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N-Bromosuccinimide oxidation of maltose and D-galactose using chloro-complex of Rh(III) in its nano-concentration range as homogeneous catalyst: A kinetic and mechanistic study

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ABSTRACT

Kinetics of oxidation of maltose (mal) and D-galactose (gal) by protonated N-bromosuccinimide (N^+BSH) using chloro-complex of Rh(III) in its nano-concentration range as homogeneous catalyst have been investigated at 40 °C for the first time. Almost constant values of pseudo-first-order rate constant (k_1) throughout the variation of N-bromosuccinimide (NBS) in the oxidation of both the reducing sugars clearly demonstrate that order of reaction with respect to [NBS] is unity. First-order kinetics with respect to each [Rh(III)], [Sugar] and [H^+] is evident from the observed values of k_1 which increase in the same proportion in which the concentration of each reactant is increased. Negligible effects of variations of [Hg(II)], [Cl^-] and [succinimide] on the rate of oxidation of each reducing sugar have been observed. Variations in ionic strength (μ) and dielectric constant (D) of the medium have not influenced the oxidation rates. Protonated N-bromosuccinimide, N^+BSH, and chloro-complex of Rh(III), $[RhCl_5(H_2O)]^{2-}$, have been postulated as the reactive species of NBS and Rh(III) chloride in acidic medium, respectively. Various activation parameters have been calculated using pseudo-first-order rate constant (k_1) values observed at four different temperatures. The proposed mechanism, involving most reactive activated complex formed as a result of interaction between the complex species $[RhCl_5{\cdot}NHBr]^-$ and a sugar molecule is supported by kinetic orders, spectrophotometric evidence, positive entropy of activation and observed zero effect of dielectric constant and ionic strength of the medium. Almost constant values of composite rate constant (k') observed for the variations of [sugar], [NBS], [Rh(III)] and [H^+] in the oxidation of each reducing sugar provide further support to the proposed reaction path. The main oxidation products of the reactions were identified as arabinonic acid and formic acid in case of maltose and lyxonic acid and formic acid in case of D-galactose.

1. Introduction

NBS which is reported [1–7] to act as a source of positive halogen has been used as an oxidant in the oxidation of a number of substrate maintaining medium of the reaction either acidic or alkaline. Literature [8] reveals that the use of NBS has been made in the reactions of biological and industrial interest viz.: oxidation of psychotropic drugs, oxidation degradation of α-amino acids, in the study of peptide cleavage, in the fragmentation of high molecular weight peptides and proteins, etc. NBS [9] has also been employed to investigate the role of tryptophan in hapten binding in anti-DNP (H-1) and anti-DNP-p-aminobenzoyl glutamate (DNP-ABG) (I-13) antibodies. The role of NBS as an oxidant in the oxidation of a large variety of organic compounds has been probed using Ru(III) [10–12], Pd(II) [13–15], Ir(III) [16,17], Pt(IV) [18] and Fe(II) [19] as homogeneous catalysts. The study has also been made for the oxidation of styrene, stilbene and phenylacetylene [20] as well as maltose and lactose [21] using Rh(III) chloride as homogeneous catalyst. Literature also reveals that Rh(III) chloride has been used as catalyst in the oxidation of mannitol [22] and cyclic ketones [23]. Very few reports are available where Rh(III) chloride has been used as catalyst in the kinetic oxidation of organic substrates of biological importance like reducing sugars and amino acids.

Rhodium complexes are reported [24] to have chemical reactivity, antitumor activity, electronic structure and catalytic functions with potential industrial applications. It is also reported [25] that Rh(III) forms complexes with nitrogen donar ligands viz. ethylene diamine, pyridine, 2,2′-bipyridine and 1,10-phenanthroline, which are reported to have antibacterial and antitumor activities.

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Rh(III) is reported [26] to form a variety of complexes such as $[RhCl]^{2+}$, $[RhCl_2]^{+}$, $RhCl_3$, $[RhCl_4]^{-}$, $[RhCl_5]^{2-}$ and $[RhCl_6]^{3-}$ in the presence of HCl with its varying concentration. The study of carbohydrates is one of the most exciting fields of organic chemistry. Besides fulfilling the nutritional role, carbohydrates are reported to have biochemical and pharmacological actions. The study of sugar containing antibiotics has provided some of most fascinating and challenging problems in the field of carbohydrate chemistry [27].

In view of the biological importance of rhodium, NBS and reducing sugars and also in view of the fact that almost no report is available in which the role of chloro-complex of Rh(III) as homogeneous catalyst taking reducing sugar as reductant and N-bromosuccinimide as oxidant is described, the present study has been performed with a view to ascertain whether:

(1) The reactive chloro-complex of Rh(III) in acidic medium participates in the reactions in the same way as reactive chloro-complex of Ir(III) [17] and Pd(II) [14] showed their involvement in the reported reaction paths for the oxidation of reducing sugars by reactive species of NBS in acidic medium.
(2) The reactive species of NBS in acidic medium for the present study of oxidation of maltose and D-galactose remains the same as is reported [14,17] for the oxidation of reducing sugars in the presence of either chloro-complex of Pd(II) or Ir(III) as homogeneous catalyst.
(3) The role of H^+ ions in the oxidation of maltose and D-galactose in the presence of chloro-complex of Rh(III) as catalyst is similar to the reported [14,17] inverse fractional order in $[H^+]$ in the oxidation of reducing sugars using Ir(III) or Pd(II) chloride as catalyst.
(4) The role of Hg(II) is limited only up to Br^- ion scavenger as is reported [14,17] for Ir(III)- or Pd(II)-catalysed oxidation of reducing sugars by NBS in acidic medium.
(5) The reductants, i.e., maltose and D-galactose interact with the reactive species of NBS and Rh(III) chloride resulting in the formation of most reactive activated complex during the course of reaction in the same way as is reported [14,17] for Ir(III)- and Pd(II)-catalysed oxidation.
(6) Effects of $[Cl^-]$ and [NHS] on the rate of oxidation in the present study are similar to the reported inverse fractional order in $[Cl^-]$ and nil effect of [NHS] in both Ir(III) [17]- and Pd(II) [14]-catalysed oxidation of reducing sugars.
(7) The chloro-complex of Rh(III) used as catalyst in the oxidation of maltose and D-galactose is more active than the chloro-complex of either Ir(III) or Pd(II) used as catalyst in the reported oxidation of reducing sugars by NBS in acidic medium.

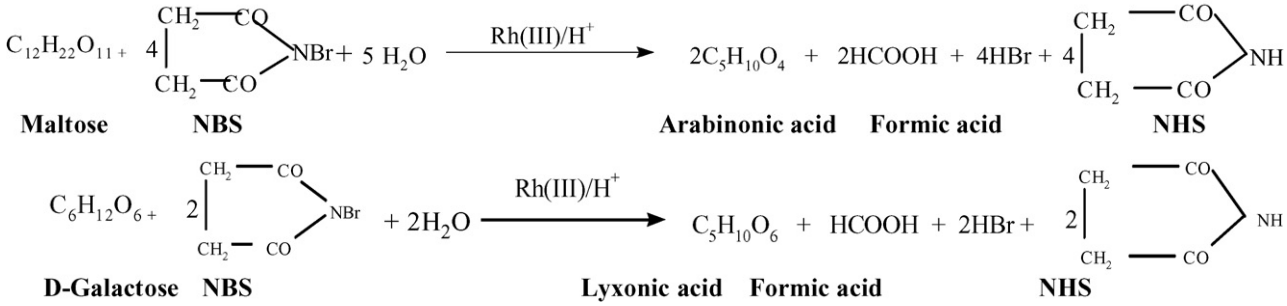
2. Experimental

A stock standard solution of NBS (E. Merck) was prepared by dissolving its known weight in doubly distilled water and its concentration was estimated iodometrically. In order to avoid photochemical deterioration, the solution of NBS was preserved in black coated flask. The standard solution of maltose (mal) and D-galactose (gal) (AR Grade) were freshly prepared. $RhCl_3{\cdot}3H_2O$ solution was prepared in 3 M HCl and its concentration was determined as 3.80×10^{-3} M. Other reagents used were of AR Grade and their solutions were also prepared in doubly distilled water. The reaction vessels were also coated black from outside to avoid photochemical effects. The kinetic runs were carried out at $40 \pm 0.1\,^{\circ}C$.

