Rh(III)-Catalysis in The Kinetic Studies of Oxidation of D-Xylose by N-Bromosuccinimide in Acidic Medium

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ABSTRACT

Kinetics of oxidation of D-xylose by acidic N-bromsuccinimide (NBS) in the presence of rhodium (III) chloride (Rh (III)) as homogeneous catalyst using mercuric acetate as Br^- ion scavenger have been studied at $40\,^0C$. First order kinetics was observed with respect to [NBS], [reducing sugar], [Rh (III)] and [H^+] in the oxidation of D-xylose. Nil effects for [Hg (II)], [Cl^-], [NHS] and ionic strength of the medium (μ) on the rate of oxidation were found. N^+BSH and $RhCl_3(H_2O)_3$ were postulated as the reactive species of NBS and Rh(III) in acidic medium. The main oxidation products of the reaction were identified as formic acid and threonic acid for the oxidation of D-xylose. A mechanism consistent with the kinetic data has been proposed for the corrosion of D-xylose by NBS which finds support from various activation parameters and spectroscopic evidence.

Keywords: Kinetics, oxidation, Rh (III)-catalysis, acidic medium, N-bromsuccinimide.

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INTRODUCTION

Oxidation of sugars has been carried out in acidic and alkaline medium by using various organic and inorganic oxidants. Besides fulfilling specific nutritional or physiological roles, sugars may also have therapeutic or pharmacological actions [1]. Transition metal catalyzed reactions have created great interest due to their involvement in many important industrial processes [2]. The octahedral rhodium complex, cis-dichloro bis(1,10 phenanthroline) rhodium(III) chloride (BISPHEN), is known to form covalent linkages with DNA involving the attachment of the metal to a base [3]. Antitumor activity of cisplatin, cis-[Pt(NH₃)₂Cl₂], was discovered by Rosenberg et al. and introduced an interest in the study of biological properties of transition metal complexes [4]. It is reported that the interest on the co-ordination chemistry of rhodium continues to be in accelerating pace due to interesting chemical reactivity, antitumor activity, electronic structure and catalytic functions of its complexes with potential industrial applications [5]. Rhodium(III) forms complexes with nitrogen donar ligands viz. ethylene diamine, pyridine, 2-2' bipyridine, 1,10-phenantroline, etc. which are reported to have antibacterial activity [6]. 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 [7]. The role of NBS as an oxidant in the oxidation of a large variety of organic compounds has been probed using Ru (III)[8,9], Pd(II) [10,11], Ir(III) [12,13], Pt(IV)

[14] and Fe(II) [15] as homogeneous catalysts. Literature also reveals that Rh(III) chloride has been used as catalyst in the oxidation of styrene, stilbene and phenylacetylene [16], mannitol [17] and cyclic ketones [18]. 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 [19-21] and amino acids [22]. In view of the antibacterial and antitumor activity of Rh (III) complexes, and specific nutritional or physiological roles and therapeutic or pharmacological actions of sugars, and also in view of biological and industrial activity of NBS, the present study in the form of the oxidation of D-xylose by NBS in acidic medium has been undertaken.

MATERIALS AND METHODS

Preparation of solutions: An aqueous solution of NBS (E. Merck) was prepared afresh by dissolving a weighed amount in doubly distilled water. The solution was standardized iodometrically against standard solution of sodium thiosulphate using starch as an indicator. The reaction mixture was prepared in a black-coated vessel to avoid photochemical deterioration. The solution of Rh (III) chloride (E. Merck) was prepared by dissolving the sample in hydrochloric acid of known strength and its strength was found 3.78 x 10^{-3} mol L^{-1}. Aqueous solution of D- Xylose was prepared daily by dissolving a weighed amount in doubly distilled water. A standard solution of mercuric acetate (E. Merck) was acidified with 20 % acetic acid. All other standardized solutions of KCl, $NaClO_4$ and succinimide (E. Merck) were prepared with doubly distilled water.

Method of study: The reactants i.e. NBS, Hg $(OAc)_2$, HCl , KCl, $NaClO_4$, NHS (succinimide) and Rh(III), were mixed in a black coated conical flask and thermostated at $40^{o}C\pm1.0$ for thermal equilibrium. A measured amount of sugar solution, also equilibrated at the same temperature, was added rapidly to the reaction mixture. As soon as the sugar solution was mixed with the reaction mixture the reaction gets initiated. To know the actual progress of the reaction, 5ml of the reaction mixture was taken out and poured in a conical containing 5ml of KI (4%) solution and 5ml of $HClO_4$ solution and was titrated iodometrically against standard hypo solution using starch as indicator.

