Kinetics Of Oxidation Of Trehalose By Protonated N-Bromosuccinimide Using Rh (III) Chloride As Homogeneous Catalyst

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ABSTRACT

The kinetic oxidation of D(+) trehalose (tre) by protonated N- bromsuccinimide (NBS) i.e. N^+BSH in presence of Rh(III) as homogeneous catalyst using $Hg(OAc)_2$ as bromide ions scavenger have been investigated at 45°C. The reaction shows first order kinetics with respect to Rh (III) throughout is variation. First order kinetics was observed with respect to lower [NBS], [trehalose] and $[H^+]$, but tends towards zero order at their higher concentrations. Nil effects of [Hg $(OAc)_2$], [succinimide], $[Cl^-]$ and ionic strength of medium were observed. Protonated N-bromsuccinimide, N^+BSH, and chloro complex of Rh(III) i.e. $[RhCl_5(H_2O)]^{2-}$, have been postulated as the reactive species of NBS and Rh(III) chloride in acidic medium respectively. On the basis of observed kinetic data, spectrophotometric evidence and various activation parameters calculated at four different temperatures, a suitable reaction mechanism has been proposed for the Rh(III)- catalyzed oxidation of D(+) trehalose by NBS in acidic medium. The main oxidation products were identified as arabinonic acid and formic acid for the aforesaid reaction.

Keywords: Kinetics, Trehalose, Oxidation, Protonated N-bromsuccinimide, Rh (III)- Catalysis.

INTRODUCTION

N-halogen compounds [1-7], such as N-bromoacetamide (NBA), N-bromsuccinimide (NBS), N-chloro succinimide (NCS) are reported to have diverse chemistry due to their ability to act as source of halonium cations, hypohalite species, nitrogen anions. Literature [8] reveals that the use of NBS has been made in the reactions of biological and industrial interest viz. oxidation of psychotropic drugs, oxidative degradation of α-amino acids, in the study of peptide cleavage, in the fragmentation of high molecular weight peptides and proteins etc. The role of NBS as an oxidant in the oxidation of a large variety of organic compound has been proved using Ru(III) [9-11], Pd(II) [12-14], Ir(III) [15,16], Pt (IV) [17] and Fe (II) [18] as homogeneous catalysts. The coordination chemistry of Rh (III) [19] has drawn considerable attention due to their chemical reactivity, anti-tumor activity, electronic structure and catalytic function of its complexes with potential industrial application. Oxidation of various reducing sugars by N-halo compounds in the presence of Rh (III)-chloride as homogeneous catalyst in acidic medium [20, 21, 22] have been reported. Till date no report is available on the oxidation of trehalose by NBS in acidic medium using Rh (III) as homogeneous catalyst, the present study has been undertaken.

MATERIALS AND METHODS

Preparation of solutions: A fresh solution of NBS (E. Merck) was prepared daily by dissolving its known weight in double distilled water and its concentration was estimated iodometrically. The solution of Rh(III) chloride was prepared by dissolving sample (E. Merck) in 3M HCl and its concentration was calculated as 3.8×10^{-3}M. Aqueous solution of trehalose (Himedia) was prepared fresh daily. All other standard solutions i.e. HCl, perchloric acid, sodium perchlorate, mercuric acetate (acidified with 20% acetic acid), succinimide, were prepared in double distilled water.

Method of study: The reaction mixture containing appropriate amount of all the reactants i.e. NBS, hydrochloric acid, Rh(III)-chloride, $Hg(OAc)_2$, $NaClO_4$, NHS and water, except substrate i.e. trehalose, was taken in a black coated conical flask to prevent any photochemical reaction, was placed in a thermostatic water bath at constant temperature 45ºC with an accuracy of ± 0.1ºC and the fresh solution of the substrate was also kept in a separate conical flask in the same water bath at the same temperature. After half an hour when reaction mixture had attained the temperature of bath, required amount of substrate solution was taken out by the help of a pipette and was poured in the reaction mixture to initiate the reaction. As soon as half of the volume of substrate solution was passed out from the pipette into the reaction mixture, the watch was started to record time. The progress of the reaction was monitored by estimating remaining amount of NBS concentration at regular time intervals against standard solution of sodium thiosulphate using starch as an indicator. The initial rates were calculated from the slope of the graph made between remaining concentration of NBS and time in initial stages of reaction.

Stoichiometry and product analysis: Different sets of experiments were performed with different [NBS]:[trehalose] ratios under the condition [NBS]>> [trehalose]. The estimation of unconsumed NBS showed that one mole of trehalose is oxidized by four moles of NBS. On the basis of equivalence and kinetic studies and also the spot test and thin layer chromatography experiments performed for the confirmation of formic acid, it can be inferred that arabinonic acid and formic acid are the oxidation products of the reaction under investigation. On the basis of above information and also on the basis of observed kinetic data together with spectrophotometric evidence collected for the redox systems, the stoichiometric equation for NBS oxidation of D(+) trehalose can be written as:
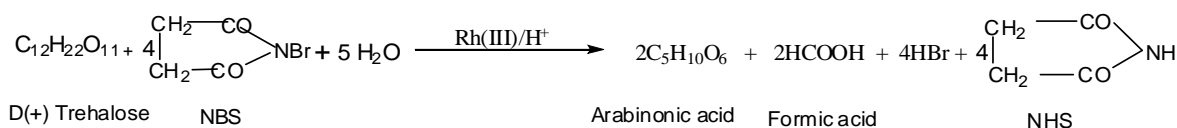
RESULTS AND DISCUSSION

