304 **RESEARCH PAPER** MAY, 304–310 JOURNAL OF CHEMICAL RESEARCH 2005

Ruthenate ion catalysed oxidation of D-galactose and D-xylose by alkaline solution of sodium metaperiodate: a kinetic study

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The kinetics of ruthenate ion (RuO_4^{2-})-catalysed oxidation of D-galactose (Gal) and D-xylose (Xyl) by alkaline species of periodate, $H_2IO_6^{3-}$, in an aqueous solution at constant ionic strength shows zero order dependence on reducing sugar and first order dependence on RuO_4^{2-}. First-order dependence of the reaction on periodate and OH^- at their low concentrations tends to zero order in their higher concentration range. A slight increase in the rate of reaction with increase in ionic strength of the medium has also been observed. Various activation parameters have been computed. Lyxonic acid and threonic acid, along with formic acid, were identified as the main oxidation products for Gal and Xyl, respectively. A general mechanism involving bidentate interaction of a species of IO_4^- with a reactive species of sugar has been proposed.

Keywords: sugars, oxidation, periodate, ruthenate ion,alkaline medium, catalysis

Periodate is a less potent oxidant in alkaline media than in acidic media. In an alkaline medium, periodate is known to exist as different species involving multiple equilibria[1] and thus it is necessary to ascertain the active form of oxidant in the reaction, since it is widely employed as a diol cleaving agent.[2] Although oxidation of aldoses by halogens[3-5] in alkaline media has been studied earlier, no report has been available in the literature on metal ion catalysed oxidation of a reducing sugar with periodate oxidant in an alkaline medium. In recent years, the use of transition metal ions, such as ruthenium,[6] iridium[7] and palladium,[8] either alone or as binary mixtures,[9] as catalysts in various redox processes has attracted considerable interest. Among the platinum metals, osmium tetroxide has been extensively used as catalyst[10] but due to its toxic[11] nature, it has largely been replaced by non-toxic and less probed ruthenium compounds. Ruthenium tetroxide is converted into ruthenate ion when dissolved in alkali.[12a] This prompted us to study ruthenate ion-catalysed oxidation of D-galactose and D-xylose by an alkaline solution of sodium metaperiodate.

Experimental

Materials and method of study

An aqueous solution of sodium metaperiodate (E.Merck) prepared by dissolving a weighed amount in double distilled water, was standardised iodometrically. A solution of RuO_4 (Sigma Chemicals) was prepared by dissolving a 1.0 g sample in NaOH solution of known strength. The concentration of the solution of RuO_4 was 6.05×10^{-3} mol dm^{-3}. The standard solutions of Gal and Xyl (Loba Chemicals) were freshly prepared.

All reactants except the sugar solution were mixed and thermostated at 45° ± 0.1°C for thermal equilibrium. The reaction was initiated by adding the requisite volume of pre-equilibrated sugar solution to the reaction mixture and the progress of the reaction was monitored by estimating the amount of unreacted periodate at regular time intervals iodometrically.

Stoichiometry and product analysis

Various experiments were performed with different $[IO_4^-]$: [reducing sugar] ratios. Determination of unconsumed periodate indicated that one mole of sugar is oxidised by 2 moles of periodate. This result showed 1:2 stoichiometry according to equations (A) and (B) for Gal and Xyl, respectively.

$$C_6H_{12}O_6 + 2IO_4^- \xrightarrow{RuO_4^{2-}} C_5H_{10}O_6 + HCOOH + 2IO_3^- \qquad A$$

D-galactose (Lyxonic acid)

$$C_5H_{10}O_5 + 2IO_4^- \xrightarrow{RuO_4^{2-}} C_4H_8O_5 + HCOOH + 2IO_3^- \qquad B$$

D-xylose (Threonic acid)

The formation of formic acid in the oxidation of both Gal and Xyl was ascertained by spot test[12b] and thin layer chromatography.[12c] For the spot test a drop of the reaction mixture was mixed with 10% mercuric chloride and one drop of buffer solution containing 1ml of glacial acetic acid and 1g of sodium acetate per 100ml water. The mixture was taken to dryness and the evaporation residue was taken up in a drop of water and to it a drop of 0.1N ammonia was added. The appearance of a black colour confirmed the presence of formic acid in the reaction mixture. The presence of formic acid in the reaction mixture was further confirmed by thin layer chromatography using *n*-butanol-diethyl amine-water in the ratio of 85:1:14 as developing solvent. The R_F value was found to be 0.39 which is very close to the reported R_F value 0.41 for formic acid in the aforesaid solvent system. The other oxidation products of the reactions, namely lyxonic acid (in case of Gal) and threonic acid (in case of Xyl) are the sole products based on equivalence, kinetic studies, and spot test as well as TLC experiment performed for the confirmation of formic acid.

