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## Kinetic Study of Oxidation of Valine by Nbromophthalimide in Presence of Iridium (III) Chloride as Homogenous Catalyst

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## Kinetic Study of Oxidation of Valine by *N*-bromophthalimide in Presence of Iridium (III) Chloride as Homogenous Catalyst

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The mechanistic study of Ir(III) chloride catalyzed oxidation of Val has been studied by by N-bromophthalimide (NBP) in aqueous perchloric acid medium at 303 K. The reaction followed first order kinetics with respect to [NBP] and zero order kinetics with respect to [Val]. At lower concentration range of Ir(III) chloride, the reaction followed first order kinetics while tending to zero order at its higher concentration. A negative effect was observed for [H<sup>+</sup>] and [NHP] (phthalimide) whereas variation in [Hg(OAc)<sub>2</sub>] (mercuric acetate), [Cl<sup>-</sup>], ionic strength (I) and dielectric constant of the medium did not bring about any significant change on the rate of reaction. The rate constants observed at five different temperatures (298 K–318 K) were used to calculate the activation parameters. A plausible mechanism from the results of kinetic studies, reaction stoichiometry and product analysis has been proposed.

Keywords Ir(III) chloride, kinetics, NBP, oxidation, valine.

#### INTRODUCTION

The versatile nature of *N*-halogeno compounds is due to their ability to act as sources of halonium cations, hypohalite species and nitrogen anions, which act as both bases and nucleophiles. *N*-halocompounds have been used widely as oxidizing and halogenating reagent in variety of organic compounds.<sup>[1–5]</sup> *N*-bromophthalimide (NBP) has recently been developed as an oxidimetric titrant for the determination of certain pharmaceuticals.<sup>[6,7]</sup> Literature survey revealed that there is limited work done on NBP.<sup>[8–10]</sup>

Val is an essential  $\alpha$ -amino acid. However, there are only few reports available for the oxidation of Val.<sup>[11,12]</sup> Recently, the use of platinum group metal ions, such as osmium, ruthenium and iridium either alone or binary mixtures, as catalyst in various redox processes has been attracted considerable interest.<sup>[13,14]</sup> The mechanism of catalysis depends on the nature of substrate, the oxidants and experimental conditions.<sup>[15]</sup> Potential of Ir(III) chloride to act as homogenous catalyst in oxidation process was recognized.<sup>[16–20]</sup> Preliminary experimental results revealed that the reaction did not proceed in the absence of catalyst, but the reaction became facile in the presence of micro quantity of Ir(III) chloride. In the present investigation, we report for the first time the results of detailed investigation on the kinetic and mechanistic aspects of Ir(III) catalyzed oxidation of Val by NBP in acidic medium at constant temperature. This study will enable us to understand the complicated biological reaction in living systems and will also help to understand the catalytic activity of Ir(III) chloride. Objectives of the present study are (i) to ascertain the reactive species of catalyst and oxidant, (ii) to identify the oxidation products, (iii) to elucidate the plausible reaction mechanism and (iv) to deduce rate law consistent with kinetic results and to calculate activation parameters.

#### Materials

Analytical reagent grade chemicals and triple distilled water were used throughout the investigation. *N*-bromophthalimide (Lancaster, 98%) was used as oxidant and melting point of the sample was found to be 481K. Solution of NBP was prepared in 80% distilled acetic acid and stored in a black-coated flask to prevent photochemical deterioration. The prepared solution of NBP was standardized iodometrically<sup>[21]</sup> against the standard solution of sodium thiosulphate using starch as indicator. Stock solution of Val was prepared by dissolving appropriate amount of sample in triple distilled water. The Ir(III) chloride solution

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was prepared by dissolving a known weight of Ir(III) chloride (S.D. fine) in HCl of known strength and stored in a blackcoated bottle to prevent photochemical decomposition. Standard solution of KCl, NaClO<sub>4</sub> and phthalimide were prepared with triple distilled water. Hg(OAc)<sub>2</sub> (Loba chem., Mumbai, India) was acidified with 20% acetic acid and perchloric acid (GR) was diluted with triple distilled water for the present investigation.

