

Mechanistic Approach to Aquachloroiridium(III) Catalysis in Oxidation of 1, 2-propanediol by alkaline N-bromosuccinimide : A Kinetic Modeling

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ABSTRACT: Kinetics of Ir(III) catalysed oxidation of 1,2-propanediol by N-bromosuccinimide (NBS) has been investigated in alkaline medium in the presence of mercuric acetate as Br⁻ ion scavenger in the temperature range of 30 to 45°C. The reaction follows complex kinetics, being first order in [NBS], zero order in 1, 2-propanediol and first order in [Ir(III)]. Increase in [OH⁻] increased the rate nonlinearly, indicating positive effect of [OH⁻] while addition of KCl decreased the rate, showing negative effect of chloride ions on the rate of the reaction. Successive addition of mercuric acetate, succinimide (NHS) and variation of ionic strength of the medium did not bring about significant change in the rate of the reaction. [IrCl₂(OH)(H₂O)₃] and NBS itself have been postulated as the reactive catalytic species of iridium (III) chloride and N-bromosuccinimide in alkaline medium, respectively. Activation parameters for the slow and rate determining step of the proposed mechanism involving the formation of most activated complex, [Cl₂Ir NBS (OH)(H₂O)₂] have been obtained from the rate measurements at 30, 35, 40 and 45°C. The rate law conforming to the observed kinetic results has been derived as:

$$\frac{-d[NBS]}{dt} = \frac{k_1 k [NBS][OH^-][Ir(III)]_T}{k_{-1}[Cl^-] + k_1[OH^-]}$$

The main oxidation products of the reaction have been identified as acetic acid and formic acid.

Keywords: Kinetics, Mechanism, Oxidation, Ir(III)catalysis, NBS, 1, 2-propanediol

INTRODUCTION

The diverse nature of the chemistry of N-halo compounds¹⁻⁵ is due to their ability to act as a source of halogenonium cations, hypohalite and nitrogen anions species which act as both bases and nucleophiles. N-Halosuccinimides are sources of positive halogens and these reagents have been exploited as oxidant for a variety of substrates^{6,7}. N-bromosuccinimide (NBS) has been extensively used as an oxidizing agent and analytical reagent especially in acid medium^{8,9} in both uncatalysed and catalysed reactions. However, there are only a few reports on the oxidation reactions of NBS in alkaline medium¹⁰⁻¹². The role of NBS as an oxidant in the oxidation of a large number of substrates has been probed using Ru (III)¹³, Pd (II)¹⁴⁻¹⁶, Pt (IV)¹⁷ and Rh (III)^{18,19} as homogeneous catalyst. Although Ir (III) catalysed^{20, 21} NBS oxidation has

been reported in aqueous acid, but no report is available on the role of Ir(III) chloride in NBS oxidation of any substrate in alkaline medium. The 1, 2-diol functionality is found in a series of synthetic intermediate. 1,2-Propanediol is non-toxic antifreeze in breweries and dairies. It finds its importance in a wide spectrum of areas^{22,23} such as (a) in the production of unsaturated polyester resins, (b) as an additive in nutrition product, (c) non-ionic detergent, (d) cosmetics, (e) brake fluid or hydraulic fluid and (f) as an de-icing agent. 1,2-Propanediol derivatives currently find use as central acting skeletal muscle relaxant. These characteristics of 1,2-propanediol interest us to study its oxidation by alkaline NBS in the presence of aquachloroiridium (III) complex as catalyst. Thus in view of biological and industrial importance of Ir (III) complexes, NBS and 1,2-propanediol and also in view of less information available in the literature on the role of

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aquachlorocomplex of Ir (III) in alkaline solution, an attempt has been made to study the kinetics and mechanism of Ir (III) catalysed oxidation of 1,2-propanediol by NBS in alkaline solution using mercuric acetate²⁴ as bromide ions scavenger. The main objectives of the present study are to ascertain (i) the reactive species of NBS in alkaline medium, (ii) the real catalytic species of Ir (III) chloride in alkaline medium, (iii) the role of chloride ions in deciding the real catalytic species of iridium (III), (iv) the role of mercuric acetate in addition to its role as bromide ions scavenger and finally (v) to elucidate the mechanistic steps and to discuss the rate law consistent with the observed kinetic results.

EXPERIMENTAL

Materials

The reagents employed in the present investigation are 1,2-propanediol (BDH Laboratory), N-bromosuccinimide of E. Merck grade, iridium(III)chloride (Johnson & Matthey), sodium hydroxide (E. Merck) and mercuric acetate (E. Merck). All other reagents used were of A. R. grade. All the solutions were prepared in doubly distilled water.

