

# OXIDATION OF SOME GLYCOL BY N-BROMOSUCCINIMIDE IN PRESENCE OF IRIIDIUM(III) CHLORIDE CATALYST IN ACIDIC MEDIUM- A KINETIC STUDY

Dr. Prasant Kumar Verma,

\*Teacher Kamla Girls +2 High School, Sitamarhi, Bihar.

## Abstract:

Investigation of various organic substrates is one of the most active areas of current research. The work reported in the present paper consist of the study of reaction between N-bromosuccinimide (NBS) as the oxidizing reagent and some Physiologically active compounds such as glycols viz. Propene glycol, Pentene glycol and heptane glycol in presence a of novel catalyst iridium(III) chloride.

These reaction have been studied from the kinetic consideration to ascertain the mechanistic pathways, product have been isolated and positively identified in each case and possible stepwise mechanism has been isolated and positively identified in each case and possible stepwise mechanism has been outlined as detailed in the last point. Role of the catalyst has also been studied in detail. The work thus introduces a novel catalyst which has yet remained somewhat unexplored in the realm of kinetic studies of various organic substrates by mild organic oxidizing agents.

**Keyword:**-N-Bromosuccinimide, Propene glycol, Pentene glycol, Heptene glycol, Iridium(III) chloride

**Introduction :** The investigation of organic reaction mechanism is one of the most active areas of current research, and still much remains to be done in this field. Much emphasis being given now-a-days to the study of organic reaction mechanism at all the levels of the study of organic chemistry on account of the following facts:-

1. An elementary grasp of how reactions occur is a great help in remembering the factual data which constitute the build of an elementary organic chemistry.
2. An understanding of reaction mechanism serves a guide in the design of sequences of reactions pertaining to synthetic organic chemistry, many of these have washed to commercial importance.
3. A study of the type of evidence which is used establish reaction mechanism introduces the research scholar to a rigorous and stimulating train of though and induces him to be critical in evaluating the significance of scientific evidences.

In the present work, scientific literature on the Ir(III) catalyst utilized in homogeneous catalyzed pcess have shown somewhat scanty in the study of kinetic and mechanistic study, its seemed worthwhile to undertake a systematic kinetic study by performing a series of experiments of the oxidation of some glycols by N-Bromosuccinimide in acidic media, catalyzed by Iridium(III) chloride.

Variation of Hydrogen ion concentration, [H<sup>+</sup>] have been provided by perchloric ion concentration as constant. Potassium chloride has been utilized for maintaining the chloride ion concentration as constant. While mercuric acetate has been employ as the scavenger for bromide ion.

**Experimental:** Present work deals with Studies on Ir(III) catalyzed N-bormosuccinimide oxidation of Propene glycol, Pentene glycol and Heptene glycol in acidic media, provided by perchloric- acid . Here mercuric acetate has been employed as bromide ion scavenger. The progress of reaction was followed by estimating the concentration of unconsumed NBS iodometrically. Full details all the chemicals utilized in the present thesis are given below.

All the solution was prepared in double distilled water.

1. The solutions of NBS were preparad by taking the appropriate amount of G.R.(E.Meerck) sample of NBS in minimum amount of warm water and then solution was made up to the mark with cold water in 100 ml volumetric flask. The solution of NBS was always freshly prepared and utilized same day and was stored in the black coated flask to prevent it photochemical decomposition<sup>2</sup>. Its strength was determine de iodometrically<sup>3</sup> using freshly prepared starch solution as indicator.
2. Aqueous solutions of propene glycol, Pentene glycol and Heptene glycol were prepared by dissolving accurately weighed amount of samples in double distilled water.
3. Mercuric acetate solution was prepared by dissolving it in doubled distilled water and acidified with little amount of glacial acetic acid.

4. Iridium(III) chloride (Johnson-Mathey) solution was prepared by dissolving its 1 sample in 0.5(N) hydrochloric acid and the volume of solution was made up to mark in 1L measuring flask.
5. Perchloric acid use was its solution of known strength and stand arising it by standard sodium hydroxide solution.
6. Standard solution of sodium hydroxide was prepared by dissolving its E. Merck sample in water and then standardized by titrating against standard oxalic acid solution using phenolphthalein as indicator.
7. For ionic strength investigation aqueous and neutral solution of sodium perchlorate was prepared.
8. 5% solution of potassium iodide (E. Merck) was prepared by dissolving it in double distilled water.
9. Succinimide sample was used by dissolving in double distilled water.
10. 1% aqueous starch solution was always prepared fresh.
11. A.R. (B.D.H.) sample of glacial acetic was used.
12. Appropriate weight of sodium thiosulphate A.R (B.D.H.) was dissolved in distilled water and then standardized using standard copper sulphate solution iodometrically.

