



## Kinetics of catalytic activities of micro amount of Ir(III) in oxidation of D(-) Galactose by N-bromosuccinimide in acidic homogeneous medium

Vinod Kumar Singh<sup>a,\*</sup>, Vineeta Singh<sup>b</sup> & Vaishali Singh<sup>a</sup>

<sup>a</sup>Department of Chemistry, Maharishi University of Information Technology, Lucknow 226 004, Uttar Pradesh, India

<sup>b</sup>Department of Chemistry, D.A.V.P.G. College (University of Lucknow), Aishbagh, Lucknow 226 004, Uttar Pradesh, India

\*E-mail: drvks151068@gmail.com

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It has been investigated how iridium(III) catalyses the oxidation of D(-)Galactose by N-bromosuccinimide (NBS) in an aqueous perchloric acid solution at 308 K. NBS kinetics is first-order, while galactose kinetics is zero-order. As a function of [Ir(III)], the reactions demonstrate first order at lower [Ir(III)] and zero-order behaviour at higher [Ir(III)]. On the rate of oxidation, inverse fractional-order has been reported in  $[H^+]$ ,  $[Cl^-]$  and [succinimide]. There is no difference in the rate of oxidation with changes in the ionic strength of the medium or with the addition of  $Hg(OAc)_2$  (a Br-ion scavenger). Galactonic acid has been identified as the major oxidation product of the process. It is possible to compute the activation parameters by utilizing the rate constants observed at four distinct temperature levels. For the sake of this research, it is hypothesised that HOBr and  $[IrCl_5H_2O]^{2-}$  are both reactive species oxidants (i.e. NBS) as well as catalysts. It is very probable that the reaction mechanism for the oxidation of galactose by NBS is supported by current kinetic data, reaction stoichiometry, and product analysis.

**Keywords:** Acidic kinetics, Ir(III)-catalysis, D(-)Galactose, N-bromosuccinimide, Oxidation

The transition metal-catalyzed reactions have important role in the pharmaceutical as well as in the chemical industry from both practical and economic points of view. Transition metal ions are found to be a good catalyst and their complexes can a wide variety of reactions like hydrogenation, decomposition, oxidation and polymerization etc. Kinetic studies on the oxidation of sugars with different oxidants have already reported<sup>1-3</sup>. There are several equilibria in acidic environments where N-bromosuccinimide (NBS) is involved and one must know the active form of NBS in the reaction to employ the oxidative capability of NBS in the reaction<sup>4,5</sup>. There have been several studies on the use of NBS in different industrial and biological processes, such as the oxidative degradation of amino acids, the oxidation of psychotropic medicines, the investigation of protein cleavage, and the fermentation of high molecular weight peptides and proteins<sup>6</sup>. There has been a lot of research into the function of NBS as an oxidant for a wide range of organic compounds<sup>7-15</sup>, but so far, nothing has been done to investigate the catalytic potential of Ir(III) in NBS oxidation. The parallel oxidation of bromine complicates NBS oxidation of organic molecules, as is well-known. Though

$Hg(OAc)_2$  may eliminate bromine ions from the reaction, nothing is known about the function of Iridium(III) chloride in NBS oxidation of sugars with acid. The economic and biological importance of carbohydrates in microbiological as well as especially their physicochemical properties/reactivates etc. depend mainly on their redox behaviour which prompted us to study the monosaccharides (an organic substrate) kinetic activity/working in the living systems. Reducing sugars plays a very significant role in pharmaceutical, patho-physicochemical (metabolic, biochemical profiles, statistical multivariate data analysis) techniques of curing tumour/cancer cells and some old age diseases in human beings. Recently (research in 2020 by INMAS- DRDO) used mimic of 2-DeoxyD(-)Glucose(2-DG) in plasma radio-therapy which shows anti-viral effects on SARS-CoV-2 infected host cells and it has been inhibiting virus multiplications & alters glycosylation of viral glycoproteins, rendering new virions incapable of infecting human cells. Now, 2-DG is approved by doctors for emergency use as a therapy in the treatment of COVID-19 patients. In order to better understand how Ir(III) catalysed oxidation by NBS of reducing sugars like D(-)Galactose (analdose) occurs

in an acidic aqueous medium with bromide ion scavenger  $\text{Hg}(\text{OAc})_2$  led to the current study.

