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Kinetics and mechanism of oxidation of lactic acid by N-bromoanisamide

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ABSTRACT

The Kinetics and mechanism of oxidation of lactic acid by N-bromoanisamide in $HC1O_4$ *and in the presence of* $Hg(OAc)_2$ *has been investigated. The reaction, studied under pseudo-first order conditions of [LA] □□ [NBA] follows a first - order dependence of the rate on [[NBA] and a fractional order on [LA]. The decreasing effect of* H^+ *ion concentration on the rate was observed. Variation of the ionic strength, dielectric constant of the medium and* $Hg(OAc)_2$ *(used as* Br^- *ion scavenger) had significant effect on the rate of the reaction. Kinetic and activation parameters are evaluated based on the temperature effect on the rate. A mechanism consistent with the observed kinetics and activation data have been proposed leading to the derived rate law.*

Keywords: lactic acid, oxidation, mechanism, N-bromoanisamide, activation parameters.

INTRODUCTION

Numerous reports are available on kinetics of oxidation of α- hydroxy acids such as glycolic acid, lactic acid, malic acid, and mandelic acid etc. by variety of oxidants like N-bromsuccinimide [1-2], N-bromacetamide [3-6], N-halosulphonamide[7-8], N-chlorosaccharin [9-10] and few others oxidants[11-13]. Lactic acid is a naturally occurring α- hydroxy acid which is widely used in food processing, biochemical products and textiles. It also finds applications in the manufacture of bioplastics, fibers, solvents and oxygenated chemicals. A literature search showed no reports on the mechanism of oxidation of Lactic acid by N-bromoanisamide in acid solution. It is therefore planned to study the details of kinetics of oxidation of Lactic acid by N-bromoanisamide in acidic medium in the presence of $Hg(OAc)_2$ which is act as Br^- ion scavenger. Kinetic data have been used to elucidate the reaction mechanism.

MATERIALS AND METHODS

N-bromoanisamide was prepared and its acetic acid solution was standardised iodometrically. The reagents employed were Lactic acid (E. Merck), $NaClO_4$ perchloric acid and all other reagents used were of AR grade. All solutions were prepared in doubly distilled water. Water (de-ionized) and glacial acetic acid were used as the solvent through the work. A thermostated water bath was used to maintain the desired temperature.

RESULTS AND DISCUSSION

The oxidation of lactic acid resulted in the formation of corresponding aldehyde. Product analysis and stoichiometric determinations indicates that the following reaction may be written as.

$$CH_3CH(OH)COOH + CH_3OC_6H_4CONHBr \longrightarrow CH_3CHO + CH_3OC_6H_4CONH_2 + HBr + CO_2$$

Effect of oxidant variation: Under the condition [LA] □□ [NBA], the disappearance of [NBA] with time followed first order kinetics as evidented by the linear plots of log (a-x) *versus* time for different initial concentrations of oxidant (table1).

Table-1: Effect of NBA on the reaction rate

Lactic acid = 5.5×10^{-3}M ; $HClO_4$ = 0.010 M; Temp.= 308K
$Hg(OAc)_2$ = 0.002M; Solvent; $AcOH-H_2O$ = 30-70 / (v/v)

NBA × 10^{-3}M	k × 10^{-3} min^{-1}
2.5	4.389
3.0	4.388
3.5	4.386
4.0	4.384
4.5	4.383
5.0	4.381

Effect of substrate variation: The reaction increases linearly with an increase in the concentration of lactic acid. The results are presented in table-2. The plot of $1/k_{obs}$ *versus* 1/[Substrate] gave linear line passing through origin suggests first order dependence on [LA].

Table-2: Effect of Substrate on the reaction rate

NBA = 3.0×10^{-3}M; $HClO_4$ = 0.010 M; Temp.= 308K
$Hg(OAc)_2$ = 0.002M; Solvent; $AcOH-H_2O$ = 30-70 / (v/v)

Substrate × 10^{-3}M	k × 10^{-3} min^{-1}
2.5	2.313
3.5	2.679
4.5	3.418
5.5	4.388
6.5	5.061
7.5	5.924

Effect of [H^+] variation: The dependence of the reaction rate on the concentration of H^+ was studied at constant concentration of oxidant, substrate and other reagents, and varying the initial concentration of $HClO_4$. The k_{obs} values measured at different initial concentration of are shown in table-3. It can be seen that the reaction rate decrease slightly with increase in the [H^+] ion concentration.

