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Kinetics and Mechanism of Oxidation of Cycloheptanol in Acid Solution of N-Bromosuccinimide

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The kinetics and mechanism of iridium(III) chloride catalysed oxidation of cycloheptanol by acidic solution of N-bromosuccinimide (NBS) have been extensively studied at constant temp. (35°C). Kinetic findings indicate first order reaction kinetics in oxidant, substrate, Ir(III) and reductant in each case. Negative effect of chloride ion has been observed on reaction rate while ionic strength of the medium and successive addition of succinimide on reaction rate do not bring any significant change in the reaction velocity. The oxidation reaction path involving NBS, *i.e.*, ΔE_a and ΔS^*, ΔF^* have also been evaluated and found to be 16.72 kcal/mole, –5.83 e.u. and 17.88 Kcal/mole respectively and a suitable mechanism consistent with the observed kinetic finding has been suggested.

INTRODUCTION

N-Bromosuccinimide (NBS) is a potential oxidising agent[1, 2] and has been used also in the estimation of several organic as well as inorganic compounds. Recently transition metal ions have been widely used as homogeneous catalysts in the oxidation of several organic compounds in acidic and alkaline media. The use of iridium(III) chloride as a homogeneous catalyst has been reported by Tandon and Krishna[3] in the oxidation of acetone. Very little work has been done on Ir(III) chloride as catalyst and no one has attempted to probe the actual catalytic potential of Ir(III) in NBS in the oxidation of cycloheptanol (cyhtol) in acidic medium. So far efforts have been made to collect the kinetic data and use them for elucidating the oxidative paths with special reference to actual catalytic activity of Ir(III) in acidic medium.

EXPERIMENTAL

All the chemicals used during the course of kinetic investigation were of AR grade (E. Merck). The solution of NBS was freshly prepared and stored in a black coated flask to prevent photochemical effect.[4] Its strength was checked iodometrically.[5] The aqueous solution of Ir(III) was prepared by dissolving 1 g sample in 0.5 M HCl.

The progress of the reaction was elucidated by estimating unreacted NBS iodometrically.[6] No oxidation of the solvent occurred under experimental conditions.

RESULTS AND DISCUSSION

The first order reaction kinetics was observed with respect to oxidant as well as substrate in acidic medium at constant temperature (35°C). A close examination of Table-1 indicates

TABLE-1

EFFECT OF [OXIDANT], [SUBSTRATE] AND [CATALYST] ON REACTION RATE

$[Hg(OAc)_2] = 2.50 \times 10^{-3}$ M; Temp. = 35°C; $[KCl] = 4.00 \times 10^{-2}$ M

[NBS] $\times 10^{-3}$ M	[Cyhtol] $\times 10^{-2}$ M	[Ir(III)] $\times 10^{-6}$ M	$[HClO_4]$ $\times 10^{-2}$ M	$k_1 \times 10^2$ min^{-1}	k_2
0.50	2.00	2.00	1.00	1.54	—
0.67	—	—	—	1.40	—
0.84	—	—	—	1.55	—
1.00	—	—	—	1.56	—
1.25	—	—	—	1.66	—
1.67	2.00	2.00	1.00	1.65	—
1.00	1.00	2.00	1.00	0.67	$0.67A^{\pm}$
—	1.33	—	—	1.07	0.80
—	2.00	—	—	1.56	0.78
—	2.50	—	—	1.96	0.78
—	4.00	—	—	3.03	0.76
1.00	8.00	2.00	1.00	6.13	0.76
1.00	2.00	1.00	1.00	0.68	$0.68B^{\pm}$
—	—	2.00	—	1.56	0.78
—	—	3.00	—	2.50	0.83
—	—	4.00	—	3.21	0.80
—	—	5.00	—	3.82	0.78
6.00	2.00	6.00	1.00	4.99	0.83

$A^{\pm} = k_2 = \frac{k_1}{[Cyhtol]} \times mole^{-1}\,min^{-1}$, $B^{\pm} = k_2 = \frac{k_1}{[IrCl_3]} \times 10^4\,mole^{-1}\,min^{-1}$

that on increasing the concentration of NBS, the value of K_1 does not significantly change and shows direct proportionality between K_1 and [Cyhtol], which is further confirmed graphically (not shown)—a straight line passing through the origin with a value of slope nearer to the average value of K_2 (log K_1 *vs*. Cyhtol). The dependence of order of reaction on perchloric acid as well as Ir(III) chloride concentration a first-order reaction kinetics, is observed. It is evident from Tables 1 and 3 that the constancy in K_2 values indicates that the reaction is susceptible to changes in $[HClO_4]$, and shows proportionality between K_1 and $[HClO_4]$. On increasing the concentration of Ir(III) chloride the value of K_1 increases which further confirms graphically (not shown) a straight line passing through the origin with a unit slope. The negative influence of chloride ion (Table-2) on redox reaction rate is observed. There is no significant influence of the addition of succinimide (Table-2), mercuric acetate (Table-3) as well as influence of ionic strength of the medium (Table-4) on reaction rate.