## Experimental Details

### Chemicals and preparation of solutions

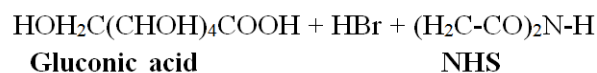
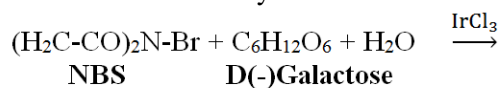
The kinetic investigations employed double recrystallized D(-)Galactose (m.p. 166 °C, mol. wt. 180.16, E. Merck). Every NBS (E. Merck) solution was produced in a dark flask to avoid photochemical degradation. In double distilled water, E. Merck grade recrystallized substance was prepared. Iodometrically, the NBS solution was compared to a conventional sodium thiosulphate(hypo) solution using starch as an indicator. Every day, D(-)Galactose aqueous solutions were made. The iridium(III) chloride solution (Johnson Matthey & Co. Ltd) was made by dissolving  $\text{IrCl}_3$  in a known strength HCl solution. The additional reagents/solutions used were mercuric acetate, perchloric acid, HCl,  $\text{NaClO}_4$ , KCl, succinimide etc., all of which were prepared in double-distilled water.

### Method of Kinetic study

An electrically operated thermo-stated water bath was maintained at the desired temperature to within  $\pm 0.1$  °C. The reaction mixture containing requisite volume (90  $\text{cm}^3$ ) of all reactants i.e., NBS,  $\text{HClO}_4$ , KCl, iridium(III) chloride,  $\text{Hg}(\text{OAc})_2$ , NHS,  $\text{NaClO}_4$ , and water excluding substrate, were introduced into a black coated reaction vessel which have been thermostatically equilibrated water bath at 35 °C. Afresh and measured volume (10  $\text{cm}^3$ ) of D(-)Galactose solution, equilibrated separately at the same temperature, was rapidly poured into the reaction vessel to initiate the reaction. The total volume of reaction mixture was 100 mL in each case. As soon as half volume of substrate was poured into reaction mixture, the stopwatch was started to record time. The 5 mL aliquots of reaction mixture was pipette out at different intervals of time and quenched with 4% acidified KI solution. The progress of the reaction was monitored by iodometric estimation of NBS by titration against a standard solution of hypo using starch as an indicator to determine unconsumed NBS at regular time intervals. Each kinetic run was investigated up to 75% reaction. The initial rate of reaction (-dc/dt) was determined by the slop of the tangent drawn between remaining [NBS] and time in initial stage of reaction, in each kinetic run. The order of reaction for each reactant was calculated with the help of log-log plot of (-dc/dt) against concentration of reactants.

### Stoichiometry and product analysis

Different sets of reaction mixture containing iridium(III) choride,  $\text{HClO}_4$ , KCl with different [NBS]: [D(-)Galactose] ratios, under the excess of [NBS] i.e.  $[\text{NBS}] \gg [\text{D}(-)\text{Galactose}]$  were kept for 72 h at 308 K. The estimation of unconsumed NBS in each set revealed that one mole of NBS was consumed for the oxidation of one mole of D(-)Galactose .On the basis of equivalence and kinetic results and also the spot test<sup>16-17</sup> and thin layer chromatography experiments performed for the confirmation of gluconic acid, which was identified as main product of reaction under investigation. On the basis above information and observed kinetic data, the following stiochiometric equation may be formulated for D(-) Galactose oxidation by NBS as:



## Result and Discussion

The kinetics studies for Ir(III)-catalyzed oxidation of D-Galactose by NBS in acidic medium have been investigated at 35 °C several initial concentrations (Table 1) of the each reactants. The initial rate of reaction determined by the slope of the tangent drawn between at fixed [NBS] i. e. (-dc/dt), the first order rate constant,  $k_1$  was calculated as:

Rate =  $-\frac{(\text{dc}/\text{dt})}{[\text{NBS}]}$  =  $k_1$ , Where (-dc/dt) is almost directly proportional to [NBS]. The first order kinetics with respect to [NBS] is also verified by the constant values of first order rate constant ( $k_1$ ) obtained at various initial concentrations of NBS, which further confirms from (-dc/dt) versus [NBS\*] plot (Fig. 1, where [NBS\*] is the concentration at which (-dc/dt) was determined) passing through the origin. Variations in [D(-)Galactose] did not influence the value of  $k_1$  appreciably (showing nearly constant values of  $k_1$  as well as also by constant (-dc/dt) values), thereby showing zero order kinetics in [D-Galactose] (Table 1). The reaction was observed to be very sensitive for catalyst [Ir(III)], its micro amount makes reaction facile. A plot of (-dc/dt) versus [Ir(III)] shows first order kinetics with respect to [Ir(III)] in its lower range of concentrations and it shift toward zero in the higher concentration range (Fig. 2) which confirms fractional order dependence