The reaction was initiated by mixing the already thermostated solution of sugar to the thermally equilibrated reaction mixture containing required volumes of solutions of NBS, H^+, Rh(III) and all other reagents. Aliquots (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% KI solution and 5 ml of dilute perchloric acid solution. The liberated iodine equivalent to unconsumed NBS was estimated with standard sodium thiosulphate solution using starch as an indicator. The initial rates were obtained from the slopes of the concentration vs. time graph in the initial stages of the reactions by plane mirror method.

2.1. Stoichiometry and products identification

Different sets of experiments were performed with different [NBS]:[sugar] ratios under the condition [NBS] ≫ [sugar]. The estimation of unconsumed NBS indicated that four moles of NBS were consumed to oxidize one mole of maltose and two moles of NBS were consumed to oxidize one mole of D-galactose. Accordingly, the following stoichiometric equations are suggested:



Formic acid and arabinonic acid in the oxidation of maltose and formic acid and lyxonic acid in the oxidation of D-galactose were identified as the main oxidation products of the reactions under investigation.

3. Kinetic results

Kinetic study of Rh(III)-catalysed oxidation of reducing sugars (mal and gal) by protonated NBS was carried out at several initial concentrations of each reactants one by one. For determining the order of reaction with respect to NBS, its concentration has been varied from 1.5×10^{-4} to 15.00×10^{-4} M at constant concentration of all other reactants at 40 °C. Initial rate $(-dc/dt)$ values have been calculated from the slopes of the plots of unconsumed [NBS] and time and first-order rate constant, k_1, was calculated as

$$k_1 = \frac{(-dc/dt)}{[NBS]}$$

The observed rate constant, k_1, remained practically constant at different initial concentrations of NBS, indicating first-order kinetics with respect to [NBS] (Table 1). When $(-dc/dt)$ values are plotted against [NBS], straight lines for both reducing sugars were obtained (Fig. 1), which clearly shows first-order dependence of the reactions on [NBS]. First-order kinetics with respect to each sugar was observed because k_1 values were found to increase linearly with increase in [sugar]. The plot of k_1 vs. [sugar] gives straight lines

Table 1
Calculated values of first-order rate constants for the variations of [NBS], [Rh(III)] and [Sugar] in the Rh(III)-catalysed oxidation of maltose and D-galactose at 40 °C.

$[NBS] \times 10^4$ (M)	$[Rh(III)] \times 10^9$ (M)	$[Sugar] \times 10^2$ (M)	$k_1 \times 10^4$ (s^{-1})	
			Maltose	D-Galactose
3.00	2.70	2.00	16.67	13.33
4.50	2.70	2.00	12.84	14.67
6.00	2.70	2.00	18.33	14.67
7.50	2.70	2.00	17.00	12.80
9.00	2.70	2.00	17.00	12.56
10.50	2.70	2.00	16.76	13.27
12.00	2.70	2.00	16.50	13.75
13.50	2.70	2.00	16.59	13.83
15.00	2.70	2.00	16.80	13.07
3.00	0.90	2.00	6.27	6.00
3.00	1.80	2.00	11.67	7.77
3.00	2.70	2.00	16.67	13.33
3.00	3.60	2.00	21.67	20.83
3.00	4.50	2.00	26.67	24.17
3.00	5.40	2.00	33.33	29.17
3.00	6.30	2.00	38.33	33.33
3.00	7.20	2.00	43.33	38.33
3.00	8.10	2.00	50.00	43.33
3.00	9.00	2.00	58.33	46.67
3.00	2.70	1.00	5.67	7.50
3.00	2.70	2.00	16.67	13.33
3.00	2.70	3.00	22.50	21.67
3.00	2.70	4.00	33.33	30.00
3.00	2.70	6.00	50.00	46.67
3.00	2.70	8.00	63.33	58.33
3.00	2.70	10.00	78.33	75.00

Solution conditions—For [NBS] variation: $[Hg(II)] = 17.50 \times 10^{-4}$ M; $[NHS] = 17.50 \times 10^{-4}$ M; $[H^+] = 20.00 \times 10^{-2}$ M; $\mu = 0.25$ M. For [Rh(III)] and [sugar] variations: $[Hg(II)] = 3.30 \times 10^{-4}$ M; $[NHS] = 3.20 \times 10^{-4}$ M & $[H^+] = 20.00 \times 10^{-2}$ M; $\mu = 0.25$ M.

passing through origin, which further supports first-order dependence of reactions on [sugar] (Fig. 2 and Table 1). The order in Rh(III) was unity as evidenced by the k_1 vs. [Rh(III)] plot, where straight lines passing through the origin have been obtained for the oxidation of both maltose and D-galactose (Fig. 3 and Table 1). The effect of $[H^+]$ on the rate was studied at a fixed ionic strength (μ) maintained by sodium perchlorate. The plot of k_1 vs. $[H^+]$ gave straight lines passing though the origin in each case, suggesting a first-order dependence of reactions on $[H^+]$ (Fig. 4). Mercuric acetate was found to have a limited role as a bromide ion scavenger only as its variation showed zero effect on the rate of oxidation of both the sugars. Addition of potassium chloride and succinimide had no effect on the reaction rate. The effect of ionic strength (μ) variation on rate of reaction was studied by carrying out investigations in the presence of different amounts of sodium perchlorate. The results indicated negligible effect of μ on the reaction rate. The reactions were studied at four different temperatures, i.e., 35, 40, 45, 50 °C. The rate constants at these temperatures led to compute E_a, $\Delta S^{\#}$, $\Delta H^{\#}$ and $\Delta G^{\#}$ in the oxidation of both maltose and D-galactose and these activation parameters are recorded in Table 2.

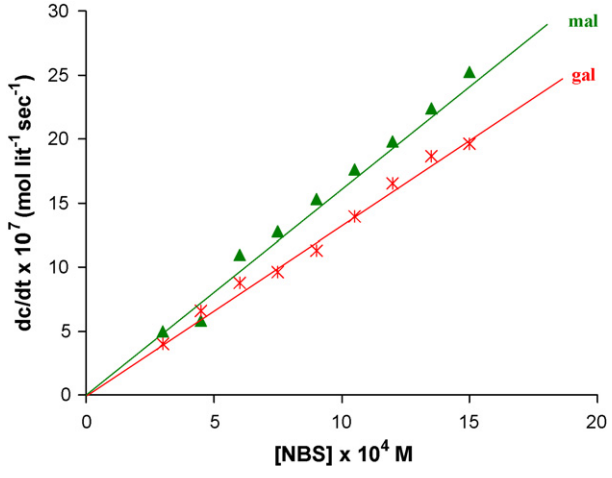


Fig. 1. Plots between (−dc/dt) and [NBS] at 40 °C. $[RhCl_3] = 2.70 \times 10^{-9}$ M; $[Sugar] = 2.00 \times 10^{-2}$ M; $[H^+] = 20.00 \times 10^{-2}$ M; $[Hg(OAc)_2] = 17.50 \times 10^{-4}$ M; $[NHS] = 17.50 \times 10^{-4}$ M; $\mu = 0.25$ M.

4. Discussion of kinetic results and mechanism

The role of NBS as an oxidant has been discussed in the reported oxidation of acetophenone [28], amino acids [29], polyhydric alcohols [11], reducing sugars [14] and 4-oxoacids [1] in acidic medium.

