Kinetic Study of Ru(III) Catalyzed Oxidation Of Alpha Hydroxy Acid By N-Bromoisonicotinamide: In aqueous Acidic Medium

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Abstract: Kinetics study of oxidation of alpha hydroxy acid by N-bromoisonicotinamide (NBIN), micro-concentration as homogeneously Ru(III) catalyst in presence of perchloric acid have been investigated at 308K using mercuric acetate as Br-ion scavenger. First-order kinetics with respect to each (NBIN) and [Ru (III)]. Zero order in [Glycolic acid], [Citric acid] and inverse fractional order [H+]. its evident from the observed values of k_1 which increase in the same proportion in which the concentration of each reactant is increased. Variations in ionic strength and dielectric constant (D_2O) have not influenced the oxidation rates. Protonated N-bromoisonicotinamide (NBINH), has been postulated as the reactive species of NBIN, HOBr, and H_2OBr. first-order rate constant ($k1$) values observed at varied different temperatures.

Keywords: kinetic, oxidation, Glycolic acid(GA), Citric acid(CA), NBIN, perchloric acid, acetic acid, etc.

1. Introduction

Kinetic studies of oxidation of reducing Hydroxy agents have been made by different Concentration of NBIN and other workers in acidic medium by Iodometric method. In the present study has been undertaken Kinetic studies regarding catalysed oxidations of reducing Glycolic and Citric acid by various oxidants agents, N- bromoisonicotinamide (NBIN),HClO4 in acidic medium in presence of mercuric acetate, HClO4,using transition metal ions, viz Ru(III) as catalyst is similar to the reported [1,2] inverse fractional order in [H+], as homogeneous catalysts are also available in literature.[3] Ru(III) complexes are reported [4] to have chemical reactivity .Oxidation of hydroxy acid and some unsaturated acid by various N-halo oxidants such as N-bromo-succinimide[5][6] ,N-bromo-acetamide[7], N-chloro-nicotinamide[8], N-bromo-benzamide[9], Chloramine–T[10], Brom-amine–T[11],1-chlorobenzotriazole[12], N-bromo-saccharin[13], N-bromo-phthalimide[14][16] and 1-chlorobenzimidazole[15] ,N-Choro benzamide [17], N-bromoisonicotinamide[18]. The availability of Ru (III) chloride as a nontoxic and homogenous catalyst has been reported [19] but slight attention has been paid to investigate the catalytic role of Ru (III) with N-halo compounds as oxidants. Oxidation of hydroxy acid by various N-halo oxidants such as N-bromo-succinimide have been reported. An extensive literature reveals that no regular kinetic work has been done.
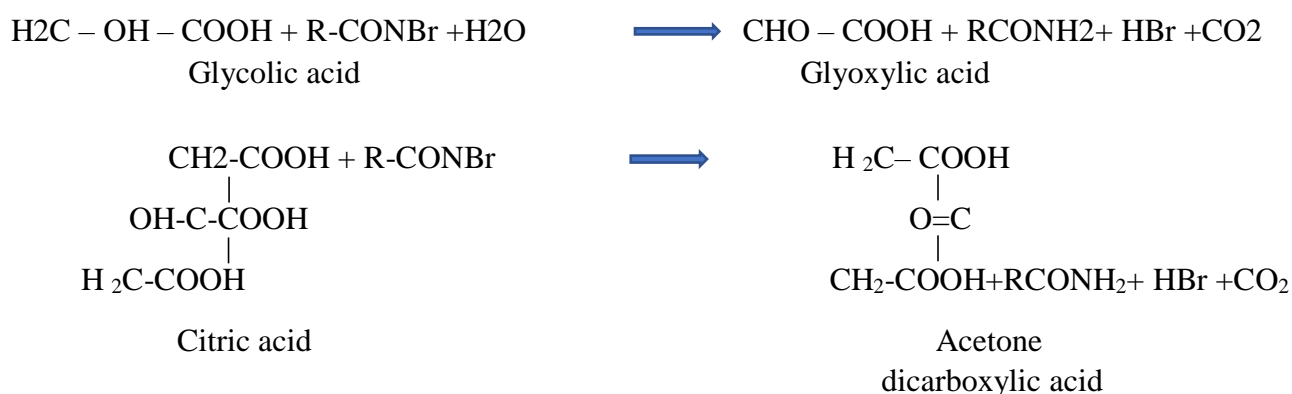
2. Materials & Experimental

