Mechanism of ruthenium (III) catalysis of periodate oxidation of aldoses in aqueous alkaline medium

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Received 11 December 2003; accepted 23 March 2004

A general mechanism for Ru(III) catalysed oxidation of L(+) arabinose (Ara) and D(+) galactose (Gal) in aqueous alkaline medium is proposed. The most reactive species of the catalyst was found to be $[RuCl_3(OH)_2H_2O]^{2-}$. The reactions exhibit pseudo-first order kinetics with respect to Ru(III) and are first order with respect to lower $[IO_4^-]$ and OH^-, but tend towards zeroth order to both higher $[IO_4^-]$ and $[OH^-]$. The reactions are zero order with respect to each aldoses. Positive effect of Cl^- on the rate of reaction is also evident in the oxidation of both reducing sugars. A mechanism, involving the interaction of the reactive species of Ru(III) and $[IO_4^-]$ leading to the formation of a complex, which in the rate determining step decomposes into another complex with the release of Cl^- ion, is proposed and the rate law is derived.

KEY WORDS: arabinose; galactose; aldoses.

1. Introduction

Although periodate is less potent oxidant in alkaline than in acidic media, it is widely employed as a diol cleaving reagent [1]. In an alkaline medium, periodate is known to exist as different species involving multiple equilibria [2] and this prompted us to know its active form in the reaction system.

The oxidation of sugars has been studied in detail by using halogens and *N*-halogeno compounds [3]. Singh and coworkers [4] have also used Cu(II), ammoniacal Ag(I) and Nessler's reagent, $[HgI_4]^{-2}$, in aqueous alkaline medium in oxidation of aldo and keto hexoses. In alkaline solutions aldoses are reported to exist as enediol anions and also undergo tautomeric change through the formation of an intermediate enediol [3]. It is necessary to know the active form of reducing sugars in the reaction.

In recent years, the use of transition metal ions such as osmium, iridium, palladium and ruthenium, either alone or as binary mixtures, as catalyst in various redox systems has attracted considerable interest. Although the mechanism of catalysis depends upon the nature of substrates, oxidants and other experimental conditions, it has been shown [5] that metal ions act as catalysts by one of these different paths such as the formation of complexes with reactants or oxidation of the substrate itself or through the formation of free radicals. Ruthenium and its chloro complexes particularly in the +3 oxidation state have evinced a great deal of interest in recent years because of their use in homogeneous catalysis [6–14]. Ruthenium(III) chloride and its EDTA complexes have, recently, been successfully employed as catalysts in the oxidation of allyl alcohol, ascorbic acid and cyclohexanol [9,10]. However, ruthenium(III) catalysed oxidation of sugars by alkaline solution of periodate has, yet, not been examined, and we have observed that ruthenium(III) catalyses periodate oxidation of Ara and Gal in alkaline medium and hence the study of these reactions is reported here with a discussion of the mechanism.

2. Experimental

Reagent grade chemicals were used. Doubly distilled water was used throughout. A stock standard solution of $[IO_4^-]$ was prepared by dissolving a known weight of $NaIO_4$ (E. Merck) in double distilled water and its concentration was ascertained iodometrically. In order to avoid photochemical deterioration the solution of $NaIO_4$ was preserved in black coated flask. The standard solutions of Ara and Gal (AR grade) were freshly prepared. A stock standard solution of Ru(III) was prepared by dissolving $RuCl_3$ (Ubichem Limited) in 0.20 mol dm^{-3} HCl and its concentration was determined as 9.64×10^{-3} mol dm^{-3} · NaOH and $NaClO_4$ (E. Merck) were employed to maintain the required alkalinity and ionic strength, respectively. The temperature was maintained constant to within ±0.10 °C.

3. Kinetic measurements

Kinetic runs were initiated by mixing the previously thermostatted reactant solutions of sugar and IO_4^- (which also contained the required amount of Ru(III), NaOH and $NaClO_4$). Aliquotes (5 ml) of the reaction mixture were pipetted out at regular intervals of time and poured into a conical flask containing 5 mL of 4%

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KI solution and 5 mL of dilute perchloric acid solution. The liberated iodine equivalent to unconsumed periodate [15,16] was titrated against $Na_2S_2O_3$ solution using starch as an indicator. The kinetic runs were carried out under pseudo-first order conditions at 45 ± 0.10 °C unless stated otherwise. The initial rates were obtained from the slopes of concentration versus time graphs in the initial stages of the reactions by plane mirror method. The rates were reproducible to within ±4.00%.

4. Stoichiometry and product analysis

Different sets of reactions containing excess $[IO_4^-]$ over [aldose] with constant concentrations of Ru(III) and $[OH^-]$ were kept for 24 h at 45 °C and then estimated. The unreacted oxidant was assayed iodometrically as mentioned earlier. The results showed 1 : 2 stoichiometry according to the equations (1) and (2).

$$\underset{\text{(Ara)}}{C_5H_{10}O_5} + 2IO_4{}^- \xrightarrow[OH^-]{Ru(III)} \underset{\text{Erythronicacid}}{C_4H_8O_5} + HCOOH + 2IO_3^- \tag{1}$$

$$\underset{\text{(Gal)}}{C_6H_{12}O_6} + 2IO_4{}^- \xrightarrow[OH]{Ru(III)} \underset{\text{Lyxonicacid}}{C_5H_{10}O_6} + HCOOH + 2IO_3^- \tag{2}$$

Formic acid and corresponding another acids were confirmed by the help of spot tests [17], equivalence, kinetic studies and thin layer chromatography.