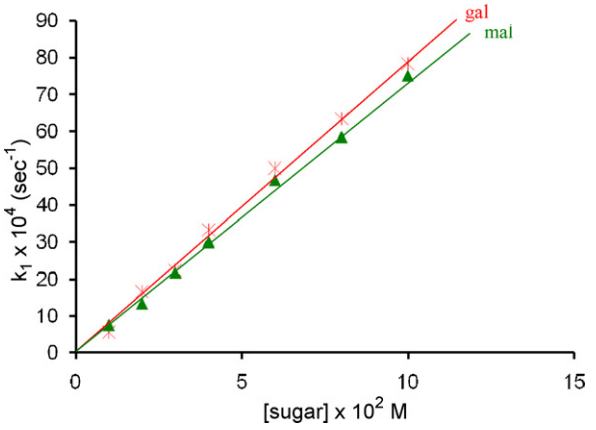


Fig. 2. Plots between k_1 and [Sugar] at 40 °C. $[NBS] = 3.00 \times 10^{-4}$ M; $[RhCl_3] = 2.70 \times 10^{-9}$ M; $[H^+] = 20.00 \times 10^{-2}$ M; $[Hg(OAc)_2] = 3.30 \times 10^{-4}$ M; $[NHS] = 3.20 \times 10^{-4}$ M; $\mu = 0.25$ M.

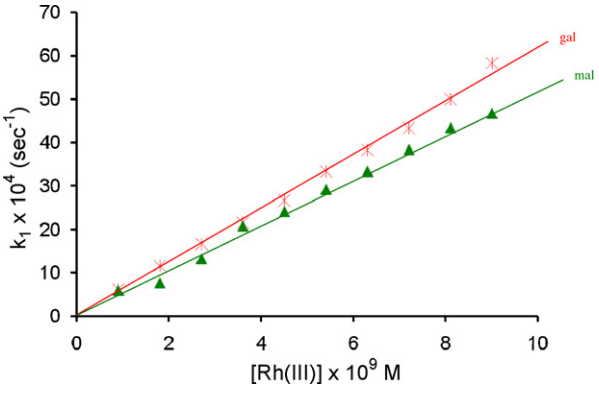


Fig. 3. Plots between k_1 and [Rh(III)] at 40 °C. $[NBS] = 3.00 \times 10^{-4}$ M; $[Sugar] = 2.00 \times 10^{-2}$ M; $[H^+] = 20.00 \times 10^{-2}$ M; $[Hg(OAc)_2] = 3.30 \times 10^{-4}$ M; $[NHS] = 3.20 \times 10^{-4}$ M; $\mu = 0.25$ M

Table 2
Activation parameters for Rh(III) chloride catalysed oxidation of reducing sugars by protonated NBS at 40 °C.

Reducing sugar	k_r ($mol^{-3}\ l^3\ s^{-1}$)	A ($mol^{-3}\ l^3\ s^{-1}$)	E_a ($kJ\ mol^{-1}$)	$\Delta H^{\#}$ ($kJ\ mol^{-1}$)	$\Delta S^{\#}$ ($J\ K^{-1}\ mol^{-1}$)	$\Delta G^{\#}$ ($kJ\ mol^{-1}$)
Maltose	1.54×10^8	0.65×10^{14}	33.90	31.27	11.48	27.67
D-Galactose	1.23×10^8	25.70×10^{14}	44.10	41.47	42.09	28.30

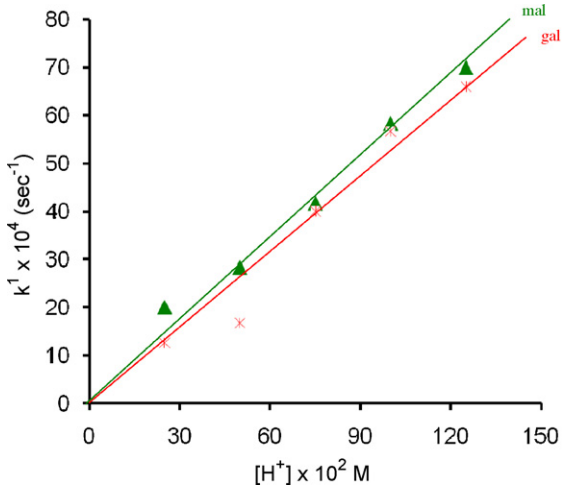


Fig. 4. Plots between k_1 and $[H^+]$ at 40 °C. $[NBS] = 3.00 \times 10^{-4}$ M; $[RhCl_3] = 2.70 \times 10^{-9}$ M; $[Sugar] = 2.00 \times 10^{-2}$ M; $[Cl^-] = 20.00 \times 10^{-2}$ M; $[Hg(OAc)_2] = 3.30 \times 10^{-4}$ M; $[NHS] = 3.20 \times 10^{-4}$ M; $\mu = 1.47$ M.

These reports indicate that the N-bromosuccinimide exists in acidic medium in the form of following equilibria:

$$\underset{(\mathbf{NBS})}{>NBr} + H^+ \rightleftharpoons \underset{(\mathbf{N^+BSH})}{>N^+HBr}$$

$$\underset{(\mathbf{NBS})}{>NBr} + H^+ \rightleftharpoons \underset{(\mathbf{NHS})}{>NH} + Br^+$$

$$Br^+ + H_2O \rightleftharpoons (H_2OBr)^+$$

From a perusal of above equilibria, it is clear that the possible oxidizing species may be any one of the four species, i.e., NBS itself, protonated NBS (N^+BSH), Br^+ and H_2OBr^+. Out of these four possible oxidizing species, the real reactive species of NBS in the present investigation has been decided on the basis of observed kinetic data and spectral information collected in this regard. If NBS as such is considered as the reactive species, then the rate law derived on this basis fails to explain the first-order kinetics with respect to $[H^+]$. Further, if Br^+ or H_2OBr^+ is taken as possible oxidizing species of NBS then it will lead to negative effect of succinimide (NHS), contrary to the observed zero effect of succinimide concentration on the rate of oxidation. Under these circumstances, we have been left with no option but to assume protonated NBS, i.e., N^+BSH as the reactive oxidizing species of NBS in the oxidation of aforesaid reducing sugars in acidic medium. Assuming N^+BSH as the reactive species of NBS, the rate law derived on the basis of proposed reaction path very well explains first-order kinetics with respect to $[H^+]$ and zero effect of addition of [NHS] on rate of reaction. Further support to this assumption was obtained by the spectra of NBS solutions with five different concentrations of H^+ ions, where an increase in absorbance with the increase in $[H^+]$ was observed. The observed increase in absorbance from 0.58 to 1.30, 1.34, 1.44 and 1.50 on increasing $[H^+]$ clearly provides support for the existence of following equilibrium in the reactions under investigation (Fig. 5(1)–(5)).

$$\underset{(\mathbf{NBS})}{>NBr} + H^+ \rightleftharpoons \underset{(\mathbf{N^+BSH})}{N^+HBr}$$

The equilibrium shown above indicates that with the increase in $[H^+]$, the equilibrium will shift towards right with more and more formation of N^+BSH. Thus observed unity order in $[H^+]$ and increase in absorbance with the increase in the concentration of hydrogen ions led us to conclude that the species N^+BSH can safely and convincingly be assumed as the reactive species of NBS in the oxidation of maltose and D-galactose in acidic medium.