Stoichiometry: In order to find out the total amount of oxidant (NBS) consumed by one mole of substrate (D-xylose), different sets of experiments were performed with varying [NBS]:[xylose] ratios under the condition   [NBS] >>[xylose]. Estimation of unconsumed NBS indicated that two mole of NBS were consumed to oxidize one mole of xylose. Accordingly, the following stoichiometric equation is suggested:
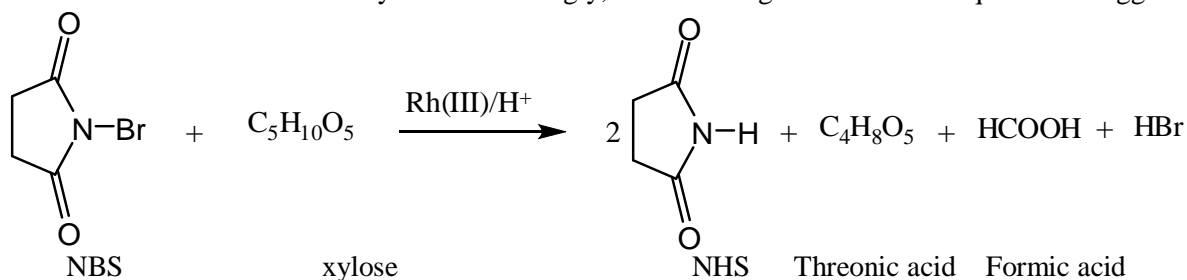
RESULTS AND DISCUSSION

Kinetics of oxidation of D-xylose using chloro-complex of Rh (III) in its nano-concentration range as homogeneous catalyst have been investigated at 40^{0} C for the first time. The initial rate i.e (–dc/dt) of reaction in each kinetic run was calculated by the slope of the tangent drawn at fixed concentration of NBS. The pseudo- first-order rate constant (k_1) was calculated as -

$$K_1 = \frac{-dc/dt}{[NBS]}$$

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The reactions was studied at different initial [NBS] and at fixed concentration of all other reactants. The values of first-order rate constant (k_1) thus obtained are recorded in table 1. It is clear from the data given in table 1 that throughout the variation of NBS, the rate of the reaction increases in the same proportion in which the concentration of NBS is increased, which leads to the conclusion that the order of reaction with respect to [NBS] is one. This result is further verified by the straight lines passing through the origin in the plots of -dc/dt versus [NBS] in the oxidation of D-Xylose (Fig.1). The observed pseudo first-order rate constant (k_1) was found to be directly proportional to the [Rh (III)] indicating first order kinetics with respect to [Rh (III)] (Table 1). A straight line passing through the origin (Fig. 2) obtained from the plot of k_1 versus [Rh (III)] further confirms the first-order dependence of the reaction on [Rh (III)] and, at the same time, it indicates that the reaction does not proceed with measurable velocity in the absence of catalyst Rh (III).
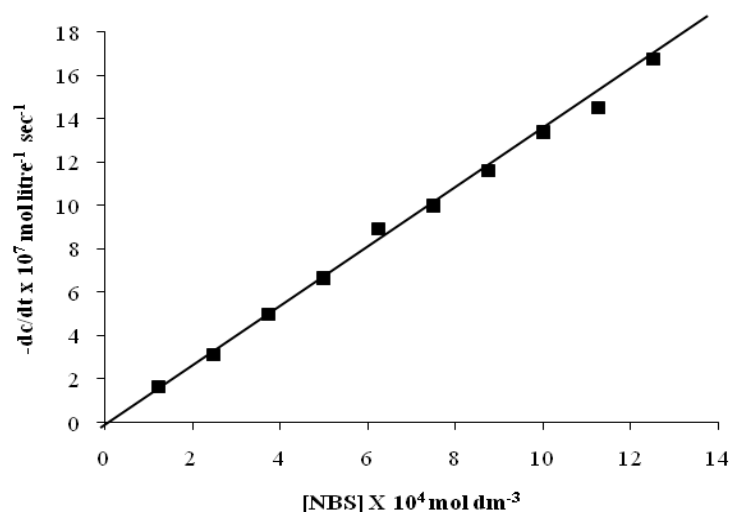

Fig. 1: Plot between –dc/dt and [NBS] at 40°C

[Sugar] = 2.00×10^{-2} M, [RhCl$_3$.3H$_2$O] = 3.03×10^{-9}M, [HCl] = 20.00×10^{-2}M [Hg(OAc)$_2$] = 26.30×10^{-4} M, [NHS] = 12.80×10^{-4}M, μ = 0.30 M

Table 1: The observed values of first order rate constants (k_1) for the variations of [NBS], [Rh(III)] and [D-Xylose] in the Rh(III)-catalyzed oxidation of D-Xylose at 40^0C.

[NBS]x10^4 (mol dm^{-3})	[Rh(III)x10^9 (mol dm^{-3})	[D-Xylose]x10^3 (mol dm^{-3})	[H$^+$]x10^2 (mol dm^{-3})	K_1x10^4 (sec^{-1})
1.25	3.03	20	20	1.33
2.50	3.03	20	20	1.25
3.75	3.03	20	20	1.33
5.00	3.03	20	20	1.33
6.25	3.03	20	20	1.43
7.50	3.03	20	20	1.33
8.75	3.03	20	20	1.33
10.00	3.03	20	20	1.34
11.25	3.03	20	20	1.29
12.50	3.30	20	20	1.34
2.50	0.75	20	20	3.96
2.50	1.52	20	20	7.32
2.50	2.27	20	20	11.44
2.50	3.03	20	20	14.96
2.50	4.55	20	20	22.00
2.50	5.31	20	20	27.48
2.50	6.06	20	20	30.80
2.50	7.58	20	20	39.60
2.50	3.03	10	20	7.92
2.50	3.03	20	20	14.64
2.50	3.03	30	20	22.00
2.50	3.03	40	20	30.80
2.50	3.03	50	20	39.60
2.50	3.03	80	20	61.60
2.50	3.03	90	20	70.40
2.50	3.03	100	20	79.20
2.50	3.03	20	25	5.48
2.50	3.03	20	50	9.52
2.50	3.03	20	75	13.20
2.50	3.03	20	100	18.68
2.50	3.03	20	125	26.40