The kinetic studies for Rh (III)-catalyzed oxidation of D(+) trehalose by NBS in acidic medium have been made at 45° C at several initial concentrations of each reactant . Initial rate i.e. –dc/dt of reaction in each kinetic run was calculated by the slope of tangent drawn at fixed concentration of NBS. The pseudo-first-order rate constant k_1, was calculated as:

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

The reaction kinetics shows first-order at lower concentration of NBS which tend towards zero-order at its higher concentration (Fig.1). When the effect of Rh (III)-chloride concentration was studied on the rate of reaction at constant concentration of all other reactants at 45ºC, the rate showed a linear dependence on

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concentration of Rh (III) (Fig.2). The reaction also shows first-order kinetics with respect to [trehalose] and [H^+] at their lower concentrations which changes to zero-order at higher concentrations (Fig. 3 and 4). Nil effects of [Hg (II)], [NHS], and [Cl^-] on the rate of oxidation was found. Ionic strength and dielectric constant of the medium did not influence the rate. The reaction has been studied at four different temperatures and by using the obtained k_1 values, the activation parameter i.e. $\Delta G^\#$, $\Delta H^\#$, A and $\Delta S^\#$ have been calculated and presented in table 1.
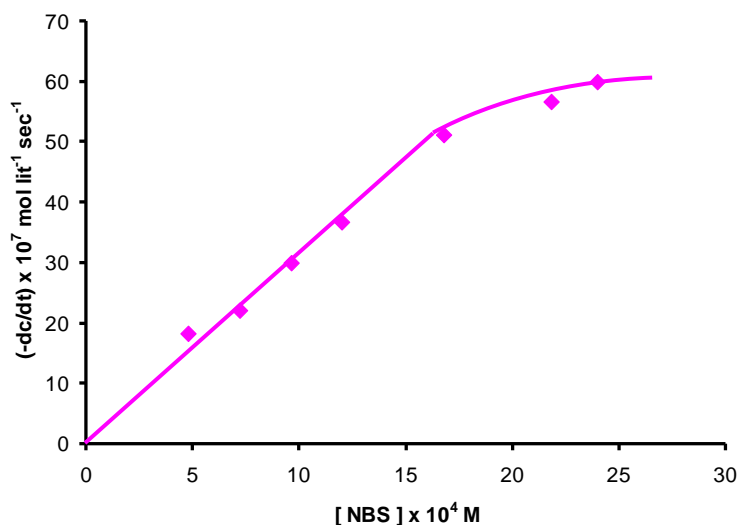
Fig.1: Plot between –dc/dt and [NBS] at 45^{0}C

[D(+) Trehalose]=2.00×10^{-2} M, [RhCl$_3$]= 8.40×10^{-8} M, [HCl] = 0.20 M, [NHS] =24.50×10^{-4} M,[Hg(OAc)$_2$] = 24.50×10^{-4} M, μ = 0.30M

Table1. Activation parameters for Rh(III)-catalyzed oxidation of trehalose
by NBS in acidic medium at 45°C

Reducing substrate	E$_a$(kCalmol^{-1})	k$_r$ (mol^{-3}lit^{3}sec^{-1})	Δ H$^\#$ (kCalmol^{-1})	Δ G$^\#$ (kCalmol^{-1})	Δ S$^\#$ (eu)	A (mol^{-3}lit^{3}sec^{-1})
D(+)Trehalose	15.20	1.14×10^7	14.56	8.38	19.45	2.74×10^{17}
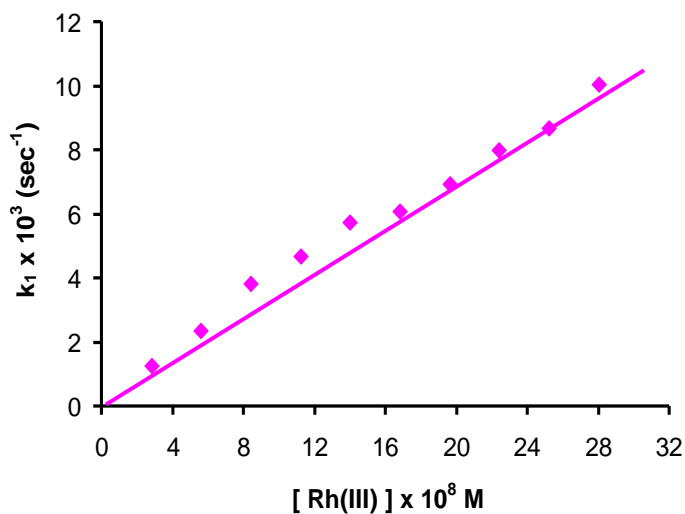
Fig.2: Plot between k_1 and [RhCl$_3$] at 45^{0}C

[NBS] =4.80×10^{-2} M, [D(+) Trehalose]=2.00×10^{-2} M, [[HCl] = 0.20 M, [NHS] =4.90× 10^{-4} M, [Hg(OAc)$_2$] = 4.90× 10^{-4} M, μ = 0.30M
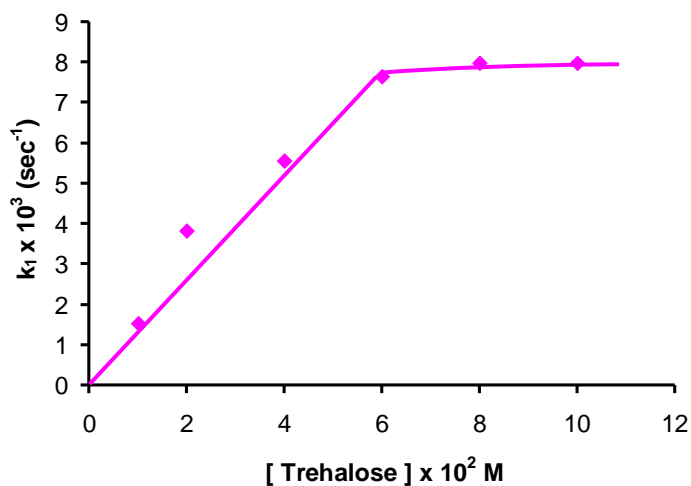
Fig.3: Plot between k_1 and [D(+) Trehalose] at 45^{0}C