The solution of iridium(III) chloride was prepared by dissolving its 1g sample in HCl (3.6 mol dm⁻³). The concentrations of iridium(III) chloride and HCl were noted in the final solution which was stored in a black coated bottle to prevent any photochemical decomposition. The solution of NBS was prepared by dissolving its weighed amount in known volume of distilled water and its strength was estimated iodometrically. The solution of 1,2-propanediol was prepared by dissolving its known amount in desired volume of distilled water. Sodium perchlorate and sodium hydroxide were used to maintain the required ionic strength and alkalinity, respectively. A standard solution of mercuric acetate was acidified with 20% (v/v) acetic acid and solutions of all other reagents viz. KCl, sodium thiosulphate of E. Merck grade were prepared by dissolving their weighed samples in known volume of distilled water.

Kinetic Procedure

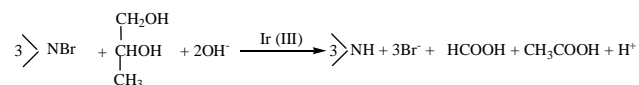
All the kinetic measurements were carried out at constant temperature 35°C (±0.1 °C). Appropriate

volumes of all reactants NBS, Ir(III), Hg(OAc)₂, KCl, NaOH and NaClO₄ were taken in a reaction bottle (Jena glass). The requisite volume of doubly distilled water was added to the reaction mixture so that total volume of the reaction mixture would become 100 ml after addition of requisite volume of 1,2-propanediol solution. The bottle containing reaction mixture was placed in an electrically operated thermostat (maintained at 35 °C) for thermal equilibrium. Appropriate volume of solution of 1,2-propanediol, also equilibrated at 35°C, was rapidly poured into the reaction mixture to initiate the reaction. The progress of the reaction was followed by estimating the amount of unconsumed [NBS] iodometrically in aliquots (5 ml) withdrawn from the reaction mixture at regular time intervals for about two half lives of the reaction.

The rate of the reaction (-dc/dt) in each kinetic run was determined by the slope of the tangent drawn at fixed concentration of NBS which is written as [NBS]*. The order of the reaction with respect to each reactant was determined by the relation between initial rate (-dc/dt) and initial [reactant].

Stoichiometry of the Reaction and Product Analysis

Varying [NBS]: [1, 2- propanediol] ratios were equilibrated at 35°C for 72 hours under the condition [NBS] >> [1,2-propanediol]. Estimation of residual [NBS] in different sets showed that one mole of [1,2-propanediol] consumed three moles of NBS. Accordingly, the following stoichiometric equation can be formulated:



Where >NBr and >NH stand for NBS and succinimide (NHS), respectively.

The main products of oxidation of 1, 2-propanediol are acetic acid and formic acid which were identified by spot test^{25,26} and thin layer chromatography (TLC)²⁷. In order to perform spot test, a drop of the reaction solution was mixed with 10% mercuric chloride and one drop of buffer solution containing 1ml of glacial acetic acid and 1g of sodium acetate per 100 ml water. The mixture was kept for dryness and the evaporated residue was taken up in a drop of water and to it a

drop of 0.1M ammonia was added. The appearance of black colour confirmed the presence of formic acid in the reaction mixture. TLC²⁸ using N-butanol, diethylamine, water in the ratio of 85:1:14 as the developing solvent was used to verify the presence of acetic acid as product in the oxidation of 1, 2-propanediol. The R_f value was found to be 0.44 which is very close to the reported R_f value, 0.45 for acetic acid in the aforesaid solvent system.

Kinetic Results

In order to study the role of reactants in the oxidation of 1,2-propanediol by NBS in the presence of aquachloroiridium(III) in alkaline medium, the oxidation kinetics was carried out at different initial concentrations of reactants at 308K. Rate $(-dc/dt)$ of the reaction increases in direct proportionality with increase in the initial [NBS], showing first-order kinetics with respect to [NBS]. This observation is also obvious from fair degree of closeness in k_{obs} value ($2.70 \times 10^{-4} \text{ s}^{-1}$) obtained from slope of plot (Fig. 1) between $(-dc/dt)$ and [NBS] and average value of k_{obs} ($2.68 \times 10^{-4} \text{ s}^{-1}$) obtained from the formula, $k_{obs} = (-dc/dt)/[\text{NBS}]^*$ at different initial [NBS]. At constant [NBS], [NaOH], [Ir(III)], [Hg(OAc)₂], [KCl] and temperature, the first-order rate constant (k_{obs}) remains practically constant on varying five-fold initial [1,2-propanediol], indicating zero-order dependence of the reaction on [1,2-propanediol]. The reaction rate $(-dc/dt)$ and first-order rate constant (k_{obs}) both increase with increase in [Ir(III)] under constant solution conditions (Table 1), indicating first order dependence of the reaction on [Ir(III)].