5. Results

The kinetics of the oxidation of Ara and Gal was investigated at several initial concentrations of the reactants. The reactions were carried out by varying the concentration of oxidant, aldose, catalyst and alkali in turn while keeping all other conditions constant (Tales 1 and 2). First order dependence of the reactions at lower $[IO_4^-]$ tends to zero-order at its higher concentrations. The order in each aldoses was found to be zero, since the initial rates were independent of the initial concentration of each aldoses. The order in Ru(III) was unity as evidenced by the slope (1.02 and 0.96 in oxidation of Ara and Gal, respectively) of the log–log plots of initial rates versus concentrations of Ru(III) whereas the order in $[OH^-]$ was less than unity which is obvious from the slopes (0.56 and 0.52) in oxidation of Ara and Gal, respectively) of the log–log plots of initial rates versus $[OH^-]$ over the range of concentrations studied. There is slight increase in the first order rate constant values with the increase in$[Cl^-]$, indicating positive effect of $[Cl^-]$ on the rate of reaction.

Approximately 15-fold variation in the ionic strength of the medium was made at constant concentrations of all the reactants and at constant temperature, 45 °C (Table 3). From the results presented in table 3, it is quite clear that the observed significant change in the rate of reaction at very low ionic strength of the medium becomes almost insignificant at higher ionic strength of the medium. The rate constants measured at 30, 35, 40 and 45 °C led to the values of Ea, $\Delta H^{\#}$ and $\Delta S^{\#}$ of the slow step in oxidation of Ara and Gal catalysed by Ru(III) by alkaline periodate solution. The values of specific rate constant (k_r), Arrhenius factor (A), energy of activation (E_a), enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were found at 40 °C in the oxidation of Ara and Gal as 6.57 and 6.79 $mol^{-2}\ dm^6 s^{-1}$, respectively, 58.20 and $2.15 \times 10^{12}\ mol^{-2}\ dm^6\ s^{-1}$, respectively, 65.86 and 69.17 $kJ\ mol^{-1}$, respectively, 63.21 and 66.57 $kJ\ mol^{-1}$, respectively, and −28.50 and −17.59 $JK^{-1}\ mol^{-1}$, respectively.

Thus on the basis of first order kinetics in lower concentrations of OH^- and $IO^-{}_4$, zero-order kinetics in reducing sugar concentrations, positive effect of $[Cl^-]$ and first-order dependence on Ru(III) concentrations, a probable rate law can be given as:

$$-\frac{d[IO_4^-]}{dt} = \frac{k[IO_4^-][OH^-][Ru(III)]_T[Cl^-]}{1 + a[Cl^-]} \tag{3}$$

5.1. *Test for free radicals*

In order to verify the presence of free radicals in the reaction, the following test was performed. A reaction mixture containing acrylamide was kept for 24 h in an inert atmosphere. On diluting the reaction mixture with methanol since no precipitate was formed hence this suggests that there is no possibility of free radical intervention in the reaction.

6. Discussion

It is reported[18] that the activity of periodate as an oxidant varies greatly as function of pH. The nature of IO_4^- in aqueous alkaline medium has received considerable attention. Periodic acid (H_5IO_6) exists in acid medium[19] and also as $[H_4\ IO_6\ ]^{-1}$ around pH 7.0 Thus, under the alkaline conditions, the main species of periodate ion are expected to be $[H_3\ IO_6\ ]^{-2}$ and $[H_2\ IO_6\ ]^{-3.}$ But, when we have collected the spectrum of IO_4^- in the presence of OH^-, it was found that there is only one peak at 237 nm, which clearly indicates that it is IO which can be taken as the reactive species of sodium metaperiodate in alkaline medium. The periodate oxidations of Ara and Gal in aqueous alkaline medium are not realisable experimentally in the absence of the catalyst, the ruthenium(III). Hence, in the presence of catalyst the reactions are understood to occur through catalysed path with negligible contributions from unrealisable uncatalysed path. Since the reactions are Ru(III) catalysed hence at this stage it would be appropriate to discuss about the actual reacting species of Ru(III) chloride in aqueous alkaline

Table 1
Effect of variation of [periodate] and [aldose] on ruthenium (III) catalysed oxidation of aldoses by periodate in aqueous alkaline medium at 45 °C, with $[OH^-] = 2.50 \times 10^{-2}$, $[Ru(III)] = 28.92 \times 10^{-5}$ (Gal), 14.46×10^{-5} (Ara), $I = 0.20$ mol dm^{-3}

$[IO_4^-] \times 10^3$ (mol dm^{-3})	[Aldose] $\times 10^2$ (mol dm^{-3})	$-dc/dt \times 10^7$ (mol dm^{-3} s^{-1})	
		Ara	Gal
0.50	2.50	0.64	0.68
0.75	2.50	0.83	–
2.00	2.50	2.76	2.08
3.00	2.50	3.34	2.77
4.00	2.50	4.16	3.34
5.00	2.50	–	4.17
6.00	2.50	5.00	4.75
8.00	2.50	5.08	5.55
2.00	0.50	2.74	2.10
2.00	1.00	2.72	2.04
2.00	2.00	2.77	2.06
2.00	4.00	2.78	2.12
2.00	6.00	2.76	2.08
2.00	10.00	2.72	2.07