A stock standard solution of NBIN 99.9% (E. Merck) was prepared by dissolving its known weight in doubly distilled water stud its concentration was estimated and the purity was checked iodometrically. All chemicals. Perchloric acid 99% (GR), Glacial acetic acid [E. Merck], $Hg(OAc)_2$ (Loba chem,mumbai) were also prepared in double distilled water. The standard solution of glycolic acid (GA)98% citric acid (CA) (99.9%sSigma Aldrich) were freshly prepared to double distilled water, Other reagents used were of SD Fine Grade, sodium sulphate (BDH) and their solutions were also prepared in doubly distilled water.

The reaction vessels were also coated black from outside to exclude photochemical Influence. The kinetic proposed were carried out at $55 \pm 0.1 \,^\circ C$. The reaction was initiated by mixing the already thermo-stated solution of hydroxy acid to the thermally equilibrated reaction mixture containing required volumes of solutions of NBIN + Ru(III) and all other reagents. Aliquots of the reaction mixture were pipetted out at regular intervals of time and poured into a conical flask containing 5 ml of 4% KI solution and 5 ml of dilute perchloric acid solution. The liberated iodine equivalent to unconsumed NBIN was estimated with standard sodium thiosulphate solution using starch as an indicator. The initial rates were obtained from the slopes of the concentration vs. time graph in the initial stages of the reactions by plane mirror method.

2.1 Stoichiometry and products identification

The reaction under condition in mixture containing excess of NBIN (over glycolic in the presence of HClO4 mercuric acetate, Na2SO4 and acetic acid was kept at different temperature 328k.The estimation of unconsumed NBIN in different set showed that one mole of hydroxy acid consumed on one mole of NBIN. In case the determined stoichiometry can be expressed according to equation for Citric and Glycolic acid.

$$H_2C - OH - COOH + R\text{-}CONBr + H_2O \longrightarrow CHO - COOH + RCONH_2 + HBr + CO_2$$

Glycolic acid $\qquad\qquad\qquad$ Glyoxylic acid

$$
\begin{array}{c}
CH_2\text{-}COOH \\
| \\
OH\text{-}C\text{-}COOH \\
| \\
H_2C\text{-}COOH
\end{array}
+ R\text{-}CONBr \longrightarrow
\begin{array}{c}
H_2C - COOH \\
| \\
O = C \\
| \\
CH_2\text{-}COOH
\end{array}
+ RCONH_2 + HBr + CO_2
$$

Citric acid $\qquad\qquad\qquad\qquad\qquad$ Acetone
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ dicarboxylic acid

The product were identified confirmed by its melting point, mixed melting point. Spectral analysis at spectrophotometer UV-1800 model. Presence of aldehyde and ketonic groups was also confirmed by Schiff regents.

that one Accordingly, the following stoichiometric equations are suggested: product formed glyoxylic acid and Acetone dicarboxylic acid were identified as the main oxidation products of the reactions under investigation.

3. Kinetic results

Kinetic study of Ru (III)-catalysed oxidation of reducing hydroxy acid by protonated NBIN was carried out at several initial concentrations of each reactant one by one in interval time. And 20% acetic acid and 50% water medium at 308 to 328K.

Initial rate $(-dc/dt)$ values have been calculated from the slopes of the plots of unconsumed [NBIN] and time and first-order rate constant, k1, was calculated as $k1 = (-dc/dt)/ [NBIN]$. When log a/a-x values are plotted against time, straight lines for reducing glycolic and citric acid were obtained.

