KINETICS STUDY OF OXIDATION OF LACTIC ACID BY N-BROMOISONICOTINAMIDE

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Abstract

Kinetics of oxidation of Lactic acid by N-Bromoisonicotinamide In aqueous acetic acid medium, in the presence of [H+] ion, have been studied in the 35^0 C range. The problems to be solved in the establishment of the rate of reaction and different factors such as concentrations of oxidant, reactants, reaction medium, etc., and interpretation of the provided further support to the proposed mechanism, intermediate possible complex, and product formation in the reaction. The reactions were found to be first-order concerning [NBIN] and fractional or zero order of the reaction concerning [substrate] and[H+]. The rate decreases with increases in the dielectric constant of the medium. The plot is linear with a negative slope. Activation parameters were evaluated.

Keywords: Kinetics, Mechanism, Lactic Acid, NBIN, Perchloric Acid.

Introduction

This research paper describes the kinetic study of the oxidation of Lactic acid by N-Bromoisonicotinamide in aqueous acetic acid medium. N- Bromoisonicotinamide is known to be a versatile reagent as an oxidant uses in kinetic studies, analytical and organic synthesis. The NBIN are referred to as positive halogen compounds. The mechanism of the Catalyst depends on the Nature of the substrate, oxidant, and the experimental work condition.

This compound has many advantages like as well as low cost, easy handling, low toxicity, and mild nature with stability [1]. The kinetic oxidation of alcohols by NBIN [2]. The perchloric acid has been used as a source of [H+] in the reaction medium [3].

The study of oxidation of organic compounds [Hydroxy acid] is of spacious importance both from a

Kinetics and mechanistic point of view. The kinetics deals with the study of such oxidation reactions through elucidation of their mechanisms and hence the investigations of reaction kinetics in chemical reactions are important aspects in chemistry [4].

N-halo compounds serve not only as the source of positive halogen but also as reagents for the oxidation of varieties of organic substrates in both acidic and alkaline media. As a result, these reagents react with a wide range of functional groups affecting an array of molecular transformations.

N-halo compounds have been extensively employed as oxidizing and halogenating reagents for organic compounds [5]. Several researchers have studied synthetic applications, kinetics, and mechanisms of oxidation reactions involving these reagents in the recent past [6].

With the above facts, we have reported for the first time, the result investigation on the kinetic and mechanism aspects of lactic acid by NBIN in an aqueous acetic acid medium at 308K. the objective of the present work is mainly to unfold the mechanistic

image of the NBIN redox system in the aqueous acetic acid medium through kinetic studies and to know the relative reactivity of lactic acid substance towards NBIN in aqueous acetic acid medium.

Experimental Materials:

An aqueous solution of lactic acid (E. Merck), NBIN was prepared by the standard method by Hauser and Renfrow (1923), and its identified melting point then was found to be 210°c with soluble in water, acetic acid, and ethanol. Stock solutions of NBIN and $NaClO_4$(E. Merck) were prepared by dissolving weighed samples in double distilled water. All other reagents were of analytical grade. The reaction mixture was kept in a Black coated bottle to prevent interaction with light and photo-chemical decompositions.

Kinetics:

The requisite volumes of all reagents, and substrate in a thermostatic water bath were maintained to attain equilibrium at the temperature of the experiment with ±0.1K accuracy. Then for initiating the chemical reaction, add the required amount of NBIN solution to the reaction mixture and start a stopwatch at the time of mixing. The solutions will be rapidly mixed and an aliquot of the reaction mixture will be withdrawn at suitable intervals of time a known amount of unconsumed NBIN was estimated iodo-metrically. The reaction mixture of 5 ml aliquots was pipette out at regular intervals of time and added KI solution in a flask to quench the reaction velocity and liberate iodine which has been titrated against standard sodium thiosulphate solution using a starch solution endpoint (endpoint indicated by the disappearance of blue color).

Stoichiometry and Product analysis:

The mixture containing in stoichiometry reaction large excess of hydroxy acids over oxidant (NBIN) in different ratios was allowed equilibrated for 24 hours at (303-328K). The estimation of unconsumed NBIN in different sets showed that one mole of hydroxy acid was consumed on one mole of NBIN. In case the determined stoichiometry can be expressed according to the equation.