Table 2
Effect of variation of [alkali] and [Ru(III)] on ruthenium (III) catalysed oxidation of aldoses by periodate in aqueous alkaline medium at 45 °C, with $[IO_4^-] = 1.00 \times 10^{-3}$ (Ara and Gal), $[aldose] = 2.50 \times 10^{-2}$, $I = 0.20$ (a), 0.026 (b) mol dm^{-3}

$[OH^-] \times 10^2$ (mol dm^{-3})	$[Ru(III)] \times 10^5$ (mol dm^{-3})	$-dc/dt \times 10^7$ (mol dm^{-3} s^{-1})	
		Ara	Gal
0.50[a]	28.92	0.38	0.35
1.00[a]	28.92	0.70	0.56
2.00[a]	28.92	0.94	0.83
2.50[a]	28.92	–	0.97
4.00[a]	28.92	1.39	1.11
6.00[a]	28.92	1.67	1.25
8.00[a]	28.92	1.94	–
10.00[a]	28.92	2.08	1.39
2.50	4.82[b]	0.13	0.08
2.50	9.64[b]	0.34	0.12
2.50	14.46[b]	0.45	–
2.50	19.28[b]	0.54	0.26
2.50	28.92[b]	0.75	0.39
2.50	38.56[b]	0.89	0.53
2.50	48.20[b]	1.16	0.70
2.50	57.85[b]	1.43	0.81

medium. It is reported [20] that at the instant of preparation Ru(III) exists in solution in the pH range 0.4–2.0 as four major species, $[RuCl_4(H_2O)_2]^{-1}$, $[RuCl_3(H_2O)_3]$ $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^{2+}$. Out of these four species, $[RuCl_2(H_2O)_4]^+$ is stabilized in its hydrolysed form, $[RuCl_2(H_2O)_3OH]$ according to the following equilibrium:

$$[RuCl_2(H_2O)_4]^+ + H_2O \rightleftharpoons RuCl_2(H_2O)_3OH] + H_3O^+ \qquad (a)$$

Since the experiments were performed with Ru(III) chloride dissolved in 0.01M HCl solution, hydrolysed species of $[RuCl_2(H_2O)_4OH]^+$ i.e. $[RuCl_2(H_2O)_3OH]$ can be assumed as the starting species of Ru(III) chloride in the present investigation. Our assumption is also supported by the peak observed at 300 nm for hydrolysed species of Ru(III) chloride as reported earlier.

Considering the slight positive effect of $[Cl^-]$ on the rate of reaction and fractional order in $[OH^-]$, the following equilibria can be assumed to exist in aqueous alkaline medium.

$$[RuCl_2(H_2O)_3OH] + Cl^- \rightleftharpoons [RuCl_3(H_2O)OH]^{-1} + H_2O \qquad (b)$$

$$[RuCl_3(H_2O)OH]^{-1} + OH^- \rightleftharpoons [RuCl_3(H_2O)(OH)_2]^{2-} + H_2O \qquad (c)$$

Since with the increase in $[OH^-]$ there is an increase in the rate of reaction hence on the basis of

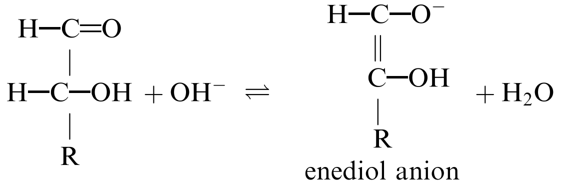
Table 3
Effect of variation of ionic strength(I) of the medium at 45°C, with $[IO_4^-] = 1.00 \times 10^{-3}$ (Ara and Gal), $[OH^-] = 2.50 \times 10^{-2}$, $[Ru(III)] = 28.92 \times 10^{-5}$ (Gal), 14.46×10^{-5} (Ara), $[aldose] = 2.50 \times 10^{-2}$ (Gal) 2.00×10^{-2} (Ara) mol dm^{-3}

$(I) \times 10^2$ (mol dm^{-3})	$(-dc/dt) \times 10^7$ (mol dm^{-3} s^{-1})	
	Ara	Gal
2.60	0.45	0.39
5.00	0.97	0.83
7.50	1.00	0.93
20.00	1.04	0.97
40.00	1.11	1.00

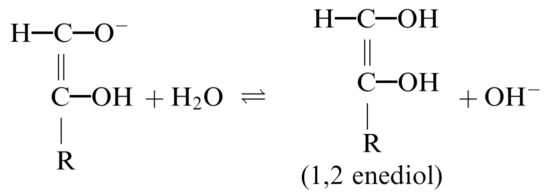
equilibrium (c) the species $[RuCl_3(H_2O)(OH)_2]^{2-}$ can be taken as the main reactive species of Ru(III) in the present investigation. This assumption is further supported by the spectra of Ru(III) observed at two different concentrations of OH^- (1.00×10^{-2} and 5.00×10^{-2} M) at 45°C (figure 1(2,3)) where increase in absorbance with the increase in $[OH^-]$ is due to shift in equilibrium (c) to the right side. The observed increase in absorbance and shift in λ_{max} towards longer wave length on one hand support the formation of reactive species $[RuCl_3(H_2O)(OH)_2]^{2-}$ and on the other hand it also support the fact that when an auxochrome (hydroxy group) is attached to a chromophore or chromophore like transition metal complex ion, the intensity of its absorption increases with an increase in λ_{max} value.