Table 1 — The observed values of first order constant ( $k_1$ )<sup>#</sup> and rate ( $-dc/dt$ ) for the variation of reactants on the rate, Ir(III)-catalyzed oxidation of D(-)Galactose by NBS in acidic medium at 308 K

$10^3 \times [\text{NBS}]$ (mol dm <sup>-3</sup> )	$10^2 \times [\text{S}]$ (mol dm <sup>-3</sup> )	$10^7(-dc/dt)$ (mol dm <sup>-3</sup> sec <sup>-1</sup> ) <sup>#</sup>	$10^4 k_1(\text{sec}^{-1})$ <sup>#</sup>
0.40	2.00	1.11	3.36
0.50	2.00	1.25	3.05
0.80	2.00	1.87	2.88
1.00	2.00	2.80	3.11
1.25	2.00	3.30	3.32
1.66	2.00	4.87	3.04
2.00	2.00	5.25	3.12
1.00	0.50	2.78	3.09
1.00	1.00	2.84	3.15
1.00	1.50	2.80	3.11
1.00	2.50	2.76	3.06
1.00	3.34	2.79	3.10
1.00	5.00	2.83	3.14

<sup>#</sup>Experimental conditions:  $[\text{HClO}_4] = 2.00 \times 10^{-2}$  mol dm<sup>-3</sup>,  $[\text{IrCl}_3] = 1.34 \times 10^{-5}$  mol dm<sup>-3</sup>,  $[\text{Hg}(\text{OAc})_2] = 3.33 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[\text{KCl}] = 1.25 \times 10^{-3}$  mol dm<sup>-3</sup>, Substrate 'S' =  $[\text{D}(-)\text{Galactose}] = 2.00 \times 10^{-2}$  mol dm<sup>-3</sup>

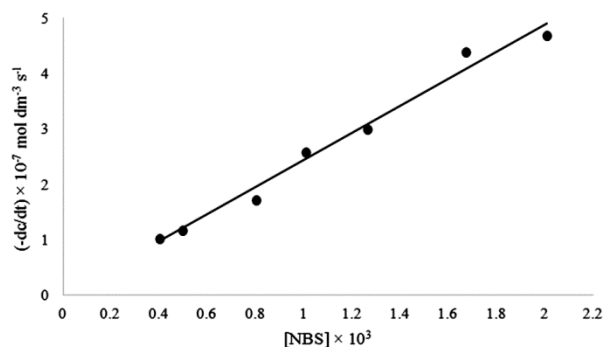


Fig. 1 — First order plots of  $(-dc/dt)$  versus  $[\text{NBS}]$ , in the Ir(III)-Catalyzed oxidation of D(-)Galactose by NBS in acidic medium at 308 K, (Experimental conditions:  $[\text{HClO}_4] = 2.00 \times 10^{-2}$  mol dm<sup>-3</sup>,  $[\text{IrCl}_3] = 1.34 \times 10^{-5}$  mol dm<sup>-3</sup>,  $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[\text{KCl}] = 1.25 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[\text{D}(-)\text{Galactose}] = 2.00 \times 10^{-2}$  mol dm<sup>-3</sup>)

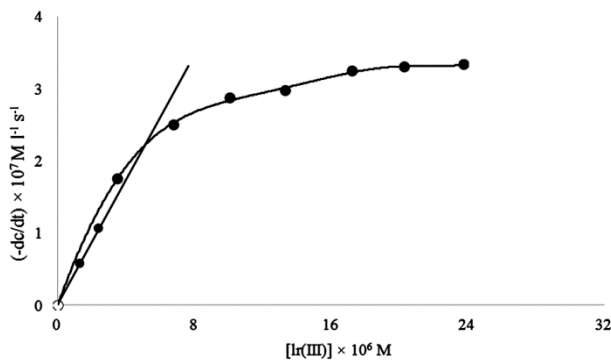


Fig. 2 — A plot between  $(-dc/dt)$  versus  $[\text{Ir(III)}]$ , in the Ir(III)-Catalyzed oxidation of D(-)Galactose by NBS in acidic medium at 308 K, (Experimental conditions:  $[\text{NBS}] = 1.00 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[\text{HClO}_4] = 2.00 \times 10^{-2}$  mol dm<sup>-3</sup>,  $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[\text{KCl}] = 1.25 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[\text{D}(-)\text{Galactose}] = 2.00 \times 10^{-2}$  mol dm<sup>-3</sup>)