Calculated values of first-order rate constants for the variations of NBIN, [α-HA] Ru(III) in the Ru(III)-catalysed oxidation of Citric and Glycolic acid at 308 and 328K.

3.1 Order of reaction with respect to NBIN, [HA] and Ru(III)

The concentration of NBIN has been varied from 2.0×10^{-4} M dm^{-3} to 15.5×10^{-4} M dm^{-3}, [α-HA] is concentration 10.0×10^{-4} M dm^{-3} to 45.0×10^{-4} M dm^{-3} at constant concentration of all other reactants at 308 and 328K. the rates were measured value of k1, respective of the concentration confirmed the first order of reaction.

The observed rate constant, k1, remained practically constant at different initial concentrations of NBIN, indicating first-order kinetics with respect to [NBIN], Ru(III) , Table 1). When k1 values are plotted against

[NBIN], straight lines for reducing glycolic and citric acid were obtained (Fig. 1). the plot of k1 vs. [α-HA] gives straight lines. (Fig. 2). straight lines with respected graph plotting time vs log a/a-x (Fig. 3).
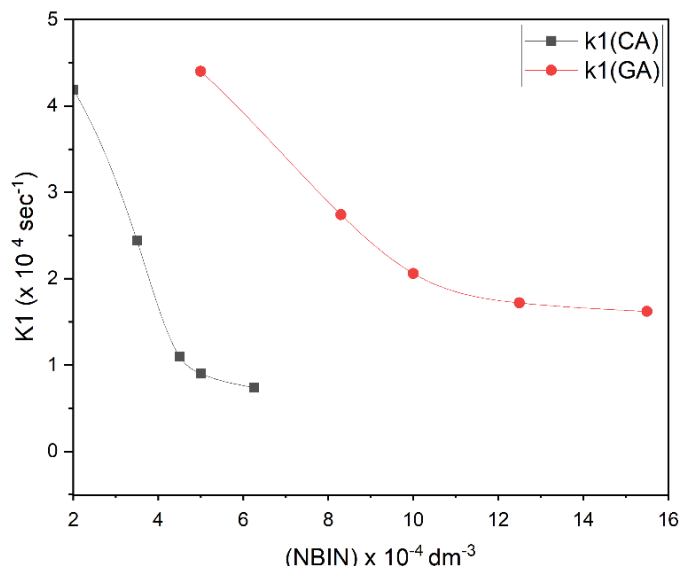

