

Studies in kinetics and mechanism of oxidation of D-glucose and D-fructose by alkaline solution of potassium iodate in the presence of Ru(III) as homogeneous catalyst

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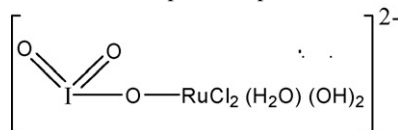
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Abstract

Kinetics of oxidation of D-glucose (glc) and D-fructose (fru) by potassium iodate has been studied for the first time in alkaline medium using Ru(III) as homogeneous catalyst. The linear dependence of the reaction rate at lower $[\text{IO}_3^-]$ and $[\text{OH}^-]$ tends towards zero-order at their higher concentrations. Experimental results also show that the order with respect to $[\text{Ru(III)}]$ is unity and the order with respect to [reducing sugar] is zero in the oxidation of both glc and fru. Variation in $[\text{Cl}^-]$ and ionic strength (μ) of the medium does not affect the oxidation rate. The species, $[\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2]^-$ and IO_3^- , were found to be the reactive species of Ru(III) chloride and potassium iodate in alkaline medium, respectively. The reactions have also been studied at four different temperatures and with the help of observed values of pseudo-first-order rate constant (k_1), the entropy of activation and other activation parameters have been calculated. A common mechanism, where the rate determining step involves the interaction between reactive species of Ru(III) chloride and reactive species of potassium iodate resulting in the formation of an activated complex,



has been proposed. The formation of activated complex is very well supported by the spectrophotometric evidence, observed kinetic data and also by the negative entropy of activation observed for the oxidation of both glc and fru. Arabinonic acid and formic acid were identified as the main oxidation products of the reactions.

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1. Introduction

Mechanistic studies of oxidation of reducing sugars have been made by different workers using *N*-halo compounds [1–3], Cu(II) [4], ammoniacal Ag(I) [5], and Nessler's reagent [6] in acidic/alkaline medium. Sen Gupta et al. [7] have described in their paper that mechanism for the oxidation of some aldoses by Cr(VI), V(V), Ce(IV), Mn(III), Ir(IV), Au(III) and periodic

acid has been investigated in acidic media. A study of the kinetics of periodates oxidation on a series of dextran oligomers and polymers has been reported recently [8]. Kinetic studies regarding catalyzed oxidations of reducing sugars by various oxidants, viz *N*-bromoacetamide (NBA), *N*-bromosuccinimide (NBS) and sodium metaperiodate in acidic or alkaline medium using transition metal ions, viz Os(VIII) [9], Pd(II) [10,11], Ru(VIII) [12], ruthenate ion [13] and Ir(III) [14], as homogeneous catalysts are also available in literature. The use of transition metal catalyst Ru(III) has not only been made in the oxidation of proline [15], atenolol [16] and phosphorous acid [17], but has also been made in the oxidation of reducing sugars where sodium metaperiodate [18], chloramine-T [19], and NBA [20] have been taken as an

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Table 1
Effect of variations of $[\text{IO}_3^-]$ and ionic strength (μ) of the medium on pseudo-first-order rate constant (k_1) in the oxidation of glc and fru at 40 °C

$[\text{IO}_3^-] (\times 10^3 \text{ mol dm}^{-3})$	$\mu (\text{mol dm}^{-3})$	$k_1 (\times 10^4 \text{ s}^{-1})$	
		glc	fru
0.40	0.60	0.88	1.53
0.80	0.60	0.92	1.56
1.00	0.60	0.97	1.67
1.20	0.60	0.89	1.56
1.60	0.60	0.91	1.51
2.00	0.60	0.94	1.53
2.40	0.60	0.91	–
2.80	0.60	–	1.38
3.20	0.60	0.81	–
3.60	0.60	0.87	1.23
4.00	0.60	0.83	1.16
1.00	0.25	1.39	1.18
1.00	0.50	1.35	1.75
1.00	0.75	1.39	1.88
1.00	1.00	1.33	1.82
1.00	1.25	1.32	1.82

Solution conditions: $[\text{OH}^-] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Sugar}] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{RuCl}_3] = 4.58 \times 10^{-6} \text{ mol dm}^{-3}$; $[\text{KCl}] = 0.50 \times 10^{-3} \text{ mol dm}^{-3}$.

$[\text{IO}_3^-]$ versus time at fixed $[\text{IO}_3^-]$, except in $[\text{IO}_3^-]$ variation when a tangent has been drawn at a fixed time (Fig. 1). The pseudo-first-order rate constant (k_1) was calculated as follows:

$$k_1 = \frac{-dc/dt}{[\text{IO}_3^-]}$$

For the determination of order of reaction with respect to $[\text{IO}_3^-]$, the concentration of IO_3^- was varied from 0.4×10^{-3} to $4.0 \times 10^{-3} \text{ M}$ at constant concentrations of all other reactants and at constant temperature, 40 °C. From the values of $(-dc/dt)$, it is obvious that they are in direct proportionality with $[\text{IO}_3^-]$ throughout its variation except at higher concentrations where the rate becomes independent of $[\text{IO}_3^-]$ (Table 1, Fig. 2). This clearly indicates that the order of reaction with respect to $[\text{IO}_3^-]$ is unity up to $2.4 \times 10^{-3} \text{ M}$ in the case of glc and up to $2.0 \times 10^{-3} \text{ M}$ in the case of fru, and there after it tends towards zero-order in case of both reducing sugars. Our conclusion about unity order with respect to $[\text{IO}_3^-]$ up to 2.4×10^{-3} and $2.0 \times 10^{-3} \text{ M}$ in the oxidation of glc and fru, respectively also finds support from the almost constant values of pseudo-first-order rate constant, k_1 (Table 1). Since throughout the study of variations of [reducing sugar], $[\text{OH}^-]$, $[\text{Ru(III)}]$, $[\text{Cl}^-]$ and ionic strength of the medium (μ), the concentration of IO_3^- was fixed at $1.00 \times 10^{-3} \text{ M}$, hence for the purpose of calculation of pseudo-first-order rate constant (k_1), order with respect to $[\text{IO}_3^-]$ has been taken as unity. After determining the order of reaction with respect to $[\text{IO}_3^-]$, the concentration of reducing sugar was varied from 1.00×10^{-2} to $10.00 \times 10^{-2} \text{ M}$ in the case of both glc and fru at constant concentrations of all other reactants and at constant temperature, 40 °C. The results thus obtained are presented in Table 2, where almost constant values of k_1 against varying concentrations of reducing sugars indicate zero-order kinetics with respect to glc