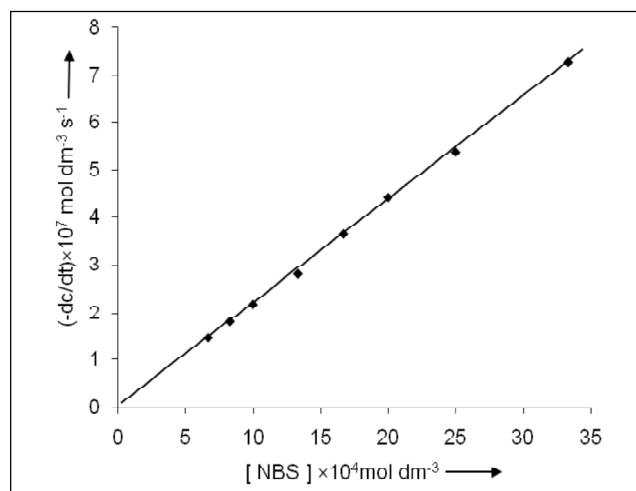


Figure 1: Plot of $(-dc/dt)$ vs. [NBS] at 35°C under the conditions of Table 1

Table 1
Effect of Variation of [NBS], [1, 2-propanediol] and [Ir (III)] on the rate at 35°C under the solution conditions: [NaOH] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$, [KCl] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ and [Hg (OAc)₂] = $2.50 \times 10^{-3} \text{ mol dm}^{-3}$

[NBS] $\times 10^3$ (mol dm ⁻³)	[1,2- propanediol] $\times 10^2$ (mol dm ⁻³)	Ir (III) $\times 10^6$ (mol dm ⁻³)	$(-dc/dt)$ $\times 10^7$ (mol dm ⁻³ s ⁻¹)	$k_{obs} \times 10^4$ s ⁻¹
0.67	2.00	3.35	1.46	2.80
0.84	2.00	3.35	1.80	2.64
1.00	2.00	3.35	2.18	2.73
1.34	2.00	3.35	2.86	2.60
1.67	2.00	3.35	3.64	2.60
2.00	2.00	3.35	4.42	2.76
2.50	2.00	3.35	5.36	2.68
3.34	2.00	3.35	7.26	2.64
1.00	1.00	3.35	2.08	—
1.00	1.34	3.35	2.20	—
1.00	2.00	3.35	2.18	—
1.00	2.50	3.35	2.24	—
1.00	3.34	3.35	2.16	—
1.00	4.00	3.35	2.30	—
1.00	5.00	3.35	2.26	—
1.00	2.00	3.35	2.18	—
1.00	2.00	5.02	3.32	—
1.00	2.00	6.70	4.00	—
1.00	2.00	8.37	5.34	—
1.00	2.00	10.00	6.56	—
1.00	2.00	11.72	7.76	—
1.00	2.00	13.40	8.80	—

Variation of ionic strength of the medium from $1.85 \times 10^{-2} \text{ mol dm}^{-3}$ to $12.85 \times 10^{-2} \text{ mol dm}^{-3}$ did not change the rate of reaction, indicating zero effect of ionic strength on the rate. Addition of succinimide (NHS) from $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ to $6.00 \times 10^{-3} \text{ mol dm}^{-3}$ was found to have no effect on the rate, showing thus negligible effect of addition of NHS on the rate of the reaction.

The results of Table 2 indicate that increase in [NaOH] increased the rate nonlinearly showing thus positive effect of [NaOH] on the rate with fractional order 0.76 obtained from $\log k_{obs}$ vs. $\log [\text{OH}^-]$ plot (figure not shown here) while successive addition of Hg(OAc)₂ to the reaction mixture indicated negligible effect on the rate of the reaction. Addition of chloride ions in the form of KCl to the reaction mixture under constant solution conditions decreased the rate $(-dc/dt)$ and a plot of $\log k_{obs}$ vs. $\log [\text{Cl}^-]$ was linear (Figure not shown) with slope (- 0.78), indicating negative effect of $[\text{Cl}^-]$ on the rate of the reaction.