Hydroxy acid   N-bromoisonicotinamide   oxo acid   Isonicotinamide
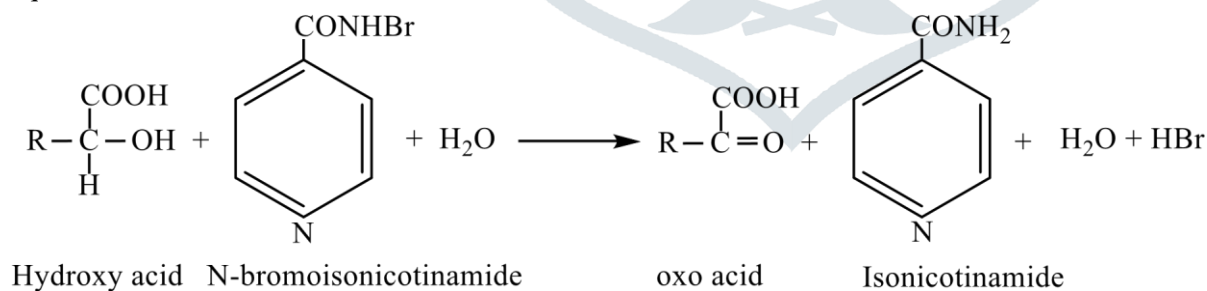
where R= CH_3 in Lactic acid [LA]

Whose Oxidation product is pyruvic acid was detected by measuring the melting point of its amide derivative as a fellow. This is also identification confirmed by spot test, 2,-4 dinitro phenyl hydrazine method[7] and its melting point.

Spectral technique

The infrared spectrum has been used for compounds recorded in the 4000- 400cm-1 region with Bruker spectrophotometer to identify the nature and oxidation reaction products (in solution) and to fellow their stretching and bending modes. This coupled with C=O stretch around 1715cm^{-1} shows that the methyl group and C=O stretch band around 1706 cm^{-1} along with the broad O-H stretch 3300 cm^{-1}observed (in dil. Solution) show that the compound is carboxylic acid. The C-H bending is observed at 1450 cm^{-1} and C-C bending around 1200 cm-1 shows the presence of saturated aliphatic acid.

Absent confirmation test of free radicals

The preparation of free radicals during the oxidation of Lactic acid with was tried by including 3-5 ml of acrylonitrile in 5-10 ml of the reaction mixture taken at various time interim. No adjustment in shading or non-appearance of off-white turbidity demonstrates that no free radical is framed in any of the reactions.

Result and discussion:

The kinetics of oxidation of lactic acid was investigated at several initial concentrations (Table 1) by NBIN in aqueous acetic acid at constant temp. of 308K. First order constant k_1, was calculated in the plots of log (a/a-x) versus time(fig.1). values of k_1 were constant at all initial concentrations of NBIN, Thus the reaction exhibited first-order dependence on the oxidant. The pseudo-first-order rate constant is nearly the same at different concentrations of lactic acid (fig.2) and perchloric acid showing fractional or zero-order dependence.

Experimental data (Table 2) show that the rate decreases with increases in the dielectric constant of the medium. Negligible effect of the Ionic strength of the medium on the rate, and the reaction is unaffected by bromide ion. The Negligible effect of $Hg(OAc)_2$ excludes the possibility of its involvement either as a scavenger for any bromide ion formed in the reaction. The kinetic study was also made in the 303-328K temp. and activation parameters were calculated (Table 4). The reactive species HOBr of NBIN, in aqueous acetic acid.

Table: 1 Effect of Variation of Oxidant, Lactic acid, and $HClO_4$ at 308K temp.

[NBIN] x 10^3mol (dm^{-3})	[Substrate]x 10^2mol (dm^{-3})	[H$^+$]x10^3 mol(dm^{-3})	K_{obs} x 10^4 sec^{-1}
1.25	2.5	1.0	2.31
2.0	2.5	1.0	2.33
3.0	2.5	1.0	2.36
5.0	2.5	1.0	2.72
6.25	2.5	1.0	2.37
2.0	2.0	1.0	3.50
2.0	2.5	1.0	3.94
2.0	3.0	1.0	4.44
2.0	5.0	1.0	4.58
2.0	6.25	1.0	4.66
2.0	2.5	1.0	4.46
2.0	2.5	1.25	3.70
2.0	2.5	2.25	3.44
2.0	2.5	2.5	3.40
2.0	2.5	5.0	3.07
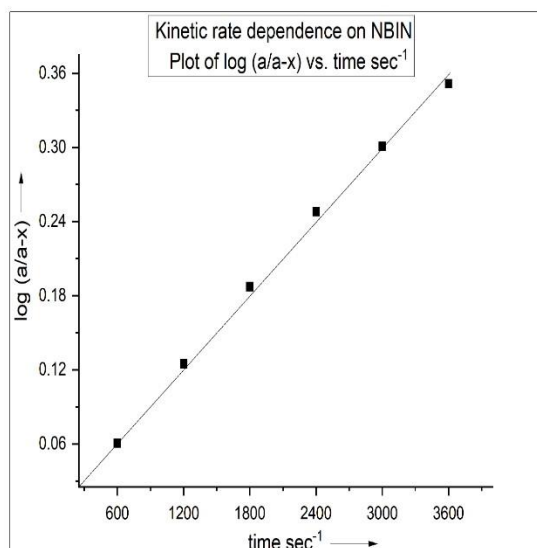
Figure 1.
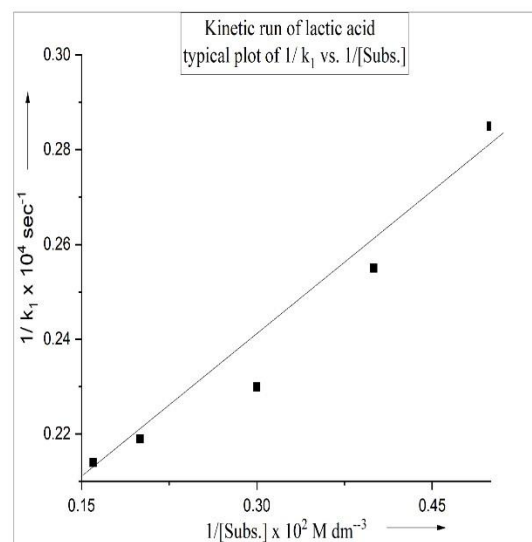
Figure 2.