It is well known [21] that in the presence of alkali the reducing sugars undergo a tautomeric change resulting in an enediol intermediate. The base catalysed formation of enediol might be visualised as

(a) **Aldehyde sugars**

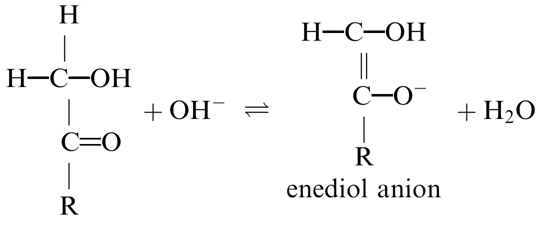


$$\begin{array}{c} H{-}C{=}O \\ | \\ H{-}C{-}OH \\ | \\ R \end{array} + OH^- \rightleftharpoons \begin{array}{c} H{-}C{-}O^- \\ \| \\ C{-}OH \\ | \\ R \\ \text{enediol anion} \end{array} + H_2O$$



$$\begin{array}{c} H{-}C{-}O^- \\ \| \\ C{-}OH \\ | \\ R \end{array} + H_2O \rightleftharpoons \begin{array}{c} H{-}C{-}OH \\ \| \\ C{-}OH \\ | \\ R \\ \text{(1,2 enediol)} \end{array} + OH^-$$

(b) **Keto sugars**



$$\begin{array}{c} H \\ | \\ H{-}C{-}OH \\ | \\ C{=}O \\ | \\ R \end{array} + OH^- \rightleftharpoons \begin{array}{c} H{-}C{-}OH \\ \| \\ C{-}O^- \\ | \\ R \\ \text{enediol anion} \end{array} + H_2O$$

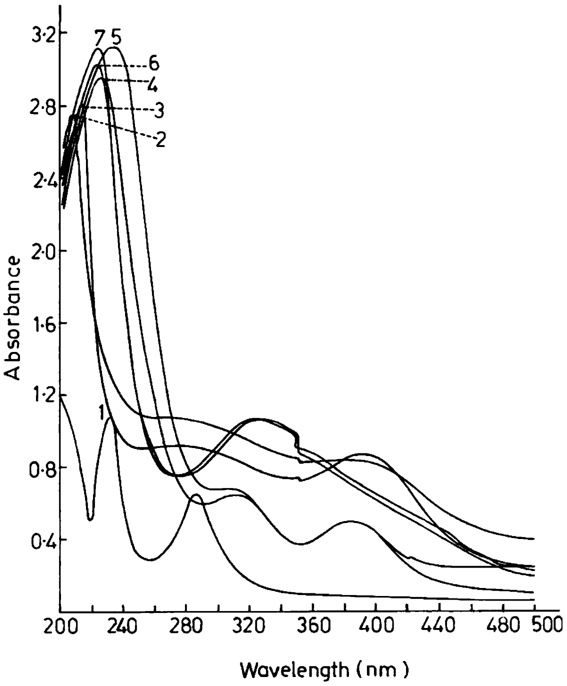
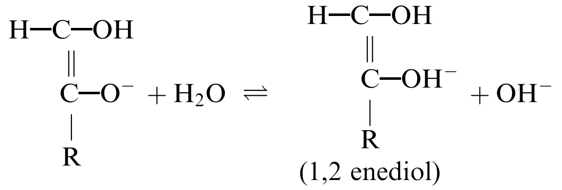


Figure 1. Spectra of sugar solution and Ru(III) solutions, Ru(III) and IO_4^- solutions, Ru(III), IO_4^- and sugar solutions in alkaline medium recorded at 45 °C. (1) $[Sugar] = 5.00 \times 10^{-1}$ mol dm^{-3}, (2) $[Ru(III)] = 2.30 \times 10^{-4}$ mol dm^{-3}, $[OH^-] = 1.00 \times 10^{-2}$ mol dm^{-3}, (3) $[Ru(III)] = 2.30 \times 10^{-4}$ mol dm^{-3}, $[OH^-] = 5.00 \times 10^{-2}$ mol dm^{-3}, (4) $[Ru(III)] = 2.30 \times 10^{-4}$ mol dm^{-3}, $[OH^-] = 5.00 \times 10^{-2}$ mol dm^{-3}, $[IO_4^-] = 1.00 \times 10^{-3}$ mol dm^{-3}, (5) $[Ru(III)] = 2.30 \times 10^{-4}$ mol dm^{-3}, $[OH^-] = 5.00 \times 10^{-2}$ mol dm^{-3}, $[IO_4^-] = 1.33 \times 10^{-3}$ mol dm^{-3}, (6) $[Ru(III)] = 2.30 \times 10^{-4}$ mol dm^{-3}, $[OH^-] = 5.00 \times 10^{-2}$ mol dm^{-3}, $[IO_4^-] = 1.00 \times 10^{-3}$ mol dm^{-3}, $[Sugar] = 1.00 \times 10^{-2}$ mol dm^{-3}, (7) $[Ru(III)] = 2.30 \times 10^{-4}$ mol dm^{-3}, $[OH^-] = 5.00 \times 10^{-2}$ mol dm^{-3}, $[IO_4^-] = 1.00 \times 10^{-3}$ mol dm^{-3}, $[Sugar] = 5.00 \times 10^{-2}$ mol dm^{-3}.



$$\begin{array}{c} H{-}C{-}OH \\ \| \\ C{-}O^- \\ | \\ R \end{array} + H_2O \rightleftharpoons \begin{array}{c} H{-}C{-}OH \\ \| \\ C{-}OH^- \\ | \\ R \\ \text{(1,2 enediol)} \end{array} + OH^-$$

Oxidation of reducing sugars might be considered either by the enediol anion or by the enediol which is in equilibrium with it. Since order with respect to $[OH^-]$ is fractional hence it is resonable to assume that it is the enediol form of sugar which is taking part in the reaction.