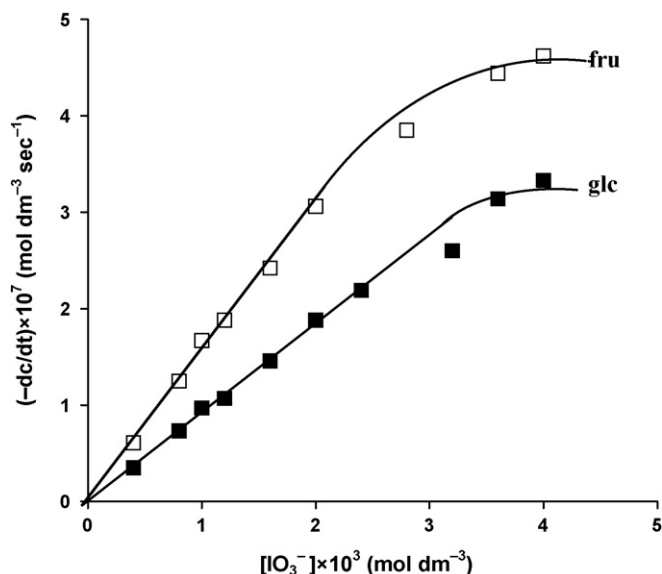


Fig. 2. Plots between $(-dc/dt)$ and $[\text{IO}_3^-]$ at 40 °C. $[\text{OH}^-] = 20.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Sugar}] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Ru(III)}] = 4.58 \times 10^{-6} \text{ mol dm}^{-3}$; $[\text{KCl}] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.6 \text{ mol dm}^{-3}$.

and fru throughout their 10-fold variations. The observed values of pseudo-first-order rate constant (k_1) presented in Table 2 against varying concentrations of OH^- in the case of both glc and fru clearly show that the unity order with respect to OH^- at its low concentration tends towards zero-order at its higher concentrations. When at constant concentrations of all other reactants and at constant temperature, 40 °C, the concentration of Ru(III) chloride was varied up to its 10-fold, it has been found that there is an increase in pseudo-first-order rate constant k_1 , values in the same proportion in which the concentration of Ru(III) chloride is increased throughout its variation (Table 2). This information led us to conclude that the order with respect to Ru(III) chloride is unity throughout its variation. The rate is unaffected by the change in $[\text{Cl}^-]$ as well as in ionic strength (μ) of the medium as there is a negligible change in pseudo-first-order rate constant (k_1) with the change in either $[\text{Cl}^-]$ or ionic strength (μ) of the medium (Table 1). The reactions have also been studied at four different temperatures, i.e. 30, 35, 40 and 45 °C and observed values of pseudo-first-order rate constant (k_1) were utilized to calculate various activation parameters including the entropy of activation (Table 3).

On the basis of observed first to zero-order kinetics with respect to IO_3^- , zero-order kinetics in reducing sugar concentration, first-order dependence on Ru(III) chloride and positive effect of $[\text{OH}^-]$ on the rate of reaction, the following experimental rate law in the form of Eq. (C) for the oxidation of both glc and fru can be expressed as

$$\frac{d[\text{IO}_3^-]}{dt} = \frac{k[\text{IO}_3^-][\text{OH}^-][\text{Ru(III)}]}{a + b[\text{IO}_3^-] + c[\text{OH}^-]} \quad (\text{C})$$

where a , b and c are constants and have different values for different organic substrates.

Table 2

Effect of variations of [NaOH], [S] and [Ru(III)] on pseudo-first-order rate constant (k_1) in the oxidation of glc and fru at 40 °C

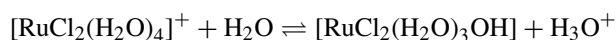
[NaOH] ($\times 10^2$ mol dm $^{-3}$)	[S] ($\times 10^2$ mol dm $^{-3}$)	[Ru(III)] ($\times 10^6$ mol dm $^{-3}$)	k_1 ($\times 10^4$ s $^{-1}$)	
			glc	fru
5.00	2.00	4.58	0.28	0.38
10.00	2.00	4.58	0.54	0.73
15.00	2.00	4.58	0.88	1.18
20.00	2.00	4.58	1.07	1.61
25.00	2.00	4.58	1.37	1.92
30.00	2.00	4.58	1.72	2.33
35.00	2.00	4.58	1.88	–
40.00	2.00	4.58	2.05	2.78
45.00	2.00	4.58	2.25	3.00
50.00	2.00	4.58	2.32	3.33
20.00	1.00	4.58	1.07	1.60
20.00	2.00	4.58	1.00	1.67
20.00	3.00	4.58	1.11	1.63
20.00	4.00	4.58	1.00	1.67
20.00	6.00	4.58	1.07	1.61
20.00	8.00	4.58	1.03	1.61
20.00	9.00	4.58	1.05	1.67
20.00	10.00	4.58	1.00	1.60
20.00	2.00	1.53	0.32	0.50
20.00	2.00	3.05	0.71	1.11
20.00	2.00	4.58	0.97	1.62
20.00	2.00	6.10	1.33	2.27
20.00	2.00	7.63	1.73	2.86
20.00	2.00	9.16	2.08	3.33
20.00	2.00	12.21	2.78	4.25
20.00	2.00	13.37	3.00	4.77
20.00	2.00	15.26	3.33	5.42

Solution conditions: $[\text{IO}_3^-] = 1.00 \times 10^{-3}$ mol dm $^{-3}$; $[\text{KCl}] = 0.50 \times 10^{-3}$ mol dm $^{-3}$; $\mu = 0.60$ mol dm $^{-3}$.