[NBS] =4.80×10^{-2} M,[RhCl$_3$]= 8.40× 10^{-8} M,, [[HCl] = 0.20 M, [NHS] =4.90× 10^{-4} M, [Hg(OAc)$_2$] = 4.90× 10^{-4} M, μ = 0.30M
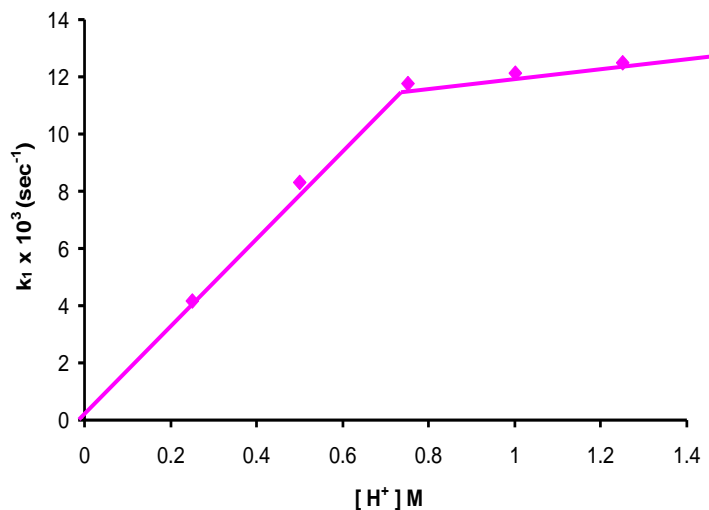
Fig.4: Plot between k_1 and [H$^+$] at 45^{0}C
[NBS] =4.80×10^{-2} M, [RhCl$_3$]= 8.40×10^{-8} M,, [D(+) Trehalose]=2.00×10^{-2} M,
[NHS] =4.90×10^{-4} M,[Hg(OAc)$_2$]= 4.90×10^{-4} M, μ = 1.50M

N-Bromosuccinimide (NBS) is a source of positive halogen and this reagent has been exploited as an oxidant for a variety of substrates in both acidic and alkaline medium [23]. The nature of active oxidizing species and the mechanism depends on the nature of the halogen atom, the groups attached to the nitrogen and the reaction condition. The species responsible for such oxidizing character may be different depending on the pH of the medium. In acidic media NBS is known [23-25] to exist in three different forms, viz. NBS itself, Br$^+$ or N$^+$BSH, in the following way

$$NBr + H^+ \rightleftharpoons N^+HBr \qquad\qquad (A)$$
(NBS)   (N$^+$BSH)

$$NBr + H^+ \rightleftharpoons NH + Br^+$$
(NBS)   (NHS)   (B)

Equilibria (A) and (B) indicated above clearly show that NBS itself, Br$^+$ or N$^+$BSH may be taken as the reactive species of NBS in acidic medium. The observed kinetic data show negligible effect of [NHS] on the rate of oxidation of D(+) trehalose. This clearly ruled out the possibility of being Br$^+$ as the reactive species of NBS in the present investigation. On the other hand if N$^+$BSH is taken as the reactive species of NBS , it will lead to a positive effect of [H$^+$] on the rate of oxidation which is in accordance with the observed positive effect of [H$^+$] on the rate of oxidation . Thus out of the species i.e. NBS itself, Br$^+$ and N$^+$BSH, the only choice left before us is to choose N$^+$BSH as the reactive species of NBS for the oxidation of trehalose in acidic medium which will satisfy the fractional positive order with respect to [H$^+$] and nil effect with respect to [NHS]. This conclusion finds further support from the spectra obtained with the help of Varian Cary 300 Bio UV-VIS spectrophotometer for various solutions of NBS with different [H$^+$] where single peak was observed at 232 nm. When spectra for NBS solution with two different [H$^+$] were taken, it is observed that there is increase in absorbance from 2.403 to 2.914 (Fig. 5 (1, 2). On the basis of this the existence of equilibrium in the following form can be assumed in the reaction.

(i)