In the present study of oxidation of maltose and D-galactose by acidic solution of N-bromosuccinimide, Rh(III) chloride has been used as homogeneous catalyst. The report of James and Rempel [30] contains the kinetic studies of chloro-complexes of rhodium as hydrogenation catalysts. They have found that in acid solution only anionic chlororhodate(III)-complexes activate molecular hydrogen for the homogeneous reduction of ferric ion. According to them the activity of the species increases with increasing number of chloride ligands attached to the metal ion in the following order:

$$[\mathbf{RhCl_6}]^{3-} > [\mathbf{Rh(H_2O)Cl_5}]^{2-} > [\mathbf{Rh(H_2O)Cl_4}]^-$$

Harrod and Halpern [31] found that $[RhCl_6]^{-3}$ is the predominant species in solution in their studies with $RhCl_3$ in 3.0–5.0 M HCl solutions. Their observation is not in line with the observation of James and Rempel where $[Rh(H_2O)Cl_5]^{2-}$ is reported as the predominant species in solution. Wolsey et al. [26] and others observed that complex species $RhCl^{2+}$, $RhCl_2^+$, $RhCl_3$, $RhCl_4^-$, $RhCl_5^{2-}$ and $RhCl_6^{3-}$ exist with change in HCl concentration from 0.010 to 2.00 M. The study relating to hydration of acetylenes catal-

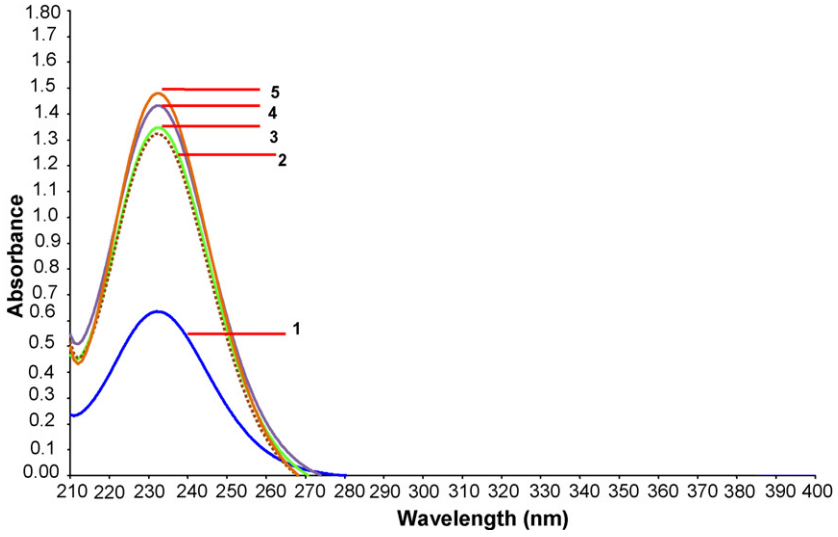


Fig. 5. Spectra of solutions [1–5] recorded at room temperature. (1) $[NBS] = 1.00 \times 10^{-4}$ M, $[H^+] = 0.2$ M; (2) $[NBS] = 1.00 \times 10^{-4}$ M, $[H^+] = 0.4$ M; (3) $[NBS] = 1.00 \times 10^{-4}$ M, $[H^+] = 0.6$ M; (4) $[NBS] = 1.00 \times 10^{-4}$ M, $[H^+] = 0.8$ M; (5) $[NBS] = 1.00 \times 10^{-4}$ M, $[H^+] = 1.0$ M.

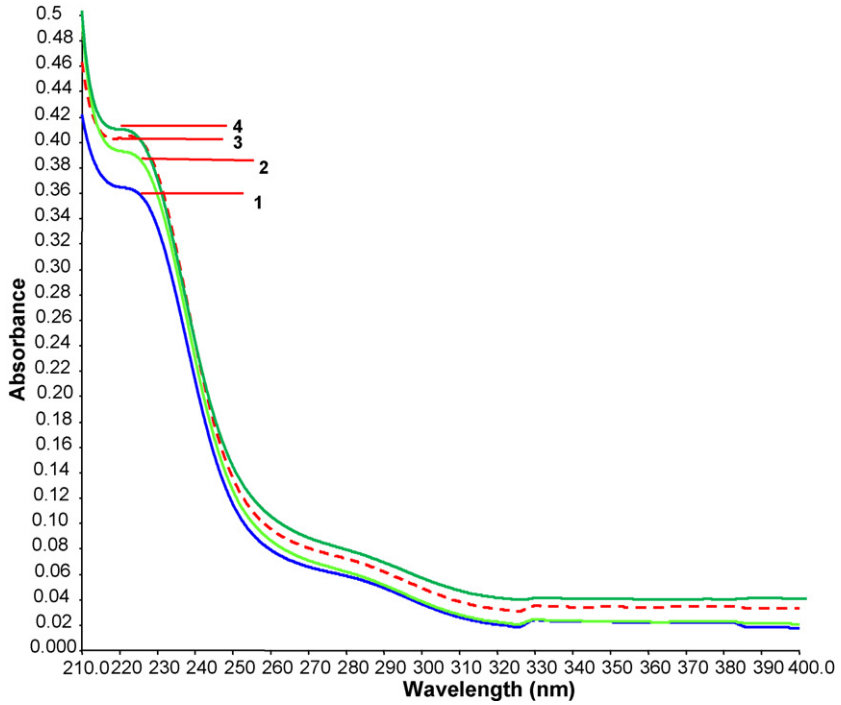


Fig. 6. Spectra of solutions [1–4] recorded at room temperature. (1) [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.1 M; (2) [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M; (3) [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.5 M; (4) [Rh(III)] = 1.90×10^{-5} M, [H^+] = 1.0 M.

ysed by rhodium(III) chloride complexes has also been reported [32], where the cationic species are reported to be completely inactive and the activity increases with increase in number of chloride ion up to a maximum of five. Hexachloro-complex is also reported as inactive.

In view of earlier reports and observed order with respect to [Rh(III)], it can be concluded that $[RhCl_5(H_2O)]^{-2}$ is the reactive species of Rh(III) chloride in oxidation of maltose and D-galactose by acidic solution of N-bromosuccinimide. This conclusion was also supported by spectral information (Fig. 6(1)– (4)). It is quite clear from Fig. 6 that with the increase in [HCl] there is an increase in absorbance at a same wavelength, i.e., at λ_{max} = 230 nm. This shows that Rh(III) chloride in solution remains as $[RhCl_5(H_2O)]^{-2}$ only because with the change in the nature of chloro-complex of Rh(III), there will be a shift in λ_{max} towards higher wavelength. The single peak observed for all the three solutions with varying concentration of HCl provides a strong evidence for the existence of the species $[RhCl_5(H_2O)]^{-2}$ as predominant species in 3 M HCl solution of Rh(III) chloride. Our assumption that the species $[RhCl_5(H_2O)]^{-2}$ is the most reactive species of Rh(III) chloride in solution of 3 M HCl

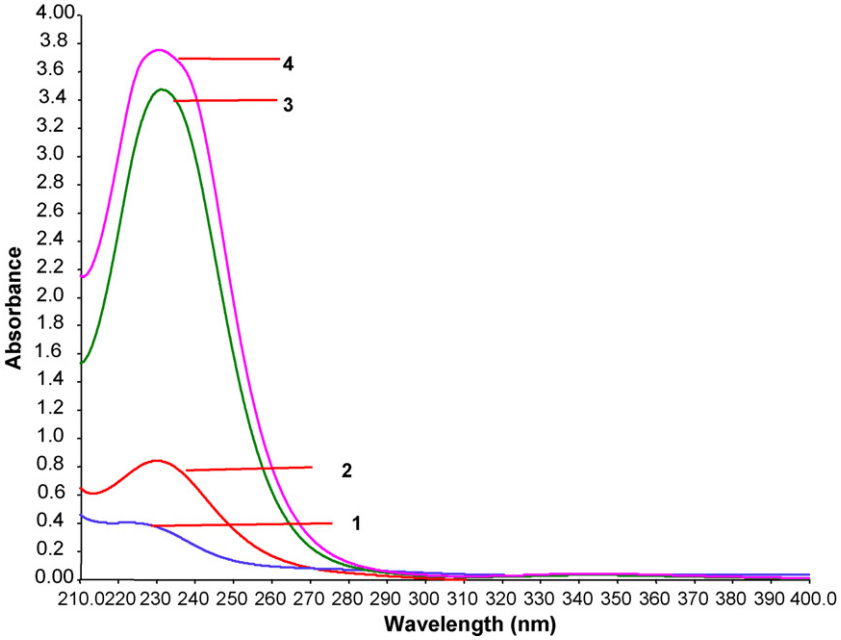


Fig. 7. Spectra of solutions [1–4] recorded at room temperature. (1) [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M; (2) [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [NBS] = 2.00×10^{-4} M; (3) [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M; [NBS] = 1.00×10^{-4} M; (4) [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [NBS] = 4.00×10^{-4} M.