[Hg(OAc)$_2$] = 2.63×10^{-4} M (for sugar, Rh(III) and H$^+$ variations) and 26.3×10^{-4} M (for NBS variation), NHS] = 2.56×10^{-4} M (for sugar, Rh(III) and H$^+$ variations) and 12.80×10^{-4} M (for NBS variation) and μ = 030 M M (for sugar, Rh(III) and NBS variations) and 1.50 M (for H$^+$ variation)
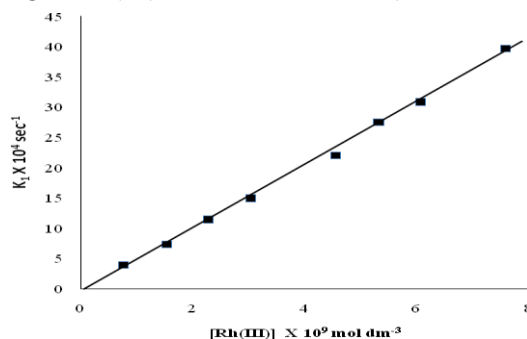
Fig. 2: Plot between k_1 and [Rh(III)] at 40°C
[NBS] = 2.50×10^{-4}M, [Substrate] = 2.00×10^{-2}M, [HCl] = 20.00×10^{-2}M ,[Hg(OAc)$_2$] = 2.63×10^{-4} M, [NHS] = 2.56×10^{-4} M, μ = 0.30 M

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Unity order in substrate up to nearly its 10-fold variation was observed (Fig. 3, Table 1). The concentration of H^+ ions in the oxidation of D-xylose was varied keeping the concentrations of all other reactants constant at constant temperature 40 °C. The observed pseudo first-order rate constants were found to be directly proportional to $[H^+]$, indicating first-order kinetics with respect to $[H^+]$ (Table 1, Fig.4). Kinetic results show negligible effects of variations of $[Hg(II)]$, $[Cl^-]$, $[NHS]$ and the ionic strength (μ) of the medium, on the rate of oxidation of D-xylose. The values of first-order rate constant, k_1, observed at temperatures 30°C, 35°C, 40°C and 45°C, were used to calculate various activation parameters(Table 2).
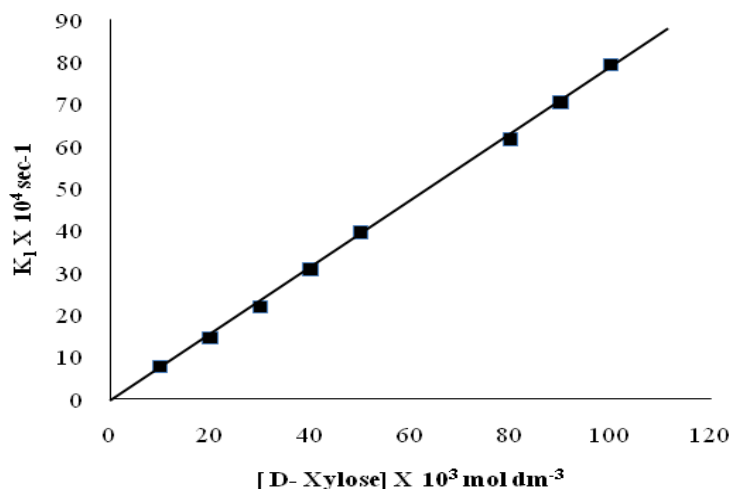
Fig. 3: Plot between k_1 and [Substrate] at 40°C

$[NBS] = 2.50 \times 10^{-4}$ M, $[RhCl_3.3H_2O] = 3.03 \times 10^{-9}$M, $[HCl] = 20.00 \times 10^{-2}$M $[Hg(OAc)_2] = 2.63 \times 10^{-4}$ M, $[NHS] = 2.56 \times 10^{-4}$M, $\mu = 0.30$ M
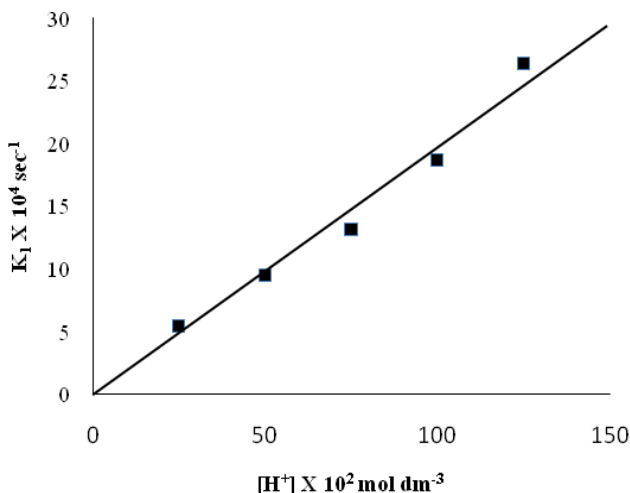