The results of our study on Ru(III) catalysed periodate oxidation of Ara and Gal suggest that there is a possibility of the formation of a complex between the reactive species of Ru(III), $[RuCl_3(H_2O)(OH)_2]^{2-}$ and the active oxidant species, IO_4. The formation of complex between the oxidant and the catalyst has also be reported earlier [22]. In order to ascertain the possible formation of complex between $[RuCl_3(H_2O)(OH)_2]^{2-}$ and IO_4^-, the spectra for the solution of Ru(III) and

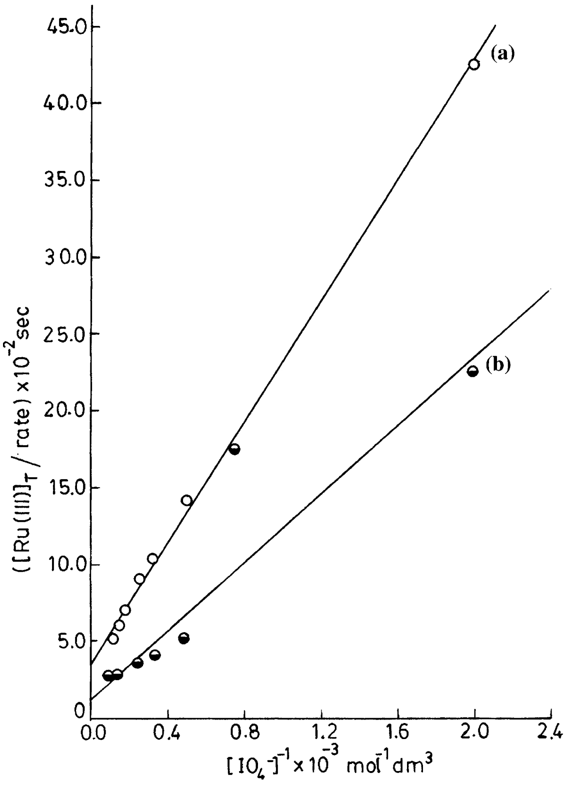


Figure 2. Verification of rate law (11) by the plot of $[Ru(III)]_T$/rate versus $1/[IO_4^-]$ under the conditions of table 1. A→galactose, B→arabinose.

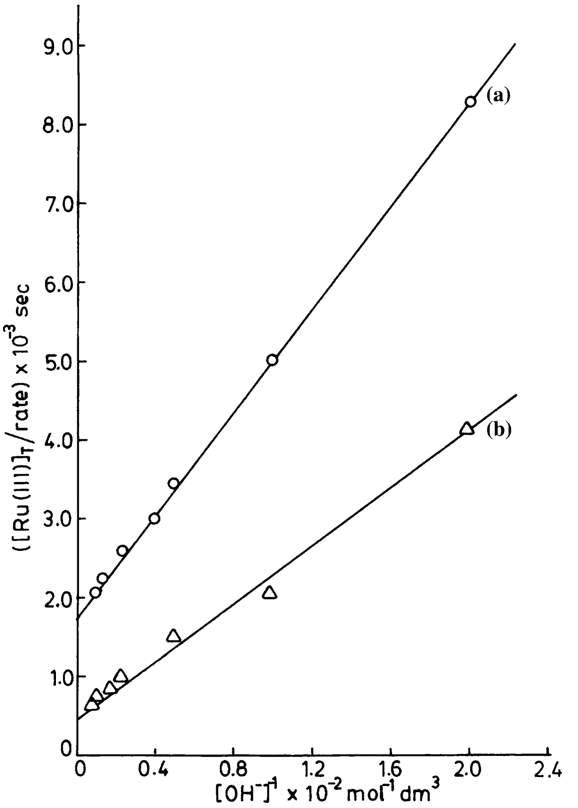


Figure 3. Verification of rate law (11) by the plot of $[Ru(III)]_T$/rate versus 1/ $[OH^-]$ under the conditions of table 2. A→galactose, B→arabinose.

OH^- as well as for the solution of Ru(III) and OH^- with two different concentrations of IO_4^- were collected (figure. 1 (3,4,5)) where it has been observed that with the addition of IO_4^- solution, there is an increase in absorbance from 2.80 to 2.96 and 3.12. The increase in absorbance with the increase in concentration of IO_4^- is due to more and more formation of the complex $[RuCl_3(OH)_2IO_4]^{3-}$ according to the following equilibrium (d)

$$[RuCl_3(H_2O)(OH)_2]^{2-} + IO_4^- \rightleftharpoons [RuCl_3(OH)_2IO_4]^{3-} + H_2O \qquad (d)$$

The absorption at longer wave length is due to the combination of a chromophore (IO_4^-) and an auxochrome (OH^-) to give rise to another chromophore.