Fig. 1 Solution condition: [NBIN] = 2.5 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-4} mol dm^{-3}, [GA] = 5.0 x 10^{-2} mol dm^{-3}, [CA] = 2.5 x 10^{-2} mol dm^{-3}, [Ru(III)] =5.0 x 10^{-5} mol dm^{-3}, [HClO4] = 2.5 X 10^{-3} mol dm^{-3}, [Hg(OAc)$_2$] = 4.0 x 10^{-3} mol dm^{-3}, [AcOH] = 20%
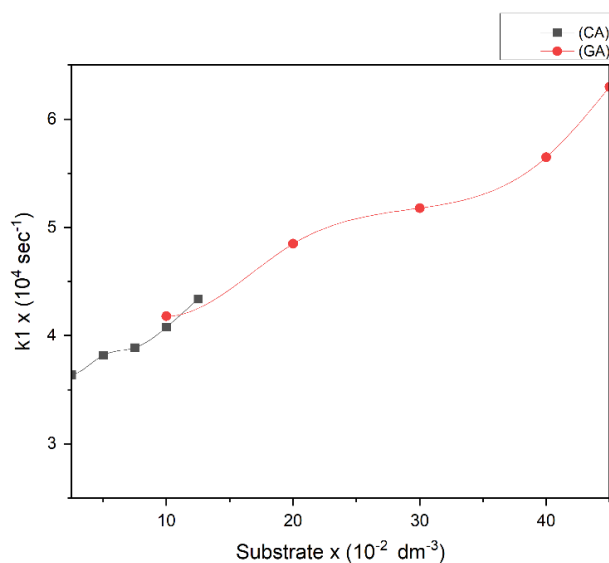
Fig. 2 Solution condition: [NBIN] = 2.5 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-4} mol dm^{-3}, [GA] = 5.0 x 10^{-2} mol dm^{-3},[CA] = 2.5 x 10^{-2} mol dm^{-3}, [Ru(III)] =5.0 x 10^{-5} mol dm^{-3}, [HClO4] = 2.5 X 10^{-3} mol dm^{-3}, [Hg(OAc)$_2$] = 4.0 x 10^{-3} mol dm^{-3}, [AcOH] = 20%
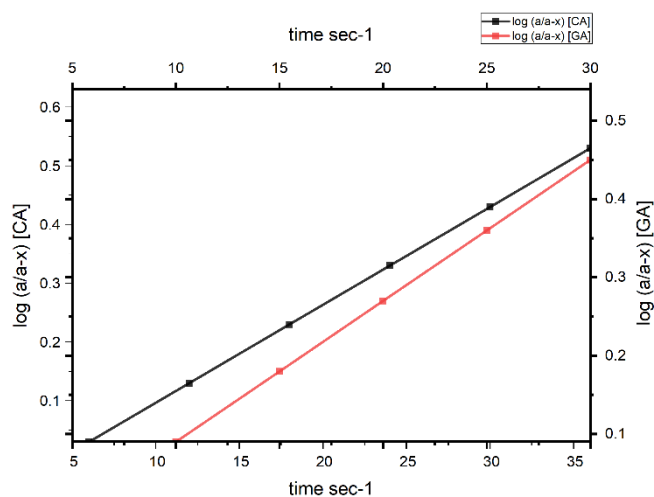
Fig. 3 Solution condition: [NBIN] = 2.5 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-4} mol dm^{-3}, [GA] = 5.0 x 10^{-2} mol dm^{-3},[CA] = 2.5 x 10^{-2} mol dm^{-3}, [Ru(III)] =5.0 x 10^{-5} mol dm^{-3}, [HClO4] = 2.5 X 10^{-3} mol dm^{-3}, [Hg(OAc)$_2$] = 4.0 x 10^{-3} mol dm^{-3}, [AcOH] = 20%

Table: 1 Influence of variation of Substrate, NBIN, HClO4, Hg(OAc)2, AcOH – H2O%. for the oxidation of glycolic, and citric acid by NBIN at 308-328K

The observed rate constant, k1, remained at different temperature 308 to 328K. rate of reaction depend on temperature. its increasing then decreasing rate of reaction. zero-order kinetics with respect to each glycolic and citric acid indicating first-order kinetics with respect to [NBIN], [Hg (OAc)2] was observed. because k1 values were found to increase linearly with increase in [α-hydroxy acid]. (Fig.2)

[HA] x 10^{-2} mol dm^{-3}	NBIN x 10^{-4} mol dm^{-3}	HClO4 x 10^{-3} mol dm^{-3}	Hg(OAc)$_2$ x 10^{-3} mol dm^{-3}	AcOH %.	K1 x 10^4 sec^{-1}	
					GA	CA
5.0	5.0	12.5	2.5	30%	3.91	3.82
7.5	5.0	7.5	2.5	30%	3.89	3.48
10	5.0	7.5	2.5	20%	4.18	4.18
12.5	5.0	15.5	4.0	20%	3.5	4.34
20	5.0	15.5	8.0	20%	4.84	5.60
15	5.0	5.0	4.0	20%	2.40	3.64
15	5.0	5.0	4.0	30%	1.70	3.48
7.5	2.5	5.0	4.0	40%	---	2.8
10	2.5	5.0	3.5	50%	---	1.73
10	3.0	5.0	2.5	20%	4.89	2.42
20	3.0	5.0	5.0	30%	3.84	6.77
20	8.3	5.0	6.0	20%	2.74	7.00
10	10	7.5	8.0	30%	2.06	5.60
10	15.5	7.5	8.0	40%	1.62	---
2.5	6.25	2.5	4.0	40%	---	0.74