Fig4 : Plot between k_1 and $[H^+]$ at 40°C

$[NBS] = 2.50 \times 10^{-4}$M, $[RhCl_3.3H_2O] = 3.03 \times 10^{-9}$M, $[Substrate] = 2.00 \times 10^{-2}$M, $[Hg(OAc)_2] = 2.63 \times 10^{-4}$ M, $[NHS] = 2.56 \times 10^{-4}$ M, $\mu = 1.50$ M

**Table 2:** Activation parameters of Rh(III)-catalyzed oxidation of D-xylose by NBS in acidic medium

E_a (KJ mol^{-1})	k_r (mol^{-3} lit^3 sec^{-1})	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	$\Delta H^{\#}$ (JK^{-1} mol^{-1})	$\Delta G^{\#}$ (JK^{-1} mol^{-1})	A (mol lit^3 sec^{-1})
38.49	1.49x10^{-3}	-184.42	35.86	93.59	3.65x10^3

In the light of above kinetic findings, the following rate law can be proposed for the reaction under investigation

$$\frac{-d[NBS]}{dt} = k^{'}[NBS][Rh(III)]_T[S][H^+] \qquad (I)$$

Where $k^{'}$ is composite rate constant.

For a variety of substrates in both acidic and alkaline medium, N-bromsuccinimide has not only been reported [10,23,24] to act as an oxidant but also has been used as a source of positive halogen. These reports indicate that the N-Bromosuccinimide exists in acidic medium in the form of following equilibria:
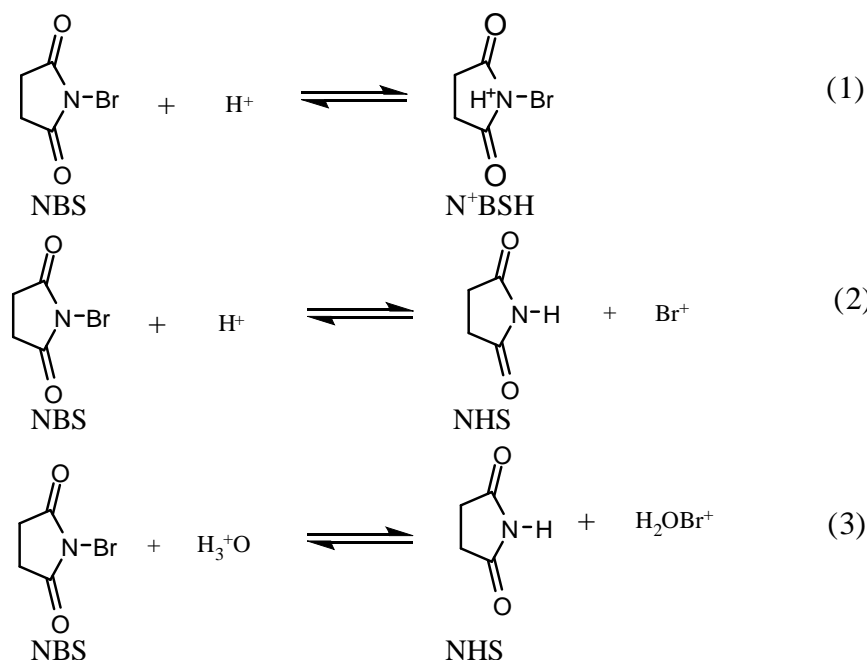
Above equilibria clearly show that NBS in acidic medium exists in four different forms i.e. NBS itself, Br$^+$, NHBr$^+$, NHS and (H$_2$OBr)$^+$. Out of these possible oxidizing species, the real reactive species of NBS in the present investigation has been decided on the basis of observed kinetic data 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$_2$OBr$^+$ 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 D-xylose 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 two different concentrations of H$^+$ ions, where an increase in absorbance with the increase in [H$^+$] was observed. The observed increase in absorbance from 0.88 to 1.84 at 230 nm on increasing [H$^+$] clearly provides support for the existence of following equilibrium in the reaction under investigation (Fig.5(1,2)).