Table 2
Effect of Variation of [NaOH], [Cl⁻] and [Hg(OAc)₂] on the rate at 35°C under the solution conditions [NBS] = 1.00 × 10⁻³ mol dm⁻³, [Ir (III)] = 3.35 × 10⁻⁶ mol dm⁻³ and [1,2-propanediol] = 2.00 × 10⁻² mol dm⁻³

[KCl] × 10 ³ (mol dm ⁻³)	[NaOH] × 10 ² (mol dm ⁻³)	[Hg(OAc) ₂] × 10 ³ (mol dm ⁻³)	(-dc/dt) × 10 ⁷ (mol dm ⁻³ s ⁻¹)
1.00	1.00	2.50	2.18
2.00	1.00	2.50	1.52
3.00	1.00	2.50	1.00
4.00	1.00	2.50	0.86
5.00	1.00	2.50	0.62
6.00	1.00	2.50	0.48
1.00	1.00	2.50	2.18
1.00	1.34	2.50	2.78
1.00	1.66	2.50	3.76
1.00	2.00	2.50	4.60
1.00	2.50	2.50	5.08
1.00	5.00	2.50	5.74
1.00	1.00	1.11	2.20
1.00	1.00	1.34	2.04
1.00	1.00	1.67	2.16
1.00	1.00	2.00	2.14
1.00	1.00	2.50	2.18
1.00	1.00	3.34	2.16

The reaction was studied at different temperatures and the rate constants measured at 30, 35, 40 and 45 °C led to compute energy of activation (E_a), enthalpy of activation (ΔH[#]), entropy of activation (ΔS[#]) and free energy of activation (ΔG[#]). Arrhenius factor (A) was calculated using specific rate constant (k_r) at 35 °C (Table 3).

Table 3
Effect of Temperature and Values of Activation Parameter for the Oxidation of 1, 2-propanediol by NBS in the presence of Ir(III) chloride as catalyst in alkaline medium at 35 °C

Temperature (K)	k _{obs} × 10 ⁴ s ⁻¹
303	1.85
308	2.73
313	4.13
318	5.85
Parameters	Values
k _r × 10 ⁻¹ (mol ² dm ⁻⁶ s ⁻¹)	1.23
Log A	11.48
E _a (kJ mol ⁻¹)	61.53
ΔH [#] (kJ mol ⁻¹)	58.95
ΔS [#] (JK ⁻¹ mol ⁻¹)	-33.86
ΔG [#] (kJ mol ⁻¹)	69.33

Solution conditions: [NBS] = 10.00 × 10⁻⁴ mol dm⁻³, [NaOH] = 1.00 × 10⁻² mol dm⁻³, [1,2-propanediol] = 2.00 × 10⁻² mol dm⁻³, [Ir(III)] = 3.35 × 10⁻⁶ mol dm⁻³, [KCl] = 1.00 × 10⁻³ mol dm⁻³, [Hg(OAc)₂] = 2.50 × 10⁻³ mol dm⁻³

Test for Free Radical

The addition of the reaction mixture to aqueous acrylamide monomer solution in dark did not initiate polymerization, indicating the absence of formation of free radical species in the reaction sequence. The control experiments were also performed under the same reaction conditions.

DISCUSSION

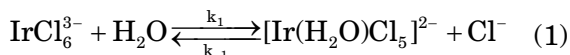
Role of Mercuric Acetate in Present Investigation

In the absence of mercuric acetate in the reaction mixture, bromide ions (reduction product of NBS) interact with NBS to form Br₂ which sets parallel oxidation of the substrate and thus creates complications in NBS oxidation. In order to prevent parallel Br₂ oxidation of the substrate, mercuric acetate²⁴ has been used as bromide ions scavenger. Hg (II) traps free bromide ions to form the complex [HgBr₄]⁻² and thus formation of complex, [HgBr₄]⁻² ensures pure NBS oxidation of 1,2-propanediol. Earlier, it is also reported that Hg(II) acts as an oxidant²⁹ as well as co-catalyst³⁰. Therefore, it needs to ascertain the role of Hg(OAc)₂ as oxidant and co-catalyst in the present investigation also in addition to its role as Br⁻ ions scavenger. In preliminary experiments, it has been observed that in the absence of NBS at constant concentrations of all other reagents viz. 1,2-propanediol, Hg(OAc)₂, NaOH, Ir(III) and KCl the reaction did not proceed at all, indicating non-involvement of Hg(OAc)₂ as oxidant. Further, in another experiments with NBS used as oxidant and at constant concentration of all other reagents including Ir(III) rate of the reaction was found to remain almost unchanged with increase in [Hg(OAc)₂], negating thus role of mercuric acetate in the reaction as co-catalyst. These observations indicate that Hg(II) is involved in the present reaction only as Br⁻ ion scavenger.