of the reactions on iridium(III) chloride. The oxidation rate decreases with increase in perchloric acid concentration used as source of H ion and a plot of  $\log k_1$  versus  $\log [\text{H}^+]$  (Fig. 3) was linear with negative slope determined as  $-0.65$  for  $[\text{D-Galactose}]$ . The results of Table 2 indicate the negative effects the addition of KCl and succinimide i.e.  $[\text{NHS}]$  on the rate constant. Variation of ionic strength of the medium i.e.,  $\mu$  (affected by addition of calculated amounts  $\text{NaClO}_4$  in reaction mixture) of the medium had not influence the oxidation and limited role of mercuric acetate i.e.,  $[\text{Hg(II)}]$  as a bromide ion scavenger is obvious from the data of Table 2. The reaction was studied at four different temperatures under identical condition of reaction mixture. The values  $E_a$ ,  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  at 308 K are count to be  $67.92$  kJ mol<sup>-1</sup>,  $-57.76$  J k<sup>-1</sup> mol<sup>-1</sup>,  $70.51$  kJ mol<sup>-1</sup> and  $88.28$  kJ mol<sup>-1</sup> respectively.

#### Reactive species of iridium(III) chloride in acidic medium

Reports are available where iridium(III) chloride has been used as homogeneous catalyst in acidic medium. A spectrophotometric study of kinetics of hydration of  $[\text{IrCl}_6]^{3-}$  and of the addition of Cl ion to  $[\text{Ir}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$  in  $1.0 - 2.5$  M  $\text{HClO}_4$  (or  $\text{HCl}$ ) at  $50^\circ\text{C}$  is reported<sup>18-21</sup>. It is known that iridium(III) chloride in hydrochloric acid solution exists as hexa-chloro complex anion i.e.  $(\text{IrCl}_6)^{3-}$  species<sup>19</sup>. It has also been reported that Ir(III) and Ir(I), ions are stable species of iridium<sup>20</sup>. Further the equation of  $(\text{IrCl}_6)^{3-}$  gives  $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ ,  $[\text{IrCl}_4(\text{H}_2\text{O})_2]^-$  and  $[\text{IrCl}_3(\text{H}_2\text{O})_3]$  species and also exists<sup>18,21,22</sup>. The

Table 2 — Observed values of first order constant( $k_1$ )<sup>#</sup> for the addition of KCl, succinimide (NHS), Hg(OAc)<sub>2</sub> and NaClO<sub>4</sub> (ionic strength variation  $\mu^*$ ) on reaction rate, in the Ir(III)-catalyzed oxidation of D(-)Galactose by NBS in acidic medium at 308 K

$10^3 \times [\text{KCl}]$ (mol dm <sup>-3</sup> )	$10^4 \times [\text{NHS}]$ (mol dm <sup>-3</sup> )	$10^3 [\text{Hg}(\text{OAc})]$ (mol dm <sup>-3</sup> )	$10^2 \times \text{NaClO}_4$ (mol dm <sup>-3</sup> )	$10^4 \times k_1$ (sec <sup>-1</sup> ) <sup>#</sup>
0.40	-	1.25	6.00	3.70
1.00	-	1.25	6.00	3.24
1.50	-	1.25	6.00	2.78
2.00	-	1.25	6.00	1.84
2.50	-	1.25	6.00	0.92
-	0.10	1.25	5.75	3.70
-	0.13	1.25	5.75	3.07
-	0.16	1.25	5.75	1.84
-	0.25	1.25	5.75	1.48
-	0.50	1.25	5.75	0.90
-	5.00	1.25	5.75	-
-	-	1.50	9.00	3.11
-	-	2.00	9.50	3.09
-	-	3.00	9.50	3.12
-	-	4.00	9.50	3.16
-	-	5.00	9.50	3.14
-	-	1.25	6.75	3.16
-	-	1.25	8.75	3.15
-	-	1.25	10.75	3.11
-	-	1.25	12.75	3.15
-	-	1.25	15.75	3.13

