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*NOTE*

# Mechanism of Ir(III) Catalysed Oxidation of Proline by N-Bromosuccinimide

VED PRAKASH SAHAY and JANAK PRASAD*
*Department of Chemsitry*
*Magadh University, Bodh Gaya-824 234, India*

Kinetics of oxidation of proline by acidic solution of N-bromosuccinimide in the presence of iridium(III) chloride as catalyst have been studied in the presence of mercuric acetate as Br scavenger. The reaction shows fractional order in both proline and Ir(III) and first order at low [NBS] tends to zero-order at high [NBS]. An inverse first-order in $H^+$ is observed. Addition of mercuric acetate, sodium perchlorate and potassium chloride does not bring about any significant change in the reaction velocity while oxidation rate is decreased with successive addition of succinimide. A suitable mechanism in agreement with observed kinetics is proposed.

Kinetics of oxidation of amino acids by hexacyanoferrate(III), periodic acid and chloramine-T has been extensively probed[1–4]. Amino acids have not been oxidised by N-bromosuccinimide involving Ir(III) chloride as catalyst in acidic medium and the kinetic features are unknown. In the present communication an attempt has been made to study the kinetics and mechanism of oxidation or proline by acidic solution of N-bromosuccinimide using Ir(III) chloride as catalyst.

Aqueous solution of proline (Fluka AG) was prepared by dissolving its desired quantity in distilled water. The reagents used were N-bromosuccinimide (S. Merck, G.R.), $NaClO_4$, $HClO_4$, $Hg(OAc)_2$ and succinimide (all E. Merck) and their solutions were prepared in doubly distilled water. The solution of iridium trichloride (Johnson-Matthey) was prepared by dissolving it in 0.01 M HCl solution.

The reaction was initiated by quickly adding desired volume of N-bromosuccinimide solution in the reaction vessel (containing requisite volumes of proline, perchloric acid, iridium(III) chloride, mercuric acetate and other reagents) maintained at a desired temperature in a thermostatic water bath (±0.1°C). The progress of the reaction was monitored by estimating unconsumed N-bromosuccinimide iodometrically at regular intervals of time till 60 to 70% of the reaction.

Table-1 records the reaction velocity constants at different concentrations of various reactants. First-order dependence in N-bromosuccinimide (NBS) at its low concentration tended to zero-order in high concentration range. Fractional order in proline is obvious from log $k_{(obs)}$ *vs.* log [Proline] with slope 0.48. A positive fractional order in Ir(III) is also obvious from slope (0.57) of log $k_{obs}$ *vs.* log [Ir(III)] plot. The rate constant decreases linearly with $[H^+]$ showing thus inverse first-order kinetics in $[H^+]$. Negligible effect of variation of ionic strength of the medium (μ), addition of mercuric acetate and chloride ions was observed (data not given) while successive addition of succinimide showed negative effect on reaction rate. The measurements of rate constant at 30, 35, 40 and 45°C led to computation of $E_a$ (energy of activation) which was found to be 87.04 kJ/mole.

TABLE-1
EFFECT OF VARIATION OF REACTANTS ON REACTION RATE AT 35°C

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $[NBS] \times 10^4$ M $l^{-1}$ | 4.00 | 5.00 | 6.00 | 8.00 | 10.00 | 12.50 | 20.00 | 25.00 |
| $\left(-\frac{dc}{dt}\right) \times 10^7$ M $l^{-1}$ $s^{-1}$ | 1.86 | 2.20 | 1.78 | 2.80 | 3.30 | 3.35 | 4.87 | 5.40 |

[Proline] = $2.00 \times 10^{-2}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M, Ir(III))] = $1.34 \times 10^{-5}$ M,
$[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M and [KCl] = $2.00 \times 10^{-3}$

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $[Proline] \times 10^2$ M $l^{-1}$ | 5.00 | 6.67 | 8.00 | 10.00 | 13.34 | 20.00 | — | — |
| $\left(-\frac{dc}{dt}\right) \times 10^7$ M $l^{-1}$ $s^{-1}$ | 2.11 | 2.30 | 2.60 | 2.50 | 2..60 | 2.58 | — | — |

[NBS] = $10.00 \times 10^{-4}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M, Ir(III))] = $1.34 \times 10^{-5}$ M,
$[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M, [KCl] = $2.00 \times 10^{-3}$ M

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $[Ir(III)] \times 10^5$ M $l^{-1}$ | 0.34 | 0.67 | 1.01 | 1.34 | 1.68 | 2.00 | — | — |
| $\left(-\frac{dc}{dt}\right) \times 10^7$ M $l^{-1}$ $s^{-1}$ | 2.00 | 3.31 | 3.37 | 4.12 | 4.50 | 5.80 | — | — |

[NBS] = $10.00 \times 10^{-4}$ M, $[HClO_4] = 1.00 \times 10^{-2}$ M, [Proline] = $2.00 \times 10^{-2}$ M,
$[Hg(OAc)_2] = 1.25 \times 10^{-3}$ M, [KCl] = $2.00 \times 10^{-3}$ M