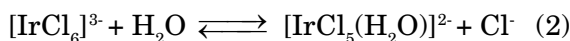
Reactive Species of Iridium(III) chloride in alkaline medium

A spectrophotometric study of the kinetics of the hydration of IrCl₆³⁻ and addition of Cl⁻ to

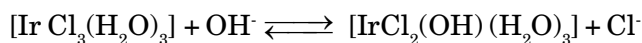
$[\text{Ir}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ in 1.0–2.5 M HClO_4 (or HCl) at 50 °C is reported, where the rate constants and the equilibrium constant K for the reversible reaction have been evaluated.



Visible and ultraviolet absorption spectra of the new Ir(III) complexes $[\text{Ir}(\text{H}_2\text{O})_2\text{Cl}_4]^-$ and $[\text{Ir}(\text{H}_2\text{O})_3\text{Cl}_3]$ together with the spectra of IrCl_6^{3-} and $[\text{Ir}(\text{OH})_2\text{Cl}_5]^{2-}$ in 2.5 F HClO_4 – 1.2 F NaClO_4 are also reported³¹ and found in reasonable agreement with the results reported by Poulsen and Garner³² in water and by Jørgensen³³. The literature on kinetic studies of Ir(III) catalysed oxidation of reducing sugars by acidic solution of NBS²⁰ and N-bromoacetamide³⁴ (NBA) indicates the existence of the following equilibrium on the basis of the effect of $[\text{Cl}^-]$ on the rate of reaction and IrCl_6^{3-} is taken as the reactive species of Ir(III) chloride in acidic medium.



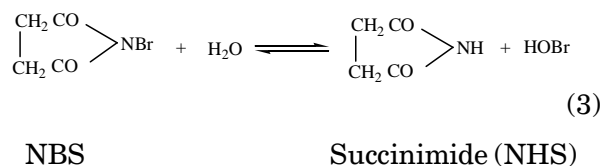
At room temperature and at 70 °C, Ir(III) chloride in 0.1 M HCl concentration is reported³⁵ to remain as $[\text{IrCl}_3(\text{H}_2\text{O})_3]$, whereas in 8.0 M HCl solution, it remains as $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ and $[\text{IrCl}_6]^{3-}$, respectively. Thus $[\text{IrCl}_3(\text{H}_2\text{O})_3]$, $[\text{IrCl}_4(\text{H}_2\text{O})_2]^-$ and $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ seem to be the predominant species between concentrations of 0.1M and 8 M HCl . In view of the reported literature, observed kinetic data and our prepared solution of Ir(III) chloride in 0.1 M HCl , it is reasonable to assume that the starting species of Ir(III) chloride is $[\text{IrCl}_3(\text{H}_2\text{O})_3]$ in the present investigation. Furthermore, since the study for Ir(III) chloride catalyzed NBS oxidation of 1,2-propanediol has been made in alkaline medium, a decision about the reactive species of Ir(III) chloride can be made only after taking into account the effect of $[\text{OH}^-]$ on the rate of oxidation of 1,2-propanediol. An increase in absorbance for Ir(III) chloride solution from 1.68 to 2.08 and 2.44 for Ir(III) chloride solution with two different concentrations of OH^- has been recently reported³⁶. On the basis of (i) the aforesaid reported literature regarding increase in absorbance for Ir(III) chloride solution with increase in $[\text{OH}^-]$, [(ii) observed positive effect of variation of $[\text{OH}^-]$ and (iii) observed negative effect of addition of $[\text{Cl}^-]$ on the oxidation rate in the present investigation, it can be concluded that the following equilibrium exists:



Out of two species $[\text{IrCl}_3(\text{H}_2\text{O})_3]$ and $[\text{IrCl}_2(\text{OH})(\text{H}_2\text{O})_3]$, the species $[\text{IrCl}_2(\text{OH})(\text{H}_2\text{O})_3]$ can be safely assumed as the reactive species of Ir(III) chloride in alkaline medium because on taking $[\text{IrCl}_2(\text{OH})(\text{H}_2\text{O})_3]$ as reactive species and considering other kinetic observations a rate law conforming to all the experimental results was derived.