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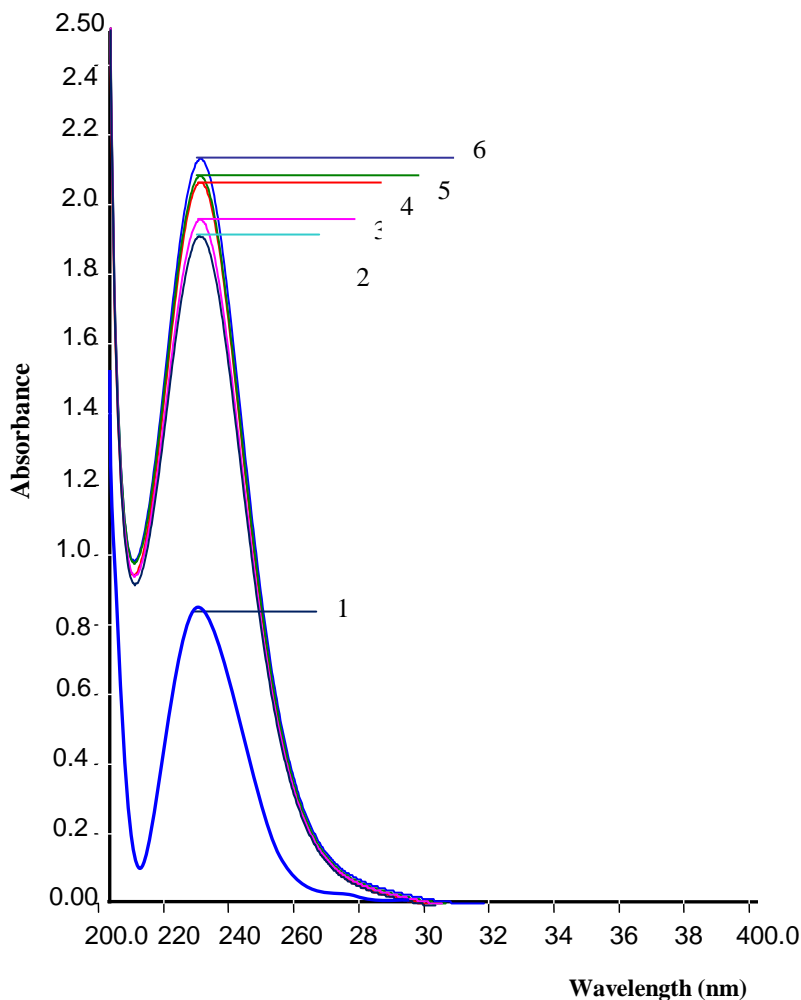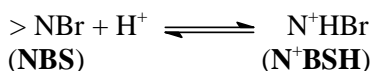**Fig. 5:** Spectra for various solutions of NBS, Rh(III), H$^+$ and D-xylose

(1). [NBS = 1.0 x 10^{-4} M,
       [H$^+$] = 0.3 M

(2). [NBS] = 1.0 x 10^{-4} M
       [H$^+$] = 1.2 M

(3). [NBS] = 1.0 x 10^{-4} M
       [H$^+$] = 0.3 M
       [Rh(III)] = 2.8 x 10^{-5} M

(4). [NBS] = 1.0 x 10^{-4} M
       [H$^+$] = 0.3 M
       [Rh(III)] = 5.6 x 10^{-5} M

(5). [NBS] = 1.0 x 10^{-4} M
       [H$^+$] = 0.3 M
       [Rh(III)] = 2.8 x 10^{-5} M
       [D-Xylose] = 20.0 x 10^{-3} M

(6). [NBS] = 1.0 x 10^{-4} M
       [H$^+$] = 0.3 M
       [Rh(III)] = 2.8 x 10^{-5} M
       [D-Xylose] = 50.0 x 10^{-3} M

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

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 D-Xylose in acidic medium.

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Wolsey et al. [25] have described the preparation of various complexes formed between rhodium (III) and chloride ion in dilute hydrochloric acid solution, and the isolation and characterization of these complexes by the ion exchange technique. In addition, the spectra of these complexes in aqueous solution have been determined and utilized for the calculation of successive formation constants by the aforesaid workers. In these solutions the chloride ion content varied from 0.002 M to 6.0 M. The spectra of the solutions have been collected which showed shifts of the absorption maxima towards longer wavelengths with increasing chloride concentration. At 0.2 M HCl solution, the predominant species was found as $[RhCl_5]^{2-}$ and at 2 M and above the predominant species was found as $[RhCl_6]^{3-}$ In the year 1966, an attempt has been made by James and Remple [26] have performed experiments with the complexes prepared from the $[Rh(H_2O)_6]^{3+}$ solution and reported that the activities of the anionic complexes decrease in the following order:

$$RhCl_6^{3-} > Rh(H_2O)Cl_5^{2-} > Rh(H_2O)_2Cl_4^{1-}$$
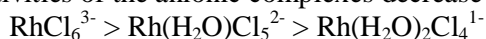
These workers have found that $RhCl_3$ in 3–5 M HCl solutions exists mainly in the form of $[Rh(H_2O)Cl_5]^{2-}$. Their findings are contrary to the results reported by Harrod and Halpern [27], who had observed that $[RhCl_6]^{3-}$ is the predominant species of $RhCl_3$ in 3–5 M HCl solutions. In the study regarding hydration of acetylenes catalyzed by Rh(III) chloride complexes, James and Remple [28] have observed that the activity of the $[Rh(H_2O)Cl_5]^{2-}$ species in 0.2 M HCl–5.80 M $HClO_4$ is about twice that in the 3 M HCl media and this is likely due to an increase in the C_2H_2 solubility by about 2. According to them, the cationic species show no reactivity and neutral $[RhCl_3 (H_2O)_3]$ species shows reactivity and this reactivity increases to a maximum for a solution containing 5:1chloro species. They have further observed that the hexachloro complex is very much less active. It is also reported [29] that on boiling aqueous solutions of the trichloride, $[Rh (H_2O)_6]^{3+}$ is formed and with excess HCl, the rose pink hexachlororhodate ion, $[RhCl_6]^{3-}$ is obtained. Between these two species there are clearly several intermediates. In aquation, $[RhCl_6]^{3-}$ produces $[RhCl_5 (H_2O)]^{2-}$, Cis-$[RhCl_4(H_2O)_2]^{1-}$ and face $RhCl_3(H_2O)_3$. In the present study, Rh (III) chloride has been used as homogeneous catalyst in the oxidation of the D-xylose by NBS in acidic medium. The solution of rhodium (III) chloride was prepared in solution of hydrochloric acid where the concentration of HCl was maintained at 3M. On the basis of reported [18,30-33] literature, it can be inferred that at 3M HCl, the lone species $[RhCl_6]^{3-}$ is present in the solution of rhodium(III) chloride at the time of its preparation, which can very easily be converted into $[RhCl_5(H_2O)]^{2-}$, $[RhCl_4(H_2O)_2]^{1-}$ and $RhCl_3(H_2O)_3$ with the dilution. It is reported that in between 0.07 M and 2.0 M $[Cl^-]$, the various species present are $[RhCl_4]^{1-}$, $[RhCl_5]^{2-}$ and $[RhCl_6]^{3-}$ $RhCl_3$ is reported as the single species at 0.035 M $[Cl^-]$ whereas $[RhCl]^+$ and $[RhCl]^{2+}$ are reported as the existing species at 0.02 M and 0.01 M respectively. Since throughout the study the concentration of Cl^- ion is maintained at 20×10^{-2} M hence it is reasonable to assume that neutral species $RhCl_3(H_2O)_3$ is the reactive species of Rh(III) chloride in acidic medium. Our assumption finds further support from observed kinetic data and spectral information collected in this regard.