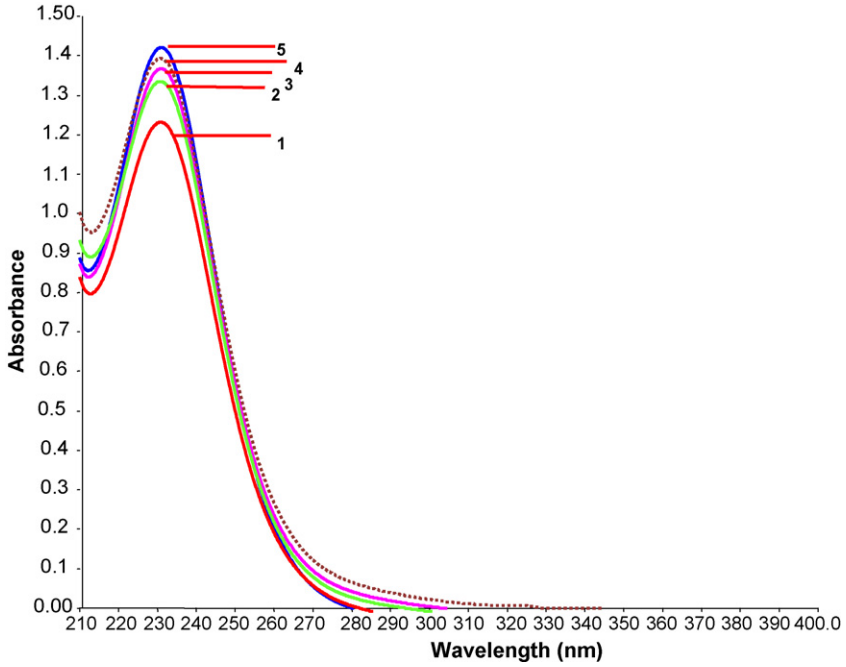
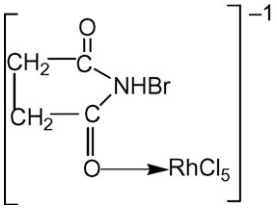


Fig. 8. Spectra of solutions [1–5] recorded at room temperature in the oxidation of maltose. (1) [NBS] = 1.00×10^{-4} M, [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [Maltose] = 1.00×10^{-2} M; (2) [NBS] = 1.00×10^{-4} M, [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [Maltose] = 3.00×10^{-2} M; (3) [NBS] = 1.00×10^{-4} M, [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [Maltose] = 5.00×10^{-2} M; (4) [NBS] = 1.00×10^{-4} M, [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [Maltose] = 7.00×10^{-2} M; (5) [NBS] = 1.00×10^{-4} M, [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [Maltose] = 9.00×10^{-2} M.

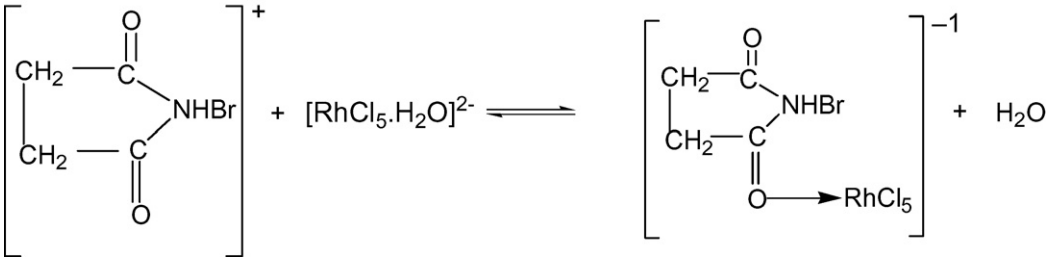
finds further support from the reported study of James and Rempel [30].

Kinetic observations show that the reactions under investigation are complex reactions, which usually take place in more than one step. In such reactions as in the present investigation, there is every possibility for the formation of complex or complexes between different reactants of the reactions.

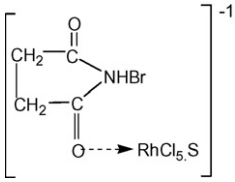
In order to verify the formation of a complex between reactive species of Rh(III) chloride and reactive species of NBS in acidic medium, the spectra for the solution containing Rh(III) chloride and H^+ alone as well as for solutions containing Rh(III) chloride and H^+ with three different concentrations of NBS have been collected by the help of UV–Vis spectrophotometer. An increase in the absorbance from 0.38 to 0.83, 3.42 and 3.67 with the increase in the concentration of NBS (Fig. 7(1)–(4)) can be regarded as due to more and more formation of the complex,

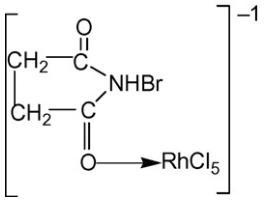


, according to the following equilibrium:



After ascertaining the formation of a complex between reactive species of Rh(III) chloride and reactive species of N-bromosuccinimide, an effort was also made to probe the possibility of formation of a complex between the aforesaid complex and a reducing sugar molecule. For this, the spectra for Rh(III) chloride, NBS and H^+ solution and for Rh(III) chloride, NBS and H^+ with five different concentrations of maltose were collected (Fig. 8(1)–(5)). The spectral information, where an increase in absorbance from 0.83 to 1.24, 1.36, 1.37, 1.38 and 1.43 with the increase in maltose concentration was indicated, led us to conclude that a complex of the type,





, is being formed between the complex,

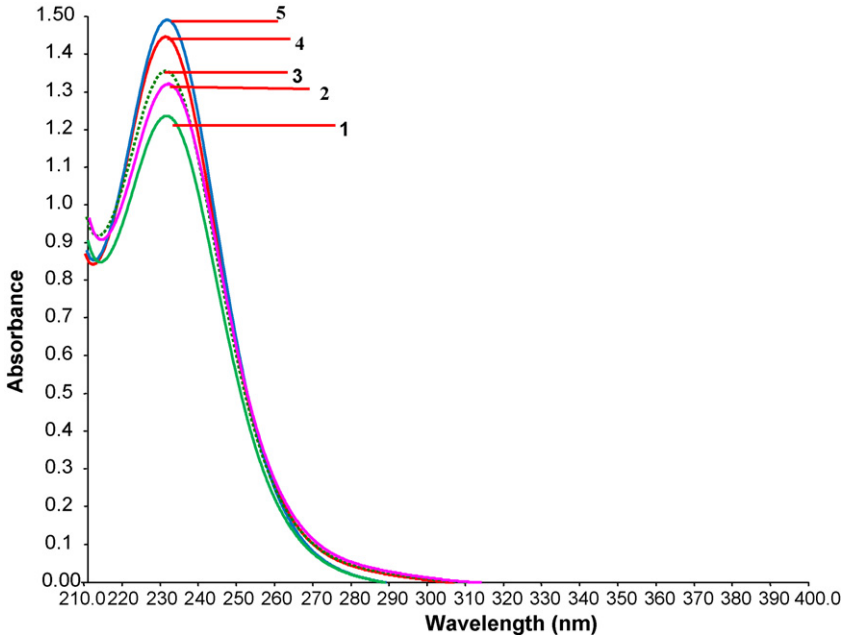
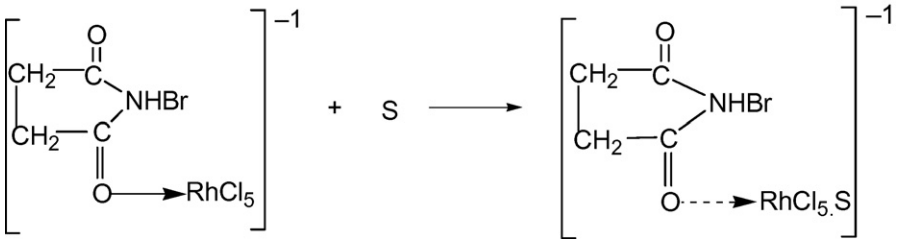
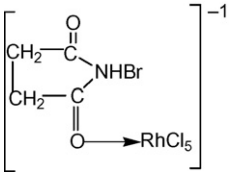