5. Discussion

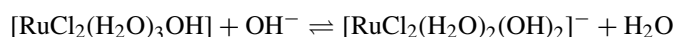
5.1. Reactive species of ruthenium(III) chloride in alkaline medium

It is reported [30] that at the instant of preparation Ru(III) exists in solution in the pH range 0.4–2.0 as four major species, $[\text{RuCl}_4(\text{H}_2\text{O})_2]^-$, $[\text{RuCl}_3(\text{H}_2\text{O})_3]$, $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ and $[\text{RuCl}(\text{H}_2\text{O})_5]^{2+}$. It is also reported that out of these four species, the species $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ is fairly stable at pH 2.0 and is stabilized in its hydrolysed form, $[\text{RuCl}_2(\text{H}_2\text{O})_3\text{OH}]$, according to the following equilibrium:



Since throughout the experiment, the required amount of catalyst was taken from the solution which was prepared by dissolving Ru(III) chloride in 0.01 M HCl (pH 2.0), it is reasonable to assume that the hydrolysed species, $[\text{RuCl}_2(\text{H}_2\text{O})_3\text{OH}]$, is the starting species of Ru(III) chloride in the present investigation. Though the solution of Ru(III) chloride was prepared by dis-

solving it in 0.01 M HCl, throughout the study in the oxidation of both, D-glucose and D-fructose, the medium was maintained alkaline by the addition of NaOH to the reaction mixture. On the basis of observed positive effect of $[\text{OH}^-]$ on the rate of oxidation of both reducing sugars, the existence of the following equilibrium in the reaction can be assumed as valid one.



Out of species $[\text{RuCl}_2(\text{H}_2\text{O})_3\text{OH}]$ and $[\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2]^-$, the species $[\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2]^-$ can be assumed as the reactive species of Ru(III) chloride in alkaline medium because by assuming only species $[\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2]^-$ as the reactive species, the observed positive effect of $[\text{OH}^-]$ on the rate of oxidation of glc and fru can be explained. Our decision about the reactive species of Ru(III) chloride in alkaline medium also finds support from the spectral information which indicate that with the addition of OH^- ions to the solution of Ru(III) chloride, there is an increase in absorbance from 3.2 to 3.28 and 3.4 (Fig. 3(2–4)). This increase in absorbance led us to conclude that the starting species, $[\text{RuCl}_2(\text{H}_2\text{O})_3\text{OH}]$, in

Table 3

Values of activation parameters for the oxidation of glc and fru at 40 °C

Reducing sugars	E_a (kJ mol $^{-1}$)	k (mol $^{-2}$ dm 6 s $^{-1}$)	ΔS^\ddagger (JK $^{-1}$ mol $^{-1}$)	ΔH^\ddagger (kJ mol $^{-1}$)	ΔG^\ddagger (kJ mol $^{-1}$)	A (mol $^{-2}$ dm 6 s $^{-1}$)
D-Glucose	50 (± 1.09)	1.06×10^2	-52 (± 0.38)	48 (± 0.05)	64 (± 0.40)	3.55×10^{10}
D-Fructose	44 (± 0.39)	1.77×10^2	-68 (± 0.46)	41 (± 0.05)	63 (± 0.26)	0.42×10^{10}

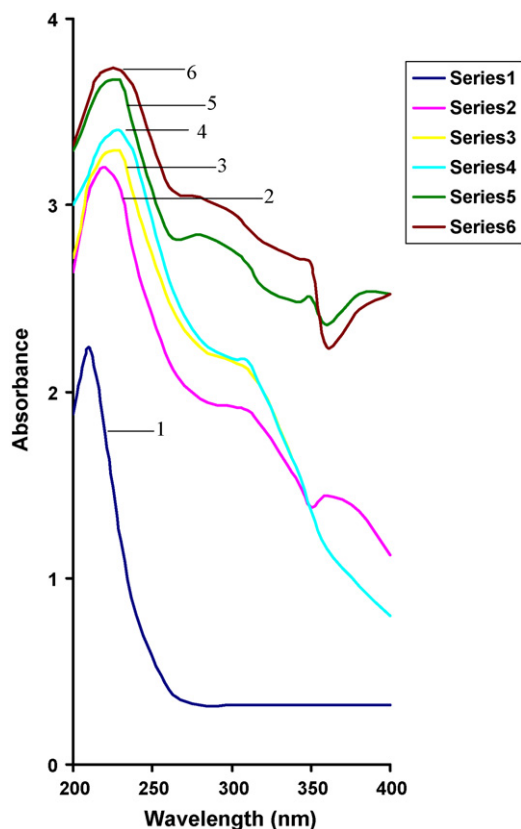


Fig. 3. Spectra: (1) $[\text{IO}_3^-] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$; (2) $[\text{Ru(III)}] = 7.63 \times 10^{-4} \text{ mol dm}^{-3}$; (3) $[\text{Ru(III)}] = 7.63 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{OH}^-] = 20.00 \times 10^{-2} \text{ mol dm}^{-3}$; (4) $[\text{Ru(III)}] = 7.63 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{OH}^-] = 50.00 \times 10^{-2} \text{ mol dm}^{-3}$; (5) $[\text{Ru(III)}] = 7.63 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 20.00 \times 10^{-2} \text{ mol dm}^{-3}$ and $[\text{IO}_3^-] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$; (6) $[\text{Ru(III)}] = 7.63 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 20.00 \times 10^{-2} \text{ mol dm}^{-3}$ and $[\text{IO}_3^-] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$.

the reaction reacts with OH^- ions to form the complex species, $[\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2]^-$, according to the equilibrium indicated above, which ultimately assumes the role of reactive species of Ru(III) chloride in the present investigation.