Results and discussion

In order to propose a probable reaction mechanism for ruthenate ion-catalysed oxidation of reducing sugars by alkaline sodium metaperiodate, it is necessary to study the effect of variation of concentration of different reactants on the rate of reaction. For determining the order of reaction with respect to periodate ion, its concentration has been varied from 0.50×10^{-3} to 8.00×10^{-3} mol dm^{-3} at constant concentrations of all other reactants and at 45°C. Initial rate ($-dc/dt$) values have been calculated from the slopes of the plots of unconsumed $[IO_4^-]$ and time with varying concentration of IO_4^-. When ($-dc/dt$) values are plotted against $[IO_4^-]$, straight lines for both reducing sugars with deviation at higher concentration, clearly show a significant change in the order of reaction with respect to $[IO_4^-]$ from one to zero (Fig. 1 and Table 1). Zero order kinetics with respect to both [Gal] and [Xyl] and first order kinetics with respect to $[RuO_4^{2-}]$ are evident from Table 2. Figure 2 shows first order kinetics with respect to OH^- ion at its lower concentrations which tends to zero order at its higher concentrations. In order to study the effect of ionic strength (I) on the rate constant of a reaction, experiments were performed at 45°C with varying ionic strength at constant concentration of all the reactants. A plot of log k_1 and $\sqrt{I}$ for each reducing sugar with positive slope clearly indicates the interaction between two similarly-charged ionic species (Fig. 3) and also shows the existence of a primary kinetic salt effect in the reaction. The first-order rate constant (k_1) values in each kinetic run were calculated by the help of equation

$$k_1 = (-dc/dt)/[IO_4^-]$$

Reactions have also been studied at four different temperatures and the values of the pseudo first-order rate constant, k_1, thus

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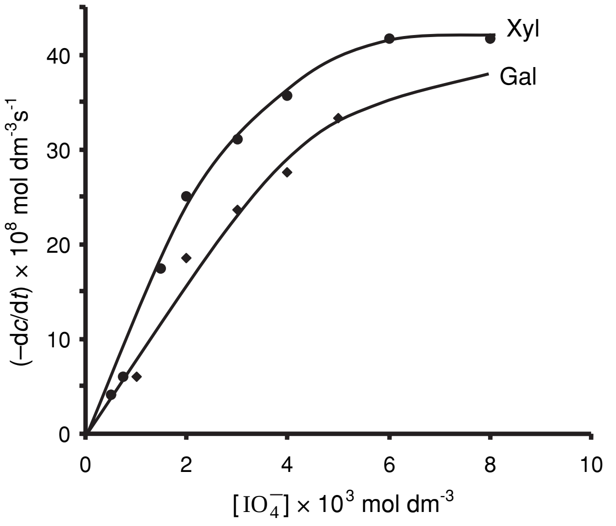


Fig. 1 Plot between (–d*c*/d*t*) and [NaIO$_4$] at 45°C, [substrate] = 1.67 × 10^{-2} mol dm^{-3} (Xyl), 2.50 × 10^{-2} mol dm^{-3} (Gal); [NaOH] = 1.67 × 10^{-2} mol dm^{-3} (Xyl), 5.00 × 10^{-2} mol dm^{-3} (Gal); [RuO$_4$] = 9.08 × 10^{-5} mol dm^{-3} (Xyl), 12.11 × 10^{-5} mol dm^{-3} (Gal); *I* = 20.00 × 10^{-2} mol dm^{-3}.

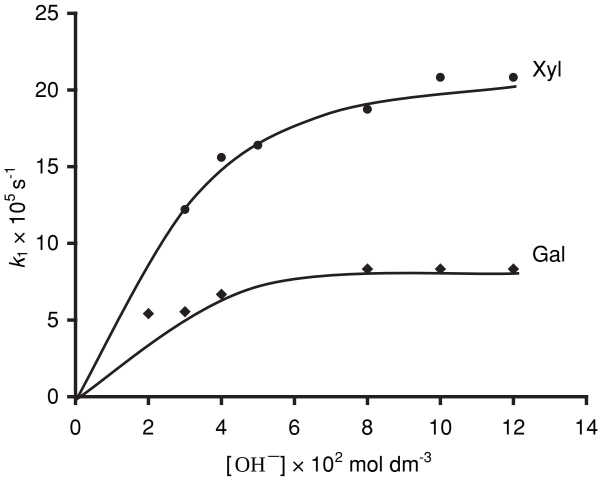


Fig. 2 Plot between (k_1) and [NaOH] at 45°C, [substrate] = 1.67 × 10^{-2} mol dm^{-3} (Xyl), 2.50 × 10^{-2} mol dm^{-3} (Gal); [NaIO$_4$] = 1.00 × 10^{-3} mol dm^{-3} (Xyl and Gal); [RuO$_4$] = 9.08 × 10^{-5} mol dm^{-3} (Xyl), 12.11 × 10^{-5} mol dm^{-3} (Gal); *I* = 20.00 × 10^{-2} mol dm^{-3}.

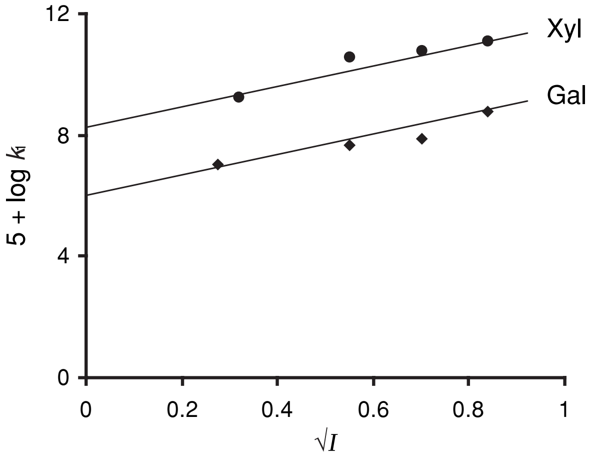


Fig. 3 Plot between log k_1 and $\sqrt{I}$ at 45°C, [NaIO$_4$]=1.00 × 10^{-3} mol dm^{-3}, [substrate] = 1.67 × 10^{-2} mol dm^{-3}(Xyl), 2.50 × 10^{-2} mol dm^{-3} (Gal); RuO$_4$=9.08 × 10^{-5} mol dm^{-3}(Xyl), 12.11 × 10^{-5} mol dm^{-3}(Gal); [NaOH] = 1.67 × 10^{-2} mol dm^{-3}(Xyl), 5.00 × 10^{-2} mol dm^{-3} (Gal).