Fig. 9. Spectra of solutions [1–5] recorded at room temperature in the oxidation of D-galactose. (1) [NBS] = 1.00×10^{-4} M, [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [D(-)Galactose] = 1.00×10^{-2} M; (2) [NBS] = 1.00×10^{-4} M, [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [D(-)Galactose] = 3.00×10^{-2} M; (3) [NBS] = 1.00×10^{-4} M, [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [D(-)Galactose] = 1.00×10^{-2} M; (4) [NBS] = 1.00×10^{-4} M, [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [D(-)Galactose] = 1.00×10^{-2} M; (5) [NBS] = 1.00×10^{-4} M, [Rh(III)] = 1.90×10^{-5} M, [H^+] = 0.2 M, [D(-)Galactose] = 1.00×10^{-2} M.

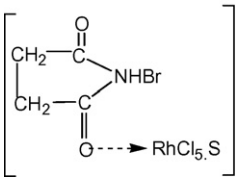
and a maltose molecule (S) during the course of reaction in the following way:



This process has been repeated with other reducing sugar, i.e., D-galactose also and the results obtained were the same (Fig. 9(1)–(5)). The formation of 1:1 complex between the complex



species, and a reducing sugar molecule was further verified by Job's plots [33,34] where $1/\Delta A$ values are plotted against 1/[substrate] in the oxidation of each reducing sugar (Fig. 10). ΔA on *y*-axis indicates the difference in the absorbance of the solution with reducing sugar molecule (S) and that of the solution without reducing sugar molecule. The formation of 1:1



complex, , is verified by the straight line with positive intercept on *y*-axis. The structure of the aforesaid complex also finds support from the literature [11].

On the basis of kinetic orders with respect to each reactant taking part in the reaction and spectral information collected for the existence of complexes as indicated above during the course of reaction, a common reaction scheme-1 in the following form can be proposed for Rh(III)-catalysed oxidation of reducing sugars by N-bromosuccinimide in acidic medium.

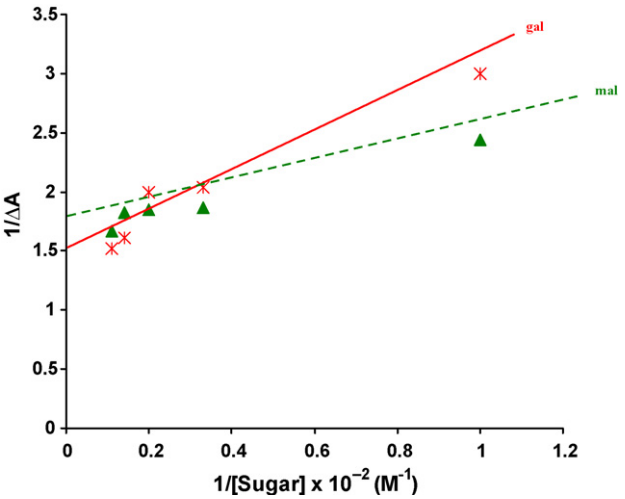
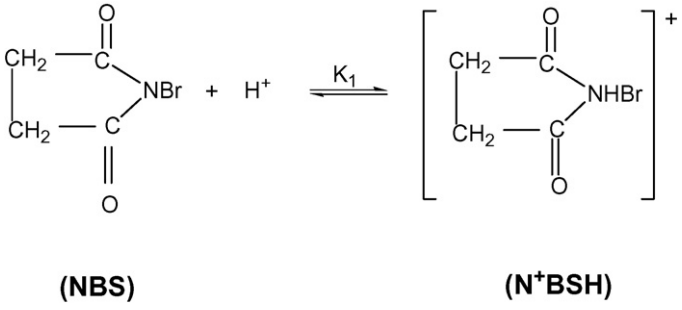
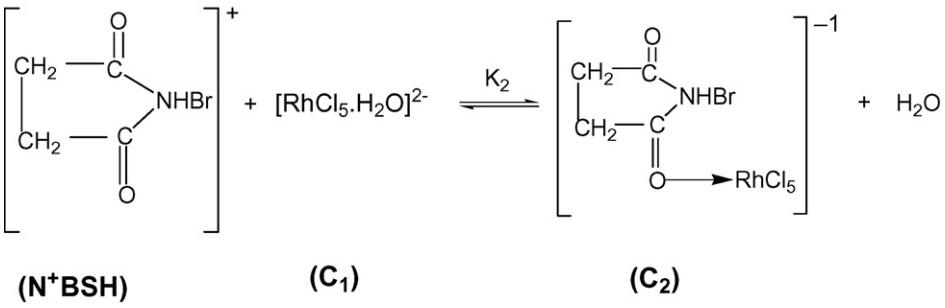


Fig. 10. Plots between $1/\Delta A$ and 1/[Sugar].

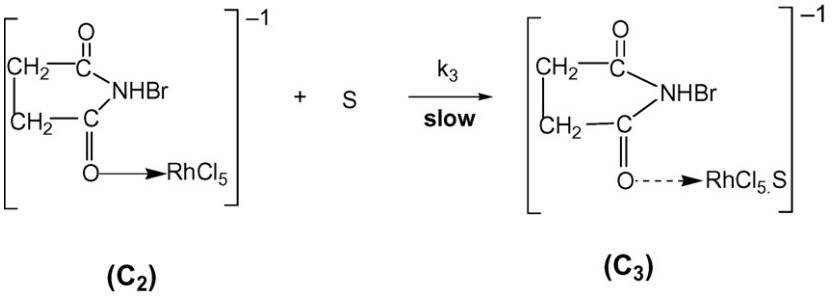
4.1. Reaction scheme-1



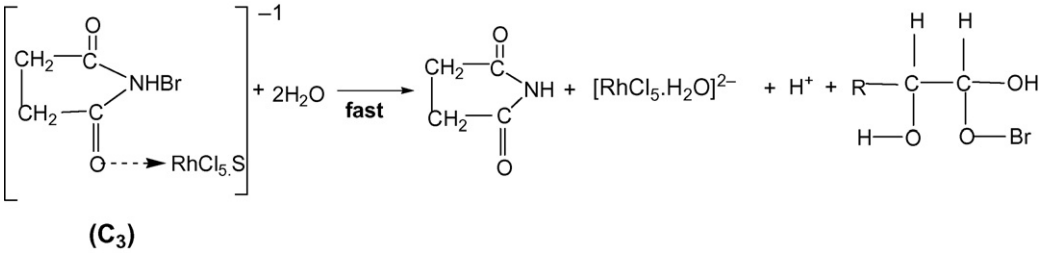
(i)



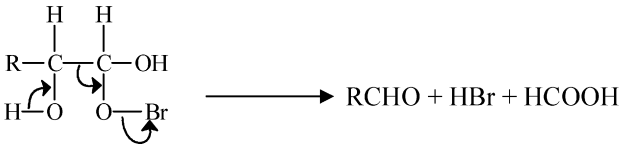
(ii)



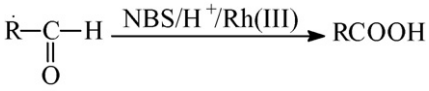
(iii)



(iv)



(v)



(vi)

where R = $C_4H_9O_4$ in the case of D-galactose and also in the case of D-glucose which is one of the units of maltose.

In the case of maltose the same process shall be repeated for its another unit which is also a D-glucose.