Solution condition: [Ru(III)] =5.0 x 10^{-5} mol dm^{-3},

Table:2 Influence of variation of solvent polarity and ionic strength on reaction rate-

The Influence of solvent composition on the reaction rate was experiment different strength of acetic acid from 30% and 70% water. Rate of reaction depend on solvent. If solvent concentration increasing then decreasing a dielectric constant. The rate of the reaction in the present study is unaffected by the change in the ionic strength(μ) by of the addition of perchloric acid medium. variation in ionic strength(μ) has no influence on the reaction rate. (Fig. 4)

μ(mol dm^{-3})	AcOH - H$_2$O (v/v)%	k1 x 10^4 sec-1	
		GA	CA
5	20% - 80%	5.4	3.64
7.5	-------	--	3.48
10.5	30% - 70%	4.3	6.11
12.5	--------	3.9	5.12
15	20% - 80%	--	4.56
2.5	30% - 70%	6.14	--
15.5	30% - 70%	3.5	--
5	10% – 90%	2.91	--
5	15% - 85%	2.71	--
2.5	20% - 80%	2.4	5.47
2.5	25% – 75%	2.02	3.64
2.5	30% - 70%	1.7	3.49
5	40% - 60%	--	2.9
5	50% - 50%	--	1.74

Solution condition: [NBIN] = 2.5 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-4} mol dm^{-3}, [GA] = 5.0 x 10^{-2} mol dm^{-3}, [CA] = 2.5 x 10^{-2} mol dm^{-3}, [Ru(III)] =5.0 x 10^{-5} mol dm^{-3}, [Hg(OAc)$_2$] = 4.0 x 10^{-3} mol dm^{-3}
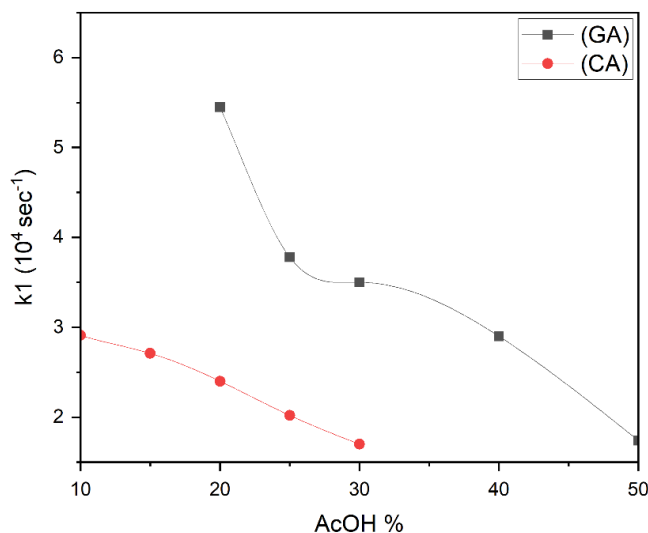
Fig. 4 Solution condition: [NBIN] = 2.5 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-4} mol dm^{-3}, [GA] = 5.0 x 10^{-2} mol dm^{-3},[CA] = 2.5 x 10^{-2} mol dm^{-3}, [Ru(III)] =5.0 x 10^{-5} mol dm^{-3}, [HClO4] = 2.5 X 10^{-3} mol dm^{-3}, [Hg(OAc)2] = 4.0 x 10^{-3} mol dm^{-3}.