Table 1 Effect of variation of [IO$_4^-$] on [RuO$_4^{2-}$]-catalysed oxidation of reducing sugars by periodate in aqueous alkaline medium at 45°C

[IO$_4^-$] × 10^3 (mol dm^{-3})	(–*dc*/*dt*) × 10^8 (mol dm^{-3} s^{-1})	
	Gal	Xyl
0.50	4.10	4.16
0.75	—	6.10
1.00	6.10	—
1.50	—	17.50
2.00	18.50	25.00
3.00	23.60	31.10
4.00	27.60	35.60
5.00	33.30	—
6.00	—	41.60
8.00	41.60	41.60

Solution condition: [sugar] = 2.50 × 10^{-2} mol dm^{-3} (Gal), 1.67 × 10^{-2} mol dm^{-3} (Xyl), [RuO$_4^{2-}$] = 12.11 × 10^{-5} mol dm^{-3} (Gal), 9.08 × 10^{-5} mol dm^{-3} (Xyl), I = 20.00 × 10^{-2} mol dm^{-3} (Gal and Xyl).

Table 2 Effect of variation of [sugar] and [RuO$_4^{2-}$] on [RuO$_4^{2-}$]-catalysed oxidation of reducing sugars by periodate in aqueous alkaline medium at 45°C

[sugar] × 10^2 (mol dm^{-3})	[RuO$_4^{2-}$] × 10^5 (mol dm^{-3})	k_1 × 10^5 (s^{-1})	
		Gal (a)	Xyl (b)
0.50	12.11^a/9.08^b	6.57	9.25
1.00	12.11^a/9.08^b	6.57	9.25
2.00	12.11^a/9.08^b	6.57	—
3.00	12.11^a/9.08^b	—	9.25
4.00	12.11^a/9.08^b	7.29	9.25
5.00	12.11^a/9.08^b	7.02	—
6.00	12.11^a/9.08^b	7.29	9.25
8.00	12.11^a/9.08^b	—	9.25
10.00	12.11^a/9.08^b	—	9.25
12.00	12.11^a/9.08^b	7.29	9.25
2.50^a/1.67^b	4.23	0.73	1.44
2.50^a/1.67^b	6.05	1.10	2.05
2.50^a/1.67^b	9.08	1.84	3.28
2.50^a/1.67^b	12.11	2.28	3.97
2.50^a/1.67^b	15.14	2.76	5.14
2.50^a/1.67^b	21.19	4.03	7.00
2.50^a/1.67^b	30.28	5.49	9.77
2.50^a/1.67^b	39.36	6.94	12.08

Solution condition: [IO$_4^-$] = 1.60 × 10^{-3} mol dm^{-3} (Gal and Xyl), [OH$^-$] = 5.00 × 10^{-2} mol dm^{-3} (Gal) and 1.67 × 10^{-2} mol dm^{-3} (Xyl).

obtained were used to calculate the energy of activation (E_a) for the oxidation of both the reducing sugars. The activation parameters, like free energy of activation ($\Delta G^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) have been calculated by the help of the rate constant, k_r, of the reaction at temperature 313K and are presented in Table 3. The Arrhenius frequency factor (A) has also been calculated using the k_r value at 313K and found to be of the same order for both Gal and Xyl.

Thus on the basis of observed first order kinetics in lower concentrations of IO$_4^-$, zero-order kinetics in reducing sugar concentrations, first-order dependence on RuO$_4^{2-}$ and positive effect of [OH$^-$], a probable rate law can be given as

$$-\frac{\mathrm{d[IO]}_4^-}{\mathrm{d}t} = \frac{k[\mathrm{IO}^-]_T[\mathrm{RuO}_4^{2-}]_T[\mathrm{OH}^-]}{1 + a[\mathrm{OH}^-]} \qquad \text{(C)}$$

Test for free radicals: In order to ascertain the presence of free radicals in the reaction, the reaction mixture containing acrylamide was kept for 24 hours in an inert atmosphere. When the reaction mixture was diluted with methanol, no precipitate was found. On the basis of this it can very easily

Table 3 Effect of variation of temperature on the rate constant and values of activation parameters

Parameters	Temp./K	Gal	Xyl
$k_1 \times 10^5$ (s^{-1})	308	5.00	6.16
$k_1 \times 10^5$ (s^{-1})	313	6.57	7.40
$k_1 \times 10^5$ (s^{-1})	318	8.76	11.11
$k_1 \times 10^5$ (s^{-1})	323	10.95	14.81
k_r ($mol^{-2}dm^6s^{-1}$)	313	6.73	15.88
10^9xA ($mol^{-2}dm^6s^{-1}$)	313	5.90	1.54
E_a (k J mol^{-1})	313	53.59	47.86
$\Delta H^\#$ (kJ mol^{-1})	313	50.96	45.23
$\Delta S^\#$ (J K^{-1} mol^{-1})	313	–66.56	–77.74
$\Delta G^\#$ (kJ mol^{-1})	313	71.79	69.54

be inferred that there is no possibility of the formation of free radicals in the reaction.

