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Kinetics and Mechanism of Oxidation of Aspartic Acid in Acid Solution of N-Bromosuccinimide in Presence of Iridium(III)

A.K. SINGH

Department of Chemistry, Magadh University, Bodh-Gaya-824 234, India

Kinetics and mechanism of iridium(III) catalyzed oxidation of aspartic acid by N-bromosuccinimide have been extensively studied under isolation condition at 30°C. The observed kinetic findings indicate first order reaction kinetics with respect to oxidant catalyst and chloride ion in each case, whereas it shows zero order reaction kinetics with respect to substrate and reductant. Successive addition of succinimide in the reaction system shows negative effect whereas addition of $Hg(OAc)_2$ shows negligible effect on reaction rate. Insignificant effect of ionic strength of the media is observed in the oxidation reaction. On the basis of the experimental findings, the proposed rate expression is $-\frac{d[NBS]}{dt}\frac{k[NBS][Ir(III)]_T[Cl^-]}{k_{-1}[NBS]+k_2[H_2O]}$.

Key Words: Kinetics, Mechanism, Aspartic acid, N-Bromosuccinimide, Iridium(III).

INTRODUCTION

N-Bromosuccinimide (NBS) is a potential oxidizing agent[1, 2] and has been used in the estimation of several organic as well as inorganic compounds. Recently transition metal ions have been widely used as an effective homogeneous catalyst in the oxidation of organic compounds in acidic and alkaline medium[3–5]. The use of Ir(III) chloride as effective homogeneous catalyst has been reported by Tondon and Krishna[6]. Very little work has been done on Ir(III) chloride as effective catalyst and no one has attempted to probe the actual catalytic potential of Ir(III) in the oxidation of aspartic acid by N-bromosuccinimide (NBS) in acidic medium. So far efforts have been made to collect the kinetic data and use them for elucidating the oxidative path with special reference to catalytic activity of Ir(III) chloride in acidic medium.

EXPERIMENTAL

All the chemicals have been used of A.R. grade (E. Merck). The solution of NBS is freshly prepared and stored in a black coated flask to prevent photochemical effect[7]. Its strength is checked iodometrically. The aqueous solution of Ir(III) chloride (Johnson & Mathey) is prepared by dissolving 1 g sample in 0.01N HCl. The entire progress of the reaction is elucidated by estimating the unreacted NBS iodometrically[8] at 30°C under isolation condition.

RESULTS AND DISCUSSION

The first order reaction kinetics is observed with respect to NBS. A close examination of Table-1 clearly indicates that on increasing the [NBS], the value of first order rate constant (K) does not change significantly. This finding has been graphically confirmed by plot of log [a/(a – x)] *vs.* t (not shown). A straight line passing through origin with a slope (k_1) = 4.60×10^{-4} sec^{-1} and evaluated K shows close resemblance. Zero order reaction kinetics is observed with respect to substrate. On changing the [organic acid], the value of K do not change significantly (Table-1).

TABLE-1
EFFECT OF VARIATION OF [OXIDANT], [SUBSTRATE], [CATALYST] AND [REDUCTANT] ON REACTION RATE AT 30°C

$[Hg(OAc)_2] = 2.00 \times 10^{-3}$ M; $[KCl] = 1.80 \times 10^{-3}$ M

[NBS] $\times 10^{-4}$ M	[Aspartic acid] $\times 10^{-2}$ M	[Ir(III)] $\times 10^{-6}$ M	[$HClO_4$] $\times 10^{-2}$ M	K_1 $\times 10^4$ sec^{-1}	$10^2 \times K_2 = K_1[Ir(III)]$ mol^{-1} sec^{-1}
4.00	1.00	1.20	1.00	4.64	—
5.00	—	—	—	4.65	—
6.70	—	—	—	4.66	—
8.30	—	—	—	4.54	—
10.00	—	—	—	4.61	—
12.50	1.00	1.20	1.00	4.41	—
10.00	0.50	1.20	1.00	4.60	—
—	1.00	—	—	4.61	—
—	1.50	—	—	4.59	—
—	2.00	—	—	4.58	—
—	2.50	—	—	4.60	—
10.00	3.00	1.20	1.20	4.58	—
10.00	1.00	0.60	1.00	2.43	4.05
—	—	1.20	—	4.61	3.84
—	—	1.80	—	7.85	4.36
—	—	2.40	—	8.98	3.76
—	—	3.00	—	12.20	4.06
10.00	1.00	3.60	1.00	14.50	4.03
12.50	1.00	1.20	0.50	4.37	—
—	—	—	1.00	4.41	—
—	—	—	1.50	4.34	—
—	—	—	3.00	4.36	—
—	—	—	4.00	4.36	—
12.50	1.00	—	5.00	4.35	—