Reactive species of N-bromosuccinimide in alkaline medium

In alkaline medium, NBS hydrolyses to give HOBr as shown by the following equilibrium:



HOBr is well known to be stable in alkaline medium. Thus reactive species of NBS in alkaline medium may be either NBS itself or HOBr. If HOBr is taken as the reactive species then the rate law derived on its basis requires negative effect of addition of NHS contrary to the observed negligible effect of NHS on the reaction rate. This rules out the possibility of taking HOBr as the reactive species of N-bromosuccinimide in alkaline medium. Hence under the circumstances the only choice left is to assume NBS as the oxidising species of N-bromosuccinimide in alkaline solution. The rate law derived on the basis of NBS also fully explains all the observed kinetic observations.

Spectral Evidence for the Formation of Complexes during the Course of the Reaction

After deciding the reactive species of both N-bromosuccinimide and Ir(III)chloride in alkaline medium and also considering zero -order kinetics with respect to 1,2-propanediol, efforts have been made to ascertain the possibility of the formation of a complex or complexes during the course of the reaction. It is reported that Ir(III)chloride forms complex with IO_3^- (oxidant) and does not form complex with xylose in its oxidation³⁶. It has been also recently reported³⁷ that Ir(III) chloride forms complex with 1,2-propanediol molecule in acidic medium and NBS is not involved in complex

formation. In the oxidation of 1,2-propanediol by NBS catalysed by Ir(III) chloride in alkaline medium, it has been observed that order with respect to [1,2-propanediol] is zero throughout its five-fold variation. This shows that in the slow and rate controlling step 1,2-propanediol is not involved, although in fast step it will react with the most reactive complex to form the reaction products along with regeneration of the catalyst for its further catalytic action. In view of the observed first order kinetics in [NBS], it is thus evident that in the present investigation there seems to be strong possibility of the formation of complex between reactive species of Ir(III) chloride and NBS in alkaline medium. In order to probe the possible formation of a complex between NBS and $[\text{IrCl}_2(\text{OH})(\text{H}_2\text{O})_3]$, spectra for the solutions of Ir(III) chloride and OH^- and for the solutions of NBS, Ir(III) chloride and OH^- have been taken (Fig. 2: spectra 1, 2, 3, 4, 5 and 6). It is clear from the spectra (Fig. 2: spectra 1, 2 and 3) that with the addition of more OH^- in the solution there is an increase in the absorbance, indicating the formation of the reactive species $[\text{IrCl}_2(\text{OH})(\text{H}_2\text{O})_3]$ in alkaline medium. When solution of NBS having spectra (4) was added to the solution of Ir(III)chloride and OH^- , again increase in absorbance was obtained (Fig. 2: spectra 5). This confirms the formation of most reactive species $[\text{IrCl}_2(\text{NBS})(\text{OH})(\text{H}_2\text{O})_2]$ in the slow and rate determining step. When the solution of 1,2-propanediol was added to the mixed solution of NBS, Ir(III) chloride and OH^- , the spectra (5) disappeared immediately and another spectra (6) with decreased absorbance was obtained which proves and suggests that the most reactive species $[\text{IrCl}_2(\text{NBS})(\text{OH})(\text{H}_2\text{O})_2]$ attacks 1,2-propanediol molecule in fast step.

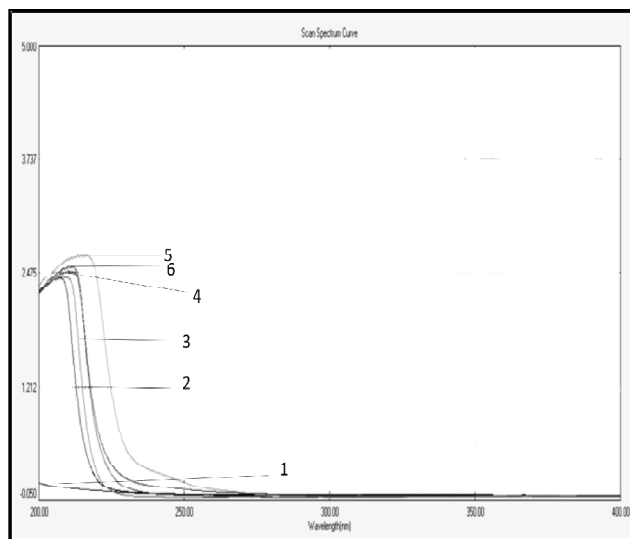
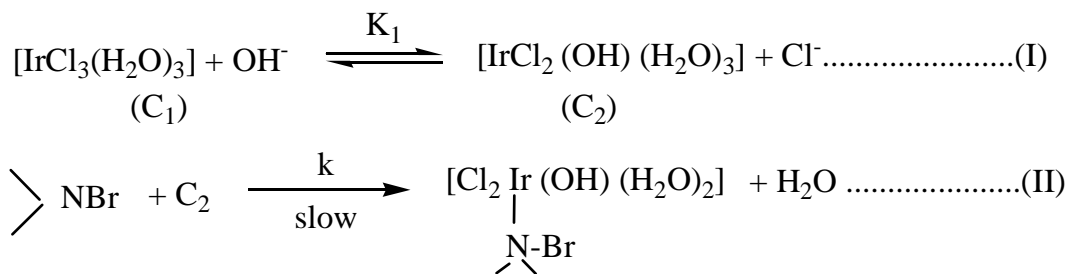