In order to ascertain the reactive species of ruthenium tetroxide in alkaline medium, uv/vis spectra were taken under different concentrations of sodium hydroxide solution (Fig. 4). It is clear from the plots of absorbance versus wavelength (λ) that ruthenium tetroxide with sodium hydroxide concentrations from 5.00×10^{-4} to 6.66×10^{-3} mol dm^{-3} remains completely in the form of Ru (VIII), as shown by a single peak (Fig. 4, curves 1,2,3) at the wavelength 380 nm. However at a sodium hydroxide concentration of (1.00×10^{-2} mol dm^{-3}) it starts converting into Ru(VI) via Ru (VII) as indicated by a peak at the wavelength 465 nm (Fig. 4, curve 4). The significant feature of RuO_4 spectra, recorded in the presence of different concentrations of NaOH, is that above 1.00×10^{-2} mol dm^{-3} sodium hydroxide concentration Ru (VIII) is converted completely into Ru (VI) (Fig. 4, curves 5, 6). Before arriving at the reactive species of Ru (VI), it is worth while to mention the works on the chemistry of ruthenium in the literature. In aqueous solution ruthenium tetroxide exists in the following equilibria.[6,13,14]

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

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

or

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

Carrington and Symons[15] have reported that both ruthenium tetroxide and potassium perruthenate decompose in alkaline solution to give oxygen.

$$4RuO_4 + 4OH^- \rightleftharpoons 4RuO_4^- + 2H_2O + O_2 \qquad (d)$$

$$4RuO_4^- + 4OH^- \rightleftharpoons 4RuO_4^{2-} + 2H_2O + O_2 \qquad (e)$$

If RuO_4 is dissolved in cold dilute KOH, virtually black crystals of $K[Ru^{VII}O_4]$ (perruthenate) are deposited.[16] These are unstable unless dried and are reduced by water, especially if alkaline, to the orange dianion $[Ru^{VI}O_4]^{2-}$ (ruthenate) by a mechanism which is thought to involve octahedral intermediates of the type $[RuO_4(OH)_2]^{3-}$ and $[RuO_4(OH)_2]^{2-}$. The Moessbauer spectrum of $[RuO_4]$ has been reported[17] as of $[RuO_3(OH)_2]^{2-}$. The existence of Ru(VI) in the form of $[RuO_3(OH)_2]^{2-}$ is also reported.[1] On the basis of the literature stated above and observed spectra (Fig.4), it can be concluded that above 1.00×10^{-2} mol dm^{-3} sodium hydroxide concentration, RuO_4^{2-} obtained from RuO_4 exists in the form of $[RuO_3(OH)_2]^{2-}$.

It is well known[18] that reducing sugars in presence of alkali exists as the enediol anion, $RC(OH)CHO^-$ and enediol RC(OH)CHOH. In view of the fractional order observed in $[OH^-]$, it can be concluded that it is the enediol form of sugar which can be considered as the reactive species.

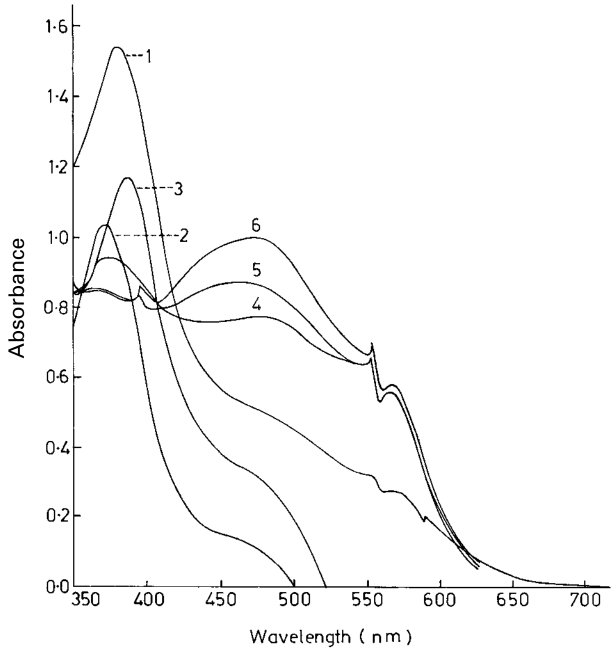


Fig. 4 UV spectra of RuO_4 at different sodium hydroxide concentrations; $[RuO_4] = 6.05 \times 10^{-4}$ mol dm^{-3} (curves 1 and 2), 3.029×10^{-5} mol dm^{-3} (curves 3,4,5 and 6); $[NaOH] = 5.00 \times 10^{-4}$ mol dm^{-3} (curve 1), 7.50×10^{-4} mol dm^{-3} (curve 2), 6.66×10^{-3} mol dm^{-3} (curve 3), 1.00×10^{-2} mol dm^{-3} (curve 4), 2.00×10^{-2} mol dm^{-3} (curve 5), 1.00×10^{-1} mol dm^{-3} (curve 6) curves (1) and (2) are taken from ref. 6a.

Crouthamel and co-workers[19] detected the following equilibria in periodate solutions and determined the various equilibrium constants.