(NBS)   **(N$^+$BSH)**
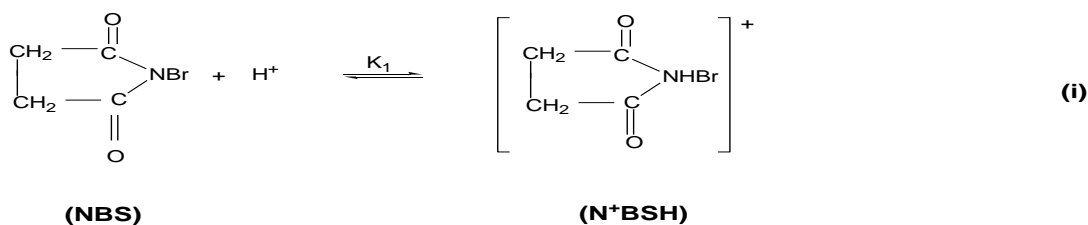
The preparation of the various complexes formed between rhodium (III) and chloride ion in dilute hydrochloric acid solution and their isolation and characterization by the ion exchange technique is reported [26] in literature. B. R. James and G. L. Rempel [27] in their kinetic studies of chloro-complexes of rhodium as hydrogenation catalysts reported that the anionic complexes such as $[RhCl_6]^{3-}$, $[Rh(H_2O)Cl_5]^{2-}$ and $[Rh(H_2O)_2Cl_4]^-$ activate molecular hydrogen for the reduction of ferric ion in aqueous acid solution. According to them cationic and neutral chloroaquorhodium-(III) complexes did not catalyse the reduction of ferric ion. The report further says that Harrod and Helpern [28] had carried out their studies with $RhCl_3$ in 3.0 M to 5.0 M HCl solutions and suggested that $[RhCl_6]^{3-}$ was the predominant species in solution but the results obtained in this report show that the 5:1 chloro species persist over this range of HCl concentration. B. R. James and G. L. Rempel [29] in an another report have described that aqueous acid solutions of some rhodium (III) complexes, $[Rh(H_2O)_{6-n}Cl_n]^{(n-3)-}$, catalysed the hydration of acetylenes under mild conditions. The report also shows that the activity of $[Rh(H_2O)Cl_5]^{2-}$ is maximum and hexachlorocomplex is inactive. In the literature, a report [21] describing the studies relating to the kinetics and mechanism of Rh(III)-catalysed oxidation of Styrene, Stilbene and Phenylacetylene by acid periodate came into existence. In the oxidation of phenylacetylene the authors have assumed $[Rh(H_2O)_3Cl_3]$ as the reactive species of Rh(III)-chloride in acidic medium. Investigations into the catalytic activity of rhodium (III) in redox reactions by capillary zone electrophoresis have been made by Svetlana S. Aleksenko and others [30]. In this paper authors have demonstrated that in perchloric acid solution Rh (III) exists entirely in the form of two positively charged complexes and in hydrochloric solutions at pH 1.0-3.5 it occurs in the form of two negatively charged chloro-complexes along with some other complex species. Literature [31, 32] also reveals that on boiling aqueous solution of rhodium (III)-chloride, $[Rh(H_2O)_6]^{3+}$ is formed and with excess HCl, the rose pink hexachlororhodate ion $[RhCl_6]^{3-}$ is formed between these two species, the existence of several intermediates are also reported. On equation $[RhCl_6]^{3-}$ produces $[RhCl_5(H_2O)]^{2-}$, Cis- $[RhCl_4(H_2O)_2]^-$ and Fac- $[RhCl_3(H_2O)_3]$. In the present study of oxidation of D (+) trehalose by NBS in acidic medium, rhodium (III)-chloride has been used as homogeneous catalyst. The solution of rhodium (III)-chloride was prepared in 3.0 M HCl solution and its concentration was determined as 3.80×10^{-3} M. This stock solution of rhodium (III)-chloride was further diluted and in each kinetic run rhodium (III)-chloride was taken in the order of 10^{-8}M. In view of the literature mentioned above it is reasonable to assume that the species $[RhCl_5(H_2O)]^{2-}$ is the lone species which exist in the reaction under investigation. This assumption finds further support by nil effect of $[Cl^-]$ on the rate of oxidation. When spectra for different solutions of Rh(III)-chloride with varying concentration of H^+ ion were recorded at 25ºC with the help of Varian Cary 300 Bio UV-VIS spectrophotometer, it is evident that in each case there is a single peak observed at fixed wavelength i.e. at 227nm.

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 NBS and H^+ with two different concentration of Rh (III)-chloride have been collected and compared with spectrum of NBS and H^+, it is found that there is an increase in absorbance from 2.403 to 2.823 and 3.258 (Fig. 5 (2, 3 and 4)). This increase in absorbance with the increase in the concentration of Rh(III)-chloride is due to more and more formation of the complex,

according to the following equilibrium:

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(N$^+$BSH)   **(C$_1$)**   **(C$_2$)**
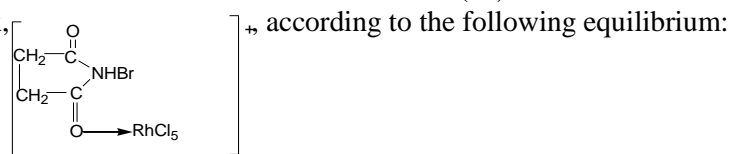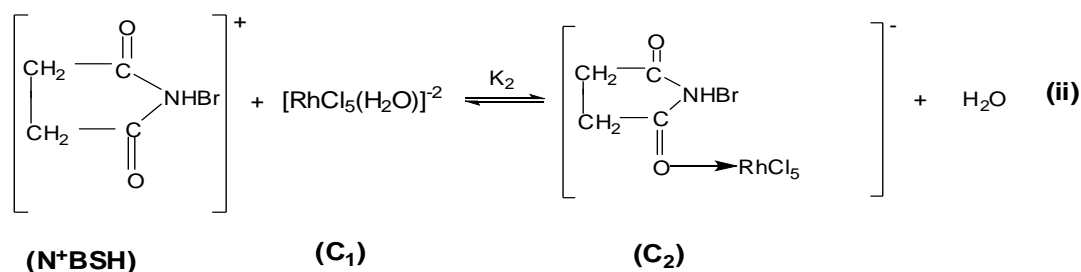
Keeping in the mind the unity order in trehalose at its low concentration and almost zero-order at its higher concentration, the spectra for solutions containing NBS, H$^+$ and Rh(III) and spectra of NBS, H$^+$ and Rh(III) with two different concentration of trehalose, it is seen that there is again an increase in absorbance from 2.823 to 3.106 and 3.177 with increase in trehalose concentration (Fig. 5 (4, 5 and 6)). This observation led us to conclude that the following equilibrium exist in the reaction under investigation.
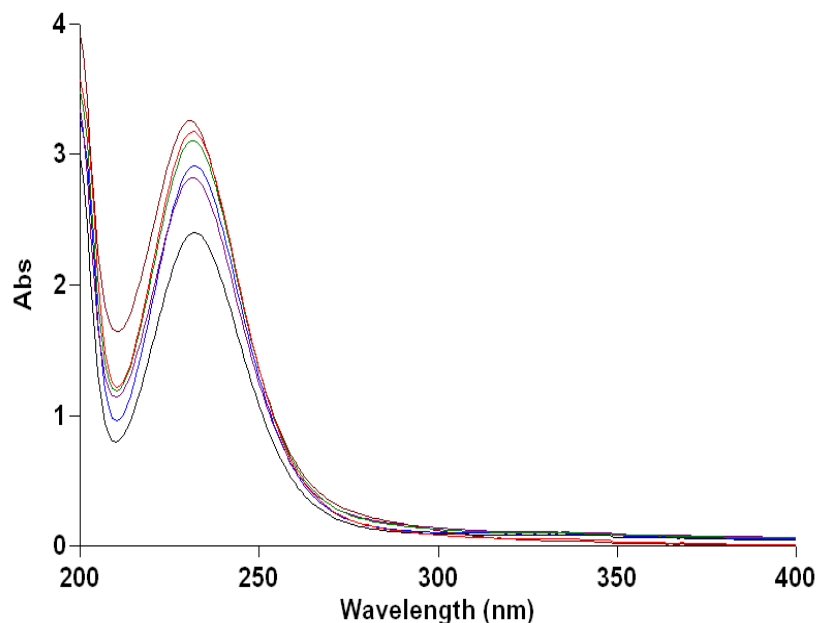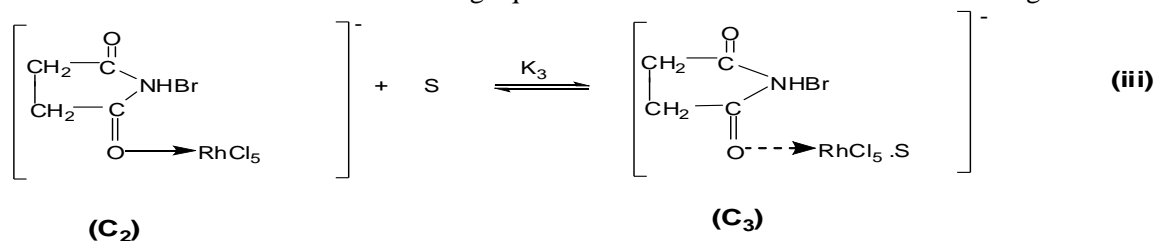

(C$_2$)   **(C$_3$)**   **(iii)**

Fig. 5: Spectra of solutions [1, 2, 3, 4, 5 and 6] recorded at room temperature

(1) [NBS] = 1.2×10^{-4} M
     [H$^+$] = 0.4 M

(2) [NBS] = 1.2×10^{-4} M
     [H$^+$] = 0.8 M

(3) [NBS] = 1.2×10^{-4} M

(5) [NBS]   = 1.2×10^{-4} M
     [H$^+$]   = 0.4 M
     [Rh(III)]   = 1.9×10^{-5} M
     [D(+) Trehalose] = 1.0×10^{-3} M

(6) [NBS]   = 1.2×10^{-4} M

$[H^+]$ = 0.4 M
$[Rh(III)]$ = 1.9×10^{-5} M

$[H^+]$ = 0.4 M
$[Rh(III)]$ = 1.9×10^{-5} M
$[D(+) \text{ Trehalose}]$ = 1.0×10^{-3} M

(4) $[NBS]$ = 1.2×10^{-4} M
$[H^+]$ = 0.4 M
$[Rh(III)]$ = 5.7×10^{-5} M

Since mercuric acetate has been used as Br$^-$ ions scavenger in each kinetic run, it was necessary to find out the effect of Hg (II) concentration on the rate of oxidation. For this concentration of mercury (II) has been varied at constant concentrations of all other reactants and at constant temperature in the oxidation of trehalose. With the help of observed relationship between pseudo-first order rate constant k_1 and mercury(II) concentration it has been concluded that there is no effect of mercury(II) concentration on the rate of oxidation. On the basis of experimental findings indicated above it can very easily be inferred that the function of mercury(II) in the present study of oxidation D(+) trehalose by NBS in acidic medium using chloro-complex of rhodium(III) as homogeneous catalyst is limited upto bromide ion scavenger only. On the basis of above findings and spectral evidence, a suitable reaction mechanism can be formulated as Reaction Scheme-1

(NBS)   (N$^+$BSH)   (i)

(N$^+$BSH)   (C$_1$)   (C$_2$)   (ii)

(C$_2$)   (C$_3$)   (iii)