#### **Kinetic Measurements**

All the kinetic measurements were carried out in a blackcoated vessel at a constant temperature, 303 K and performed under pseudo first order condition with [Val]  $\gg$  [NBP]. The reaction was initiated by the rapid addition of known amounts of oxidant to reaction mixture containing the required amount of Val, perchloric acid, Ir(III) chloride, Hg(OAc)<sub>2</sub>, acetic acid and water in glass stoppered pyrex boiling tubes, and thermosttated at the same temperature. The progress of reaction was monitored by iodometric determination of unconsumed [NBP] in known aliquots of the reaction mixtures at different time intervals. The rate of reaction (-dc/dt) in each kinetic run was determined by the slope of tangent drawn at fixed [NBP]. Each kinetic run was studied for two half lives of the reaction. The observed rates of reaction were reproducible within  $\pm$  5% in replicate kinetic run. The order of reaction in each reactant was determined with the help of log-log plot of (-dc/dt) versus concentration of reactant.

#### **Stoichiometry and Product Analysis**

Different ratios of NBP to Val were equilibrated at 303 K in the presence of requisite amount of perchloric acid, mercuric acetate and acetic acid under the condition of  $[NBP] \gg [Val]$ for 48 h. Determination of unconsumed NBP revealed that more than two mole of NBP were required for the oxidation of each mole of Val as in the following equation.

The products were identified as a mixture of nitrile, aldehyde and trace of ammonia. Nitrile was identified by the color reaction<sup>[22]</sup> and was later confirmed by FT-IR and GC-MS techniques. Presence of aldehyde was also confirmed by Schiff's reagent. Ammonia was detected by Nessler's reagent. The consumption of more than two moles of NBP per mole of amino acid may be due to the reaction of ammonia with NBP and may also be due to the further oxidation of aldehyde. In the spot method, one drop of liquid sample was placed in a test tube to which 2 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> hydroxyl ammonium chloride in propylene glycol and 1 cm<sup>3</sup> of potassium hydroxide in propylene were added. The mixture was heated at its boiling point for 2 min. and allowed to cool, followed by addition of 0.5 to 1 cm<sup>3</sup> of ferric chloride solution. A red to violet color in the solution mixture was seen, indicating the presence of nitrile. In the FT-IR analysis, a sharp peak around  $2250 \text{ cm}^{-1}$  also suggested the nitrile. For GC-MS analysis, the oxidized product was extracted with diethyl ether and the ether layer was concentrated by slow evaporation. The concentrated sample was then analyzed by GCMS using a JEOL-JMS (Mate-MS System, Japan) instrument.



FIG. 1. Plot between unconsumed [NBP] versus Time at T = 303 K; [NBP]  $= 2.00 \times 10^{-4}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] = 0.50 mol dm<sup>-3</sup>; [Val] =  $2.00 \times 10^{-3}$  mol dm<sup>-3</sup>, [Ir(III)] =  $1.00 \times 10^{-5}$  mol dm<sup>-3</sup>; and [Hg(OAc)<sub>2</sub>] =  $3.00 \times 10^{-4}$  mol dm<sup>-3</sup> and CH<sub>3</sub>COOH = 20%.

#### **KINETIC RESULTS**

The kinetics of the oxidation of Val by NBP in an aqueous acidic medium in the presence of Ir(III) chloride was investigated at different concentration of all the reactants. The value of the initial rate in each kinetic run was calculated from the slope of the tangent of plot of unconsumed [NBP] versus time at fixed [NBP] (written as [NBP]\*) except in variation of [NBP] when a tangent was drawn at a fixed time. Plots of log [NBP] versus time under different initial concentrations of [NBP] are shown in Figure 1. The pseudo first order rate constant  $k_1$  was calculated as

$$k_1 = \frac{-(\mathrm{dc}/\mathrm{dt})}{[\mathrm{NBP}]^*}$$

Each kinetic run was studied for two half lives of the reaction. The observed rates of reaction were reproducible within  $\pm$  5% in replicate kinetic run. The order of reaction in each reactant was determined with the help of log-log plot of (-dc/dt) versus concentration of reactant. For the determination of the order of reaction with respect to each reactant, the help of Ostwald's isolation methods in conjuction with Van't Hoff's differntial method has been taken. Considering NBP, Val, H<sup>+</sup>, Ir(III) chloride as the main reactants, the general form of the rate equation for the reaction can be written as

Rate = k[NBP]<sup>$$\alpha$$</sup>[Val] <sup>$\beta$</sup> [catalyst] <sup>$\gamma$</sup> [H+] <sup>$\delta$</sup> 