5.2. Reactive species of potassium iodate in alkaline medium

Potassium iodate has been reported to be used as an oxidant in Os(VIII) [31] and Ru(III) [25,31]-catalyzed oxidation of organic compounds in acidic medium. In these cases, reactive species of KIO_3 in acidic medium is taken either as HIO_3 or as IO_3^- . Kinetic studies for the oxidation of acetophenones [22], ferrocyanide [32], thiocyanate [33] and 1,3-dihydroxybenzene [34] by acidic solution of iodate are also reported, where IO_3^- has been assumed as the reactive species of KIO_3 in acidic medium. Literature reveals that there is only one report [26] where KIO_3 has been used as an oxidant in Ir(III)-catalyzed oxidation of reducing sugars in alkaline medium. In this case, also on the basis of observed kinetic data and spectral evidence, IO_3^- has been assumed as the reactive species of KIO_3 in alkaline medium. In ruthenate ion [13] and Ru(III) [18]-catalyzed oxidation of reducing sugars in alkaline medium, NaIO_4 has been taken as an oxidant. Both the reports [13,18] contain IO_3^- as one of the

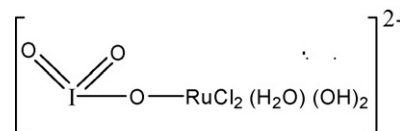
oxidation products indicating the existence of IO_3^- in alkaline medium. In view of the reported literature shown above and also in view of the fact that iodate in alkaline medium exists in the form of IO_3^- only, it is most appropriate to infer that IO_3^- is the reactive species of KIO_3 in alkaline medium. Kinetic data observed for Ru(III)-catalyzed oxidation of glc and fru and single peak observed for KIO_3 solution in alkaline medium at 210 nm also support the above experimental finding (Fig. 3(1)).

5.3. Reactive form of sugar in alkaline medium

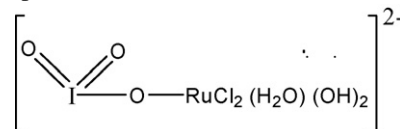
It is well known [35,36] that the reducing sugars undergo a tautomeric change in presence of alkali and exists as the enediol anion, $\text{RC}(\text{OH})\text{CHO}^-$, and enediol, $\text{RC}(\text{OH})\text{CHOH}$. Taking into account the base catalyzed formation of enediol anion and enediol and also the positive effect of $[\text{OH}^-]$ 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.

5.4. Spectrophotometric evidence for the formation of complexes in the reactions under investigation

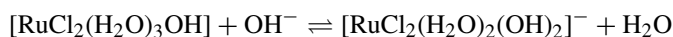
When on the basis of kinetic orders with respect to each reactant of the reactions, the reactive species of Ru(III) chloride as $[\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2]^-$ and reactive species of potassium iodate as IO_3^- , an effort was made to formulate a reaction mechanism, it was found that there is a possibility of the formation of a complex,



by the interaction of $[\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2]^-$ and IO_3^- . In order to verify the existence of the complex species, $[\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2]^-$, and also the existence of most reactive activated complex,

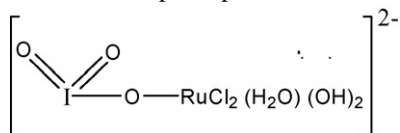


spectra for Ru(III) chloride solution, Ru(III) chloride solution with two different concentrations of OH^- and Ru(III) chloride and OH^- with two different concentrations of IO_3^- solution have been collected (Fig. 3). From the recorded spectra, it is clear that with the addition of OH^- solution to the solution of Ru(III) chloride, there is an increase in absorbance from 3.2 to 3.28 and 3.4 with the very small change in λ_{max} from 220 to 225 nm (Fig. 3(2–4)). This increase in absorbance with the increase $[\text{OH}^-]$ can be considered as due to more and more formation of a complex between $[\text{RuCl}_2(\text{H}_2\text{O})_3\text{OH}]$ and OH^- according to the following equilibrium

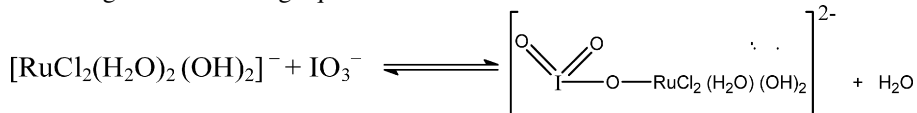


The existence of above equilibrium in the reaction is supported by the positive effect of $[\text{OH}^-]$ on pseudo-first-order

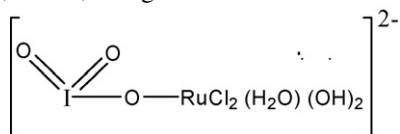
rate constant, k_1 . Further, when comparison is made between the spectrum recorded for the solution of Ru(III) chloride and OH^- and spectra recorded for the solutions of Ru(III) chloride and OH^- with two different concentrations of IO_3^- , it was found that with the addition of KIO_3 solution there is an increase in absorbance from 3.4 to 3.68 and 3.72 with a shift in λ_{max} towards longer wavelength (Fig. 3(4–6)). This increase in absorbance with the increase in $[\text{IO}_3^-]$ clearly indicates that there is a formation of complex species,



according to the following equilibrium



The shift in λ_{max} value towards longer wavelength is due to the combination of a chromophore, IO_3^- , and an auxochrome, OH^- , to give rise to another chromophore,



according to the equilibrium indicated above.