TABLE-2

EFFECT OF [Cl⁻] AND [SUCCINIMIDE] ON REACTION RATE

$[NBS] = 1.00 \times 10^{-3}$ M $[Ir(III)] = 2.00 \times 10^{-6}$ M

$[Cyhtol] = 2.00 \times 10^{-2}$ M $[HClO_4] = 1.00 \times 10^{-2}$ M

$[Hg(OAc)_2] = 2.50 \times 10^{-3}$ M Temp. = 35°C

$[KCl] \times 10^2$ M	$[Succinimide] \times 10$ M	$k_1 \times 10^2$ min^{-1}
2.00	—	2.46
3.00	—	1.84
4.00	—	1.56
5.00	—	1.38
6.00	—	1.28
8.00	—	1.08
10.00	—	0.86
20.00	—	0.68
4.00	0.00	1.56
4.00	1.00	1.50
—	2.00	1.52
—	3.00	1.60
—	4.00	1.54
—	6.00	1.48
4.00	8.00	1.54

TABLE-3

EFFECT OF [HYDROGEN] AND [BROMIDE ION] ON REACTION RATE

$[NBS] = 1.00 \times 10^{-3}$ M $[Ir(III)] = 2.00 \times 10^{-6}$ M

$[Cyhtol] = 2.00 \times 10^{-2}$ M $[KCl] = 4.00 \times 10^{-2}$ M

$[HClO_4]$ $\times 10^2$ M	$[Hg(OAc)_2]$ $\times 10^3$ M	$k_1 \times 10^2$ min^{-1}	$k_2 = k_1/[HClO_4] \times 10^2$ mole^{-1} min^{-1}
0.50	2.50	0.65	1.30
1.00	—	1.56	1.56
1.25	—	1.90	1.52
1.50	—	2.43	1.62
2.00	—	3.11	1.55
3.00	2.50	4.65	1.55
1.00	2.50	1.56	—
—	4.00	1.60	—
—	6.00	1.58	—
—	8.00	1.56	—
—	12.00	1.54	—
1.00	16.00	1.57	—

TABLE-4

EFFECT OF IONIC STRENGTH AND TEMPERATURE ON REACTION RATE

$[NBS] = 1.00 \times 10^{-3}$ M $[Ir(III)] = 2.00 \times 10^{-6}$ M

$[Cyhtol] = 2.00 \times 10^{-2}$ M $[KCl] = 4.00 \times 10^{-2}$ M

Temp (°C)	$[HClO_4] \times 10^2 M$	$[NaClO_4] \times 10^2 M$	$\mu \times 10^2$ M	$k_1 \times 10^2\ min^{-1}$
35	1.0	0.00	5.00	1.56
—	—	5.00	10.00	1.55
—	—	10.00	15.00	1.58
—	—	20.00	25.00	1.54
—	—	30.00	35.00	1.52
—	—	40.00	45.00	1.56
35	1.00	50.00	55.00	1.56
30	1.00	0.00	5.00	1.07
35	—	—	—	1.56
40	—	—	—	2.35
45	1.00	0.00	5.00	3.16

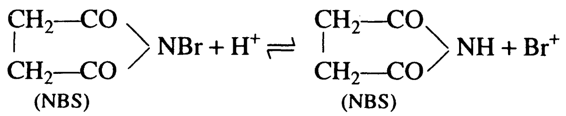
The value of energy of activation and other related thermodynamical parameters have been evaluated at four different temperatures as follows.

$\Delta E_A = 16.72$ kcal/mol

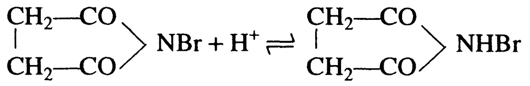
$\Delta S^* = -5.83$ e.u.