Uniform pseudo first order rate constant  $(k_1)$  values of [NBP] (from  $0.50 \times 10^{-4}$  mol dm<sup>-3</sup> to  $3.00 \times 10^{-4}$  mol dm<sup>-3</sup>) clearly show that the order with respect to [NBP] is unity. This is also obvious from the plot of (-dc/dt) versus [NBP] (Figure 2, Table 1). The reactions have been studied ten fold variation in



FIG. 2. Plot between rate of reaction (-dc/dt) versus [NBP] and [Ir(III)] at T = 303 K; [H<sup>+</sup>] = 0.50 mol dm<sup>-3</sup>, [Val] =  $2 \times 10^{-3}$  mol dm<sup>-3</sup>; and [Hg(OAc)<sub>2</sub>] =  $3 \times 10^{-4}$  mol dm<sup>-3</sup> and CH<sub>3</sub>COOH = 20%.

[Val] (from  $0.50 \times 10^{-3}$  mol dm<sup>-3</sup> to  $5.00 \times 10^{-3}$  mol dm<sup>-3</sup>) at constant concentration of all reactants at constant temperature. The rate of reaction was found to be nearly the same for all concentrations of Val, exhibiting zero order kinetics with respect

TABLE 1 Effect of variation [NBP], [Val] and Acetonitrile on the rate of oxidation of value at 303K

$\frac{[\text{NBP}] \times 10^4}{\text{mol dm}^{-3}}$	$\begin{array}{l} [\text{Val}] \times 10^3 \\ \text{mol } \text{dm}^{-3} \end{array}$	Acetonitrile % by volume	$k_1 \times 10^4 \text{ s}^{-1}$ (obs.)
0.50	2.00	_	$1.21\pm0.21$
1.00	2.00		$1.23\pm0.17$
1.50	2.00	_	$1.20\pm0.32$
2.00	2.00	_	$1.26\pm0.21$
3.00	2.00	—	$1.22\pm0.09$
2.00	0.50		1.33±0.11
2.00	1.00	_	$1.42\pm0.26$
2.00	1.50	_	$1.31\pm0.17$
2.00	2.00	_	$1.35 \pm 0.24$
2.00	3.00	_	$1.61\pm0.22$
2.00	4.00	_	$1.57\pm0.17$
2.00	5.00	—	$1.29\pm0.31$
2.00	2.00	0	$1.41 \pm 0.81$
2.00	2.00	5	$1.23 \pm 0.15$
2.00	2.00	10	$1.20 \pm 0.24$
2.00	2.00	15	$1.29\pm0.22$
2.00	2.00	20	$1.39 \pm 0.25$
2.00	2.00	30	$1.25 \pm 0.15$
2.00	2.00	40	$1.22\pm0.21$

**Solution conditions**:  $[Hg(OAc)_2] = 3.00 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[Ir(III)] = 1.00 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[H^+] = 0.50 \text{ mol dm}^{-3}$  and  $CH_3COOH = 20\%$ .

 TABLE 2

 Effect of varying [NHP], [H<sup>+</sup>] and [Ir(III)] on the rate of oxidation of value at 303 K

$\frac{[\text{NHP}] \times 10^4}{\text{mol dm}^{-3}}$	$[\mathrm{H^+}]  \mathrm{mol} \\ \mathrm{dm^{-3}}$	$[Ir(III)] \times 10^5$ mol dm <sup>-3</sup>	$k_1 \times 10^4 \text{ s}^{-1}$ (obs.)	$k_1 \times 10^4 \mathrm{s}^{-1}$ (cal.)
1.00	0.50	1.00	$1.39 \pm 0.19$	1.20
3.00	0.50	1.00	$1.18\pm0.41$	1.10
5.00	0.50	1.00	$0.66\pm0.25$	0.52
7.00	0.50	1.00	$0.45\pm0.20$	0.37
10.00	0.50	1.00	$0.27\pm0.09$	0.21
	0.10	1.00	$3.95\pm0.19$	4.21
	0.20	1.00	$3.27\pm0.12$	2.98
	0.30	1.00	$2.27\pm0.07$	1.94
	0.50	1.00	$1.40\pm0.24$	1.21
	0.60	1.00	$1.06\pm0.20$	1.05
	0.80	1.00	$0.90\pm0.16$	0.81
	1.00	1.00	$0.65\pm0.29$	0.62
		0.30	$0.50\pm0.24$	0.41
		0.60	$1.06\pm0.29$	0.78
	—	1.00	$1.69\pm0.19$	1.38
		1.30	$2.22\pm0.27$	1.71
		1.60	$2.85\pm0.31$	1.86
		2.30	$2.94\pm0.11$	2.61

