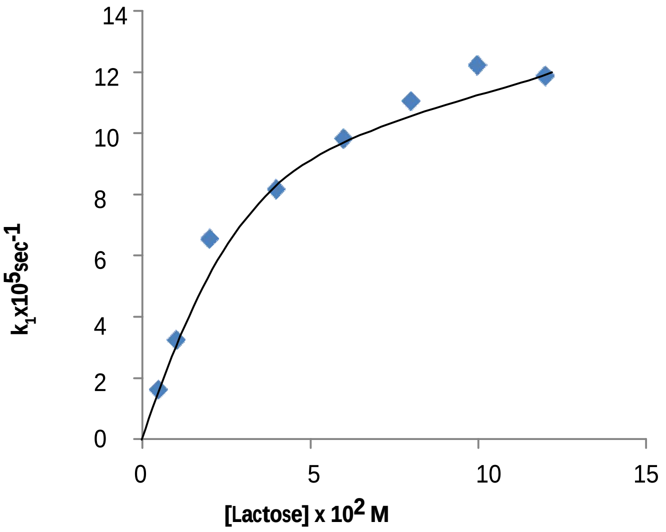


Figure 3. Plot between [Lactose] and (k_1)

Solution conditions: [$NaIO_4$] =100 x 10^{-3} M, [NaOH] = 2.00 x 10^{-2} M, [$RuCl_3$] = 28.92 x 10^{-6} M

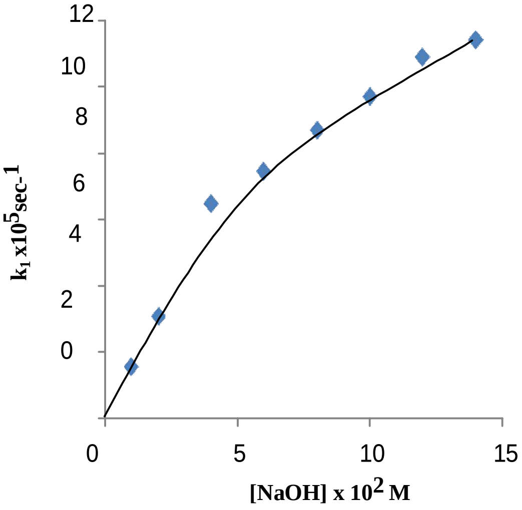


Figure 4. Plot between [NaOH] and (k_1) at 40^0C
Solution conditions: [$NaIO_4$] =1.00 x 10^{-3} M, [Lactose] = 10.00 x 10^{-2} M, [$RuCl_3$] = 28.92 x 10^{-6} M

Reactive species of Sodium metaperiodate in alkaline medium: Rao *et al.,* [5] have reported that the observance of Michaelis type of kinetics with respect to periodate ion, under the conditions [Periodate]>> [Ru(III)], and suggests the formation of 1:1 complex between catalyst and periodate, the complex being the reactive oxidizing species. The UV and Raman spectral studies [6-9] indicate that in aqueous acid media (<5M), periodate mainly exists in the form of tetrahedral IO_4^- and octahedral $H_4IO_6^-$ and at higher acidities. It is further protonated giving $[H_6IO_6]^+$or $[I(OH)_6]^+$. Galliford et al [6] reported that at pH < 2, the dilute periodate solutions are mainly in the form of H_5IO_6 and IO_4^-. Hence under these conditions which also pertain to the experimental conditions employed by the author $H_4IO_6^-$ activity is believed to be negligibly small. Rosa Pascual *et al.,* [9] reported that the pH dependence of the oxidation rate together with the pk_a values, suggests that in the lower pH range (pH<4) the oxidation of substrate must be brought about by the periodate monoanion. In the pH range 4-8 where we must consider only reaction between dipolar amino acid and periodate monoanion, changes of the rate constant are not expected and the increase in the rate in the pH range 6-8 can be attributed to the catalysis of the phosphate buffer. In analyzing the variation of the reaction rate with pH, we assume that the effective reactants to be the monoanion (H_4IO_6+IO^-_4) of periodate and the protonated dipolar ionic form of the amino acid. In alkaline medium periodate ion is assumed to be involved in the following equilibrium.