According to the proposed reaction scheme-1, the rate in terms of disappearance of NBS can be shown as

$$\text{rate} = -\frac{d[\text{NBS}]}{dt} = nk_3[C_2][S] \quad (1)$$

where n as per the stoichiometric equation is four for maltose and two for D-galactose.

On applying the law of chemical equilibrium to steps (i) and (ii), we have Eqs. (2) and (3), respectively.

$$K_1 = \frac{[N^+BSH]}{[NBS][H^+]} \quad \text{or} \quad [N^+BSH] = K_1[NBS][H^+] \quad (2)$$

$$\text{and} \quad K_2 = \frac{[C_2]}{[N^+BSH][C_1]} \quad \text{or} \quad [C_2] = K_2[N^+BSH][C_1] \quad \text{or} \quad [C_2] = K_1K_2[NBS][H^+][C_1] \quad (3)$$

From Eqs. (1) and (3), we obtain Eq. (4):

$$\text{rate} = -\frac{d[\text{NBS}]}{dt} = nk_3K_1K_2[NBS][H^+][C_1][S] \quad (4)$$

At any time in the reaction, the total concentration of Rh(III) can be expressed as

$$[\text{Rh(III)}]_T = [C_1] + [C_2] \quad (5)$$

Table 3
Calculated values of composite rate constants for the variations of [NBS], [H+], [Rh(III)] and [Sugar] in the Rh(III)-catalysed oxidation of maltose at 40 °C.

[NBS] × 10^4 (M)	[H+] × 10^2 (M)	[Rh(III)] × 10^9 (M)	[Sugar] × 10^2 (M)	k′ × 10^8 (s^−1)
3.00	20.00	2.70	2.00	1.54
4.50	20.00	2.70	2.00	1.91
6.00	20.00	2.70	2.00	1.70
7.50	20.00	2.70	2.00	1.57
9.00	20.00	2.70	2.00	1.57
10.50	20.00	2.70	2.00	1.55
12.00	20.00	2.70	2.00	1.53
13.50	20.00	2.70	2.00	1.54
15.00	20.00	2.70	2.00	1.56
3.00	25.00	2.70	2.00	1.48
3.00	50.00	2.70	2.00	1.05
3.00	75.00	2.70	2.00	1.03
3.00	100.00	2.70	2.00	1.08
3.00	125.00	2.70	2.00	1.00
3.00	20.00	0.90	2.00	1.74
3.00	20.00	1.80	2.00	1.62
3.00	20.00	2.70	2.00	1.54
3.00	20.00	3.60	2.00	1.50
3.00	20.00	4.50	2.00	1.48
3.00	20.00	5.40	2.00	1.54
3.00	20.00	6.30	2.00	1.52
3.00	20.00	7.20	2.00	1.50
3.00	20.00	8.10	2.00	1.54
3.00	20.00	9.00	2.00	1.62
3.00	20.00	2.70	1.00	1.05
3.00	20.00	2.70	2.00	1.54
3.00	20.00	2.70	3.00	1.39
3.00	20.00	2.70	4.00	1.54
3.00	20.00	2.70	6.00	1.54
3.00	20.00	2.70	8.00	1.47
3.00	20.00	2.70	10.00	1.45

Solution conditions—For [NBS] variation: [Hg(II)] = 17.50 × 10^−4 M; [NHS] = 17.50 × 10^−4 M; μ = 0.25 M. For [Rh(III)] and [sugar] variations: [Hg(II)] = 3.30 × 10^−4 M; [NHS] = 3.20 × 10^−4 M; μ = 0.25 M. For [H+] variation: [Hg(II)] = 3.30 × 10^−4 M; [NHS] = 3.20 × 10^−4 M; μ = 1.47 M.

On substituting the value of $[C_2]$ from Eq. (3) in Eq. (5), we get:

$$\begin{aligned} [\mathrm{Rh(III)}]_T &= [C_1] + K_1K_2[\mathrm{NBS}]\,[\mathrm{H^+}]\,[C_1] \\ \text{or}\quad [\mathrm{Rh(III)}]_T &= [C_1]\{1 + \mathrm{K_1K_2[NBS][H^+]}\} \\ \text{or}\quad [C_1] &= \frac{[\mathrm{Rh(III)}]_T}{1 + \mathrm{K_1K_2[NBS][H^+]}} \end{aligned} \tag{6}$$

From Eqs. (4) and (6), we obtain Eq. (7):

$$\text{rate} = -\frac{\mathrm{d[NBS]}}{dt} = \frac{nk_3K_1K_2[\mathrm{NBS}][\mathrm{H^+}][\mathrm{S}][\mathrm{Rh(III)}]_T}{1 + K_1K_2[\mathrm{NBS}][\mathrm{H^+}]} \tag{7}$$

At low concentrations of NBS and H^+, the inequality $1 \gg K_1K_2[\mathrm{NBS}][\mathrm{H^+}]$ can be assumed as valid one and under this condition Eq. (7) will be reduced to Eq. (8).

$$\text{rate} = -\frac{\mathrm{d[NBS]}}{dt} = nk_3K_1K_2[\mathrm{NBS}][\mathrm{H^+}][\mathrm{S}][\mathrm{Rh(III)}]_T \tag{8}$$

Eq. (8) is the required rate law because it is in accordance with the observed first-order kinetics with respect to NBS, H^+, S and $[\mathrm{Rh(III)}]_T$ in the oxidation of maltose and D-galactose.

On the other hand if we assume that the inequality $1 \ll K_1K_2[\mathrm{NBS}][\mathrm{H^+}]$ is valid at higher concentrations of NBS and H^+, then under this condition Eq. (7) will take the shape of Eq. (9).

$$\text{rate} = -\frac{\mathrm{d[NBS]}}{dt} = nk_3[\mathrm{S}][\mathrm{Rh(III)}]_T \tag{9}$$

Rate equation (9) indicates that the reactions under investigation will follow zero-order kinetics with respect NBS and H^+ at their higher concentrations. Since our entire study is at low concentrations of NBS and H^+, hence in our case the rate law (8) is applicable and can be treated as the final rate law. Further, since the rate law (8) derived on the basis of reaction scheme-1 is strictly in accordance with our experimental findings hence mechanism proposed in the form of reaction scheme-1 is the most probable reaction mechanism for the oxidation of maltose and D-galactose by N-bromosuccinimide in acidic medium using $[\mathrm{RhCl_5{\cdot}H_2O}]^{-2}$ as homogeneous catalyst.

According to Eq. (8):

$$\text{rate} = -\frac{\mathrm{d[NBS]}}{dt} = nk_3K_1K_2[\mathrm{NBS}][\mathrm{H^+}][\mathrm{S}][\mathrm{Rh(III)}]_T$$

Since n is equal to four in the case of maltose and two in the case of D-galactose, hence for the oxidation of both maltose and D-galactose above equation can be written as Eqs. (10) and (11), respectively.

$$\begin{aligned} \text{rate} &= -\frac{\mathrm{d[NBS]}}{dt} = 4k_3K_1K_2[\mathrm{NBS}][\mathrm{H^+}][\mathrm{S}][\mathrm{Rh(III)}]_T \\ \text{or} \\ \text{rate} &= -\frac{\mathrm{d[NBS]}}{dt} = k'[\mathrm{NBS}][\mathrm{H^+}][\mathrm{S}][\mathrm{Rh(III)}]_T \end{aligned} \tag{10}$$

where $k' = 4k_3K_1K_2$.

and

$$\begin{aligned} \text{rate} &= -\frac{\mathrm{d[NBS]}}{dt} = 2k_3K_1K_2[\mathrm{NBS}][\mathrm{H^+}][\mathrm{S}][\mathrm{Rh(III)}]_T \\ \text{or} \\ \text{rate} &= -\frac{\mathrm{d[NBS]}}{dt} = k''[\mathrm{NBS}][\mathrm{H^+}][\mathrm{S}][\mathrm{Rh(III)}]_T \end{aligned} \tag{11}$$

where $k'' = 2k_3K_1K_2$.