(C$_3$)   (iv)

$$RCHO + HBr + HCOOH \qquad \textbf{(v)}$$

$$\textbf{(vi)}$$
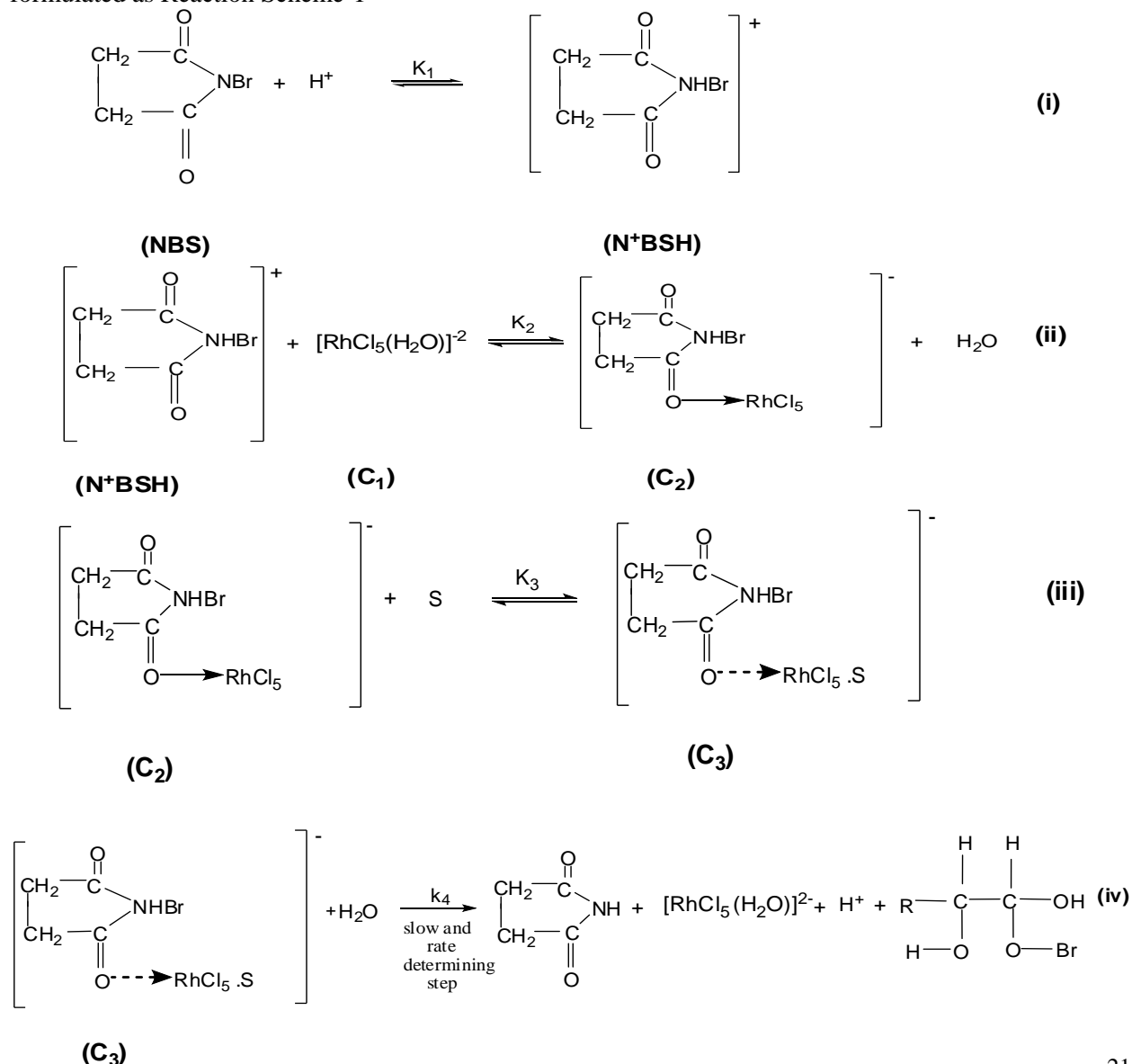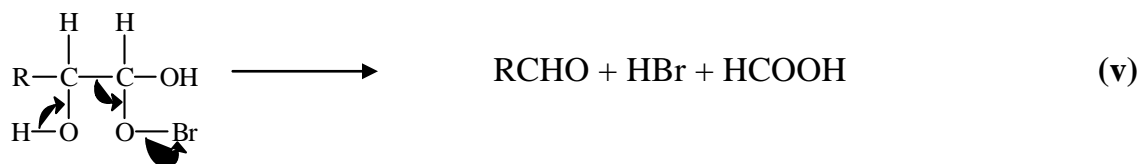
Where $R = C_4H_9O_4$

Reaction Scheme-1

Since D (+) trehalose contains two glucose units and the aforesaid steps (i-vi) are presented for the oxidation of one glucose unit only, hence the same process shall be repeated for its another glucose unit. According to the reaction scheme-1 proposed for the oxidation of D(+) trehalose by NBS using Rh(III) as homogeneous catalyst in acidic medium, the rate in terms of decrease in [NBS] can be expressed as

$$\text{rate} = -\frac{d[NBS]}{dt} = 4k_4[C_3] \qquad (1)$$

Where 4 indicate that one mole of trehalose is oxidized by four moles of NBS.