5.5. Reaction scheme

A reaction scheme, based on the kinetic results observed for the oxidation of glc and fru and also based on the spectral information collected for the formation of complex or complexes during the course of reaction, is presented at the end of the article.

On the basis of proposed reaction scheme, the rate of reaction in terms of decrease in the concentration of IO_3^- can be written as

$$\text{rate} = -\frac{d[\text{IO}_3^-]}{dt} = 2k_2[\text{IO}_3^-][\text{C}_2] \quad (1)$$

where '2' indicates that 1 mole of glc and fru is oxidized by 2 moles of KIO_3 .

On applying the steady state approximation to $[\text{C}_2]$, we get Eq. (2)

$$[\text{C}_2] = \frac{k_1[\text{C}_1][\text{OH}^-]}{k_{-1} + k_2[\text{IO}_3^-]} \quad (2)$$

According to the proposed mechanism, the total concentration of Ru(III), i.e. $[\text{Ru(III)}]_{\text{T}}$ at any moment in the reaction can be expressed as

$$[\text{Ru(III)}]_{\text{T}} = [\text{C}_1] + [\text{C}_2] \quad (3)$$

On substituting the value of $[\text{C}_2]$ from Eq. (2) to (3), we have Eq. (4)

$$[\text{C}_1] = \frac{\{k_{-1} + k_2[\text{IO}_3^-]\}[\text{Ru(III)}]_{\text{T}}}{k_{-1} + k_2[\text{IO}_3^-] + k_1[\text{OH}^-]} \quad (4)$$

On substituting the value of $[\text{C}_2]$ from Eq. (2) to (1), we get Eq. (5)

$$\text{rate} = -\frac{d[\text{IO}_3^-]}{dt} = \frac{2k_1k_2[\text{IO}_3^-][\text{OH}^-][\text{C}_1]}{k_{-1} + k_2[\text{IO}_3^-]} \quad (5)$$

From Eqs. (4) and (5), we get Eq. (6)

$$\text{rate} = -\frac{d[\text{IO}_3^-]}{dt} = \frac{2k_1k_2[\text{IO}_3^-][\text{OH}^-][\text{Ru(III)}]_{\text{T}}}{k_{-1} + k_2[\text{IO}_3^-] + k_1[\text{OH}^-]} \quad (6)$$

Eq. (6) is the final rate law which very well explains the observed positive effects of $[\text{IO}_3^-]$ and $[\text{OH}^-]$ on the rate of oxidation and also the observed first-order kinetics with respect to $[\text{Ru(III)}]_{\text{T}}$ throughout its variation.

On reversing Eq. (6), we get Eq. (7)

$$\frac{[\text{Ru(III)}]_{\text{T}}}{\text{rate}} = \frac{k_{-1}}{2k_1k_2[\text{IO}_3^-][\text{OH}^-]} + \frac{1}{2k_1[\text{OH}^-]} + \frac{1}{2k_2[\text{IO}_3^-]} \quad (7)$$

where $\text{rate} = -d[\text{IO}_3^-]/dt$.

According to Eq. (7), if a plot is made between $[\text{Ru(III)}]_{\text{T}}/\text{rate}$ and $1/[\text{IO}_3^-]$ or $1/[\text{OH}^-]$ for the oxidation of each reducing sugar, a straight line having positive intercept on y-axis will be obtained. When plots were made between $[\text{Ru(III)}]_{\text{T}}/\text{rate}$ and $1/[\text{IO}_3^-]$ and between $[\text{Ru(III)}]_{\text{T}}/\text{rate}$ and $1/[\text{OH}^-]$, straight lines having positive intercepts on y-axis were obtained (Figs. 4 and 5). This not only proves the validity of rate law (6) but also gives support to the proposed reaction scheme. From the slopes and intercepts of the straight lines, the values of k_2 , k_1 and k_{-1} have been calculated and found as $0.83 \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, 0.83 s^{-1} and 0.97 s^{-1} , respectively for the oxidation of D-glucose and $3.64 \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$,