**Solution conditions:** [NBP] =  $2.00 \times 10^{-4}$  mol dm<sup>-3</sup>, [Val] =  $2.00 \times 10^{-3}$  mol dm<sup>-3</sup>, [Hg(OAc)<sub>2</sub>] =  $3.00 \times 10^{-4}$  mol dm<sup>-3</sup> and CH<sub>3</sub>COOH = 20%.

to Val (Table 1). The reaction follows first order kinetics with respect to [Ir(III)] at lower concentration but tends to zero order at higher concentration. This result was further verified by the plot of -dc/dt versus [Ir(III)] (Figure 2, Table 2). The values of rate of reaction decreased with increase in proton concentration (Figure 3, Table 1). This may be related to protonation equilibrium of Val, which has two forms in the acidic region of the study (Eq. 2).

$$\text{RCHN}^+\text{H}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{RCHNH}_2\text{COO}^-\text{ pH} = 2.39$$
 [1]

The equilibrium of Eq. (1) suggests that the positive species of Val increases with increase in the proton concentration while the neutral species of Val decreases. If positive species of Val involved in the reaction, the rates were expected to increase with increase in proton concentration. This is contrary to the results of Figure 3. Hence the neutral species of Val is possibly involved in the oxidation by NBP. Variation of [Cl<sup>-</sup>] ion, dielectric constant and ionic strength to the reaction mixture did not affect the rate significantly, indicating chloride ion is not involved in any step prior to the rate determining step in the scheme (1) proposed and effect of ionic strength suggesting involvement of a nonionic species in the rate determining step. Subsequently the ionic strength of the reaction mixture was not kept constant for kinetic runs. There was no significant effect of increase in concentration of Hg(OAc)<sub>2</sub> on rate of reaction. But as the concentration of NHP increased rate of reaction decreased, indicating negligible



FIG. 3. Plot between rate of reaction (-dc/dt) versus [H<sup>+</sup>] at T = 303 K; [NBP] =  $2 \times 10^{-4}$  mol dm<sup>-3</sup>, [Ir(III)] =  $1.00 \times 10^{-5}$  mol dm<sup>-3</sup>; [Val] =  $2 \times 10^{-3}$  mol dm<sup>-3</sup>, [Hg(OAc)<sub>2</sub>] =  $3 \times 10^{-4}$  mol dm<sup>-3</sup> and CH<sub>3</sub>COOH = 20%.

effect of NHP on the rate of reaction. The rate of oxidation depends on the polarity of medium. When the polarity of the solvent was increased, the rate of reaction was unaffected. To determine the activation parameters, the reaction was performed at five different temperatures (298–313 K). Arrhenius plot of log  $k_1$  versus 1/T (Figure 4) was used to calculate activation energy (Ea). On the basis of Ea, and with the help of specific constant  $(k_r)$ , values of the other activation parameters such as enthalpy of activation ( $\Delta H^{\#}$ ), entropy of activation ( $\Delta S^{\#}$ ), Gibb's free of activation ( $\Delta G^{\#}$ ) and frequency factor (A) were evaluated and these values are given in (Table 3).

#### **Test for Free Radicals**

To test the presence of free radicals in the reaction, the reaction mixture with acryl amide was placed in an inert atmosphere for 24 h. When the reaction mixture was diluted with methanol, it was found that there is no precipitate in the reaction mixture. This clearly showed that there was no formation of free radical in the redox reaction under investigation.



FIG. 4. Plot between  $\log k_1$  versus 1/T; [NBP] =  $2 \times 10^{-4}$  mol dm<sup>-3</sup>, [Ir(III)] =  $1.00 \times 10^{-5}$  mol dm<sup>-3</sup>, [Val] =  $2 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] = 0.50 mol dm<sup>-3</sup>; and [Hg(OAc)<sub>2</sub>] =  $3 \times 10^{-4}$  mol dm<sup>-3</sup> and CH<sub>3</sub>COOH = 20%.