When reducing sugar solution of two different concentrations (1.00×10^{-2} and 5.00×10^{-2} mol dm^{-3}) were added to the solution of Ru(III), IO_4^- and OH^-, it was observed that with the increase in sugar concentration there is an increase in absorbance from 2.96 to 3.02 and 3.12 at 222 nm (figure 1 (4,6,7)). This increase in absorbance can be considered as due to increase in the concentration of a complex formed according to the equilibrium (*f*) to the right side. Since the complex between $[RuCl_3(OH)_2IO_4]^{3-}$ and E, the enediol form of sugar is formed at a wave length 222 nm less than the wave length 225 nm at which the [Ru(III)–IO_4] complex is formed hence before the equilibrium (*f*) is established, a rate determining step (*e*) can be assumed to exist in the reaction.

$$[RuCl_3(OH)_2(IO_4)]^{3-} \longrightarrow [RuCl_2(OH)_2IO_4]^{2-} + Cl^- \qquad (e)$$

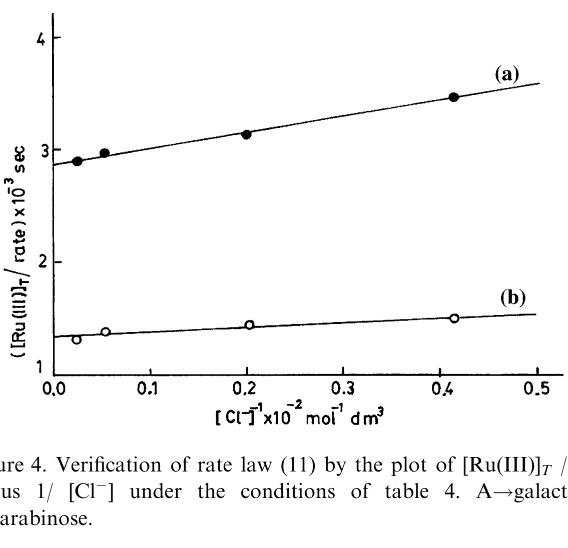


Figure 4. Verification of rate law (11) by the plot of $[Ru(III)]_T$ /rate versus 1/ $[Cl^-]$ under the conditions of table 4. A→galactose, B→arabinose.

$$[RuCl_2(OH)_2(IO_4)]^{2-} + E \rightleftharpoons [RuCl_2(OH)_2(IO_4)E]^{2-} \qquad (f)$$

The shift in λ_{max} towards shorter wave length is due to release of an auxochrome (Cl^-) from the reactive activated complex, $[RuCl_3(OH)_2IO_4]^3$. Equilibrium (*e*) will find a place in the proposed mechanism just after the rate determining step because observed order with respect to reducing sugar concentration is zero. All the experimental results are in agreement with scheme 1.

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 (4)

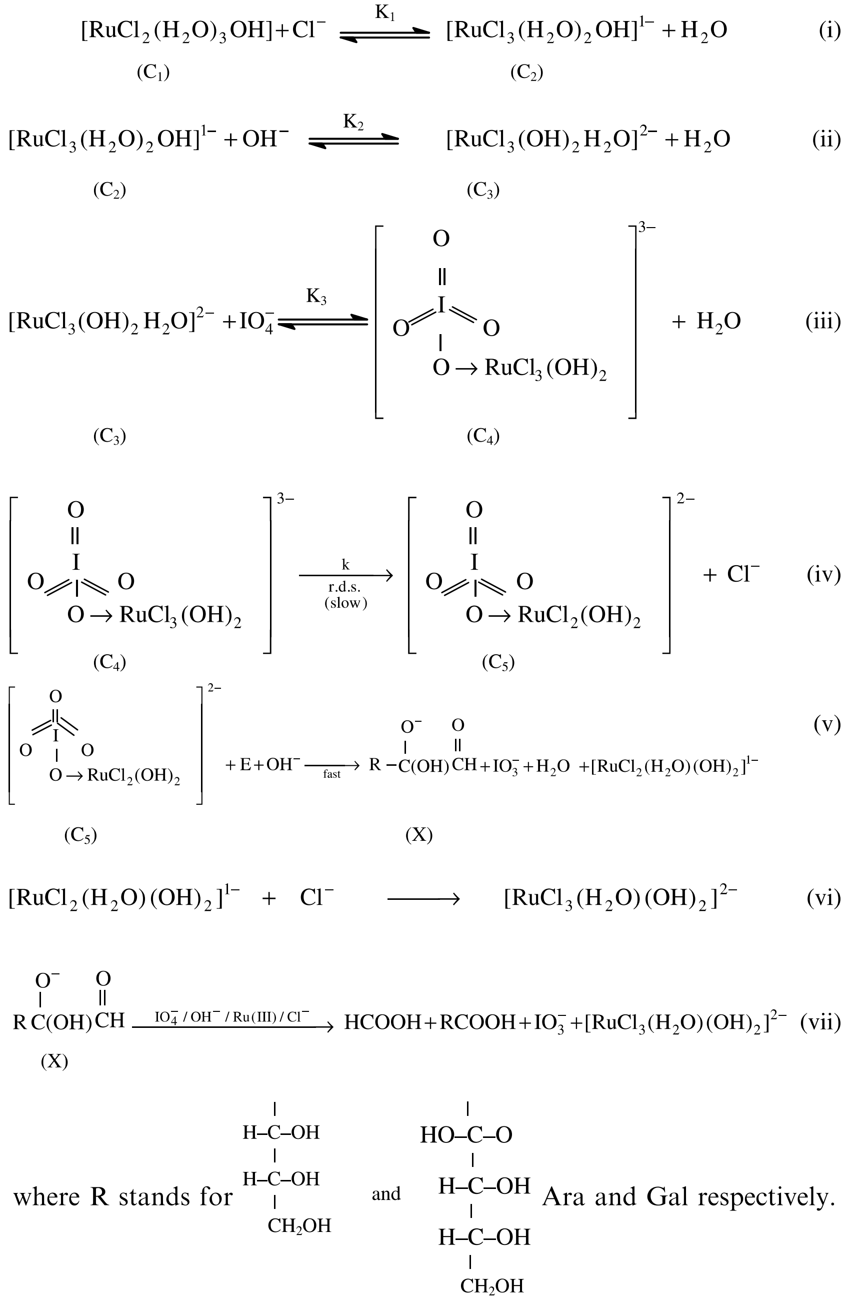
$$\text{rate} = \frac{d[\text{Product}]}{dt} = \frac{-d[IO_4^-]}{dt} = 2k[C_4] \qquad (4)$$