Table:3 Influence of varying different concentration [Ru(III)]

The concentration if Ruthenium (III) chloride is varied range of 5.0 X 10^-5 mol dm^-3 to 21.5 X 10^-5 mol dm^-3 at constant [NBIN], [α-HA] and [H+] at 308 and 313K and rate constants were measured. First order kinetics with respect to**[Ru(III)].** We observing that the rate constants increase with increasing concentration of Ruthenium (III) chloride. (Fig. 5)

10^{-5} [Ru(III)] (mol dm^{-3})	K1 x 10^4 sec^{-1}	
	GA	CA
5.0	5.40	2.5
7.0	5.81	---
8.3	6.53	---
16.5	7.27	---
21.5	7.50	---
1.25	---	1.3
2.5	---	1.45
3.75	---	1.74
6.25	---	3.5

Solution condition: [NBIN] = 2.5 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-4} mol dm^{-3}, [GA] = 5.0 x 10^{-2} mol dm^{-3}, [CA] = 2.5 x 10^{-2} mol dm^{-3}, [HClO4] = 2.5 X 10^{-3} mol dm^{-3}, [Hg(OAc)2] = 4.0 x 10^{-3} mol dm^{-3}, **[AcOH] = 20%**
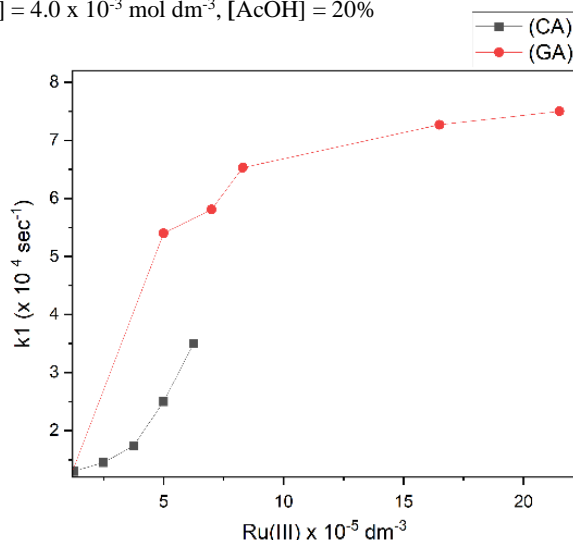
Fig. 5 Solution condition: [NBIN] = 2.5 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-4} mol dm^{-3}, [GA] = 5.0 x 10^{-2} mol dm^{-3},[CA] = 2.5 x 10^{-2} mol dm^{-3}, [Ru(III)] =5.0 x 10^{-5} mol dm^{-3}, [HClO4] = 2.5 X 10^{-3} mol dm^{-3}, [Hg(OAc)2] = 4.0 x 10^{-3} mol dm^{-3}.

Table:4 Influence of varying different temperature and Rate constants for Thermodynamics parameters

The observed rate constant, k1, remained at different temperature 308 to 328K. rate of reaction depend on temperature. its increasing then decreasing rate of reaction. The kinetics rate of oxidation of alpha hydroxy acids was study at five temperatures viz.308, 313, 318 ,323, 328K.The Arrhenius plots of log k1 versus 1/T is found to be linear. The thermodynamics parameters were calculated from k1 at varying temperature 308-328k The first order rate constant were calculated table:4, Fig. 6 etc.
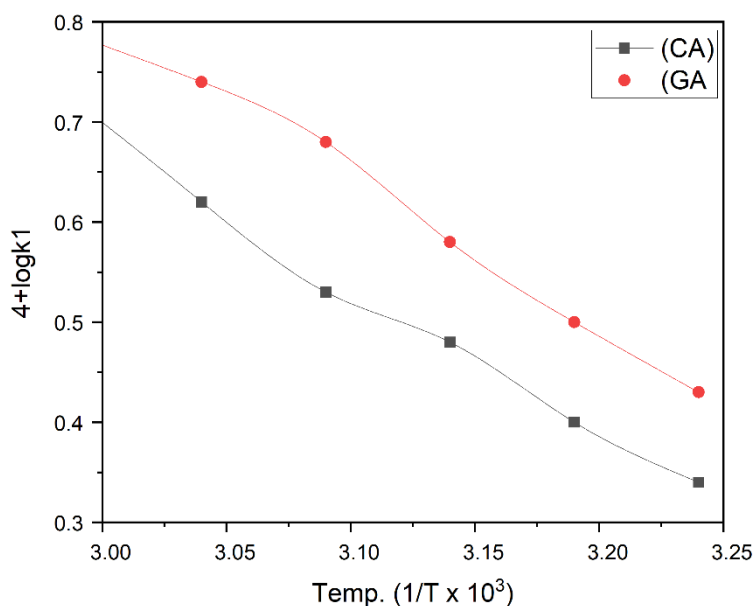