TABLE 3 Effect of temperature and corresponding activation parameter on the rate of oxidation of Val

Temperature K	$k_1 \times 10^4 \text{ s}^{-1} \text{ (obs.)}$	
298	$1.00 \pm 0.36$	
303	$1.38 \pm 0.11$	
308	$2.11\pm0.18$	
313	$3.42 \pm 0.20$	
318	$4.52\pm0.24$	
Ea (kJ mol $^{-1)}$	51.69	
$\Delta H^{\#}$ (kJ mol <sup>-1</sup> )	$49.17\pm0.06$	
$\Delta S^{\#}$ (JK mol <sup>-1</sup> )	$119.23 \pm 1.16$	
$\Delta G^{\#}$ (kJ mol <sup>-1</sup> )	$13.67\pm0.68$	
log A	$5.10 \pm 0.4$	
$k_r \times 10^{-1} s^{-1}$	2.50	

**Solution conditions**: [NBP] =  $2.00 \times 10^{-4}$  mol dm<sup>-3</sup>, [Val] =  $2.00 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] = 0.50 mol dm<sup>-3</sup>, [Hg(OAc)<sub>2</sub>] =  $3.00 \times 10^{-4}$  mol dm<sup>-3</sup> [Ir(III)] =  $1.00 \times 10^{-5}$  mol dm<sup>-3</sup> and CH<sub>3</sub>COOH = 20%.

#### **Stoichiometry of the Reaction**

Stoichiometric experiments were conducted by mixing different amounts of Val and NBP at a molar ratio of 1:10 ([NBP]: [Val]). The results are reported in Table 4. The results clearly demonstrate the consumption of more than two moles of NBP per mole of Val. This stoichiometric reactant ratio and the formation of NHP, nitrile, aldehyde, ammonia and CO<sub>2</sub> in the product analysis indicate the following stochiometric equation.

$$Val + 2.6 NBP \rightarrow Products$$
 [2]

#### DISCUSSION

#### **Reactive Species of NBP**

It has been reported earlier by several workers<sup>[23–29]</sup> that NBP is good oxidizing and brominating agent because of large

TABLE 4 Consumption of NBP in the oxidation of Val with NBP at 303 K

	$[NBP] \times 10^4$	$[NBP] \times 10^4$	$[NBP] \times 10^4$	
$[Val] \times 10^4$	mol $dm^{-3}$	mol $dm^{-3}$	$mol dm^{-3}$	[NBP] :
mol $dm^{-3}$	initial	final	consumed	[Val]
2.00	20.00	14.66	5.34	1:2.67
4.00	40.00	29.00	11.00	1:2.75
6.00	60.00	43.20	16.80	1:2.80

**Solution conditions:**  $[Hg(OAc)_2] = 3 \times 10^{-4} \text{ mol dm}^{-3}, [Ir(III)] = 1.00 \times 10^{-5} \text{ mol dm}^{-3}, [H^+] = 0.50 \text{ mol dm}^{-3} \text{ and } CH_3COOH = 20\%.$ 

polarity of >N-Br bond. NBP, like other similar N-halo imides, may exist in various forms in acidic medium, i.e., free NBP, protonated NBP,  $Br^+$ , HOBr,  $(H_2OBr)^+$ , as per the following equilibria:

 $NDD + U^+ \rightarrow NUD + D_r$ 

$$NBP + H_2O \rightleftharpoons HOBr + NHP \qquad [3]$$

$$NBP + H^+ \rightleftharpoons NHP + Br$$
 [4]

$$NBP + H^+ \rightleftharpoons (NBPH)^+$$
 [5]

$$\text{HOBr} + \text{H}^+ \rightleftharpoons (\text{H}_2\text{OBr})^+$$
 [6]

When  $(H_2OBr)^+$  is taken as reactive species, the rate law obtained shows first order kinetics with respect to hydrogen ion concentrations, contrary to our observed negative fractional order in [HClO<sub>4</sub>]. Therefore, the possibility of  $(H_2OBr)^+$ and cationic bromine  $(Br)^+$  as reactive species is ruled out. When HOBr is assumed as the reactive species, the derived rate is lawfully capable to explain negative effect of phthalimide. Thus, the only choice left is HOBr, which when considered as the reactive species, leads to a rate law capable of explaining all the kinetic observations and other effects. Hence, in the light of kinetic observation, HOBr can safely be assumed to be the main reactive species for the present reaction.