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

$$H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O$$

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

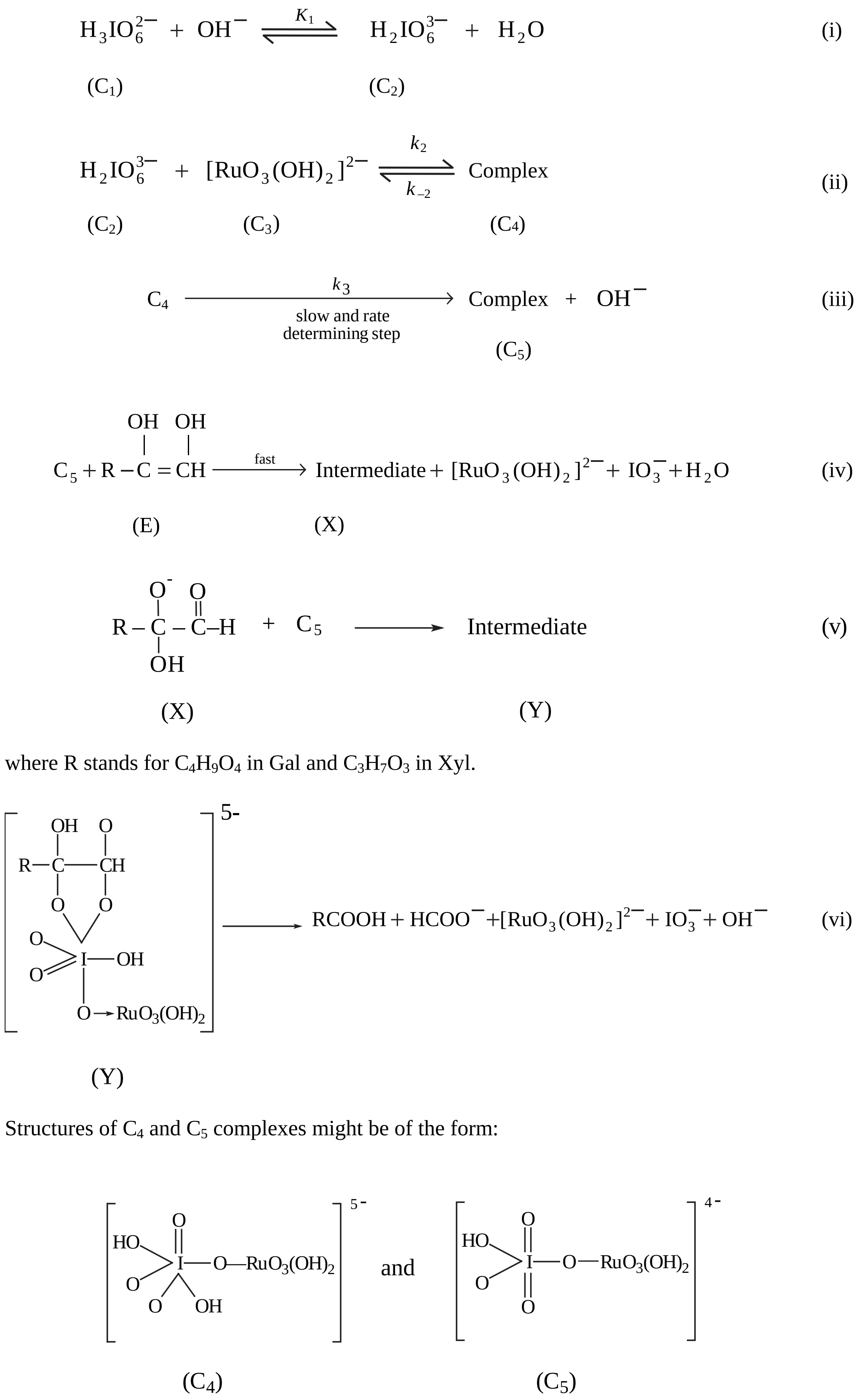
$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+$$

The concentrations of H_5IO_6, IO_4^- and $H_3IO_6^{2-}$ in the periodate solutions of this study were determined using the observed absorption intensities and the extinction coefficients reported by Crouthamel *et al.*,[20] for these species at 222.5 μm. On the basis of the plots between extinction coefficient and wavelength for periodate solution at several pH's, it is reported[21] that at pH 1.00, 75% of periodate remains in the form of H_5IO_6 whereas at pH 6.5, it remains 97% in the form of IO_4^- and 3% in the form of $H_4IO_6^-$. It is further reported[21] that at pH 10.2, 100% of periodate is $H_3IO_6^{2-}$ and at pH 13.6, 100% of periodate is $H_2IO_6^{3-}$. Thus with the change in pH from 10.2 to 13.6 the species trihydrogen-*para* periodate, $H_3IO_6^{2-}$ starts converting into the species dihydrogen-*para* periodate, $H_2IO_6^{3-}$ and at pH 13.6 it is finally converted into $H_2IO_6^{3-}$. In ruthenate ion-catalysed oxidation of D-galactose and D-xylose, since the concentration of OH^- has been varied from 2.00×10^{-2} to 12.00×10^{-2} mol dm^{-3} the pH of the system is varied between 12.30 to 13.08, hence it is reasonable to assume that there exists an equilibrium between two types of species, $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$ as shown below

$$H_3IO_6^{2-} + OH^- \rightleftharpoons H_2IO_6^{3-} + H_2O$$

It is clear from the above equilibrium that with increase in the concentration of OH^-, the equilibrium will shift to the right side with more and more formation of $H_2IO_6^{3-}$. Further, since the rate of reaction increases with the increase in $[OH^-]$, hence it can safely be assumed that $H_2IO_6^{3-}$ is the reactive species of periodate ion in the present investigation.