Table:2 Effect of Variation AcOH-H_2O%(V/V), KCl, and $Hg(OAc)_2$ at 308K temp.

[AcOH]-H_2O% (v/v)	[KCl]x10^3mol (dm^{-3})	[Hg(OAc)$_2$]x10^3 mol (dm^{-3})	K_{obs} x 10^4 sec-1
15-85%	1.0	1.0	4.87
20-80%	1.0	1.0	4.53
25-75%	1.0	1.0	4.32
30-70%	1.0	1.0	3.66
40-60%	1.0	1.0	2.88
30-70%	1.0	1.0	4.15
30-70%	1.25	1.0	3.49
30-70%	2.25	1.0	3.50
30-70%	2.5	1.0	3.19
30-70%	5.0	1.0	3.31
30-70%	1.0	1.0	4.09
30-70%	1.0	1.25	5.21
30-70%	1.0	2.25	5.96
30-70%	1.0	2.5	3.72
30-70%	1.0	5.0	3.17

Table 3 Effect of the temperature on the reaction rate constant

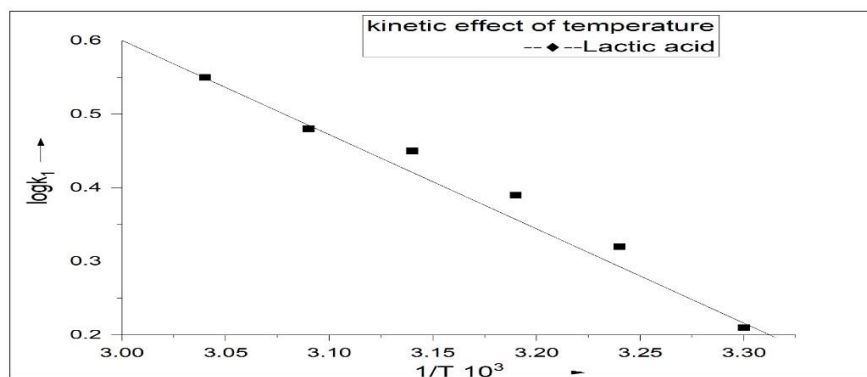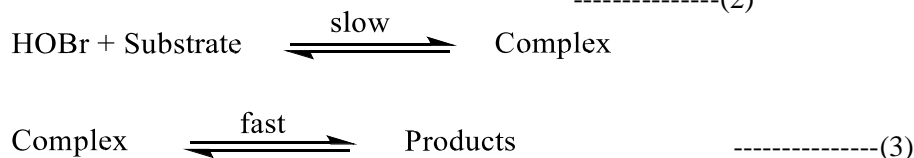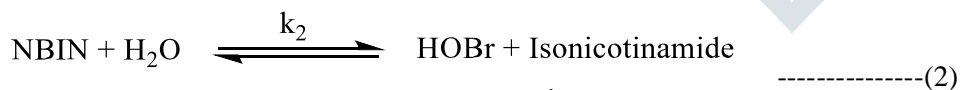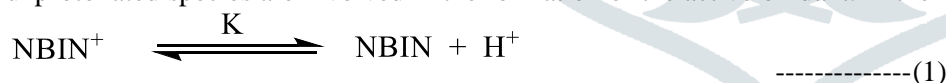| Temp. K	Kr x 10^4
303	1.61
308	2.13
313	2.50
318	2.97
323	3.03
328	3.57