#### **Reactive Species of Ir(III) Chloride**

A spectrophotometric study of the kinetics of the hydration of  $IrCl_6^{3-}$  and of the addition of  $Cl^-$  to  $[Ir(H_2O)Cl_5]^{2-}$  in 1.0–2.5 M HClO<sub>4</sub> (or HCl) at 50°C was reported.<sup>[30]</sup>

$$\operatorname{IrC1}_{6}^{3-} + \operatorname{H}_{2}O \xrightarrow[k_{-1}]{k_{1}} [\operatorname{IrC1}_{5}(\operatorname{H}_{2}O)]^{2} + C1^{-}$$
 [7]

Visible and ultraviolet absorption spectra of the new Ir(III) complexes  $[IrCl_4(H_2O)_2]^-$  and  $[IrCl_3(H_2O)_3]$ , together with the spectra of  $[IrCl_6]^{3-}$  and  $[IrCl_5H_2O]^{2-}$  in 2.5F HClO<sub>4</sub> - 1.2F Na-ClO4 were also reported [31] and found in reasonable agreement with those reported by Poulsen and Garner<sup>[30]</sup> and Jorgensen.<sup>[32]</sup> When Ir(III) chloride dissolved in 0.1 M HCl solution,  $[IrCl_6]^{3-1}$ and  $[IrCl_5H_2O]^{2-}$  species were formed. On the basis of negligible effect of chloride ion on the rate of reaction and also assuming the existence of the above equilibrium in the reaction,  $[IrCl_6]^{3-}$  is taken as the reactive species of Ir(III) chloride in the acidic medium.

Considering the reactive species of Ir(III) chloride and NBP and with the help of above experimental findings, the probable reaction mechanism is proposed and considering the fact that 1 mole of Val is oxidized by 2 moles of NBP.

Step (III) is a slow step in the proposed scheme (1), hence the rate can be written as

$$Rate = 2k[C_2]$$
[8]

On the basis of steps (I) to (V), Eqs (9) can be obtained in the following equations, respectively:

$$rate = \frac{2k K_1 K_2 [Ir(III)] [NBP]}{[H^+] [NHP]}$$
[9]

At any time in the reaction, the total concentration of NBP, i.e. [NBP]<sub>T</sub> can be represented as

$$[NBP]_{T} = [NBP] + [HOBr] + [C_{2}]$$
 [10]

Substitution of [HOBr] and  $[C_2]$  into Eq. 10 and rearrange it

$$[NBP] = \frac{[NBP]_{T} [H^{+}] [NHP]}{[H^{+}] [NHP] + K_{1} [H^{+}] + K_{1} K_{2} [Ir(III)]}$$
[11]

Substitution of Eq. (11) into Eq. (9) gives Eq. (12) as

rate = 
$$\frac{2kK_1K_2[Ir(III)][NBP]_T}{[H^+][NHP] + K_1[H^+] + K_1K_2[Ir(III)]}$$
[12]

The rate expression obtained in equation (12) can be rewritten as

$$\frac{[\text{NBP}]_{\text{T}}}{\text{rate}} = \frac{[\text{H}^+] [\text{NHP}]}{2kK_1K_2[\text{Ir}(\text{III})]} + \frac{[\text{H}^+]}{2kK_2[\text{Ir}(\text{III})]} + \frac{1}{2k} \qquad [13]$$

According to the Eq. (13), the plot between [NBP]<sub>T</sub>/rate and [H<sup>+</sup>] or 1/[Ir(III)] or [NHP] would be a straight line having an intercept on the y-axis. A reasonably linear relationship was obtained in this plot (Figure 5). The value of k,  $K_1$  and  $K_2$ calculated from the slope and intercept of the plot were 1.07  $\times$  $10^{-3}$ s<sup>-1</sup>,  $3.82 \times 10^{-6}$  mol dm<sup>-3</sup> and  $8.18 \times 10^{3}$ , respectively. Utilizing these values of the constants, the reaction rate were calculated for the variations of [Ir(III)], [H<sup>+</sup>] and [NHP]. Almost the same values of two rates, i.e., the calculated and observed, further proves the validity of the rate law (5) and hence the proposed reaction scheme.