The order of reaction with respect to Ir(III) is found to be first order. It is evident from Table-1 that on increasing the concentration of [Ir(III)], the value of K increases linearly. This finding has been further confirmed graphically (not shown). Plot of K *vs*. [Ir(III)], a straight line with a slope k_1 4.00×10^2 mol^{-1} sec^{-1}, which is very close to average value of k_2 (4.0×10^2 mol^{-1} sec^{-1}). But on increasing the [$HClO_4$], the value of K remains constant, suggesting zero order dependence with respect to H^+ ions. On increasing the [KCl], the value of K increases (Table-2), showing first order reaction kinetics with respect to KCl, which has been confirmed graphically. Plot of [KCl] *vs*. k_1 is a straight line with a slope value 2.66×10^2. It is evident from Table-2, *i.e.*, on successive addition of succinimide it shows decreasing effect whereas in the case of ionic strength (Table-3) and $Hg(OAc)_2$ (Table-2) it shows insignificant influence on redox reaction rate. The energy of activation and related thermodynamical parameters have been evaluated at four temperature variation studies ranging from 30 to 45°C (Table-3).

$K_s = 2.03 \times 10^{-2}$ mol^{-1} sec^{-1}, $\Delta E = 15.18$ kcal/mol, $\Delta S = 0.91$ e.u.,
$\Delta G = 14.90$ kcal/mol

TABLE-2

EFFECT OF [Cl], [SUCCINIMIDE] AND [$Hg(OAc)_2$] ON REACTION RATE AT 30°C

[NBS] = 10.00×10^{-4} M [Aspartic acid] = 1.00×10^{-2} M
[$HClO_4$] = 1.00×10^{-2} M [Ir(III)] = 1.20×10^{-6} M

[KCl] $\times 10^{-3}$ M	[Succinimide] $\times 10^{-4}$ M	[$Hg(OAc)_2$] $\times 10^{-3}$ M	K_1 $\times 10^4$ sec^{-1}	$10^2 \times K_2 = \frac{K}{[KCl]}$ $\times mol^{-1}$ sec^{-1}
0.60	—	2.00	1.54	2.56
0.90	—	—	2.34	2.60
1.20	—	—	3.17	2.64
1.80	—	—	4.61	2.56
2.40	—	2.00	7.34	3.05
1.80	0.00	2.00	4.61	—
—	1.00	—	4.00	—
—	2.00	—	3.56	—
—	3.00	—	3.08	—
—	4.00	—	2.72	—
—	5.00	—	2.42	—
—	6.00	—	2.02	—
—	7.50	—	1.56	—
1.80	10.00	2.00	0.39	—
1.80	—	1.00	4.62	—
—	—	2.00	4.61	—
—	—	2.50	4.63	—
—	—	3.00	4.64	—
—	—	5.00	4.66	—
—	—	7.50	4.65	—
—	—	10.50	4.62	—
1.80	—	15.00	4.63	—

TABLE-3

EFFECT OF [$NaClO_4$] AND TEMPERATURE ON REACTION RATE

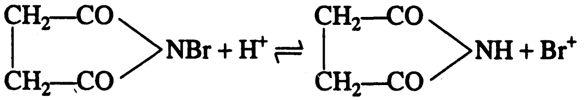
[NBS] = 10.00×10^{-4} M [Aspartic acid] = 1.00×10^{-2} M

[$HClO_4$] = 1.00×10^{-2} M [Ir(III)] = 1.200×10^{-6} M

[$NaClO_4$] $\times 10^{-2}$ M	[KCl] $\times 10^{-2}$ M	[$Hg(OAc)_2$] $\times 10^{-3}$ M	K $\times 10^4$ sec^{-1}
0.00	1.80	2.00	4.61
1.00	—	—	4.63
2.00	—	—	4.62
3.00	—	—	4.60
5.00	—	—	4.59
7.00	—	—	4.64
9.00	1.80	2.00	4.62
Temp. (°C)			
30	1.80	2.80	2.43
35	—	—	3.68
40	—	—	5.14
45	1.80	2.00	7.24

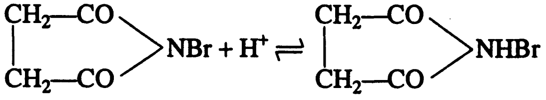
Note: ±indicates the respective variation.