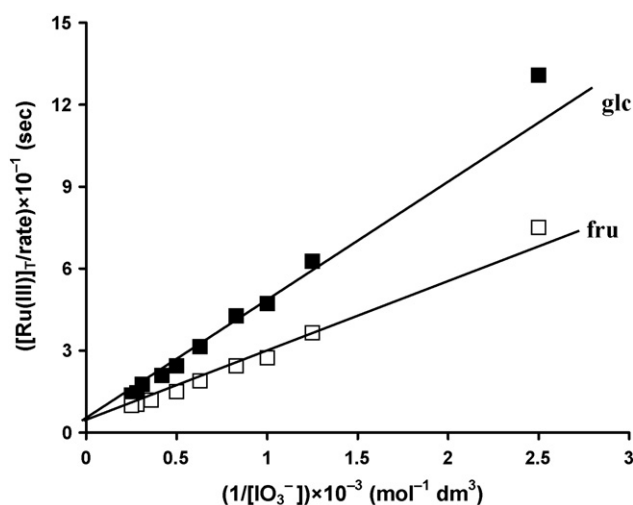
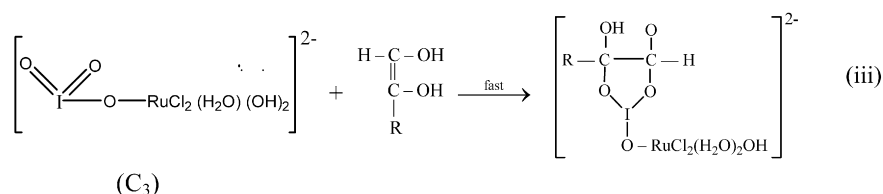
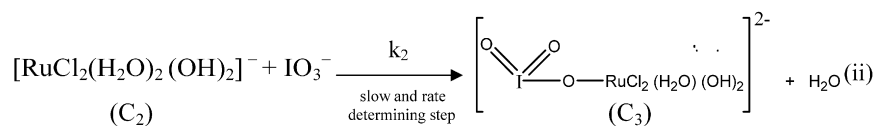
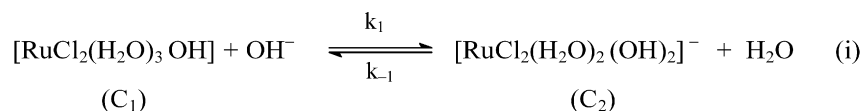
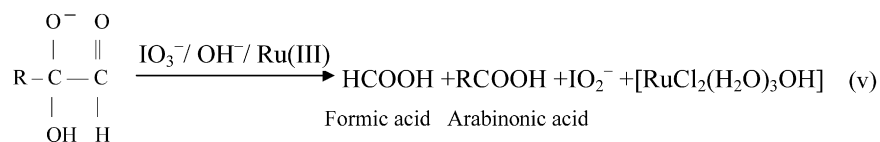
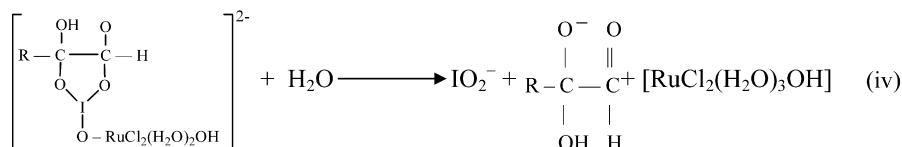


Fig. 4. Plots between $[\text{Ru(III)}]_{\text{T}}/\text{rate}$ and $1/[\text{IO}_3^-]$ at 40°C . $[\text{OH}^-] = 20.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Sugar}] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Ru(III)}] = 4.58 \times 10^{-6} \text{ mol dm}^{-3}$; $[\text{KCl}] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.6 \text{ mol dm}^{-3}$.



where R stands for C₄H₉O₄



Scheme 1.

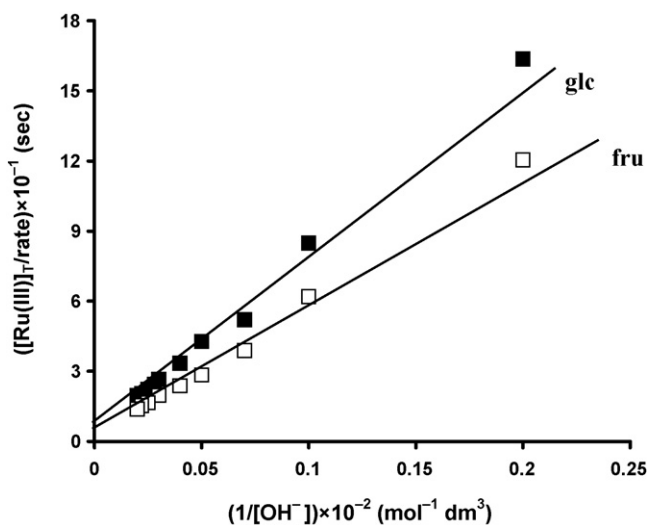


Fig. 5. Plots between $[\text{Ru(III)}]_{\text{T}}/\text{rate}$ and $1/[\text{OH}^-]$ at 40°C , $[\text{IO}_3^-] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{Sugar}] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Ru(III)}] = 4.58 \times 10^{-6} \text{ mol dm}^{-3}$; $[\text{KCl}] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.6 \text{ mol dm}^{-3}$.

1.2 s^{-1} and 4.88 s^{-1} , respectively for the oxidation of D-fructose. Utilizing these values of rate constants, the reaction rates for the variations of $[\text{Ru(III)}]$, $[\text{OH}^-]$ and $[\text{IO}_3^-]$ have been calculated according to the rate law (6) and found to be in close agreement with the observed rates (Tables 4–6). This further confirms the validity of rate law (6).

For the reaction between ions of unlike sign there is generally an entropy increase going from reactants to activated complex and for ions of like sign, there is an entropy decrease [37]. In the present study of oxidation of glc and fru by alkaline solution of KIO_3 in presence of Ru(III) chloride as homogeneous catalyst, the entropy of activation was found as $-52 (\pm 0.38) \text{ J K}^{-1} \text{ mol}^{-1}$ and $-68 (\pm 0.46) \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The observed negative entropy of activation clearly supports the interaction between the species, $[\text{RuCl}_2(\text{H}_2\text{O})_2(\text{OH})_2]^-$ and the species IO_3^- , leading to the formation of most reactive activated complex,

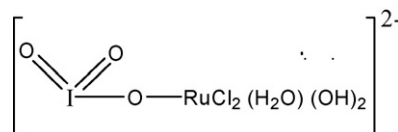


Table 4

Comparison of observed rates with the rates calculated on the basis of rate law (6) under the conditions of Table 2