FIG. 5. Plot between  $[NBP]_T$ /rate versus  $[H^+]$  and  $1/[Ir(III)]; [NBP] = 2 \times$  $10^{-4} \text{ mol dm}^{-3}$ , [Val] = 2 × 10<sup>-3</sup> mol dm<sup>-3</sup>; and [Hg(OAc)<sub>2</sub>] = 3 × 10<sup>-4</sup> mol dm<sup>-3</sup> and CH<sub>3</sub>COOH = 20%.

49.17

 TABLE 5

 Activation parameters for Val with different catalyst (for isokinetic temperature)

The values of  $\Delta S^{\#}$  and  $\Delta H^{\#}$  were both favorable for electron transfer processes. The favorable enthalpy was due to release of energy on solution changes in the transition state. In the present study of Ir(III) catalyzed oxidation of Val observed positive entropy of activation ( $\Delta S^{\#}$ ) very well supports the reaction step A reaction scheme proposed for the oxidation of Val supports from the order of frequency factor (A) and values of free energy of activation ( $\Delta G^{\#}$ ) for the redox system.

2.11

1.38

NBP + H<sub>2</sub>O 
$$k_1$$
 HOBr + NHP  
[IrCl<sub>6</sub>]<sup>3-</sup> + HOBr  $k_2$  [IrCl<sub>6</sub>OBr]<sup>4-</sup> + H<sup>+</sup>  
C<sub>1</sub> C<sub>2</sub>

$$[IrCl_6OBr]^{4-} \xrightarrow{k} [IrCl_5OBr]^{3-} + Cl^{-1}$$

$$C_2 \qquad C_3$$

$$[IrCl_5OBr]^{3-} + \underset{\text{R-C-C=O}}{\text{H}} \xrightarrow{\text{H}^+} [IrCl_5H_2O]^{2-} + \underset{\text{NH}_2}{\text{H}} \xrightarrow{\text{H}^-} \overset{\text{H}^-}{\underset{\text{NH}_2}{\text{H}}}$$



FIG. 6. **Reaction scheme:** Reaction path for the oxidation of Val by NBP in the presence of Ir(III) chloride.

The activation parameters for the oxidation of Val with different catalyst by NBP are summarized in Table 5. The entropy of activation for the title reaction change within the observed range.The isokinetic temperature ( $\beta$ ) has been evaluated from the Exner equation<sup>[33]</sup>

$$\beta = T_1 T_2 (b - 1) / T_2 b - T_1$$
[14]

13.67

present work

A plot of log  $k_2$  at 303 K versus log  $k_1$  at 308 K gave isokinetic temperature as 392.04. Higher values of  $\beta$  (392.04) than the experimental temperature (303 K) indicates that the rate is governed by the enthalpy of activation.<sup>[34]</sup>

#### **Activation Parameters**

119.23

The reaction was studied at five different temperatures (25– 45°C), for the catalyzed reaction. From the plot of  $\log k_1$  versus 1/T (Arrhenius plot), the activation energy (Ea) was evaluated. The proposed mechanism is also supported by the moderate values energy of activation and other thermodynamic parameters. The positive values of free energy of activation and of the enthalpy of activation suggest that the transition state is highly solvated, while the high positive entropy of activation indicates that the formation of rigid associated transition states. The order of frequency factor (A) and values of free energy of activation ( $\Delta G^{\#}$ ) for the redox system also supports a reaction scheme proposed for the oxidation of Val by NBP in the presence of Ir(III) chloride under acidic conditions.

#### CONCLUSIONS

Oxidation of Val by NBP in perchloric acid media was found to be very sluggish, but oxidation became facile in the presence of micro-quantities of Ir(III) chloride catalyst. HOBr and RCHNH<sub>3</sub><sup>+</sup>(COO<sup>-</sup>) were the reactive species for the NBP and Val, respectively. Among the various species of Ir(III) chloride in an acidic medium,  $[IrCl_6]^{3-}$  was determined to be the catalytic species. In the proposed reaction scheme, the equilibrium of  $[IrCl_6]^{3-}$  and HOBr gave  $[IrCl_6OBr]^{4-}$ , which on dissociation formed  $[IrCl_5OBr]^{3-}$  through a slow rate-determining step. The species formed was responsible for oxidation of Val. In the scheme, each molecule of Val consumed more than two moles of NBP to give nitrile, aldehyde, NHP, CO<sub>2</sub>, and Br<sup>-</sup> in agreement with the experimentally observed stoichiometry. The deduced rate law for the reaction scheme was also consistent with the kinetics of the reaction.

Val + Ir(III)

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