On the basis of above experimental findings and considering $[RuO_3(OH)_2]^{2-}$ and $H_2IO_6^{3-}$ as the main reactive species of ruthenate ion and periodate ion, respectively, the following reaction mechanism can be proposed for the oxidation of reducing sugars by alkaline solutions of periodate.



$$\underset{(C_1)}{H_3IO_6^{2-}} + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} \underset{(C_2)}{H_2IO_6^{3-}} + H_2O \qquad \text{(i)}$$

$$\underset{(C_2)}{H_2IO_6^{3-}} + \underset{(C_3)}{[RuO_3(OH)_2]^{2-}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{(C_4)}{\text{Complex}} \qquad \text{(ii)}$$

$$C_4 \xrightarrow[\text{slow and rate determining step}]{k_3} \underset{(C_5)}{\text{Complex}} + OH^- \qquad \text{(iii)}$$

$$C_5 + \underset{(E)}{R-\overset{OH}{\overset{|}{C}}=\overset{OH}{\overset{|}{CH}}} \xrightarrow{\text{fast}} \underset{(X)}{\text{Intermediate}} + [RuO_3(OH)_2]^{2-} + IO_3^- + H_2O \qquad \text{(iv)}$$

$$\underset{(X)}{R-\overset{O^-}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-H} + C_5 \longrightarrow \underset{(Y)}{\text{Intermediate}} \qquad \text{(v)}$$

where R stands for $C_4H_9O_4$ in Gal and $C_3H_7O_3$ in Xyl.

$$(Y) \longrightarrow RCOOH + HCOO^- + [RuO_3(OH)_2]^{2-} + IO_3^- + OH^- \qquad \text{(vi)}$$

(Y)

Structures of C_4 and C_5 complexes might be of the form:

(C_4) and (C_5)

Scheme 1

It is clear from the proposed Scheme 1 that the complex (C_4), resulting from the interaction of active species of periodate with active species of the catalyst *i.e.* $[\mathrm{RuO_3(OH)_2}]^{2-}$ (step-ii), decomposes in a slow and rate determining step (iii), forming another complex (C_5) which interacts with enediol (E) in a fast step (iv) followed by subsequent fast steps (v) and (vi) to regenerate the active species of the catalyst for further recycling and formation of products. The bidentate interaction of the active species of periodate present in C_5 with sugar species (X) formed in step (iv) causes C—C splitting (step vi), resulting in the formation of final products.

On the basis of the above reaction mechanism, the rate of the reaction can be written in terms of loss of concentration of periodate ion as Eqn (1).

$$\text{Rate} = -\frac{\mathrm{d}[\mathrm{IO_4^-}]}{\mathrm{d}t} = 2k_3[\mathrm{C_4}] \qquad (1)$$

On applying the law of chemical equilibrium to the step (i), we have Eqn (2)

$$[\mathrm{C_2}] = K_1[\mathrm{C_1}][\mathrm{OH^-}] \qquad (2)$$

On applying the steady state approximation to the concentration of C_4, we have Eqn (3)

$$[\mathrm{C_4}] = \frac{k_2[\mathrm{C_2}][\mathrm{C_3}]}{(k_{-2}+k_3)} \qquad (3)$$

On substituting the value of $[C_2]$ from Eqn (2) to Eqn (3), we have Eqn (4)

$$[\mathrm{C_4}] = \frac{K_1k_2[\mathrm{C_1}][\mathrm{OH^-}][\mathrm{C_3}]}{(k_{-2}+k_3)} \qquad (4)$$

Total concentration of periodate ion *i.e.* $[\mathrm{IO_4^-}]_\mathrm{T}$ at any time in the reaction can be written as Eqn (5)

$$[\mathrm{IO_4^-}]_\mathrm{T} = [\mathrm{C_1}] + [\mathrm{C_2}] \qquad (5)$$

Considering Eqn (2) and (5), $[C_1]$ can be written as Eqn (6)

$$[\mathrm{C_1}] = \frac{[\mathrm{IO_4^-}]_T}{1+K_1[\mathrm{OH^-}]} \qquad (6)$$

On substituting the value of $[C_1]$ from Eqn (6) to Eqn (4), we get

$$[\mathrm{C_4}] = \frac{K_1k_2[\mathrm{OH^-}][\mathrm{C_3}][\mathrm{IO_4^-}]_\mathrm{T}}{\left(1+K_1[\mathrm{OH^-}]\right)\left(k_{-2}+k_3\right)} \qquad (7)$$

On putting the value of $[C_4]$ from Eqn (7) to Eqn (1), we have Eqn (8)

$$\text{Rate} = -\frac{\mathrm{d}[\mathrm{IO_4^-}]}{\mathrm{d}t} = \frac{2k_3k_2K_1[\mathrm{OH^-}][\mathrm{C_3}][\mathrm{IO_4^-}]_T}{(1+K_1[\mathrm{OH^-}])(k_{-2}+k_3)} \qquad (8)$$

According to the reaction Scheme 1, the total concentration of ruthenate ion *i.e.* $[\mathrm{RuO_4^{2-}}]_\mathrm{T}$ at any time in the reaction can be written as Eqn (9)

$$[\mathrm{RuO_4^{2-}}]_T = [\mathrm{C_3}] + [\mathrm{C_4}] \qquad (9)$$

Considering Eqn (7) and (9), we have Eqn (10)

$$[\mathrm{C_3}] = \frac{(1+K_1[\mathrm{OH^-}])(k_{-2}+k_3)[\mathrm{RuO_4^{2-}}]_\mathrm{T}}{(1+K_1[\mathrm{OH^-}])(k_{-2}+k_3) + K_1k_2[\mathrm{OH^-}][\mathrm{IO_4^-}]_T} \qquad (10)$$

On substituting the value of $[C_3]$ from Eqn (10) to Eqn (8), we have Eqn (11)

$$\text{Rate} = -\frac{\mathrm{d}[\mathrm{IO_4^-}]}{\mathrm{d}t} = \frac{2k_3k_2K_1[\mathrm{OH^-}][\mathrm{IO_4^-}]_\mathrm{T}[\mathrm{RuO_4^{2-}}]_\mathrm{T}}{\left(1+K_1[\mathrm{OH^-}]\right)\left(k_{-2}+k_3\right)+K_1k_2[\mathrm{OH^-}][\mathrm{IO_4^-}]_T} \qquad (11)$$

Eqn (11) is the rate law which is well in accordance with our experimental findings.