### Elucidation of the order of the reaction:

Throughout the course of experiment the concentration of NBS (Oxidant) was kept sufficiently much smaller than that of the reducing substrate as determined stoichiometrically. Thus in each investigation rate of oxidation depends upon the concentration of the oxidant.

In all oxidation, the reactions were found to follow first order kinetic with respect to NBS. The rate constants for NBS were calculated using the equation.

$$K_1 = 2.303/t \log_{10} a/(a-x)$$

Where,  $a$  = initial concentration of NBS,

$(a-x)$  = remaining concentration of NBS at time 't'.

i.e.  $K_1 = -2.303 \times \text{slope}$

The order with respect to either substrate or hydrogen ion was elucidated by dividing rate of reaction values with NBS denoted by [NBS]. The value of  $k_1$  thus obtained was found to be constant for different initial concentration of substrate or hydrogen ions, hence the order was also assumed to be one with respect to substrate or hydrogen ions or with respect to Ir(III) when similar procedure was followed.

### Results and discussion:-

This Chapter deals with the interpretation of the experimental kinetic data obtained and shown in chapter (III-V), in order to suggest the most probable reaction mechanism for Ir(III) catalyzed oxidation of propene glycol, pentene glycol and heptene glycol by N-bromosuccinimide in acidic medium.

NBS is an excellent mild oxidizing agent which has been initially used for the volumetric estimation of many organic substrates<sup>1,2</sup>. It has been utilized in the oxidation of alcohol and the redox reaction has been investigated kinetically and the results have been reported<sup>3,4</sup>. Ir(III) chloride as catalyst in the oxidation of organic substrate has been reported somewhat scantily and thus induce us to undertake the present research work.

Summary of experimental results in Ir(III)-catalyzed oxidation of propene glycol, pentene glycol and Heptene glycol by N-Bromosuccinimide in acidic medium.

The kinetic results are as follows:

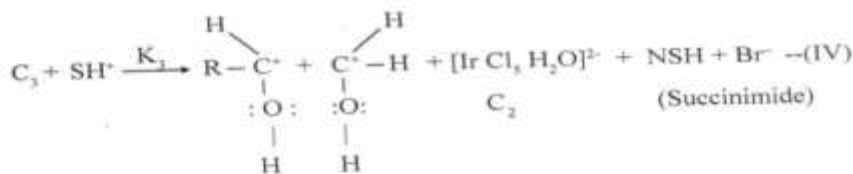
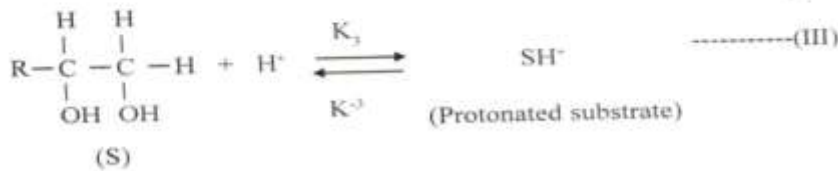
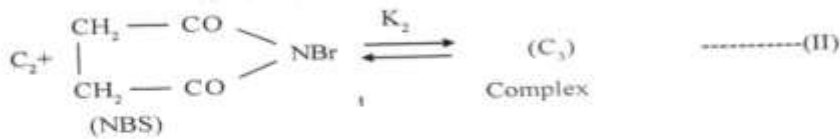
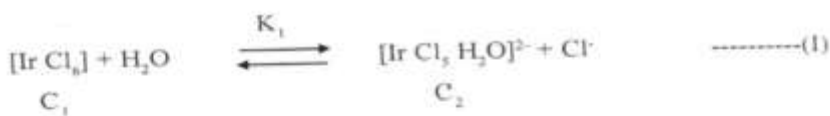
1. All the redox reactions follow first order kinetics with respect to N-bromosuccinimide.
2. The redox reaction exhibits first order dependence on each of the glycols.
3. The aforesaid redox reactions have shown to obey first order dependence with respect to hydrogen ion concentration  $[H^+]$ .
4. The redox reactions have shown to obey first order kinetics with respect to Ir(II) concentration.
5. Addition of chloride ion slows down the rate of reaction.
6. The rate of reaction was unaffected by the addition of mercuric acetate.
7. The rate of reaction remains also unaffected by the addition of succinimide.
8. The rate of reaction increases markedly with increase in temperature.
9. Variation of ionic strength did not affect the rate of the redox reaction.
10. The redox reaction followed 1:1 stoichiometry with each of the three experimental glycols.