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $[HClO_4] \times 10^2$ M $l^{-1}$ | 5.00 | 6.67 | 8.00 | 13.33 | 20.00 | 40.00 | — | — |
| $\left(-\frac{dc}{dt}\right) \times 10^7$ M $l^{-1}$ $s^{-1}$ | 4.79 | 4.50 | 3.63 | 2.30 | 1.45 | 0.94 | — | — |

[NBS] = $10.00 \times 10^{-4}$ M, [Proline] = $2.00 \times 10^{-2}$ M, [Ir(III)] = $1.34 \times 10^{-5}$ M,
$[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M, [KCl] = $2.00 \times 10^{-3}$ M

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $[Succinimide] \times 10^2$ M $l^{-1}$ | 3.34 | 6.67 | 10.00 | 12.50 | 20.00 | 25.00 | — | — |
| $\left(-\frac{dc}{dt}\right) \times 10^7$ M $l^{-1}$ $s^{-1}$ | 26.00 | 22.00 | 15.40 | 13.00 | 10.10 | 6.20 | — | — |

[NBS] = $10.00 \times 10^{-4}$ M, [Proline] = $2.00 \times 10^{-2}$ M, [Ir(III)] = $1.34 \times 10^{-5}$ M,
$[Hg(OAc)_2] = 3.34 \times 10^{-3}$ M, [KCl] = $2.00 \times 10^{-3}$ M and $[HClO_4] = 1.00 \times 10^{-2}$ M

Zero effect of mercuric acetate indicates its involvement only as $Br^-$ scavenger. It eliminates the oxidation of proline by $Br_2$ which would bave been formed in the reaction and thus ensures pure NBS[5] oxidation. Insignificant effect of successive addition of $Cl^-$ suggests that neutral molecule $IrCl_3(H_2O)_3$ is involved in the reaction as catalytic species.

The following equilibria are reported to exist in acidic solution of NBS:

$$\underset{\text{(NBS)}}{>NBr} + H^+ \rightleftarrows \underset{\text{(NSH)}}{>NH} + Br^+ \tag{1}$$

$$Br^+ + H_2O \rightleftarrows (H_2OBr)^+ \tag{2}$$

$$>NBr + H^+ \rightleftarrows \underset{\text{(NBSH)}}{\overset{+}{N}HBr} \tag{3}$$

$$>\mathrm{NBr} + \mathrm{H_2O} \rightleftarrows >\mathrm{NH} + \mathrm{HOBr} \qquad (4)$$

Considering the kinetic features with respect to $[\mathrm{H^+}]$ and succinimide (NSH), the rate law expression obtained on the basis of HOBr as oxidising species conforms well to all observed kinetic data while NBS as such, cationic bromine ($\mathrm{Br^+}$ or $\mathrm{H_2OBr^+}$) or protonated NBS $(\overset{+}{\mathrm{N}}\mathrm{HBr}$ fail to give rate expression in agreement with kinetic observations. Therefore, HOBr has been safely assumed as oxidising species of NBS.

The following reaction scheme is suggested on the basis of reactive species of Ir(III) chloride, NBS and other kinetic features in the present investigations where S is written for proline and Ir(III) stands for $\mathrm{IrCl_3(H_2O)_3}$.

$$\mathrm{NBS} + \mathrm{H_2O} \overset{K_1}{\rightleftarrows} \mathrm{NHS} + \mathrm{HOBr} \qquad (5)$$

$$\mathrm{Ir(III)} + \mathrm{HOBr} \overset{K_2}{\rightleftarrows} [\mathrm{Ir(III)(HOBr)}]^{3+} \qquad (6)$$

$$\mathrm{Ir(III)(HOBr)}]^{3+} + \mathrm{S} \overset{K_3}{\rightleftarrows} [\mathrm{Ir(III)(OBr)S}]^{2+} + \mathrm{H^+} \qquad (7)$$

$$\mathrm{Ir(III)(OBr)S}]^{2+} \xrightarrow[\text{determining step}]{\text{Slow and rate}} [\mathrm{Ir(III)(H)}]^{2+} + \mathrm{OBr^-} + \mathrm{S^+} \qquad (8)$$

$$[\mathrm{Ir(III)(H)}]^{2+} + \mathrm{HOBr} \xrightarrow[\text{fast}]{} \mathrm{Ir(III)} + \mathrm{H_2O} + \mathrm{Br^-} \qquad (9)$$

$$\mathrm{S^+} + \mathrm{H_2O} \xrightarrow[\text{fast}]{} \text{Product} \qquad (10)$$

Considering the above reaction steps (5–8) the rate of oxidation of proline in terms of rate of loss of [NBS] may be written as Eqn. (11)

$$\frac{-d[\mathrm{NBS}]}{dt} = \frac{K'[\mathrm{NBS}][\mathrm{Ir(III)}][\mathrm{Proline}]}{K_{-3}[\mathrm{H^+}]\{K_3[\mathrm{Proline}](K_{-1}[\mathrm{NHS}] + K_2[\mathrm{Ir(III)}] + K_1K_2[\mathrm{NBS}])\}} \qquad (11)$$

where $K' = K_dK_2K_3$, $K_1 = K_1/K_{-1}$, $K_3 = K_3/K_{-3}$.

The rate law (11) agrees fully with all kinetic observations.

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