Upon applying the law of chemical equilibrium to steps (i), (ii) and (iii) of the mechanism, we have

$$[C_2] = K_1[C_1][Cl^-] \qquad (5)$$

$$[C_3] = K_1K_2[C_1][Cl^-][OH^-] \qquad (6)$$

$$[C_4] = K_1K_2K_3[C_1][Cl^-][OH^-][IO_4^-] \qquad (7)$$



Scheme 1.

On substituting the value of $[C_4]$ from equation (7) to rate equation (4), we get

$$\frac{-d[IO_4^-]}{dt} = 2kK_1K_2K_3[C_1][Cl^-][OH^-][IO_4^-] \qquad (8)$$

According to the mechanism, the total concentration of Ru(III) can be written as equation (9)

$$[Ru(III)]_T = [C_1] + [C_2] + [C_3] + [C_4] \qquad (9)$$

On substituting the values of $[C_2]$, $[C_3]$ and $[C_4]$ from equation (5), (6) and (7) respectively to equation (9), we get

$$[Ru(III)]_T = [C_1](1 + K_1[Cl^-]) + K_1K_2[Cl^-][OH^-] + K_1K_2K_3[OH^-][Cl^-][IO_4^-]$$

or

$$[C_1] = \frac{[Ru(III)]_T}{1 + K_1[Cl^-] + K_1K_2[Cl^-][OH^-] + K_1K_2K_3[OH^-][Cl^-][IO_4^-]} \qquad (10)$$

Now equations (8) and (10) will give

$$\frac{-d[IO_4^-]}{dt} = \frac{2kK_1K_2K_3[Cl^-][OH^-][IO_4^-][Ru(III)]_T}{1 + K_1[Cl^-] + K_1K_2[Cl^-][OH^-] + K_1K_2K_3[OH^-][Cl^-][IO_4^-]} \qquad (11)$$

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

$$\frac{[Ru(III)]_T}{rate} = \frac{1}{2kK_1K_2K_3[Cl^-][OH^-][IO_4^-]} + \frac{1}{2kK_2K_3[OH^-][IO_4^-]} + \frac{1}{2kK_3[IO_4^-]} + \frac{1}{2k} \qquad (10)$$

where rate = $-d[IO_4^-]dt$

According to equation (12), when $\frac{[Ru(III)]_T}{rate}$ values are plotted against $\frac{1}{[IO_4^-]}$, $\frac{1}{[OH^-]}$ and $\frac{1}{[Cl^-]}$ straight lines with positive intercepts on *Y*-axis were obtained (figures 2, 3, 4) which prove the validity of the rate law (11) and hence the proposed mechanism. These positive intercepts in each case on one hand supports the observed fractional order with respect to each $[IO_4^-]$, $[OH^-]$, $[Cl^-]$ and on the other hand confirms the formation of a complex between the reactive species $[RuCl_3(OH)_2H_2O]^{2-}$ and IO_4^- prior to the rate determining step. From the slopes and the intercepts of the straight lines, the values of *k*, K_1, K_2 and K_3 were calculated at 45 °C in the oxidation of Ara and Gal as 8.835×10^{-3} and 1.5×10^{-3} s^{-1} respectively, 5.238×10^2 and 0.76×10^2 mol^{-1} dm^3 respectively, 0.23×10^2 and 0.53×10^2 mol^{-1} dm^3 respectively and 1.164×10^2 and 2.312×10^2 mol^{-1} dm^3 respectively. Using these values, the rates for the variation of chloride ion concentration at constant concentration of all other reactants and at 45 °C were calculated with the help of rate law (11) under the conditions of Table 4 and were found to be in agreement with the observed rates (Table 5). A close resemblance between the calculated and observed rates for both the reducing sugars clearly supports the rate law (11) and hence the proposed mechanism.