Insignificant effect of $Hg(OAc)_2$ suggests that it is not involved in NBS oxidation. It simply acts as scavenger[8a] for any Br^- ions formed. NBS is expected to exist in the following equilibria in acidic medium as reported earlier[9–11]:



...(1)

$$\begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\!\!>NBr + H^+ \rightleftharpoons \begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\!\!>NH + Br^+ \quad ...(1)$$



...(2)

$$\begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\!\!>NBr + H^+ \rightleftharpoons \begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\!\!>NHBr \quad ...(2)$$

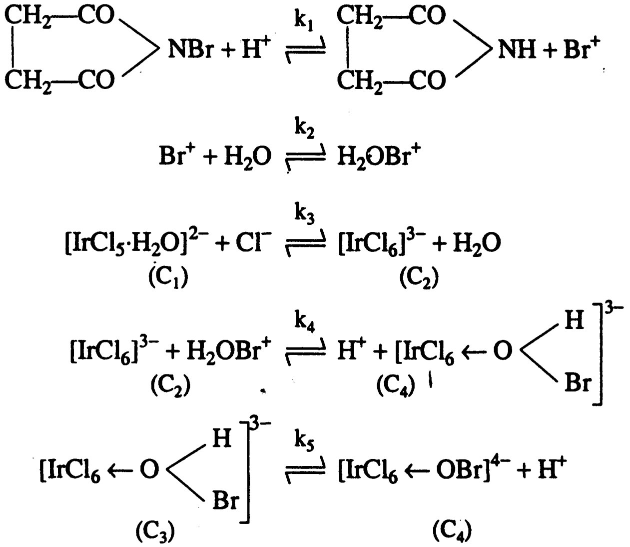
$$Br^+ + H_2O \rightleftharpoons H_2OBr^+ \quad ...(3)$$

Thus in acidic medium the possible oxidizing agents of NBS are NBS itself, H_2OBr^+ and NBSH. Neither NBS itself nor protonated N^+BSH can be assumed to be actual reactive species of NBS. Hence it fails to explain the zero order dependence of H^+ ions and the –ve effect of succinimide on reaction rate as well as NBS not involved in the oxidation reaction supported by Srinivasan and Venkatasubramaniam[12]. Hence the only choice left is hydrated brominium ion (H_2OBr^+) which is involved in the oxidation reaction as reactive species in acidic media.

The first order dependence of chloride ion suggests that the actual reactive species of Ir(III) chloride[13] is $[IrCl_6]^{3-}$ in acidic media[14].

$$[IrCl_5(H_2O)]^{2-} + Cl \rightleftharpoons [IrCl_6]^{3-}$$

Zero order reaction kinetics with respect to substrate suggests that substrate are involved in fast process. Keeping in view the following reaction paths have been suggested:



$$\begin{matrix}CH_2-CO\\ |\\ CH_2-CO\end{matrix}\!\!>NBr + H^+ \overset{k_1}{\rightleftharpoons} \begin{matrix}CH_2-CO\\ |\\ CH_2-CO\end{matrix}\!\!>NH + Br^+ \qquad \ldots(i)$$

$$Br^+ + H_2O \overset{k_2}{\rightleftharpoons} H_2OBr^+ \qquad \ldots(ii)$$

$$\underset{(C_1)}{[IrCl_5{\cdot}H_2O]^{2-}} + Cl^- \overset{k_3}{\rightleftharpoons} \underset{(C_2)}{[IrCl_6]^{3-}} + H_2O \qquad \ldots(iii)$$

$$\underset{(C_2)}{[IrCl_6]^{3-}} + H_2OBr^+ \overset{k_4}{\rightleftharpoons} H^+ + \underset{(C_4)}{\left[IrCl_6 \leftarrow O\begin{matrix}H\\ \\ Br\end{matrix}\right]^{3-}} \qquad \ldots(iv)$$

$$\underset{(C_3)}{\left[IrCl_6 \leftarrow O\begin{matrix}H\\ \\ Br\end{matrix}\right]^{3-}} \overset{k_5}{\rightleftharpoons} \underset{(C_4)}{[IrCl_6 \leftarrow OBr]^{4-}} + H^+ \qquad \ldots(v)$$