On applying law of chemical equilibrium to steps (i)-(iii), we get equations (2)-(4) respectively.

$$K_1 = \frac{[N^+BSH]}{[NBS][H^+]}$$

or $\quad [N^+BSH] = K_1[NBS][H^+] \qquad (2)$

$$K_2 = \frac{[C_2]}{[C_1][N^+BSH]}$$

or $\quad [C_2] = K_1K_2[C_1][H^+][NBS] \qquad (3)$

and $\quad K_3 = \frac{[C_3]}{[C_2][S]}$

or $\quad [C_3] = K_1K_2K_3[C_1][H^+][NBS][S] \qquad (4)$

On putting the value of $[C_3]$ from equation (4) to equation (1), we have

$$\text{rate} = -\frac{d[NBS]}{dt} = 4k_4K_1K_2K_3[C_1][H^+][NBS][S] \qquad (5)$$

According to the reaction mechanism, total concentration of Rh (III) i.e. [Rh (III)]$_T$ at any time in the reaction can be shown as:

$[Rh(III)]_T = [C_1] + [C_2] + [C_3] \qquad (6)$

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On substituting the values of $[C_2]$ and $[C_3]$ from equations (3) and (4) respectively to equation (6),we get equation (7)

$[Rh(III)]_T = [C_1] + K_1K_2[C_1] [H^+] [NBS] + K_1K_2K_3 [C_1] [H^+] [NBS] [S]$

or

$[Rh(III)]_T = [C_1] \{1+ K_1K_2 [H^+] [NBS] + K_1K_2K_3 [H^+] [NBS] [S]\}$

or

$$[C_1] = \frac{[Rh(III)]_T}{1+ K_1K_2[H^+][NBS] + K_1K_2K_3[H^+][NBS][S]} \tag{7}$$

From equation (7) and equation (5), we have equation (8)

$$rate = -\frac{d[NBS]}{dt} = \frac{4k_4K_1K_2K_3[H^+][NBS][S][Rh(III)]_T}{1+ K_1K_2[H^+][NBS] + K_1K_2K_3[H^+][NBS][S]} \tag{8}$$

The proposed reaction scheme shows that the total concentration of NBS can be expressed as

$[NBS]_T = [NBS] + [N^+BSH]$ (9)

On putting the value of $[N^+BSH]$ from equation (2) to equation (9), we get equation (10)

$$[NBS] = \frac{[NBS]_T}{1+ K_1[H^+]} \tag{10}$$

When [NBS] in the rate equation (8) is replaced by $[NBS]_T$ with the help of equation (10), we get equation (11) as given below

$$rate = -\frac{d[NBS]}{dt} = \frac{4k_4K_1K_2K_3[H^+][NBS]_T[S][Rh(III)]_T}{1+ K_1[H^+] + K_1K_2K_3[H^+][NBS]_T[S]} \tag{11}$$

Equation (11) can also be written as

$$rate = -\frac{d[NBS]}{dt} = \frac{4k_4K_1K_2K_3[H^+][NBS]_T[S][Rh(III)]_T}{1+ K_1[H^+]\{1+ K_2K_3[NBS]_T[S]\}} \tag{12}$$

Equation (12) is the required rate law because it is in complete agreement with the first-order kinetics with respect to [Rh(III)] and first to zero-order kinetics with respect to each [NBS], [H$^+$] and [S] in the catalyzed oxidation of D(+) trehalose.

At low concentrations of [NBS] and [S], the inequality $K_2K_3[NBS]_T[S]<<1$ can be assumed as valid one and under this condition equation (12) will be reduced to equation (13).

$$rate = -\frac{d[NBS]}{dt} = \frac{4k_4K_1K_2K_3[H^+][NBS]_T[S][Rh(III)]_T}{1+ K_1[H^+]} \tag{13}$$

Further, when inequality $K_1 [H^+] <<1$ is taken into consideration at low concentration of H$^+$ then equation (13) will take the shape of equation (14)

$$rate = -\frac{d[NBS]}{dt} = 4k_4K_1K_2K_3[H^+][NBS]_T[S][Rh(III)]_T \tag{14}$$

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Equation (14) is the rate law at low concentrations of [NBS], [S] and $[H^+]$ where first-order kinetics with respect to these reactants was observed. Equation (13) can also be written in the form of equation (15) as:

$$\text{rate} = -\frac{d[NBS]}{dt} = k'[H^+][NBS]_T[S][Rh(III)]_T \tag{15}$$

where $k' = 4k_4K_1K_2K_3$

When validity of rate law (14) or (15) was tested by calculating the values of k' for the variations of [NBS], $[H^+]$, $[Rh(III)]_T$ and [S] at their low concentrations, it was found that values of k' are almost the same for all the four aforesaid variations (Table-2). This proves the validity of rate law (14) or (15) and hence the proposed mechanism in the form of reaction scheme-1.

Again, at high concentrations of $[NBS]_T$ and [S] the inequality $K_2K_3[NBS]_T[S] \gg 1$ can be assumed as valid one and under this condition equation (12) will take the shape of equation (16)

$$\tag{16}$$

$$rate = -\frac{d[NBS]}{dt} = \frac{4k_4K_1K_2K_3[H^+][NBS]_T[S][Rh(III)]_T}{1 + K_1K_2K_3[NBS]_T[H^+][S]}$$

Further, under our experimental conditions i.e. at very high concentrations of NBS, H^+ and S, one being very-very small in comparison to $K_1K_2K_3[NBS]_T[H^+][S]$ in the denominator of equation (16) can be neglected. With the assumption $K_1K_2K_3[NBS]_T[H^+][S] \gg 1$ equation (16) will be converted into equation (17)

$$\text{rate} = -\frac{d[NBS]}{dt} = 4k_4[Rh(III)]_T \tag{17}$$

The rate law (17) is in accordance with our experimental observations valid at very high concentrations of NBS, H^+ and S.