Table-3: Effect of $HClO_4$ on the reaction rate
NBA = 3.0 × 10^{-3}M ; Lactic acid = 5.5×10^{-3} ;Temp.= 308K
$Hg(OAc)_2$ = 0.002M; Solvent; $AcOH$-H_2O = 30-70 / (v/v)

$HCLO_4$ ×10^{-2}M	k × 10^{-3} min^{-1}
0.5	4.831
1.0	4.388
2.0	4.056
3.0	3.566
4.0	3.091
5.0	2.470

Effect of temperature variation: Kinetic runs were performed at various temperatures (308-323K) while keeping other experimental conditions the same and the results are summarized in table-4. Using Arrhenius equation the energy of activation for substrate has been calculated and this value subsequently utilized in computing various other thermodynamic parameter and all the results are presented in table-5.

Table4. Effect of Temperature, on the reaction rate

NBA = 3.0 ×10^{-3}M ; Lactic acid = 5.5×10^{-3} ; $HClO_4$ = 0.010M;
$Hg(OAc)_2$ = 0.002M; Solvent; $AcOH$-H_2O = 30-70 / (v/v)

Temperature	k × 10^{-3} min^{-1}
308	4.388
313	5.937
318	9.173
323	12.218

Effect of dielectric constant and anisamide: The effect of dielectric constant of reaction medium was studied by adding acetic acid in the reaction medium at constant concentration of other reactants. Addition of anisamide (one of the reaction product) in reaction mixture at constant concentration of oxidant and lactic acid, decreases the rate of reaction.

Table 5. Activation parameters for the oxidation of Lactic acid
NBA =3.0×10^{-3}M; Lactic acid = 5.5×10^{-3} M; $HClO_4$ = 0.010 M;
$Hg(OAc)_2$ = 0.002M; Temp = 308K; Solvent; $AcOH$-H_2O = 30-70 / (v/v)

Substrate	Ea (k.J mol^{-1})	ΔH^* (k.J mol^{-1})	$-\Delta S^*$ ($Jk^{-1}mol^{-1}$)	ΔG^* (k J mol^{-1})
Lactic Acid	60.06	57.50	95.38	86.87

Reaction Mechanism: The following reaction mechanism is suggested in which the protonated hydroxy acid react with active form of the oxidant HOBr in the rate determining step.

$$CH_3OC_6H_4CONHBr + H_2O \underset{k_1^{-1}}{\overset{k_1}{\rightleftharpoons}} HOBr + CH_3OC_6H_4CONH_2 \qquad (I)$$

$$CH_3CH(OH)COOH + H^+ \underset{k_2^{-1}}{\overset{k_2}{\rightleftharpoons}} CH_3CH(O^+H_2)COOH \qquad (II)$$

$$CH_3CH(O^+H_2)COOH + HOBr \underset{k_3^{-1}}{\overset{\text{slow } k_3}{\rightleftharpoons}} CH_3CH(OBr)COOH + H_2O + H^+ \qquad (III)$$

$$CH_3CH(OBr)COOH \xrightarrow{\text{fast}} CH_3CHO + CO_2 + HBr \qquad (IV)$$

From the above mechanism, the following rate law is derived.

$$\text{Rate} = k_1 k_2 k_3 [NBA][H^+][Sub] / [Anisamide]$$

$$k_{obs} = k_1 k_2 k_3 [H^+] [Sub] / [Anisamide]$$

which support the observed kinetic parameter like first order with respect to [substrate], [oxidant] and [H^+] and inhibition by anisamide and also non-involvement of water molecule in rate determining step.

APPLICATIONS

The details of kinetics of oxidation of Lactic acid by N-bromoanisamide in acidic medium in the presence of $Hg(OAc)_2$ which is act as Br^- ion scavenger . Obtained Kinetic data have been used to elucidate the reaction mechanism.

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