[Ru(III)] ($\times 10^6$ mol dm $^{-3}$)	$-dc/dt$ ($\times 10^7$ mol dm $^{-3}$ s $^{-1}$)			
	glc		fru	
	Experimental	Calculated	Experimental	Calculated
1.53	0.32	0.35	0.50	0.49
3.05	0.71	0.70	1.11	0.97
4.58	0.97	1.03	1.62	1.46
6.10	1.33	1.38	2.27	1.94
7.63	1.73	1.72	2.86	2.43
9.16	2.08	2.07	3.33	2.92
12.21	2.78	2.76	4.25	3.89
13.37	3.00	3.02	4.77	4.37
15.26	3.33	3.45	5.42	4.86

Table 5

Comparison of observed rates with the rates calculated on the basis of rate law (6) under the conditions of Table 2

[NaOH] ($\times 10^2$ mol dm $^{-3}$)	$-dc/dt$ ($\times 10^7$ mol dm $^{-3}$ s $^{-1}$)			
	glc		fru	
	Experimental	Calculated	Experimental	Calculated
5.00	0.28	0.28	0.38	0.38
10.00	0.54	0.56	0.73	0.75
15.00	0.88	0.80	1.18	1.11
20.00	1.07	1.03	1.61	1.46
25.00	1.37	1.25	1.92	1.80
30.00	1.72	1.45	2.33	2.14
35.00	1.88	1.64	–	–
40.00	2.05	1.82	2.78	2.79
45.00	2.25	2.00	3.00	3.11
50.00	2.32	2.15	3.33	3.42

Table 6

Comparison of observed rates with the rates calculated on the basis of rate law (6) under the conditions of Table 1

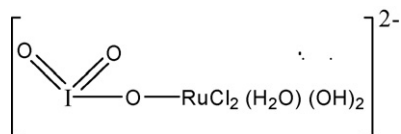
[KIO $_3$] ($\times 10^2$ mol dm $^{-3}$)	$-dc/dt$ ($\times 10^7$ mol dm $^{-3}$ s $^{-1}$)			
	glc		fru	
	Experimental	Calculated	Experimental	Calculated
0.40	0.35	0.43	0.61	0.61
0.80	0.73	0.84	1.25	1.18
1.00	0.97	1.03	1.67	1.46
1.20	1.07	1.22	1.88	1.73
1.60	1.46	1.59	2.42	2.25
2.00	1.88	1.93	3.06	2.74
2.40	2.19	2.26	–	–
2.80	–	–	3.85	3.61
3.20	2.60	2.88	–	–
3.60	3.14	3.16	4.44	4.48
4.00	3.33	3.43	4.62	4.87

(step II) and hence the proposed reaction mechanism. The mechanism, common for both glc and fru, also finds support from the observed Arrhenius frequency factor (A), which is of the same order of magnitude for both the reducing sugars.

6. Comparative studies

Efforts have been made to compare the findings of this paper with the results reported for the oxidation of glc and fru by acidic solution of NBA in presence of either Pd(II) [10] or Ir(III) [14].

As far as order of reaction with respect to oxidant is concerned, it is first order at its low concentrations which changes towards zero-order at its higher concentrations. Zero-order kinetics with respect to each substrate in the present study and also in the reported Ir(III)-catalyzed [14] oxidation of glc and fru is contrary to the first to zero-order kinetics reported for Pd (II)-catalyzed [10] oxidation of glc and fru. Observed first-order kinetics in [Ru(III)] in the present study shows similarity with the reported Pd(II)-catalyzed [10] oxidation but differs from Ir(III)-catalyzed [14] oxidation, where first- to zero-order kinetics in [Ir(III)] was observed. The nil effect of $[Cl^-]$ on the rate in Ru(III)-catalyzed oxidation clearly shows that there is no role of $[Cl^-]$ in deciding the reactive species of Ru(III) chloride in alkaline medium but the observed negative effect of $[Cl^-]$ in both Pd(II)-catalyzed [10] and in Ir(III)-catalyzed [14] oxidation shows that there is a significant role of Cl^- ions in deciding the reactive species of Pd(II) chloride and Ir(III) chloride in acidic medium. The negative effect of $[H^+]$ on the rate of oxidation of glc and fru in Pd(II) [10] and Ir(III) [14]-catalyzed oxidation was made one of the basis for taking HOBr as the reactive species of NBA in acidic medium whereas in the present study of Ru(III)-catalyzed oxidation, positive effect of $[OH^-]$ was made a basis to conclude that $[RuCl_2(H_2O)_2(OH)_2]^-$ is the reactive species Ru(III) chloride in alkaline medium. The formation of most reactive activated complex,

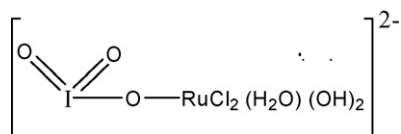


in step II of the proposed reaction scheme is supported by negative entropy of activation whereas in the reported Pd(II) [10]- and Ir(III) [14]-catalyzed oxidation it is supported by the positive entropy of activation.

7. Conclusions

The conclusions drawn, from the observed kinetic data and from the spectral information collected for the Ru(III)-catalyzed oxidation of glc and fru by potassium iodate in alkaline medium, are as follows

- (i) IO_3^- and $[RuCl_2(H_2O)_2(OH)_2]^-$ have been found as the reactive species of potassium iodate and Ru(III) chloride in alkaline medium, respectively.
- (ii) In the rate determining step, the most reactive activated complex,

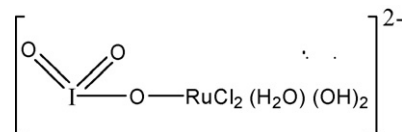


is formed by the interaction of reactive species of Ru(III) chloride and reactive species of potassium iodate in alkaline medium.

- (iii) The observed negative entropy of activation for the oxidation of both glc and fru supports step II of the proposed

reaction scheme, where two negatively charged species interact to form the most reactive activated complex.