To ascertain the formation of possible complex or complexes during the course of reaction, spectra were collected by using Perkin Elmer lambda 35 UV-vis spectrophotometer for different acidic solutions of NBS, Rh(III), and reducing sugar either alone or in the form of mixture. Spectra for NBS solutions with two different concentrations of H^+ ions were taken. It is evident from the spectra that with the increase in concentration of H^+ ion there is increase in the absorbance from 0.88 to 1.84 at 230 nm (Fig. 5((1) and (2)). This gives support to the existence of protonated NBS i.e. N^+BSH as the reactive species of NBS in acidic medium. We also collected the spectrum for acidic solution of Rh (III) chloride where single peak was observed which shows the existence of lone neutral species $RhCl_3 (H_2O)_3$ as the reactive species of Rh(III) chloride in acidic medium. Further, when Rh (III) chloride solution of two different concentrations were added to the acidic solution of NBS it was observed that with the addition of Rh(III) chloride solution, there is an increase in absorbance from 0.88 to 1.89 and 2.00 at 230 nm (Fig.5 (1,3 and 4)), which can be assigned to the existence of equilibrium step (i) proposed in the reaction scheme 1.
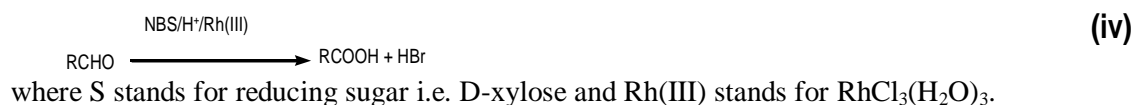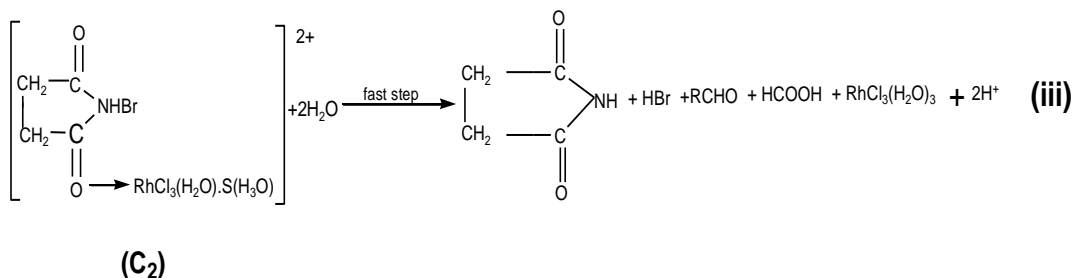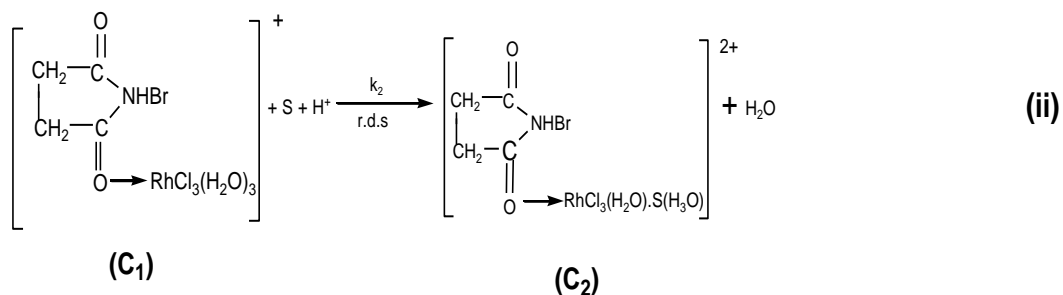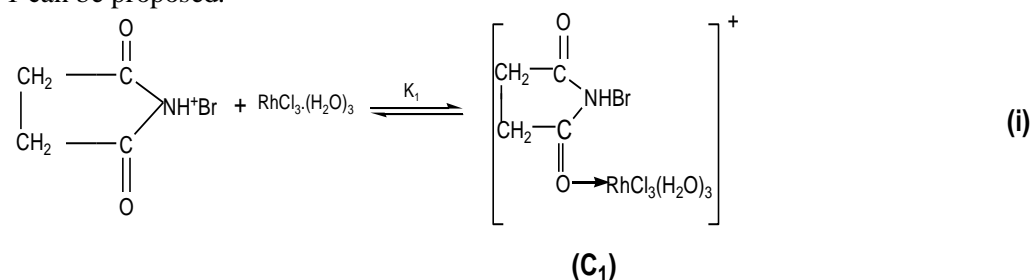
On the basis of observed kinetic data, an effort was also made to ascertain the formation of a complex between a complex formed as a result of interaction between reactive species of Rh(III) chloride and acidic