Eqn (11) can also be written as Eqn (12)

$$\text{Rate} = -\frac{\mathrm{d}[\mathrm{IO_4^-}]}{\mathrm{d}t} = \qquad (12)$$

$$\frac{2k_3k_2K_1[\mathrm{OH^-}][\mathrm{IO_4^-}]_\mathrm{T}[\mathrm{RuO_4^{2-}}]_\mathrm{T}}{(k_{-2}+k_3)\left\{1+K_1[\mathrm{OH^-}]\left(1+\frac{k_2}{(k_{-2}+k_3)}[\mathrm{IO_4^-}]_T\right)\right\}}$$

According to Eqn (3)

$$[\mathrm{C_4}] = \frac{k_2[\mathrm{C_2}][\mathrm{C_3}]}{(k_{-2}+k_3)}$$

$$\text{or} \quad \frac{k_2}{(k_{-2}+k_3)}[\mathrm{C_2}] = \frac{[\mathrm{C_4}]}{[\mathrm{C_3}]} \qquad (13)$$

C_2 *i.e.* $\mathrm{H_2IO_6^{3-}}$ is the reactive species of $\mathrm{IO_4^-}$, hence it can be taken as approximately equal to $[\mathrm{IO_4^-}]_T$ and under this condition Eqn (13) will take the shape of Eqn (14)

$$\frac{k_2}{(k_{-2}+k_3)}[\mathrm{IO_4^-}]_T = \frac{[\mathrm{C_4}]}{[\mathrm{C_3}]} \qquad (14)$$

Since C_4, is a very reactive intermediate complex, it will not accumulate to a significant extent during the reaction and C_3 is the reactant, hence under the experimental conditions $[C_4]$ will always be very much less than $[C_3]$.

When $[C_4] << [C_3]$ and kinetic data for the variation of concentration of all other reactants have been collected at low, $[\mathrm{IO_4^-}]_T$,

then according to Eqn (14) the inequality $\frac{k_2}{(k_{-2}+k_3)}[\mathrm{IO_4^-}]_T << 1$ can be assumed as valid and under this condition Eqn (12) will be reduced to Eqn (15)

$$\text{Rate} = -\frac{\mathrm{d}[\mathrm{IO_4^-}]}{\mathrm{d}t} = \frac{2k_3k_2K_1[\mathrm{OH^-}][\mathrm{IO_4^-}]_T[\mathrm{RuO_4^{2-}}]_T}{(k_{-2}+k_3)(1+K_1[\mathrm{OH^-}])} \qquad (15)$$

Eqn (15) can also be written as Eqn (16)

$$\text{Rate} = -\frac{\mathrm{d}[\mathrm{IO_4^-}]}{\mathrm{d}t} = \frac{2k'k_3K_1[\mathrm{OH^-}][\mathrm{IO_4^-}]_T[\mathrm{RuO_4^{2-}}]_T}{1+K_1[\mathrm{OH^-}]}$$

$$\text{where} \quad k' = \frac{k_2}{k_{-2}+k_3} \qquad (16)$$

Eqn (16) is the rate law valid for first order kinetics in lower concentration of $[\mathrm{IO_4^-}]$, first order kinetics in $[\mathrm{RuO_4^{2-}}]_T$ and positive effect of $[\mathrm{OH^-}]$ on the rate of reaction.

When the rate law (16) is compared with the proposed rate law (C), it is found that the values of k and a are 0.48×10^2 $\mathrm{mol^{-2}\,dm^6\,s^{-1}}$ and 63.13 $\mathrm{mol^{-1}\,dm^3}$ respectively for Gal and 1.50×10^2 $\mathrm{mol^{-2}\,dm^6\,s^{-1}}$ and 60.39 $\mathrm{mol^{-1}\,dm^3}$ respectively for Xyl.

Eqn (16) can also be written as Eqn (17)

$$\frac{[IO_4^-]_T\,[RuO_4^{2-}]_T}{\text{rate}} = \frac{1}{2k'k_3K_1[OH^-]} + \frac{1}{2k'k_3}$$

or

$$\frac{[RuO_4^{2-}]_T}{k_1} = \frac{1}{2k'k_3K_1[OH^-]} + \frac{1}{2k'k_3} \qquad (17)$$

where $k_1 = \frac{\text{rate}}{[IO_4^-]_T}$

According to Eqn (17) if a plot is made between $\frac{[RuO_4^{2-}]_T}{k_1}$ and $\frac{1}{[OH^-]}$, a straight line having a positive intercept on the *y*-axis should be obtained. When $\frac{[RuO_4^{2-}]_T}{k_1}$ values were plotted against $\frac{1}{[OH^-]}$ for both the reducing sugars, straight lines having positive intercepts on *y*-axis were obtained (Fig. 5), proving the validity of the rate law (16) and hence the proposed mechanism. From the values of the slopes and intercepts of the straight lines, the values of K_1 and k_3k' have been calculated for both the sugars and found to be 63.13 mol^{-1} dm^3 and 3.84 × 10^{-1} mol^{-1} dm^3 s^{-1} respectively for Gal and 60.39 mol^{-1} dm^3 and 12.42 × 10^{-1} mol^{-1} dm^3 s^{-1} respectively for Xyl. The existence of equilibrium step (i) of the proposed reaction mechanism is supported by almost the same values of K_1 being obtained for RuO_4^{2-} catalysed oxidation of both Gal and Xyl.