<sup>#</sup>Experimental conditions: [NBS] =  $1.00 \times 10^{-3}$  mol dm<sup>-3</sup>, [HClO<sub>4</sub>] =  $2.00 \times 10^{-2}$  mol dm<sup>-3</sup>, [IrCl<sub>3</sub>] =  $1.34 \times 10^{-5}$  mol dm<sup>-3</sup>, [D(-)Galactose] =  $2.00 \times 10^{-2}$  mol dm<sup>-3</sup>

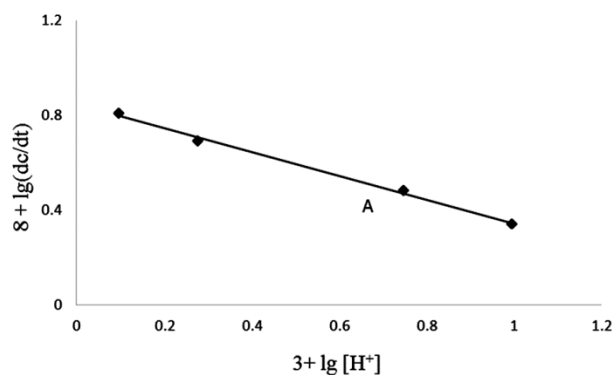
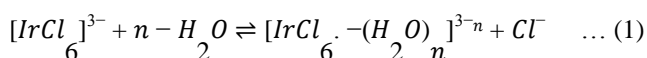


Fig. 3 — Effect of [H<sup>+</sup>] on the rate of reaction at 308 K, (Experimental conditions: [NBS] =  $1.00 \times 10^{-3}$  mol dm<sup>-3</sup>; [IrCl<sub>3</sub>] =  $1.34 \times 10^{-5}$  mol dm<sup>-3</sup>, [Hg(OAc)<sub>2</sub>] =  $1.25 \times 10^{-3}$  mol dm<sup>-3</sup>, [KCl] =  $1.25 \times 10^{-3}$  mol dm<sup>-3</sup>, [D(-)Galactose] =  $2.00 \times 10^{-2}$  mol dm<sup>-3</sup>)

reversible equation reaction of [IrCl<sub>6</sub>]<sup>3-</sup> species with equilibrium constant (K) were shown as general in Eqn. (1):



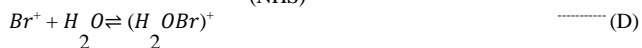
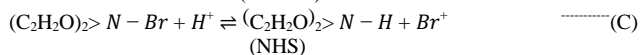
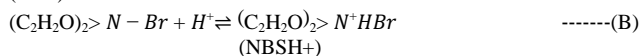
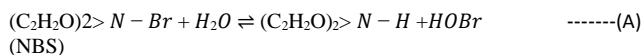
The UV-visible absorption spectra of the new Ir(III) complexes [IrCl<sub>3</sub>.(H<sub>2</sub>O)<sub>3</sub>], [IrCl<sub>4</sub>.(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup> together with spectra of [IrCl<sub>6</sub>]<sup>3-</sup> and [IrCl<sub>5</sub>.(H<sub>2</sub>O)]<sup>2-</sup> in 2.5 M – 1.2 M HClO<sub>4</sub> were also reported and found

in reasonable agreement with those reported in literature<sup>18,21,22</sup>. When iridium(III) chloride dissolved in 0.1 M HCl solution, [IrCl<sub>6</sub>]<sup>3-</sup> and [IrCl<sub>5</sub>.(H<sub>2</sub>O)]<sup>2-</sup> species were formed. So, the [IrCl<sub>6</sub>]<sup>3-</sup> is taken as the starting species of iridium(III)chloride in acidic medium. On the basis of the effect of [Cl<sup>-</sup>] ion on the rate of reaction and also assuming that existence of above equilibrium (Eqn. 1) in present reaction. Change in oxidation state of Ir(III) in Ir(III)hexachloro complex anion during the course of reaction may result via removal of Cl<sup>-</sup> ions, leading to their negative effect on the reaction velocity, which was observed in present investigation, suggesting that equilibrium is favoured to right side<sup>23</sup> in acidic solution of iridium(III) chloride in present study.