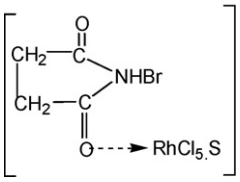
For the variations of [NBS], $[H^+]$, $[\mathrm{Rh(III)}]_T$ and [S] in the oxidation of maltose and D-galactose, the values of composite rate constants (k' for maltose and k'' for D-galactose) have been calculated at 40 °C. Almost constant values of k' and k'' throughout the variation of [NBS], $[H^+]$, $[\mathrm{Rh(III)}]_T$ and [S] in the oxidation of maltose and D-galactose, respectively clearly prove the validity of rate laws (10) and (11) and hence the proposed reaction scheme-1 (Tables 3 and 4).

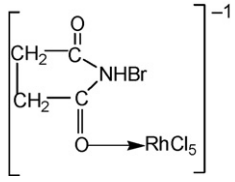
Observed positive entropy of activation in the case of both reducing sugar supports the rate determining step (iii)

Table 4
Calculated values of composite rate constants for the variations of [NBS], [H^+], [Rh(III)] and [Sugar] in the Rh(III)-catalysed oxidation of D-galactose at 40 °C.

[NBS] × 10^4 (M)	[H^+] × 10^2 (M)	[Rh(III)] × 10^9 (M)	[Sugar] × 10^2 (M)	k'' × 10^8 (s^{-1})
3.00	20.00	2.70	2.00	1.23
4.50	20.00	2.70	2.00	1.36
6.00	20.00	2.70	2.00	1.36
7.50	20.00	2.70	2.00	1.19
9.00	20.00	2.70	2.00	1.16
10.50	20.00	2.70	2.00	1.23
12.00	20.00	2.70	2.00	1.27
13.50	20.00	2.70	2.00	1.28
15.00	20.00	2.70	2.00	1.21
3.00	25.00	2.70	2.00	0.93
3.00	50.00	2.70	2.00	0.62
3.00	75.00	2.70	2.00	1.03
3.00	100.00	2.70	2.00	1.05
3.00	125.00	2.70	2.00	0.99
3.00	20.00	0.90	2.00	1.67
3.00	20.00	1.80	2.00	1.08
3.00	20.00	2.70	2.00	1.23
3.00	20.00	3.60	2.00	1.45
3.00	20.00	4.50	2.00	1.34
3.00	20.00	5.40	2.00	1.35
3.00	20.00	6.30	2.00	1.32
3.00	20.00	7.20	2.00	1.33
3.00	20.00	8.10	2.00	1.34
3.00	20.00	9.00	2.00	1.30
3.00	20.00	2.70	1.00	1.39
3.00	20.00	2.70	2.00	1.23
3.00	20.00	2.70	3.00	1.34
3.00	20.00	2.70	4.00	1.39
3.00	20.00	2.70	6.00	1.44
3.00	20.00	2.70	8.00	1.35
3.00	20.00	2.70	10.00	1.39

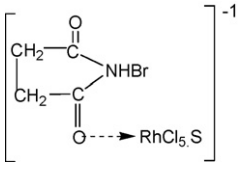
Solution conditions—For [NBS] variation: [Hg(II)] = 17.50 × 10^{-4} M; [NHS] = 17.50 × 10^{-4} M; μ = 0.25 M. For [Rh(III)] and [sugar] variations: [Hg(II)] = 3.30 × 10^{-4} M; [NHS] = 3.20 × 10^{-4} M; μ = 0.25 M. For [H^+] variation: [Hg(II)] = 3.30 × 10^{-4} M; [NHS] = 3.20 × 10^{-4} M; μ = 1.47 M.

of reaction scheme-1 where most reactive activated complex, 

, formed by the interaction of a charged species, 

and a neutral molecule (S) becomes less polar than the initial state because of being dispersed over a greater volume. The order of Arrhenius frequency factor being the same in the oxidation of both the reducing sugars, i.e., maltose and D-galactose is an evidence for the operation of single reaction mechanism in the form of reaction scheme-1.

5. Comparative studies

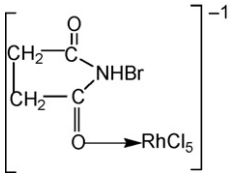
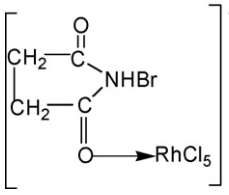
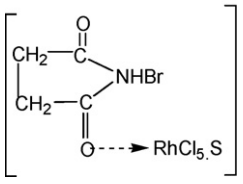
Efforts have also been made to compare the findings of this paper with the results already reported for Pd(II)-catalysed [14] oxidation of reducing sugars by NBS in acidic medium and also with the results reported for Ir(III)-catalysed [17] oxidation of reducing sugars by NBS in acidic medium. The present study being similar in orders with respect to the oxidant, shows significant change as far as order with respect to H^+ ions and Cl^- ions are concerned. Observed order with respect to H^+ ions being unity in Rh(III)-catalysed oxidation of maltose and D-galactose differs from reported Pd(II)- [14] and Ir(III) [17]-catalysed oxidation of reducing sugars where inverse fractional order has been found. The observed nil effect of [Cl^-] on the rate of oxidation is contrary to the reported negative effect of [Cl^-] in the oxidation of reducing sugars using chloro-complex of Ir(III) [17] and Pd(II) [14] as catalyst. First order kinetics in reductants throughout their 10-fold variations distinguishes the present study from the study reported for Ir(III)-catalysed [17] oxidation in which order with respect to substrates remained zero throughout their variations. The present study seems to be similar in nature with the reported [14] Pd(II)-catalysed oxidation as far as order with respect to sugar at its low concentration is concerned. The unity order in [Rh(III)] on one hand is similar to reported [14] unity order in [Pd(II)] but on the other hand, it differ slightly from reported [17] Ir(III)-catalysed oxidation where order in [Ir(III)] varies from first to zero. On the basis of kinetic results and spectrophotometric information regarding the formation of various complexes during the course of reaction, a reaction mechanism with the formation of most reactive activated complex of the type, 

is proposed.

The nature of this activated complex is entirely different form the complex $[IrCl_5{\cdot}OBr]^{3-}$ reported as most reactive in Ir(III)-catalysed [17] oxidation. Protonated NBS, i.e., N^+BSH in the form of reactive species of NBS in acidic medium makes the present study entirely different from other two studies where HOBr has been proposed as the reactive species of NBS in acidic medium. Hg(II) acts as Br^- ions scavenger not only in the present study but also in reported Pd(II)- [14] and Ir(III)-[17] catalysed oxidation. On the basis of the facts mentioned above, it can be inferred that the present study differs in many respects from the studies reported for Ir(III)- and Pd(II)-catalysed oxidation.

6. Conclusions

The following conclusions can be derived in the present study of oxidation of maltose and D-galactose by N-bromosuccinimide in acidic medium using chloro-complex of Rh(III) as homogeneous catalyst.

1. Protonated N-bromosuccinimide, N^+BSH, is the reactive species of NBS in acidic medium.
2. Chloro-complex of Rh(III), i.e. $[RhCl_5{\cdot}H_2O]^{2-}$ is the reactive species of Rh(III) chloride in acidic medium.
3. The formation of a reactive complex,  , between reactive species of NBS and reactive species of Rh(III) chloride in acidic medium is well supported by the observed kinetic data and spectral information collected in this regard.
4. The rate determining step of the proposed reaction scheme-1 involves the interaction between reactive complex,  and a neutral substrate molecule resulting in the formation of a most reactive activated complex  . This step of the proposed reaction scheme-1 is not only supported by the observed positive entropy of activation but also by the spectroscopic evidence also.
5. Hg(II) used in the reactions under investigation as Br^- scavenger did not show the role of either a co-catalyst or as an inhibitor.
6. The chloro-complex of Rh(III) is more reactive in its nano-concentration (10^{-9} M) range than its hexa (10^{-6} M), hepta (10^{-7} M) and octa (10^{-8} M) ranges.

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