Actual reactive species of N-bromosuccinimide in acidic medium N-bromosuccinimide (NBS) has been reported to exist in the equilibria and in acidic media.<sup>5,2</sup>

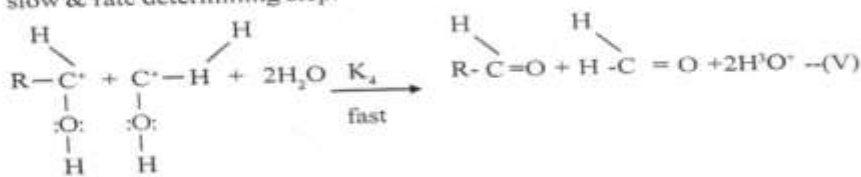
Thus NBS itself or protonated NBS i.e.  $N^+BSH$  or  $H_2OBr^+$  seem to be the probable oxidizing species of NBS in acidic medium. Since addition of succinimide did not alter the rate of reaction, it implies that neither  $H_2OBr^+$  i.e. bromonium cation nor protonated NBS i.e.  $N^+BSH$  is involved in the oxidation process. Had there been involvement, addition of succinimide must have shown a marked negative effect.<sup>7-10</sup>

**Most Probable mechanism of Ir(III) catalyzed oxidation of glycols by NBS in acidic medium:**

The conclusion drawn from experimental kinetic data reported in below clearly suggest that all the title redox reaction follow similar kinetics. Following reaction steps are suggested.



slow & rate determining step.



Where, R=CH<sub>3</sub> - for Propene glycol  
 R = -C<sub>3</sub>H<sub>7</sub> for Pentene glycol  
 R = n-C<sub>7</sub>H<sub>11</sub> for Heptene glycol

$$\Rightarrow [C_3] = \frac{K_1 K_2 [NBS] [Ir(III)]_T}{[Cl^-] + K_1 + K_1 K_2 [NBS]} \quad \text{-----(6)}$$

Now substituting the value of [C<sub>3</sub>] from equation (6) in equation (1), we get have

$$\Rightarrow -\frac{d[NBS]}{dt} = \frac{K K_1 K_2 [NBS] [Ir(III)]_T [S^+ H]}{[Cl^-] + K_1 + K_1 K_2 [NBS]}$$

$$\Rightarrow -\frac{d[NBS]}{dt} = \frac{K K_1 K_2 [NBS] [Ir(III)]_T [S^+ H]}{[Cl^-] + K_1 \{1 + K_2 [NBS]\}} \quad \text{-----(7)}$$

Assuming  $1 \gg K_2 [NBS]$  i.e.  $1 + K_2 [NBS] \cong 1$ , Equation (7) reduces to

$$\Rightarrow -\frac{d[NBS]}{dt} = \frac{K K_1 K_2 [NBS] [Ir(III)]_T [S^+ H]}{[Cl^-] + K_1} \quad \text{-----(8)}$$

From step (III) and (IV) on applying steady state approximation principle to [S<sup>+</sup> H] we have

$$\Rightarrow -\frac{d[S^+ H]}{dt} = K_3 [S] [H^+] - K^{-3} [S^+ H] - K [C_3] [S^+ H]$$

$$\Rightarrow \text{At steady state, } -\frac{d[S^+ H]}{dt} = 0$$

$$\Rightarrow 0 = K_3 [S] [H^+] - K^{-3} [S^+ H] - K [C_3] [S^+ H]$$

$$\Rightarrow 0 = K_3 [S] [H^+] - [S^+ H] \{K^{-3} + K [C_3]\}$$

$$\Rightarrow [S^+ H] \{K^{-3} + K [C_3]\} = K_3 [S] [H^+]$$

$$\Rightarrow [S^+ H] = \frac{K_3 [S] [H^+]}{K^{-3} + K [C_3]} \quad \text{----- (9)}$$