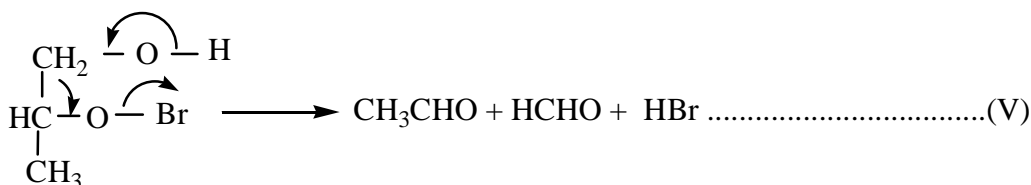
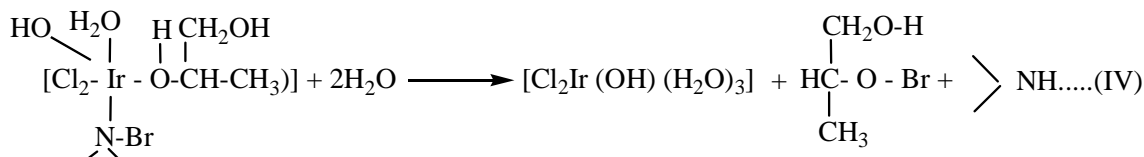
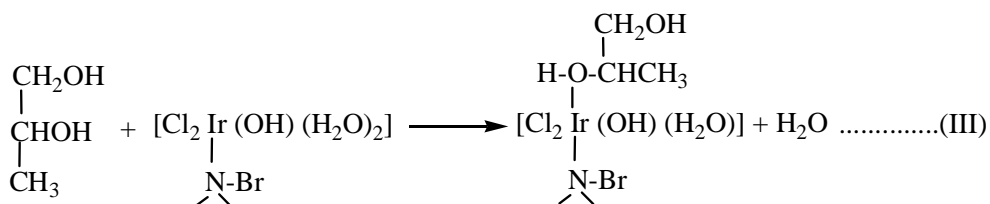
Figure 2: Conditions for Spectra of Various Solutions

1. $[\text{Ir(III)}] = 6.70 \times 10^{-6} \text{ mol dm}^{-3}$
2. $[\text{Ir(III)}] = 6.70 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$
3. $[\text{Ir(III)}] = 6.70 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 4.00 \times 10^{-2} \text{ mol dm}^{-3}$
4. $[\text{NBS}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$
5. $[\text{Ir(III)}] = 6.70 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 4.00 \times 10^{-2} \text{ mol dm}^{-3}$ and $[\text{NBS}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$
6. $[\text{Ir(III)}] = 6.70 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 4.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{NBS}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{1,2-propanediol}] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$

Elucidation of Reaction Mechanism and Derivation of Rate Law

In the light of reactive species of N-bromosuccinimide and Ir(III)chloride in alkaline solution as NBS itself and $[\text{IrCl}_2(\text{OH})(\text{H}_2\text{O})_3]$ respectively, statement regarding the role of $\text{Hg}(\text{OAc})_2$ in the reaction and on the basis of all other observed kinetic results the following reaction scheme -1 is suggested.





Interaction of NBS with species C_2 (step II) increases the oxidizing capacity of NBS due to the presence of more electron deficient Br atom in NBS of $[\text{IrCl}_2(\text{NBS})(\text{OH})(\text{H}_2\text{O})_2]$ complex which rapidly attacks electron rich 1,2-propanediol molecule leading to the formation of reaction products with regeneration of catalytic species for further catalytic action (fast steps III-VII).