Fig. 6 Solution condition: [NBIN] = 2.5 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-4} mol dm^{-3}, [GA] = 5.0 x 10^{-2} mol dm^{-3}, [CA] = 2.5 x 10^{-2} mol dm^{-3}, [Ru(III)] =5.0 x 10^{-5} mol dm^{-3}, [HClO4] = 2.5 X 10^{-3} mol dm^{-3}, [Hg(OAc)$_2$] = 4.0 x 10^{-3} mol dm^{-3}, [AcOH] = 20%

Substrate [HA] X 10^{-2} mol	K1 x 10^4 sec-1					Temp. coeff.	Log A 10^4 m^{-1} Sec^{-1}	Ea KJ mol^{-1}	ΔH$^{\#}$ KJ mol^{-1}	ΔS# JK^{-1} mol^{-1}	ΔG KJ mol^{-1}
	308K	313K	318K	323K	328K						
Citric	2.21	2.49	3.08	3.29	4.2	1.670	2.040	94.91	92.30	-58.55	50.93
Glycolic	2.7	3.4	3.67	4.89	5.52	1.747	1.747	105.8	103.2	-68.26	84.78

Solution condition: [NBIN] = 2.5 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-4} mol dm^{-3}, [GA] = 5.0 x 10^{-2} mol dm^{-3}, [CA] = 2.5 x 10^{-2} mol dm^{-3}, [Ru(III)] =5.0 x 10^{-5} mol dm^{-3}, [HClO4] = 2.5 X 10^{-3} mol dm^{-3}, [Hg(OAc)$_2$] = 4.0 x 10^{-3} mol dm^{-3}, [AcOH] = 20%

4. Products analysis report

product concentration on the change of the wavelength of minimum and maximum absorbance in the solution, show in fig. Sample set course of UV and Visible absorbance spectra of glyoxylic and acetone dicarboxylic acid in acetic medium in presence perchloric acid and Ru (III) that a maximum absorbance alternates as 560nm and 525nm with 5-6 time intervals at 313K. The existence of above equilibrium in the reaction is supported by the positive effect of [HOBr] on pseudo-first-order rate constant, k1. Further, when comparison is made between the spectrum recorded for the solution of Ru(III) chloride and OH− and spectra recorded for the solutions of Ru(III) chloride and OH− with different concentrations of INA, it was found that with the addition of NBIN solution there is an increase in absorbance from 1.1 to 1.5 and 1.8 with a shift in λmax 400 to 560nm towards longer wavelength (Fig.7) [Glyoxylic acid] . it was found that with the addition of NBIN solution there is an increase in absorbance from o.5 to 0.9 and 2.6 with a shift in λmax 200 to 525nm towards longer wavelength (Fig.8). This increase in absorbance with the increase in [NBIN] clearly indicates that there is a formation of complex variant.
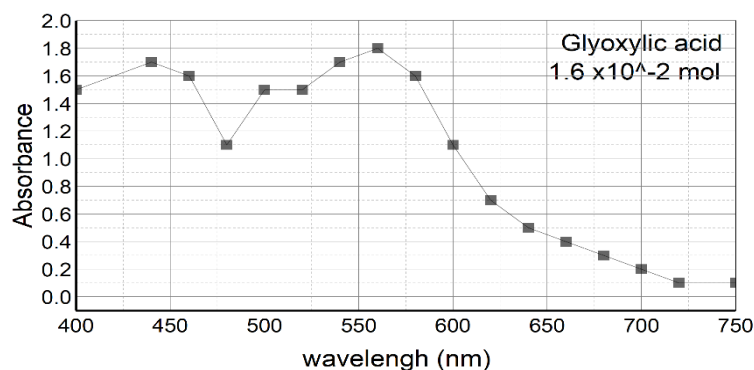
Fig 7. Solution condition: [Glyoxylic acid] = 0.5 x 10^{-2} mol dm^{-3} to 1.6 x 10^{-2} mol dm^{-3} , [NBIN] = 2.5 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-4} mol dm^{-3}