In the present study of oxidation of reducing sugars by IO_4^- in the presence of ruthenate ions, the activated state will be a more highly charged ion and would be strongly solvated due to the reactants $H_2IO_6^{3-}$ and $[RuO_3(OH)_2]^{2-}$. The large decrease in entropy is due to more solvation of the activated state than the reactants. The common mechanism for both the reactions is obvious from the order of the frequency factor, A, which is the same for both reducing sugars *i.e.* Gal and Xyl. The formation of complex C_4 in the activated state resulting from the reaction between $H_2IO_6^{3-}$ and $[RuO_3(OH)_2]^{2-}$, is also supported by the observed positive effect of ionic strength on the rate constant of the reaction. The spectral information collected for two different concentrations of Ru(VIII) with varying hydroxide concentrations, clearly prove the involvement of $[RuO_3(OH)_2]^{2-}$ *i.e.* Ru(VI) in the oxidation of Gal and Xyl.

Efforts have also been made to compare the findings of this paper with the results already published[6a] for ruthenium tetroxide-catalysed oxidation of aldoses by alkaline N-bromoacetamide. The present study, being very similar in kinetic order with respect to [oxidant] and [reducing sugar], differs in order with respect to OH^-, showing a positive effect of OH^- on the pseudo first-order rate constant as against zero-order observed for Ru(VIII)- catalysed oxidation of reducing sugars. The observed increase in the rate of reaction with the increase in OH^- led us to assume that $H_2IO_6^{3-}$ is the reactive species of IO_4^- ions in alkaline medium while the reported[6a] zero effect of OH^- on the rate of reaction was made a basis for taking OBr^- as the reactive species of N-bromoacetamide in alkaline medium. In RuO_4^{2-}- catalysed oxidation of Gal and Xyl, $[RuO_3(OH)_2]^{2-}$ has been assumed as the reactive species of ruthenate ions whereas in the reported[6a] ruthenium tetroxide-catalysed oxidation of aldoses, $HRuO_5^-$ has been taken as the reactive species of RuO_4 in alkaline medium. Our conclusion for the reaction being RuO_4^{2-} or RuO_4 catalysed, is based on the spectra which we have collected for RuO_4 solutions with varying concentrations of OH^- ions. It is already reported[6a] that below 1.00 × 10^{-2} mol dm^{-3} concentration of NaOH, ruthenium tetroxide remains in the form of Ru(VIII) only and at 1.00 × 10^{-2} mol dm^{-3} concentration of OH^-, it remains in the form of both Ru(VI) and Ru(VII). On the basis of spectral information (Fig. 4), it is also concluded that above 1.00 × 10^{-2} mol dm^{-3} concentration of OH^-, ruthenium tetroxide remains in the form of Ru(VI) only. Thus the present study carried out in the range of $[OH^-]$ from 2.00 × 10^{-2} mol dm^{-3} to 12 × 10^{-2} mol dm^{-3} is RuO_4^{2-} catalysed and the previous study[6a] carried out between 0.10 × 10^{-3} mol dm^{-3} and 1.00 × 10^{-3} mol dm^{-3} concentration of OH^- ions was Ru(VIII) catalysed.

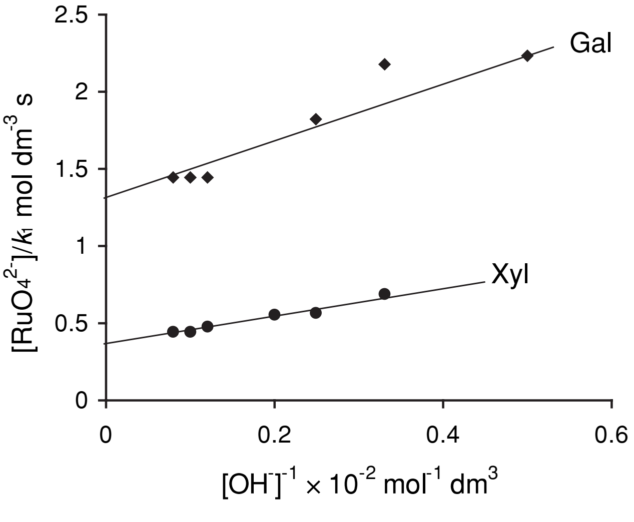


Fig. 5 Plot between ($[RuO_4^{2-}]_T/k_1$) and ($1/[OH^-]$) at 45°C, $[NaIO_4]$ = 1.00 × 10^{-3} mol dm^{-3} (Xyl and Gal); [substrate] = 1.67 × 10^{-2} mol dm^{-3} (Xyl), 2.50 × 10^{-2} mol dm^{-3}(Gal); $[RuO_4]$ = 9.08 × 10^{-5} mol dm^{-3} (Xyl), 12.11 × 10^{-5} mol dm^{-3} (Gal), I = 20.00 × 10^{-2} mol dm^{-3} (Xyl and Gal).

Received 20 July 2004; accepted 23 December 2004
Paper 04/2651

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