#### Reactive species of NBS in acidic medium

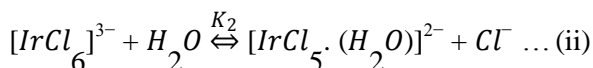
NBS is a source of positive halogen and this reagent has been exploited as an oxidant for variety of substrates in both acidic and alkaline media<sup>14</sup>. The nature of active oxidizing species and the mechanism depends on the nature of the halogen atom, the group attached to the nitrogen and reaction condition. The species responsible for such oxidizing character may be different depending on the pH of the medium. In acidic media NBS is known<sup>14-16</sup> to exist in four different forms, viz. NBS itself HOBr, protonated

NBS i.e., ( $N^+BSH$ ),  $(H_2OBr)^+$  as shown by the following equilibriums,

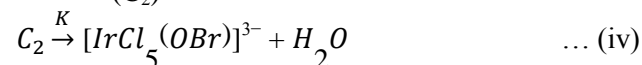
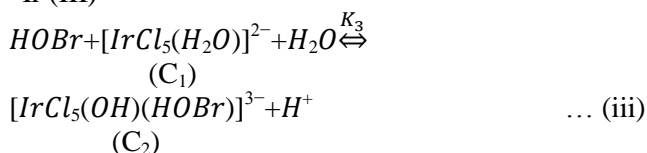


Thus NBS itself, HOBr, protonated NBS i.e., ( $N^+BSH$ ),  $Br^+$  or  $(H_2OBr)^+$  may be the possible oxidizing species in acidic media. Negative effect of  $[H^+]$  on the reaction rate observed here, does not allow us to assume protonated NBS i.e. ( $N^+BSH$ ) as reactive species of NBS. The observed kinetic data show negative effect of succinimide (NHS) on rate of oxidation of D(-)Galactose restricts us to take  $Br^+$  or  $(H_2OBr)^+$  as oxidizing species. If NBS as such taken as reactive species, then rate law should be independent of effect of [Succinimide] which is contrary to its negative effect. This clearly ruled out the possible role of oxidant for NBS as such in the reaction, although all of these species {i.e.  $Br^+$ , HOBr,  $(H_2OBr)^+$ } except ( $N^+BSH$ ) successfully explain the negative effect of succinimide. Hence, none of these three species is involved in the present investigation due to aforesaid reason. Under these circumstance the only choice left before us is to choose HOBr as the reactive species of the oxidant NBS which will satisfy negative fractional order with respect to the  $[H^+]$  and of [NHS] and gives rate law capable of explaining all the kinetic observations and other effects. On the basis of above experimental findings and kinetic data, a probable reaction mechanism as Scheme-I is formulated for the oxidation of D(-)Galactose, which have been designated as "S".

#### Scheme-I

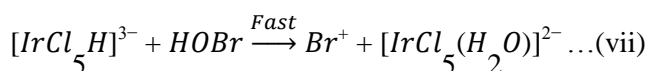
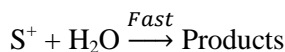
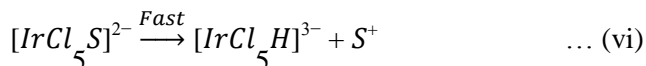
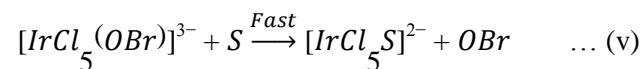


Ir (III)



Slow and rate determining step

$C_2 = [IrCl_5(OH)(HOBr)]^{3-}$  is an intermediate complex



#### Mechanism and derivation of rate law

On the basis of reaction Scheme-I, and consider the fact that one mole of D(-)Galactose is oxidized by one mole of NBS, the in terms of decreasing in concentration of NBS, rate law can be expressed as:

$$\text{Rate} = -\frac{d[NBS]}{dt} = k[C_2] \quad \dots (1)$$

On applying the law of chemical equilibrium in steps (ii) and (iii), in the above scheme, we have

$$[C_1] = K_2 [Ir(III)] / [Cl^-]$$

$$[C_2] = K_3 [HOBr][C_1] / [H^+]$$

When we applying the law of chemical equilibrium for step (ii) of scheme-I, then we get