[GA] = 5.0 x 10^{-2} mol dm^{-3}, [Ru(III)] =5.0 x 10^{-5} mol dm^{-3}, [HClO4] = 2.0X 10^{-3} mol dm^{-3}, **[AcOH]** = 20%
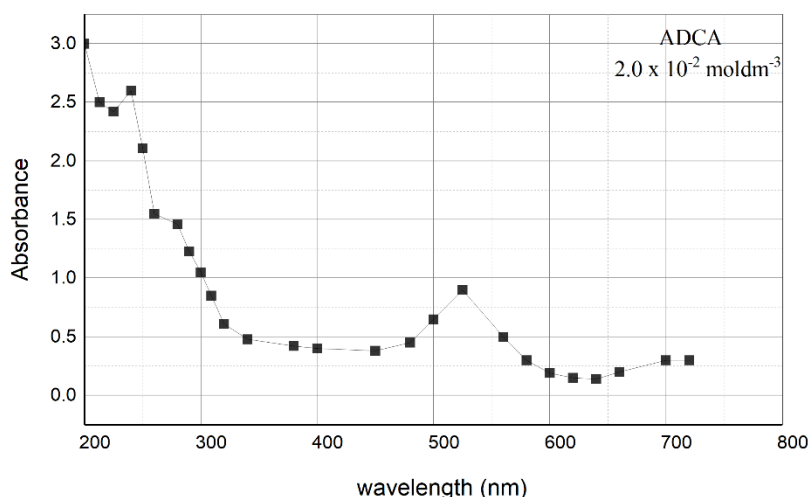

Fig 8. Solution condition: [Acetone dicarboxylic acid] = 0.5 x 10^{-2} mol dm^{-3} to 2.5 x 10^{-2} mol dm^{-3} , [NBIN] = 2.5 x 10^{-4} mol dm^{-3} to 5.0 x 10^{-4} mol dm^{-3}, [CA] = 2.5 x 10^{-2} mol dm^{-3} [Ru(III)] =5.0 x 10^{-5} mol dm^{-3}, [HClO4] = 2.0X 10^{-3} mol dm^{-3}, **[AcOH]** = 20%

4.1 Proof of the involvement of an intermediate:

When the integrated rate law suggestion provided the participation of an intermediate, the main direct support is established by measurement of its physicochemical properties. This approach needs the existence of an experimental technique for its recognition. Frequently, it is essential that the intermediate is formed in very high concentration (equivalent to the reactants in the case of a rapid equilibrium). Based on the life-time of the intermediate, the detection can use classical techniques or some arrangements intended for rapid reactions.

4.2 Proof for rejection of intermediate existence-s:

When there is large difference between electronic spectra (UV-VIS) of reactants and products, the consecutive recordings isf spectra throughout the reaction can convey information on the involvement of intermediate. the concentrations of the species, suggesting that the reactants is converted directly into the product without any intermediate. If this is not observed or appears only within a short period at the start of the reaction and the intersection position is changed, so it suggests some intermediate of significant concentration is formed.

5. Conclusion:

Several kinetic studies have been carried out to the mechanistic aspects of initial concentration of the reactants, oxidation of hydroxy acid by NBIN in the presence of perchloric acid. Under pseudo- first order conditions [HA] >> [NBIN]. indicates that's the reactions is zero- order in [HA]. It can be concluded a premilarly that oxidation became facile in the presence of low quantity of Ru(III) catalyst. The kinetics and oxidation of hydroxy acids by the rate determining step of the proposed mechanism have been elegant is also supported by the moderated values of energy of activation and other activation parameters and the relevant rate law.

6. Acknowledgments:

Reference:

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