Since the rate (IV) is slowest and rate determining step, hence K is very small and equation (9) reduces to

$$\Rightarrow [S^+H] = \frac{K_3[S][H^+]}{K^{-3}}$$

$$\Rightarrow [S^+H] = K'_3[S][H^+] \dots\dots\dots(10)$$

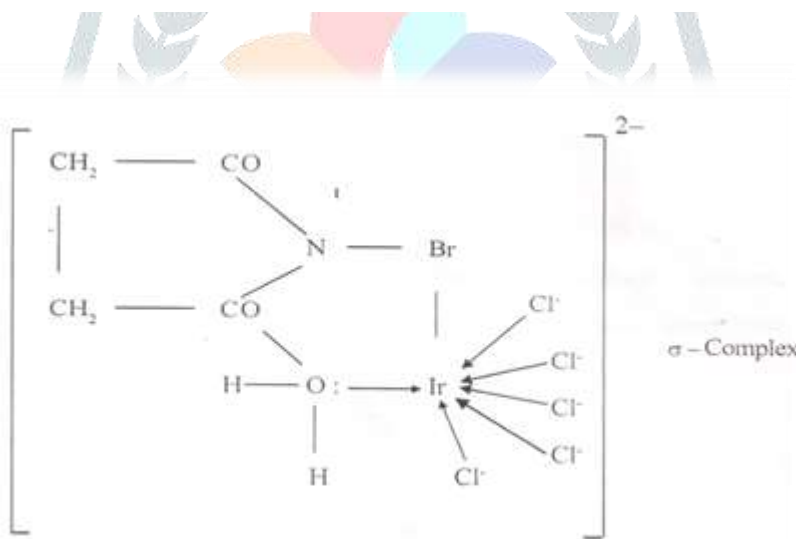
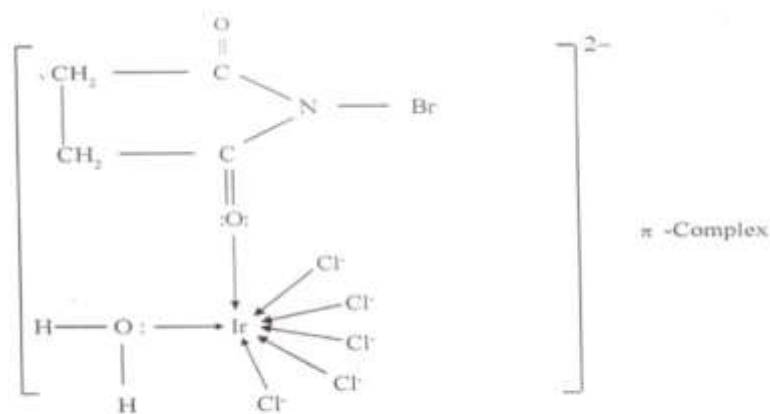
$$\text{Where } K'_3 = \frac{K_3}{K^{-3}}$$

Now the substituting the value of  $[S^+H]$  from equation (10) in equation (8), we get

$$\Rightarrow -\frac{d[NBS]}{dt} = \frac{KK_1K_2K'_3[NBS][Ir(III)_T][S^+H]}{[Cl^-]+K_1} \dots\dots\dots(11)$$

This derived rate law (11) is valid for the Ir(III) chloride catalyzed oxidation of all the three experimental glycols by NBS on acidic medium as it is consistent and satisfactorily explains all the observed kinetic results.

The structure of complexes formed is not known with certainty but in order to explain the formation of products in step (IV) following structures may be assigned for the  $\pi$ -Complex and  $\sigma$ -Complex.



#### References :

1. R. Filter,;Chem.Rev. 63, 21(1963)
2. N. K. Matur and C. K. Narang : The determination of organic compounds with N-bromosuccinimide Acad. Press New York (1975).
3. N.Venkatasubramanian V. Thiagrajan : Can J. Chem.,47, 694,(1969).
4. N. S. Srinivasan and N.Venkatasubramanian : Indian J. Chem., 9, 726, (1971).
5. N.S. Pandey et al :Tetrahedron, 38,169, (1982).
6. M .B. Singh et al : J. Mol. Catalysis, 40, 49, (1987)
7. O. Kotluka and W. Von Niessen, : Swit. Sci. 401, 185, (1998)
8. J.H.B.J. Hoebink et al ; Chem. Engg. Sci., 55, 1573, (2000)
9. A. De. Sarkar and B. C. Khanra: Ind. J. Phys., 77A, 603, (2003).
10. Abir De Sarkar and B. C. Khanra: Ind. J. Chem., 43A, 1033, (2004).