$$\text{For equilibrium constant } K_2 = [\text{Product}]/[\text{Reactant}]$$

$K_2 = [IrCl_5(H_2O)]^{2-} [Cl^-] / [IrCl_6]^{3-} [H_2O]$   
 $K_2 = [C_1] [Cl^-] / [Ir(III) \times 1]$ , where  $[H_2O] = 1$  which is in excess

$$\text{Or } [C_1] = K_2 [Ir(III)] / [Cl^-] \quad \dots (2)$$

Similarly, way for step (iii) of scheme-I

$$\text{Equation constant } K_3 = [\text{Product}]/[\text{Reactant}]$$

$$K_3 = [IrCl_5(OH)(HOBr)]^{3-} [H^+] / [IrCl_5(H_2O)]^{2-} [HOBr] [H_2O]$$

$$K_3 = [C_2] [H^+] / [C_1] [HOBr]$$

$$\text{Or } [C_2] = K_3 [C_1] [HOBr] / [H^+] \quad \dots (3)$$

On substituting the value of  $[C_1]$ , in Eqn. (3) we have

$$[C_2] = K_2 K_3 [HOBr] [Ir(III)] / [Cl^-] [H^+] \quad \dots (4)$$

The total concentration of Ir(III) can be written as in Eqn. (5)

$$[Ir(III)]_T = [Ir(III)] + [C_1] + [C_2] \quad \dots (5)$$

Substituting the values of  $[C_1]$  and  $[C_2]$  in Eqn. (5), we have

$$[Ir(III)] = \frac{[Ir(III)]_T [Cl^-] [H^+]}{[Cl^-] [H^+] + K_2 [H^+] + K_2 K_3 [HOBr]} \quad \dots (6)$$

Now on applying steady-state approximation to the concentration of highly reactive, HOBr species:

$$[HOBr] = k_f [NBS] / k_b [NHS] + K_3 [C_1] \quad \dots (7)$$

Where  $K_1 = k_f / k_b$

Now on substituting the value of  $[Ir(III)]$  from Eqn. (6) in Eqn. (4), we have

$$[C_2] = \frac{K_2 K_3 [HOBr] [Ir(III)]_T}{[H^+] [Cl^-] + K_2 K_3 [HOBr]} \quad \dots (8)$$

On assuming  $[H^+] \{ [Cl^-] + K_2 \} \gg K_2 K_3 [HOBr]$ . Then Eqn. (8) becomes Eqn. (9)

$$[C_2] = \frac{K_2 K_3 [HOBr] [Ir(III)]_T}{[H^+] \{ [Cl^-] + K_2 \}} \quad \dots (9)$$

On substituting the value of  $[C_2]$  from Eqn. (9) to Eqn. (1).

$$\text{Rate} = -\frac{d[NBS]}{dt} = \frac{K_2 K_3 [HOBr] [Ir(III)]_T}{[H^+] \{ [Cl^-] + K_2 \}} \quad \dots (10)$$

Under the condition  $[H^+] \{ [Cl^-] + K_2 \} \gg K_2 K_3 [HOBr]$ . Eqn. (6) will take shape of Eqn. (11)

$$[Ir(III)] = \{ [Ir(III)]_T [Cl^-] \} / \{ [Cl^-] + K_2 \} \quad \dots (11)$$

Considering Eqn. (2) and Eqn. (11) we have,

$$[C_1] = \{ K_2 [Ir(III)]_T \} / \{ [Cl^-] + K_2 \}, \quad \dots (12)$$

By putting the value of  $C_1$  in Eqn. (7), we have,

$$[HOBr] = \frac{k_f [NBS] \{ [Cl^-] + K_2 \}}{k_b [NHS] [Cl^-] + k_b K_2 [NHS] + K_3 K_2 [Ir(III)]_T} \quad \dots (13)$$

On substituting the value of  $[HOBr]$  from Eqn. (13) to Eqn. (10)

$$\text{Rate} = -\frac{d[NBS]}{dt} = \frac{k' [NBS] \{ [Cl^-] + K_2 \} [Cl^-]}{[H^+] \{ k_b [NHS] [Cl^-] + k_b K_2 [NHS] + K_3 K_2 [Ir(III)]_T \}} \quad \dots (14)$$