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solution of N-bromsuccinimide and a reducing sugar molecule. When reducing sugar solution of two different concentration was added to the solution of NBS, H^+ and Rh(III), a substantial increase in absorbance was noted (Fig. 5 (4,5 and 6)) This indicates the formation of an unstable activated complex,
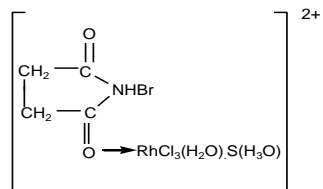
in the reactions under investigation as shown in a slow and rate determining step (ii) of reaction scheme 1.

On the basis of observed kinetic orders, spectroscopic information collected for the possible formation of complex or complexes in the reaction and taking cognizance of the fact that the observed entropy of activation is negative; a probable reaction path for the oxidation of xylose by NBS in acidic medium in the form of scheme 1 can be proposed.

(i)

(C$_1$)

(ii)

(C$_1$)   **(C$_2$)**

(iii)

(C$_2$)

(iv)

where S stands for reducing sugar i.e. D-xylose and Rh(III) stands for $RhCl_3(H_2O)_3$.

Reaction Scheme1

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

$$\text{rate} = \frac{-\,d[NBS]}{dt} = 2k_2[C_1][S][H^+] \tag{1}$$

On applying the law of chemical equilibrium to step-(I), we have

$$K_1 = \frac{[C_1]}{[N^+BSH][Rh(III)]}$$

$$\text{or} \qquad [C_1] = K_1[N^+BSH][Rh(III)] \tag{2}$$

With the help of equations (1) and (2), we can get

$$\text{rate} = \frac{-\,d[NBS]}{dt} = 2K_1k_2[N^+BSH][Rh(III)][S][H^+] \tag{3}$$

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

$$[Rh(III)]_T = [Rh(III)] + [C_1]$$

$$\text{or} \qquad [Rh(III)]_T = [Rh(III)] + K_1[N^+BSH][Rh(III)]$$

$$\text{or} \qquad [Rh(III)]_T = [Rh(III)]\{\,1 + K_1[N^+BSH]\}$$

$$\text{or} \qquad [Rh(III)] = \frac{[Rh(III)]_T}{1 + K_1[N^+BSH]} \tag{4}$$

On substituting the value of free concentration of Rh(III) i.e. [Rh(III)] from equation (4) to equation (3), we get

$$\text{rate} = \frac{-\,d[NBS]}{dt} = \frac{2K_1k_2[N^+BSH][Rh(III)]_T[S][H^+]}{1 + K_1[N^+BSH]} \tag{5}$$

Since, total [NBS] in the solution remains in the form of [N$^+$BSH], hence it is reasonable to assume that

$$[NBS] = [N^+BSH]$$

Now, under the condition indicated above, equation (5) showing the relationship between the rate of reaction and concentration of reaction components can be written as

$$\text{rate} = \frac{-\,d[NBS]}{dt} = \frac{2K_1k_2[NBS][Rh(III)]_T[S][H^+]}{1 + K_1[NBS]} \tag{6}$$

Since the concentration of NBS throughout the experiments was very very small in comparison to [S], hence under this condition the inequality $K_1[NBS]\ll 1$ can be assumed as valid one. With the inequality indicated above, equation (6) will be reduced to equation (7) as demonstrated earlier

$$\text{rate} = \frac{-\,d[NBS]}{dt} = nK_1k_2[NBS][Rh(III)]_T[S][H^+] \tag{7}$$

Equation (7) is the rate law which is strictly in accordance with observed first-order kinetics with respect to each [NBS], [S], [Rh(III)]$_T$ and [H$^+$].

Equation (7) can be written in the following way

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

where k' is $2K_1k_2$ for the oxidation of D-xylose.

According to equation (8), the values of composite rate constant (k') were calculated for the variation of [NBS], [S] and [Rh(III)] in the oxidation of aforesaid reducing sugar at 40ºC under uniform condition and are presented in Table 3 . Almost constant values of composite rate constant (k') clearly show the validity of rate law (7) and (8) and hence the proposed reaction scheme-1.

Table 3: The calculated values of composite rate constants (k') for the variations of [NBS], [Rh(III) and [Substrate] in the Rh(III)-catalyzed oxidation of D-xylose at 40^OC.