Table 2: Calculated values of composite rate constant for the variation of [NBS], $[Rh(III)]_T$ and [Substrate] in the Rh(III)-catalyzed oxidation of D(+) Trehalose at 45^0C

$[NBS] \times 10^4$ (M)	$[Rh(III)]_T \times 10^8$ (M)	$[Substrate] \times 10^2$ (M)	$k' \times 10^{-7}$ (sec^{-1})
4.80	8.40	2.00	1.13
7.20	8.40	2.00	0.92
9.60	8.40	2.00	0.93
12.00	8.40	2.00	0.91
16.80	8.40	2.00	0.91
4.80	2.80	2.00	1.14
4.80	5.60	2.00	1.05
4.80	8.40	2.00	1.14
4.80	11.20	2.00	1.05
4.80	14.00	2.00	1.02
4.80	16.80	2.00	0.90
4.80	19.60	2.00	0.92
4.80	22.40	2.00	0.90
4.80	25.20	2.00	0.86
4.80	28.00	2.00	0.90
4.80	8.40	1.00	0.93
4.80	8.40	2.00	1.14
4.80	8.40	4.00	0.83
4.80	8.40	6.00	0.76

Solution Conditions:

For [NBS] variation	For [Rh (III)] and [Substrate] variations
$[Hg(II)] = 24.50 \times 10^{-4}$ M	$[Hg(II)] = 4.9 \times 10^{-4}$ M
$[NHS] = 24.50 \times 10^{-4}$	$[NHS] = 4.9 \times 10^{-4}$ M
$[H^+] = 0.2$ M	$[H^+] = 0.2$ M
$\mu = 0.3$M	$\mu = 0.3$ M

Utilizing the value of rate constant at 45°C and also the observed entropy of activation, the entropy of activation and others activation parameters were calculated for the Rh (III)-catalyzed oxidation of D(+) trehalose at the temperature indicated above. The values thus obtained are presented in table-1. Observed positive entropy of activation is due to most reactive activated complex of the type,
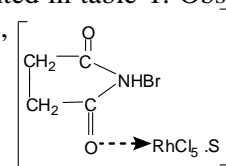

being less polar than the initial state where interaction is being made between a charge species,
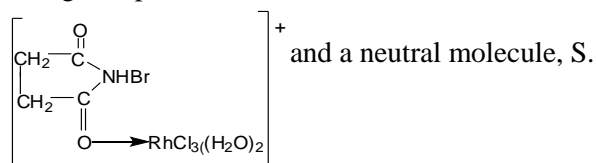
and a neutral molecule, S.

Comparative Studies: The results of present study of the Rh(III) catalysed oxidation of trehalose by NBS in acidic medium can be compared with the results for the Pd(II) catalysed [13] oxidation of reducing sugar by NBS in acidic medium and also with the results reported for Ir(III) catalysed [16] oxidation of reducing sugar by NBS in acidic medium. The first-order kinetics which shows retardation in rate at higher concentration of NBS were different from reported Pd(II) and Ir(III) catalysed oxidation where reaction shows first-order with respect to [NBS] throughout its variation. The present reaction shows first-order with respect to [Rh(III)] which is similar to the Pd(II) catalysed oxidation as well as Ir(III) catalysed oxidation at lower concentration. The present study on the one hand were similar to Pd(II) catalysed oxidation of reducing sugar with respect to [sugar] but on the other hand it differs to Ir(III) catalysed oxidation of reducing sugar where nil effect of reducing sugar was observed. Present study shows remarkable change with respect to[H$^+$] ion and [Cl$^-$] ion. The Rh(III) catalysed oxidation shows first-order with respect to [H$^+$] ion at lower concentration which changes to zero-order at higher concentration whereas Pd(II) and Ir(III) catalysed oxidation shows inverse-fractional order with respect to [H$^+$] ion. The observed nil effect of [Cl$^-$] ion concentration on the rate of oxidation is also contrary to the observed negative effect of [Cl$^-$] ion concentration in the oxidation of reducing sugar using chloro-complex of Ir(III) and Pd(II) as catalyst.

On the basis of above 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,
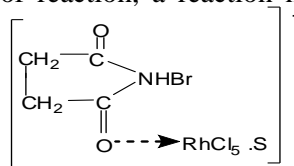
is proposed. The nature of the activated complex is entirely different from the complex $[IrCl_5OBr]^{3-}$ reported as most reactive in Ir(III) catalysed oxidation. Protonated NBS i.e. N$^+$BSH in the form of reactive species of NBS in acidic medium formed.

APPLICATIONS

A most probable reaction mechanism has been proposed for Rh (III)- catalyzed oxidation of D(+) trehalose by NBS in acidic medium which finds support from observed kinetic data, spectrophotometric evidence and various activation parameters.

CONCLUSIONS

The conclusions drawn for Rh(III)- catalyzed oxidation of D(+) trehalose by NBS in acidic medium on the basis of observed kinetic data and spectrophotometric evidence are as follows:

1. Protonated N-bromsuccinimide, N^+BSH, and chlorocomplex of Rh (III) i.e. $[RhCl_5(H_2O)]^{2-}$, have been postulated as the reactive species of NBS and Rh(III) chloride in acidic medium respectively.

2. The function of mercury (II) in the present study is limited upto bromide ion scavenger only.

3. On the basis of kinetic results and spectrophotometric information, the formation of most reactive activated complex of the type, , is proposed.
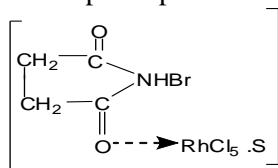
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