Scheme-1

Rate law derivation

The rate of the reaction may be written in terms of rate of loss of [NBS] in the light of aforesaid reaction scheme -1 as:

$$\frac{-d[\text{NBS}]}{dt} = k[\text{C}_2][\text{NBS}] \quad (1)$$

Considering steady state to $[\text{C}_2]$ from steps (I) and (II) we have

$$[\text{C}_2] = \frac{k_1[\text{C}_1][\text{OH}^-]}{k_{-1}[\text{Cl}^-] + k[\text{NBS}]} \quad (2)$$

Where $K_1 = k_1 / k_{-1}$

On substituting the value of $[\text{C}_2]$ from eq. (2) in eq. (1) we have

$$\frac{-d[\text{NBS}]}{dt} = \frac{k k_1 [\text{C}_1][\text{OH}^-][\text{NBS}]}{k_{-1}[\text{Cl}^-] + k[\text{NBS}]} \quad (3)$$

The total concentration of Ir (III) i.e. $[\text{Ir(III)}_T]$ may be written as eq. (4)

$$[\text{Ir(III)}_T] = [\text{C}_1] + [\text{C}_2] \quad (4)$$

Considering eq. (2) and (4) and on further solving for $[\text{C}_1]$ we get eq. (5)

$$[\text{C}_1] = \frac{(k_{-1}[\text{Cl}^-] + k[\text{NBS}])[\text{Ir(III)}_T]}{k_{-1}[\text{Cl}^-] + k[\text{NBS}] + k_1[\text{OH}^-]} \quad (5)$$

Considering eq. (3) and (5) we have eq. (6)

$$\frac{-d[\text{NBS}]}{dt} = \frac{k k_1 [\text{OH}^-] [\text{NBS}] [\text{Ir(III)}]_T}{(k_{-1} [\text{Cl}^-] + k_1 [\text{OH}^-]) + k [\text{NBS}]} \quad (6)$$

Since k is small therefore in the light of inequality, $(k_{-1} [\text{Cl}^-] + k_1 [\text{OH}^-]) \gg k [\text{NBS}]$ the final rate law can be written as eq. (7)

$$\frac{-d[\text{NBS}]}{dt} = \frac{k_1 k [\text{NBS}] [\text{OH}^-] [\text{Ir(III)}]_T}{k_{-1} [\text{Cl}^-] + k_1 [\text{OH}^-]} \quad (7)$$

The rate law (7) agrees well with all the observed kinetic results. It also explains zero effect of ionic strength of the medium indicating dipole – dipole interaction which is evident from the slow step (II).

Further verification of the above rate law can be achieved on rearranging the eq. (7).

$$\frac{1}{\text{rate}} = \frac{k_1 [\text{Cl}^-]}{k_1 k [\text{NBS}] [\text{OH}^-] [\text{Ir(III)}]_T} + \frac{1}{k [\text{NBS}] [\text{Ir(III)}]_T} \quad (8)$$

According to eq.(8) when plots were made between $1/\text{rate}$ and $[\text{Cl}^-]$ (Plot-A) and between $1/\text{rate}$ and $1/[\text{OH}^-]$ (Plot-B), straight lines (Figures not shown here), having positive intercept on y-axis should be obtained and these were found to be so. This not only proves the validity of rate law (7) but also gives support to the proposed reaction scheme-1. The fair degree of closeness in k values ($1.93 \times 10^2 \text{ mol dm}^{-3} \text{ s}^{-1}$ obtained from plot-A and $1.99 \times 10^2 \text{ mol dm}^{-3} \text{ s}^{-1}$ from plot-B) also supports the validity of proposed mechanism. Similarly almost near K_1 values (6.41×10^{-2} and 6.24×10^{-2}) obtained from slopes of aforesaid plots also support the proposed reaction scheme-1.

CONCLUSIONS

On the basis of our study on Ir(III) catalysed oxidation of 1,2-propanediol by alkaline NBS the following conclusions are drawn:

1. NBS itself is the reactive species of N-bromosuccinimide in alkaline medium.
2. $[\text{IrCl}_2(\text{OH})(\text{H}_2\text{O})_3]$ is the reactive species of Ir(III) chloride in alkaline medium.
3. Hg (II) plays only the role of Br^- ion scavenger in the present investigation and its role as oxidant and co-catalyst is negated.

4. In the slow and rate determining step a most reactive oxidizing complex, $[\text{IrCl}_2(\text{OH})(\text{NBS})(\text{H}_2\text{O})_2]$ is formed by the interaction of $[\text{IrCl}_2(\text{OH})(\text{H}_2\text{O})_3]$ and NBS.
5. Acetic acid and formic acid have been identified as the main oxidation products of the reaction.
6. A high negative value of ΔS^\ddagger suggests that transition state is more ordered than the reactants.
7. A high positive value of ΔG^\ddagger indicates that the transition state is highly solvated.

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