Table 4
Effect of variation of chloride ion concentration at 45°C with $[IO_4^-] = 1.00 \times 10^{-3}$ (Ara and Gal), $[OH^-] = 2.50 \times 10^{-2}$, $[Ru(III)] = 28.92 \times 10^{-5}$ (Gal), 14.46×10^{-5} (Ara), [aldose] = 2.50×10^{-2} (Gal) 2.00×10^{-2} (Ara) mol dm^{-3} and I = 0.20 mol dm^{-3}

$[KCl]\times10^2$ (mol dm^{-3})	$(-dc/dt) \times 10^7$ (mol dm^{-3} sec^{-1})	
	Ara	Gal
2.40	9.72	8.33
4.90	10.00	9.25
17.42	10.42	9.72
37.45	11.10	10.00

Table 5
Observed and calculated rates under the conditions of Table 4 at 45° C

$[KCl] \times 10^2$ (mol dm^{-3})	$(-dc/dt) \times 10^7$ (mol dm^{-3} s^{-1})			
	Ara		Gal	
	Observed	Calculated	Observed	Calculated
02.40	09.72	09.93	08.33	08.36
04.90	10.00	10.17	09.25	09.17
17.42	10.42	10.35	09.72	09.82
37.45	11.10	10.98	10.00	09.97

Since solvation in general increases with the charge on the ion, hence in the case of a reaction between two ions of opposite charge, their union will result in a lowering of the net charge and as result the activated state will be less polar than the reactants. On the other hand, for ions of same sign, the activated state will be a more highly charged ion and as a result it would be expected to be strongly solvated than the reactants. In the present study of oxidation of Ara and Gal by IO_4^- in the presence of Ru(III), the activated state will be a highly charged ion due to the reactants $[RuCl_3(OH)_2\ H_2O]^{2-}$ and IO_4^- . The observed decrease in entropy is due to activated state being strongly solvated than the reactant. The order of the frequency factor being the same for both reducing sugars clearly shows that the reactions have common mechanism (scheme 1). The increase in the rate with the increase in the ionic strength (I) of the medium is an indication for the existence of a primary kinetic salt effect and supports the involvement of two negative ions in the reaction step (III) of proposal reaction scheme 1.

References

[1] C.A. Burton, *Oxidation in Organic Chemistry Part A*, ed. K.B. Wiberg (Academic Press, New York, 1965). p. 368.

[2] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry A Comprehensive Text*, 5th ed, (Wiley – Interscience New York, 1988) p. 569.

[3] H.S. Isbell, J. Res. Bur Stand, 8 (1932) 615; J. Am. Chem. Soc. 54 (1932) 1692; 55 (1933) 2166; N. Bhattacharya and M.L. Sen Gupta, India J. Chem. (1948) 810; 5 (1967) 554; O.G. Ingles and G.C. Israel, J. Chem. Soc. 810 (1948); B. Capon, Chem. Rev. 69 407 (1969); M.C. Agrawal and S.P. Mushran, J. Chem. Soc. Perkin II, (1973) 762; A.K. Singh, A. Singh, R. Gupta, M. Saxena and B. Singh, Transition. Met. Chem. 17 (1992) 413; A.K. Singh, D. Chopra, S. Rahmani and Bharat Singh, Carbohydrate Res 314 (1998) 157.
[4] M.P. Singh, O.C. Saxena and S.V. Singh, J. Am. Chem. Soc. 92 (1970) 537.
[5] P. Vecrasomaiah, K.B. Reddy, B. Sethuram and T.N. Rao, Indian J. Chem. 26A (1987) 402.
[6] M.M.T. Khan, G. Ramachandraiah and A.P. Rao, Inorg. Chem. 25 (1986) 665.
[7] M.M.T. Khan and G. Ramachandraiah, Inorg. Chem. 21 (1982) 2109.
[8] M.M.T. Khan, Pure Appl. Chem. 55(1) (1983) 159.
[9] H.C. Bajaj and M.M.T. Khan, React. Kinet. Catal. Lett. 28 (1985) 339.
[10] M.M.T. Khan and R.S. Shukla, J. Mol. Catal. 34 (1985) 19.
[11] E.S. Gore, Platinum Met. Rev. 27 (1983) III.
[12] J. Halpern, B.R. James and A.L.W. Kemp, J. Am. Chem. Soc 83 (1961) 4097.
[13] J.E. Harrod, S. Coccone and J. Halpern, Can. J. Chem. 39 (1961) 1372.
[14] M.P. Singh, H.S. Singh and M.K. Verma, J. Phys. Chem. 84 (1980) 256.
[15] N. Swarnalakshmi, V. Uma, B. Sethuram and T. Navaneeth Rao, Indian J. Chem. 26A (1987) 595.
[16] Kenneth A. Connors, *A Text Book of Pharmaceutical Analysis* 3rd ed. (Wiley-Interscience, New York, 1982) p. 494 and 507.
[17] F. Feigl, *Spot Tests in Organic Chemistry*, (Elsevier, New York, (1975) p. 452.
[18] G.A. Hiremath, P.L. Timmanagoudar, R.B. Chougale and S.T. Nandibewoor, J. Indian Chem. Soc. 75 (1998) 363.
[19] C.E. Crouthmel, H.V. Mech and D.V. Martin, J. Am. Chem. Soc. 73 (1951) 82, S.M. Tuwar, S.T. Nandibewoor and J.R. Raju, J. Indian Chem. Soc. 69 (1992) 651.
[20] M.M. Taqui Khan, G. Rama Chandraiah and A.P. Rao, Inorg. Chem. 25 (1986) 665.
[21] M.P. Singh, B. Krishna and S. Ghosh, Z. Phys. Chem. 204 (1955) 1; 205 (1956) 285; 208 (1958) 273.
[22] A.M. Balodo, B.C. Galan and F.J.P. Martin, An Quim 88 (1992) 170.