[NBS]x10^4 (mol dm^{-3})	[Rh(III)x10^9 (mol dm^{-3})	[Subsrate]x10^3 (mol dm^{-3})	k'x10^8 (sec^{-1})
1.25	3.03	20	1.09
2.50	3.03	20	1.03
3.75	3.03	20	1.10
5.00	3.03	20	1.10
6.25	3.03	20	1.10
7.50	3.03	20	1.10
8.75	3.03	20	1.09
10.00	3.03	20	1.10
11.25	3.03	20	1.06
12.50	3.30	20	1.10
2.50	0.75	20	1.32
2.50	1.52	20	1.20
2.50	2.27	20	1.25
2.50	3.03	20	1.23
2.50	4.55	20	1.20
2.50	5.31	20	1.29
2.50	6.06	20	1.27
2.50	7.58	20	1.30
2.50	3.03	10	1.32
2.50	3.03	20	1.20
2.50	3.03	30	1.20
2.50	3.03	40	1.26
2.50	3.03	50	1.30
2.50	3.03	80	1.26
2.50	3.03	90	1.28
2.50	3.03	100	1.30

Reaction scheme-1 finds further support from Job's plot [34], where $1/\Delta A$ values were plotted against $1/[S]$ (Fig.6). For the calculation of ΔA values, spectra for solution of Rh(III), H^+ and NBS with varying concentration of reducing sugar were collected. The values of ΔA was collected by the difference in absorbance of solutions of Rh(III), H^+ and NBS with and without reducing sugar. The straight lines with positive intercept obtained for the oxidation of D-xylose clearly support the rate determining step (i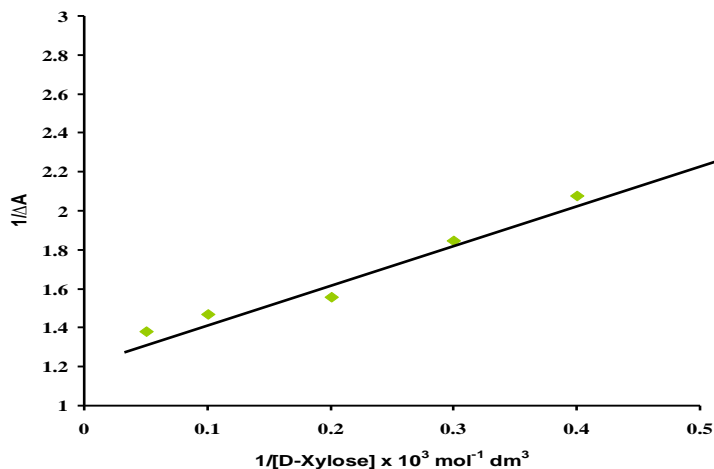i) of reaction scheme-1, where formation of 1:1 complex, by the interaction of a complex , and a sugar molecule (S) is indicated (Fig.6).
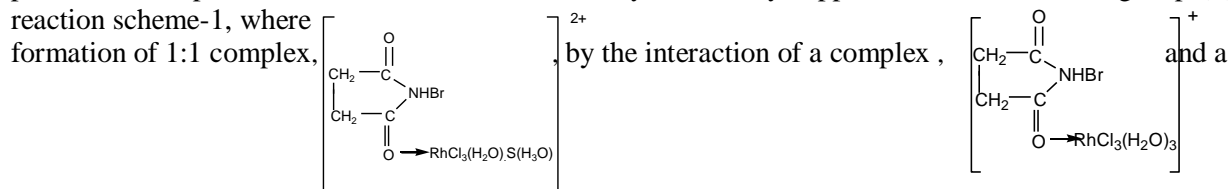
Fig.6: Plot between $1/\Delta A$ and $1/$[D-Xylose]

It is known fact [35] that reactions for ions of opposite charges there is generally an increase in entropy in going from reactant to activated complex and for ions of like charges, there is an entropy decrease. Observed negative entropy of activation of oxidation of D-Xylose clearly supports reaction scheme- 1, where in the rate determining step the interaction in between two similarly charged species result in the formation of very reactive complex, which in the fast process converts in to reaction products with
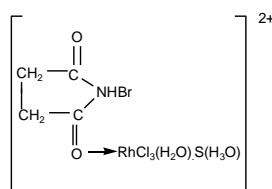
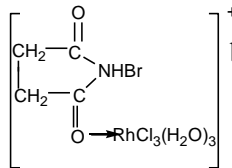regeneration of catalyst $RhCl_3 \cdot (H_2O)_3$.

APPLICATIONS

On the basis of observed kinetic orders, spectroscopic information collected for the possible formation of complex or complexes in the reaction and taking cognizance of the fact that the observed entropy of activation in each case is negative, a probable reaction path in the form of scheme 1 has been proposed.

CONCLUSIONS

The following conclusions can be drawn from the observed kinetic data as well as the spectroscopic information for Rh(III)-catalysed oxidation of D-xylose by NBS in acidic medium.
1. Protonated N-bromosuccinimide, N^+BSH, is the reactive species of NBS in acidic medium.
2. Chloro-complex of Rh(III), i.e. $[RhCl5 \cdot H2O]2-$ 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, , H$^+$ 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 negative 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.

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