Where  $k' = k k_f K_2 K_3$

On rearranging Eqn. (14), Eqn. (15) is obtained:

$$\frac{1}{\text{rate}} = \frac{k_b [H^+] [NHS] (K_2 + [Cl^-])}{k' [NBS] [Ir(III)]_T} + \frac{K_3 [H^+]}{k k_f [NBS]} \quad \dots (15)$$

Rate law (Eqn. 14) has been complete agreement with observed data and proposed mechanism. The rate law shows that the rate of the reaction is inversely proportional to  $[H^+]$  i.e., order of reaction with respect to  $[H^+]$  should be negative one (i.e. = -1.0), but observed order with respect to  $[H^+]$  is -0.65 for the D-Galactose. The deviation of order in  $[H^+]$  from -1.0

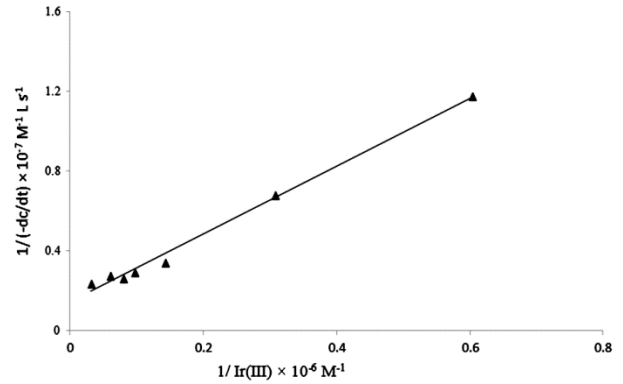
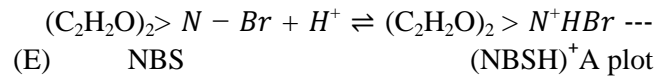


Fig. 4 — Plot of  $1/\text{rate}$  versus  $1/[Ir(III)]_T$  (Experimental conditions;  $[NBS] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[HClO_4] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[Hg(OAc)_2] = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[D(-)Galactose] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[Galactose] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$ )

to -0.65 ascribed as the involvement of  $H^+$  in the formation of unreactive protonated species of NBS in investigation, as given Eqn.(E) below:



NBS  $(NBSH)^+$  A plot of  $1/\text{rate}$  versus  $[NHS]$  or  $1/\text{rate}$  versus  $1/[Ir(III)]_T$  at constant  $[NBS]$ ,  $[H^+]$ ,  $[Cl^-]$  should yield a straight line with a positive intercept on the  $1/\text{rate}$  axis (Fig. 4). Such plots were obtained for showing validity of rate law, hence the proposed mechanism. The constant value of  $K_3/kk_f$  calculated from the intercept was  $4.54 \times 10 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}$  at particular temperature also confirm the validity of the proposed mechanism. The rate law (Eqn.14) and (Eqn.15) has been again proved via complete support with observed data of different activation parameters. The high positive values of the free energy of activation ( $\Delta G^\ddagger$ ) and enthalpy ( $\Delta H^\ddagger$ ) indicated that transition state is highly solvated, while the negative value of entropy of activation ( $\Delta S^\ddagger$ ) suggest formation of activated complex in reaction mechanism with the reduction of degree of freedom of reacting molecules.

## Conclusions

In light of the obtained kinetic data for Ir(III)-catalyzed oxidation of D-Galactose by NBS in acidic medium and activation conditions, the following conclusions may be drawn. The presence of very low (micro) amount of Ir(III) catalyst makes this sluggish reaction facile, indicates that Ir(III) is very potent catalyst. The deleterious effects of  $[NHS]$   $[Cl^-]$  and  $[H^+]$  is very well supported by stem (i), (ii) and (iii) respectively of Scheme 1. The function of  $Hg(II)$  is limited upto bromide ion ( $Br^-$ ) scavenger only not as

co-catalyst / promotor or as an inhibitor. In step (iii) of reaction, Scheme 1 an interaction between charged species 'C1' and a neutral molecules, leads the formation of most reactive activated complex 'C2', which is also proven by the negative entropy of activation. Before the rate deforming step, interaction of a charged species and a neutral molecule, is confirmed by nil effect of ionic strength on the rate. The high positive values of free energy of activation and enthalpy indicated that endothermic nature of transition state. During the whole process of investigation the extrications released are not environmentally adverse products or byproducts, confirming its ecofriendly behaviour. So, it is an efficient and safe chemical process.

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