$$IO_4^- + OH^- \rightleftharpoons HIO_5^{2-}$$

Thus in view of existence of IO_4^- in alkaline medium as HIO_5^{2-}I t is proposed that HIO_5^{2-} is reactive species. Reactive species of Ru(III) chloride in alkaline medium: Oxidation of Ru(III) by periodate is known to be very fast[21-23]. Thus it appears that the conversion of Ru(III) to Ru(VIII) takes place much more rapidly than oxidation of sugar. Hence, it is reasonable to postulate the Ru(VIII) is the species responsible for the catalysis. In aquous solution ruthenium tetraoxide exist the following equilibria-

$$RuO_4 + H_2O \rightleftharpoons H_2RuO_5 \qquad (I)$$

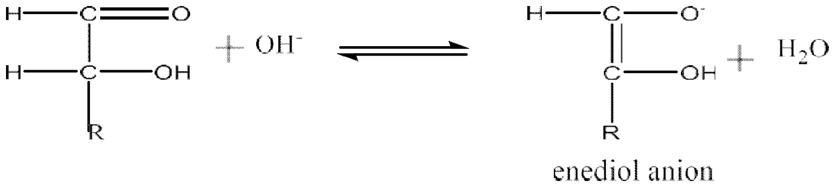
$$H_2RuO_5 + OH^- \rightleftharpoons H_2O + HRuO_5^- \qquad (II)$$

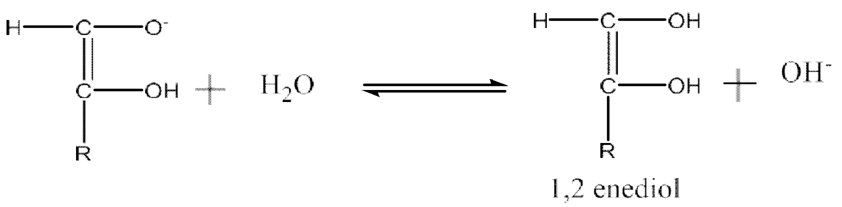
$$RuO_4 + OH^- \rightleftharpoons HRuO_5^- \qquad (III)$$

It appears from above equilibria that ruthenium tetroxide may catalyze the reaction under investigation either by RuO_4 or through $HRuO_5^-$. If $HRuO_5^-$is assumed to be active species then rate law requires positive effect of hydroxide ion. In our case the observed positive effect of hydroxide ion on the rate of reaction clearly shows that the reactive species of ruthenium tetroxide in alkaline medium is $HRuO_5^-$.

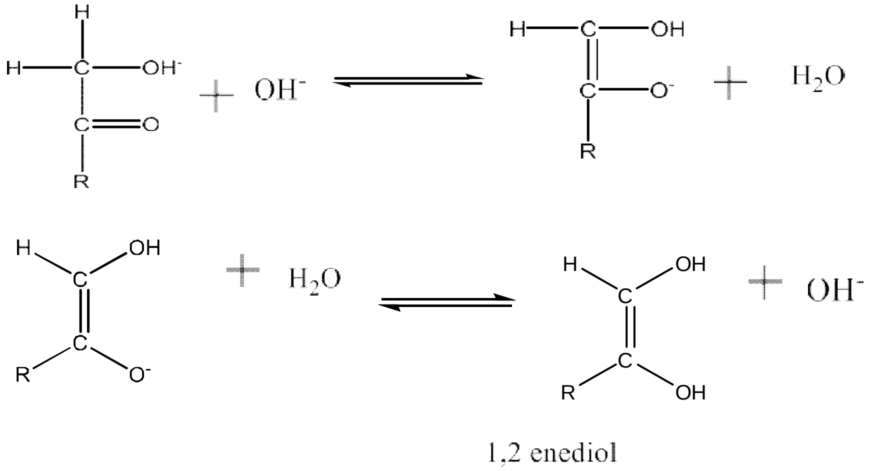
Reactive species of lactose in alkaline medium: It is well known that in the presence of alkali the reducing sugar undergoes tautomeric change resulting in an enediol intermediate as an intermediate. The formation of enediol as an intermediate in the inter conversion of reducing sugar was first suggested by Wohl and Neuberg [24] and later on by Nef Evans [25]. Further evidence of enediol is afforded by the ability of the alkaline sugar solution to take up large quantities of iodine [26] by the observations that sugars are oxidized with cleavage C_1 and C_2 in alkaline solutions and by studies of ultraviolet spectra which show a maximum characteristic dicarbonyl compounds attributed to an enediol. The evidence for the enediol [27] formation is also furnished bythe observed ability of the alkaline sugar solutions to decolorize the solutions of 2, 6-dichlorophenol indophenol. The alkali catalyzed formation of enediol might be as follows.