- (iv) The existence of the complex species $[RuCl_2(H_2O)_2(OH)_2]^-$ and



is supported by the spectral information collected in this regard.

- (v) On the basis of observed positive effect of $[OH^-]$ on the rate of reaction, it is concluded that the enediol form of reducing sugar participates in the fast step of the common reaction scheme proposed for the oxidation of glc and fru.

References

- [1] T.A. Iyengar, Puttaswamy, D.S. Mahadewappa, Carbohydr. Res. 204 (1990) 197–206.
- [2] K.S. Rangappa, H. Manjunathaswamy, M.P. Raghvendra, D.C. Gowda, Carbohydr. Res. 307 (1998) 253–262.
- [3] K.S. Rangappa, M.P. Raghvendra, D.S. Mahadewappa, D.C. Gowda, Carbohydr. Res. 306 (1998) 57–67.
- [4] M.P. Singh, A.K. Singh, V. Tripathi, J. Phys. Chem. 82 (1978) 1222–1225.
- [5] M.P. Singh, H.S. Singh, S.C. Tiwari, K.C. Gupta, A.K. Singh, V.P. Singh, R.K. Singh, Ind. J. Chem. 13 (1975) 819–822.
- [6] M.P. Singh, R.K. Singh, A.K. Singh, A. Srivastava, Ind. J. Chem. 19A (1980) 547–549.
- [7] K.K. Sen Gupta, B.A. Begum, B. Pal, Carbohydr. Res. 309 (1998) 303–310.
- [8] S. Tiziani, F. Sussich, A. Cesaroi, Carbohydr. Res. 338 (2003) 1083–1095.
- [9] R. Tripathi, S.K. Upadhyay, Int. J. Chem. Kinet. 36 (2004) 441–448.
- [10] A.K. Singh, J. Srivastava, S. Rahmani, V. Singh, Carbohydr. Res. 341 (2006) 397–409.
- [11] A.K. Singh, D. Chopra, S. Rahmani, B. Singh, Carbohydr. Res. 314 (1998) 157–160.
- [12] A.K. Singh, A. Singh, R. Gupta, M. Saxena, B. Singh, Trans. Met. Chem. 17 (1992) 413–416.
- [13] A.K. Singh, N. Chaurasia, S. Rahmani, J. Srivastava, A.K. Singh, J. Chem. Res. (2005) 304–310.
- [14] A.K. Singh, S. Rahmani, B. Singh, R.K. Singh, M. Singh, J. Phys. Org. Chem. 17 (2004) 1–8.
- [15] S. Srivastava, S. Singh, J. Indian. Chem. Soc. 81 (2004) 295–298.
- [16] R.M. Mulla, G.C. Hiremath, S.T. Nandibewoor, J. Chem. Sci. 117 (1) (2005) 33–42.
- [17] M. Bhasin, S. Dubey, I. Sharma, P.D. Sharma, Ind. J. Chem. 39A (2000) 1036–1040.
- [18] A.K. Singh, N. Chaurasia, S. Rahmani, Jaya Srivastava, Bharat Singh, Catal. Lett. 95 (3–4) (2004) 135–142.
- [19] N. Kambo, S.K. Upadhyay, Trans. Met. Chem. 25 (2000) 461–464.
- [20] A.K. Singh, V. Singh, A.K. Singh, N. Gupta, B. Singh, Carbohydr. Res. 337 (2002) 345–351.
- [21] P.V. Ramana, R.V. Appa Rao, Ind. J. Chem. 30A (1991) 971–973.
- [22] P. Munikyamba, P. Raghunath Rao, E.V. Sundaram, J. Ind. Chem. Soc. LX (1983) 652–655.
- [23] P. Munikyamba, P. Raghunath Rao, E.V. Sundaram, Ind. J. Chem. 20A (1981) 1217–1219.
- [24] A. Brahmaiah, P. Manikyamba, Ind. J. Chem. 34A (1995) 900–903.
- [25] G.K. Muthakia, S.B. Jonnalagadda, Int. J. Chem. Kinet. 21 (1995) 519–533.
- [26] A.K. Singh, S. Srivastava, J. Srivastava, R. Singh, Carbohydr. Res. 342 (2007) 1078–1090.
- [27] Z. Khan, P.S.S. Babu, Kabir-ud-Din, Carbohydr. Res. 339 (2004) 133–140.
- [28] F. Feigl, Spot Tests in Organic Analysis, Elsevier, New York, 1960, p. 368.
- [29] F. Gutbauer, J. Chromatogr. 45 (1969) 104.

- [30] M.M. Taqui Khan, G. Ramachandraiah, A. Prakash Rao, *J. Inorg. Chem.* 25 (1986) 665–670.
- [31] P.S. Radhakrishnamurti, K.S. Tripathy, *Ind. J. Chem.* 25A (1986) 762–763.
- [32] Y. Sulfab, H.A. Elfaki, *Can. J. Chem.* (1974) 52.
- [33] R.H. Simoyi, M. Manyonda, J. Masere, M. Mtambo, I. Ncube, H. Patel, *J. Phys. Chem.* 95 (1991) 770–774.
- [34] J.F. Iyun, P.O. Ukaha, *Ind. J. Chem.* 38A (1999) 180–182.
- [35] M.P. Singh, B. Krishna, S. Ghosh, *Z. Phys. Chem.* 204 (1955) 1; 205 (1956) 285; 208 (1958) 273.
- [36] H.S. Isbell, H.L. Frush, C.W. Wade, C.E. Hunter, *Carbohydr. Res.* 9 (1969) 163.
- [37] A.A. Frost, R.G. Pearson, *Kinetics and Mechanism: A Study of Homogeneous Chemical Reactions*, 2nd ed., Wiley Eastern Private Limited, New Delhi, 1961, p. 143.