The rate determining step

$$\underset{(C_4)}{[IrCl_6 \leftarrow OBr]^{4-}} + S \xrightarrow[\text{fast}]{} [IrCl_6H]^{4-} + \text{Product} \qquad \ldots(vi)$$

$$[IrCl_6H]^{4-} + H_2OBr^+ \xrightarrow[\text{fast}]{} [IrCl_6]^{3-} + H_2O + HBr \qquad \ldots(vii)$$

The formation of $[IrCl_6H]^{4-}$ is well known.

Now considering the above oxidation paths of aspartic acid, the rate of loss of NBS may be expressed as:

$$\frac{-d[NBS]}{dt} = K_5[C_3] \qquad \ldots(1)$$

The total $[Ir(III)]_T$ may be:

$$[Ir(III)] = [C_1] + [C_2] + [C_3] + [C_4] \qquad \ldots(2)$$

Considering the steps (iii), (iv), and (v) we know the values of C_1, C_2, C_3 and C_4 respectively, and substituting its proper value in (2), we have

$$[Ir(III)]_T = \frac{[C_3][H^+]}{k_3k_4[Cl^-][H_2OBr^+]} + \frac{[C_3][H^+]}{k_4[H_2OBr^+]} + C_3 + \frac{K_3[C_3]}{[H^+]}$$

or $$[Ir(III)]_T = \frac{[Cl][H^+]^2 + k_3[H^+]^2[Cl^-] + k_3k_4[H^+][Cl^-][H_2OBr^+] + LY}{k_3k_4[Cl^-][H_2OBr^+][H^+]} \qquad \ldots(3)$$

where $Y = k_3k_4k_5[Cl^-][H_2OBr^+]$.

On comparing (1) and (3), we have

$$\frac{-d[NBS]}{dt} = \frac{k_3k_4k_5[Cl^-][H^+][H_2OBr^+][Ir(III)]_T}{[H^+][H^+] + k_3[H^+][Cl^-] + [X][Y]} \quad \ldots (4)$$

where $X = k_3k_4[H_2OBr^+][Cl^-]$

On assuming $Y \ll [H^+][H^+] + k_3[H^+][Cl^-] + [X]$, we have

$$\frac{-d[NBS]}{dt} = \frac{k_3k_4k_5[Cl^-][H_2OBr^+][Ir(III)]_T}{[H^+] + k_3[H^+][Cl^-] + [X]} \quad \ldots (5)$$

Again on considering the inequality, $[H^+] \gg [Cl^-][H^+] + [X]$, from (5), we have

$$\frac{-d[NBS]}{dt} = \frac{k_3k_4k_5[Cl^-][Ir(III)]_T[H_2OBr^+]}{[H^+]} \quad \ldots (6)$$

Again considering the oxidative path (ii), we have

$$k_2 = \frac{[H_2OBr^+]}{[Br^+][H_2O]}$$

or $$[H_2OBr^+] = k_2[Br^+][H_2O] \quad \ldots (7)$$

On applying steady state to Br^+,

$$\frac{d[Br^+]}{dt} = k_1[NBS][H^+] - k_{-1}[NBS][Br^+] - k_2[Br^+][H_2O] = 0$$

or $$[Br^+] = \frac{k_1[NBS][H^+]}{k_{-1}[NBS] + k_2[H_2O]} \quad \ldots (8)$$

On comparing (7) and (8), we have

$$\frac{-d[NBS]}{dt} = \frac{k_1k_5k_2k_3k_4[Cl^-][NBS][Ir(III)]_T[H_2O]}{k_{-1}[NBS] + k_2[H_2O]}$$

$$\frac{-d[NBS]}{dt} = \frac{K[NBS][Ir(III)]_T[Cl^-]}{k_{-1}[NBS] + k_2[H_2O]} \quad \ldots (9)$$

where $$k = k_1k_5k_2k_3k_4[H_2O].$$

It is obvious from the above expression that the rate of the reaction is proportional to [NBS], $[Ir(III)]_T$ and $[Cl^-]$ while on successive addition of succinimide the rate decreases. This expression also clearly explains the zero order dependence on aspartic acid and H^+ ions on redox reaction rate.

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