Aldehyde Sugars





Keto Sugars



On the basis of evidence discussed above, it is concluded that the reducing sugar in the presence of alkali first changes into enediol anion and then into 1,2enediol. Reaction mechanism and derivation of rate law thus in view of existence of RuO_4 and IO_4^- in alkaline medium as $HRuO_5^-$ and HIO_5^{2-} respectively and considering the observed kinetic results, the following reaction scheme is suggested.

$$RuO_4 + OH^- \overset{K_1}{\rightleftharpoons} HRuO_5^- \qquad (I)$$

$$IO_4^- + OH^- \overset{K_2}{\rightleftharpoons} HIO_5^{2-} \qquad (II)$$

$$HRuO_5^- + HIO_5^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Complex(C_1) + OH^- \qquad (III)$$

$$S + OH^- \overset{K_4}{\rightleftharpoons} S + H_2O \qquad (IV)$$

Where S stands for substrate

Slow the rate determining step

$$HRuO_4^- + IO^-_4 \xrightarrow{\text{fast}} HRuO_5^- + IO_3^- \qquad (VI)$$

Considering above mechanistic steps, the rate of the reaction maybe expressed in terms of loss of sodium periodate concentration as equation (1)

$$-\frac{d[IO_4^-]}{dt} = k_5\,[C_1][S^-] \qquad (1)$$

On applying steady state approximation to $[C_1]$ and considering steps (III) and (IV) we have

$$C_1 = \frac{k_3[HRuO_5^-][HIO_5^{2-}]}{k_{-3}[OH^-] + k[S^-]} \qquad (2)$$

By considering equation no.(1) and (2) we have

$$= k_5k_3\,[S^-]\,[HRuO_5^-]\,[\,HIO_5^{2-}] \qquad (3)$$

The total concentration of $HRuO_5^-$ may be written as-

$$[HRuO_5^-] = \frac{k_{-3}[OH^-] + k_5[S^-][HRuO_5^-]_T}{k_{-3}[OH^-] + k_5[S^-] + k_3[HIO_5^{2-}]} \qquad (4)$$

On substituting the value of $[HRuO_5]$ from equation (4) in equation (3) we have

$$-\frac{d[IO_4^-]}{dt} = \frac{k_5k_3[S^-][HIO_5^{2-}]\,(k_{-3}[OH^-] + k_5[S^-])\,[HRuO_5^-]_T}{(k_{-3}[OH^-] + k[S^-])\,(k_{-3}[OH^-] + k[S^-] + k_3[HIO_5^{2-}]}$$

$$-\frac{d[IO_4^-]}{dt} = \frac{k_5k_3[S^-][HIO_5^{2-}][HRuO_5^-]_T}{(k_{-3}[OH^-] + k_5[S^-]) + k_3[HIO_5^{2-}]} \qquad (5)$$

From step (IV) we have

$$K_4 = \frac{[S^-]}{[S]\,[OH^-]}$$

Or $[S^-] = K_4[S][OH^-]$ (6)

By substituting value of $[S^-]$ from equation (6) in equation (5)

$$-\frac{d[IO_4^-]}{dt} = \frac{k_5k_3K_4[S^-][OH^-][HIO_5^-][HRuO_5^-]_T}{k_{-3}[OH^-] + k_5K_4[S][OH^-] + k_3[HIO_5^{2-}]} \qquad (7)$$

But since [OH-] >> $[RuO_4]$, Hence $[HRuO_5^-]_T = [RuO_4]$. Similarly, since $[OH^-] >> [IO_4^-]$, Hence $[HIO_5^{2-}] = [IO_4^-]$

In the light of above statement equation (7) may be written as equation (8)

$$-\frac{d[IO_4^-]}{dt} = \frac{k_5k_3K_4[S][OH^-][IO_4^-][RuO_4]}{k_{-3}[OH^-] + k_5K_4[S][OH^-] + k_3[IO_4^-]} \qquad (8)$$

Further on assuming $k_{-3} < k_5K[S]$, equation (8) may be written as equation (9)

$$-\frac{d[IO_4^-]}{dt} = \frac{k_5k_3k_4[S][OH^-][IO_4^-][RuO_4]}{k_5K[S][OH^-] + k_3[IO_4^-]}$$

$$\text{Or} \quad -\frac{d[IO_4^-]}{dt} = \frac{k'[S][OH^-][IO_4^-][RuO_4]}{k''[S][OH^-] + k_3[IO_4^-]} \qquad (9)$$

The rate law (9) is in good agreement with experimental observations

APPLICATION

Based on the observed kinetic data and a most probable reaction path for Ru(III)- catalyzed oxidation of by sodium meta periodate in alkaline medium has been proposed. Oxidation of lactose depends on both reaction conditions and catalyst activity. For industrial purposes, it would be desirable that the lactose kinetic model were be able to describe accurately the conversion as a function of time, from time zero to nearly complete reduction of the substrate.

CONCLUSIONS

The following conclusions were derived from the observed kinetic data for Ru(III)-catalyzed oxidation of lactose by sodium metaperiodate in alkaline medium-

1. $[HIO_5^{2-}]$ and $[HRuO_5^-]$ have been determined as the reactive species of the metaperiodate and Ru[III] chloride in alkaline medium, respectively.
2. First order kinetics with respect to [Ru(III)] and nil effect of $[Cl^-]$ was noted.
3. There is no effect of ionic strength of the medium (μ) on the rate of oxidation of lactose.
4. The rate law (9) is in good agreement with experimental observations.

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