$\Delta F^* = 17.88$ kcal/mole

NBS exists in the following equilibria in acidic medium as reported earlier.[7, 9]



$$\underset{(NBS)}{\begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array}} \rangle NBr + H^+ \rightleftharpoons \underset{(NBS)}{\begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array}} \rangle NH + Br^+ \qquad (i)$$



$$\begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array} \rangle NBr + H^+ \rightleftharpoons \begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array} \rangle NHBr \qquad (ii)$$

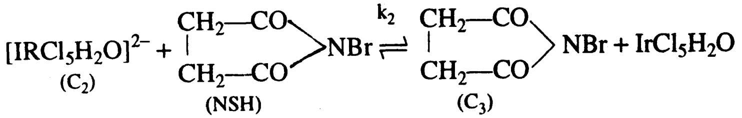
$$Br^+ + H_2O \rightleftharpoons H_2OBr^+ \qquad (iii)$$

Thus in acidic medium NBS itself (N^+BSH) and (H_2OBr^+) might be possible oxidising species. NSH has no significant influence on reaction rate suggesting thereby that neither cationic bromine (H_2OBr^+) nor protonated NBS (N^+BSH) is involved in the oxidation process. Hence the only choice left is NBS which is involved in the oxidation reaction as a reactive species.

In view of the negative effect of the chloride ions, $[IrCl_5(H_2O)]^{2-}$ can be considered as the actual reactive species[10] of Ir(III) in acidic medium.

On the basis of the above observed facts the following reaction path has been suggested:

$$\underset{(C_1)}{[IrCl_6]^{3-}} + H_2O \overset{k_1}{\rightleftharpoons} \underset{(C_2)}{[IrCl_5{\cdot}H_2O]^{2-}} + Cl^- \tag{i}$$



(ii)

$$>CHOH + H^+ \overset{k_3}{\rightleftharpoons} >CHOH^+ + S^+H \tag{iii}$$

$$C_3 + S^+H \xrightarrow{k} >C^+—O—H + C_2 + NSH + HBr \tag{iv}$$

Slow and rate determining step is

$$>C^+—OH + H_2O \xrightarrow{k_4} >C{=}O + H_3O^+ \tag{v}$$

Now the rate of oxidation of cyhtol may be expressed as:

$$\frac{-d[NBS]}{dt} = k[C_3][S] \tag{1}$$

On simplifying, the value of C_3 is as

$$[C_3] = \frac{k_1k_2[NBS][Ir(III)]_r}{[Cl^-] + k_1 + k_1k_2[NBS]} \tag{2}$$

Puting $[C_3]$ from (2) in (1), we have

$$\frac{-d\,[NBS]}{dt} = \frac{kk_1k_2[NBS][Ir(III)]_T[S^+H]}{[Cl^-] + k_1 + (1 + k_2)[NBS]} \tag{3}$$

Assuming $1 \gg k_1$ [NBS],

$$\frac{-d\,[NBS]}{dt} = \frac{kk_1k_2[NBS][Ir(III)]_T[S^+H]}{[Cl^-] + k_1} \tag{4}$$

On applying steady state approximation to $[S^+H]$, we have

$$[S^+H] = \frac{k_3[S][H^+]}{k_3 + k[C_3]} \tag{5}$$

k is small; then $k_1 \gg k[C_3]$,

$$[S^+H] = \frac{k_3[S][H^+]}{k_{-3}}$$

$$[S^+H] = k_3[S][H^+] \tag{6}$$

where $k_3 = k_3/k_{-3}$

On comparing (4) and (6), we have

$$\frac{-d\,[NBS]}{dt} = \frac{kk_1k_2k_3[NBS][Ir(III)]_T[S][H^+]}{[k_1] + [Cl^-]}$$

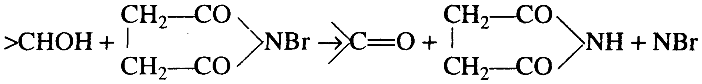
$$= \frac{k_1[NBS][Ir(III)]_T[S][H^+]}{k_1 + [Cl^-]}$$

where $k^1 = kk_1k_2k_3$

The above proposed rate expression is valid for the oxidation of cyhtol by N-bromosuccinimide in presence of acidic solution of Ir(III) choride which explains all the observed reaction kinetics.

Stoichiometry

The reaction mixture containing excess of NBS over cycloheptanol has been allowed to equilibrate under experimental conditions. The observed experimental findings showed that one mole of NBS is consumed in the oxidation of one mole of cycloheptanol in accordance to the stoichiometric equation:



$$>CHOH + \begin{array}{l} CH_2{-}CO \\ | \\ CH_2{-}CO \end{array}\!\!>NBr \rightarrow >C{=}O + \begin{array}{l} CH_2{-}CO \\ | \\ CH_2{-}CO \end{array}\!\!>NH + NBr$$

(C_3)

where >CHOH → Cycloheptanol (Cyhtol)

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