Table:4 Activation Parameters

Substrate	Temperature Coeff.	$[\Delta Ea]$ KJMol^{-1}	Arrhenius Factor [Log A]	$[\Delta S^*]$ JK$_{-1}$Mol$_{-1}$	$[\Delta H^*]$ KJMol^{-1}	$[\Delta G^*]$ KJMol^{-1}
Lactic acid	1.2857	34.50	2.21	-194.10	31.90	71.15

Mechanism:

In the present section, the reaction Plan is based on kinetic results through which the reaction between NBIN and substrates in an acetic solution takes place. has been proposed. The rate of reaction decreases with the increases in [H+]. The protonated and unprotonated species are involved in the formation of the active oxidant. In the next steps following as well as

$$NBIN^+ \xrightleftharpoons{K} NBIN + H^+ \qquad \text{--------------(1)}$$

$$NBIN + H_2O \xrightleftharpoons{k_2} HOBr + Isonicotinamide \qquad \text{--------------(2)}$$

$$HOBr + Substrate \xrightleftharpoons{slow} Complex$$

$$Complex \xrightleftharpoons{fast} Products \qquad \text{--------------(3)}$$
$$\text{--------------(4)}$$

$$Rate = k_2[NBIN] [H_2O] \qquad \text{--------------(5)}$$

Applying equilibrium approximation to step (1)

$$K = \frac{[NBIN] [H^+]}{[NBINH^+]} \qquad \text{--------------(6)}$$

$$K [NBINH^+] = [NBIN] [H^+] \qquad \text{--------------(7)}$$

$$[NBIN]_e = \frac{K[NBINH^+]}{[H^+]}$$

$$\text{--------------(8)}$$

Where [NBIN]e is the concentration of NBIN at reaction equilibrium, Substituting [NBIN]e in the rate equation.

$$\text{Rate} = \frac{k_2 K\,[NBINH^+][H^+]}{[H^+]}$$

---------------(9)

The total effective concentration of NBIN is $[NBIN]t$,

$$[NBIN]t = [NBIN]e + [NBINH+]$$ --------------(10)

$$[NBIN]_t = \frac{K[NBINH^+]}{[H^+]} + [NBINH^+]$$

----------------(11)

$$[NBIN]_t = [NBINH^+]\left[\frac{K}{[H^+]} + 1\right]$$

--------------(12)

$$[NBINH^+] = \frac{[NBIN]_t}{(K/[H^+]) + 1}$$

----------------(13)

Substituting for $[NBIN+]$ in the rate equation

$$\text{Rate} = k_2K[H_2O]/[H^+] \;\; x \;\; \frac{[NBIN]_t}{^+(K/[H^+]) + 1}$$

$$\text{Rate} = k_2K\,[H_2O]/[H^+] \;\; x \;\; \frac{[NBIN]_t}{\{(K+[H^+])/[H^+]\}}$$

-----------------(14)

-----------------(15)

$$\text{Rate} = \frac{k_2K[H_2O][NBIN]_t}{(K + [H^+])}$$

------------------(16)

$$\text{Rate} = \frac{k\,[NBIN]_t}{(K+[H^+])}$$

------------------(17)

Whereas, $k = k_2K\,[H_2O]$

The above equation can be written as follows:

$$\frac{1}{k'} = \frac{(K+[H^+])}{k\,[NBIN]_t}$$

$$\frac{1}{k'} = \frac{K}{k\,[NBIN]_t} + \frac{[H^+]}{k\,[NBIN]_t}$$

----------------(18)

------------------(19)

When $1/k'$ is plotting against $[H+]$, a straight line is obtained. The slope of the line is $1/k\,[NBIN]t$. From the value of intercept and substituting the value of $k\,[NBIN]t$, the equilibrium constant K is calculated.

Since $K < [H+]$.

$$\text{Rate} = \frac{k\,[NBIN]_t}{[H^+]} \qquad \text{-------------------(20)}$$

The rate law showed that the reaction follows first-order kinetics concerning [NBIN] and inverse fractional order kinetics concerning [H+]. This may be clarified by looking balance between protonated and unprotonated oxidants.

The unprotonated species is attached to the evolution of the effective oxidant.

Rate = k_2[NBIN] [H$_2$O] The rate law shows that the response pursues the first request energy regarding [NBIN].

Acknowledgment

Conclusion:

From observed kinetic data the following conclusion can be drawn:

i). HOBr is reactive oxidizing species of NBIN in aqueous acetic acid medium.

ii). The oxidation rate of lactic acid did not depend on the ionic strength of the reaction medium.

iii). Mercuric acetate as one of the reactants plays the role of inhibitor in addition to its role as Br$^-$ as a scavenger.

iv). The observed negative values of entropy of activation for lactic acid support the formation of a rigid activated complex as proposed in equation (2) of the mechanism.

v). The following chemical reaction, pyruvic acid was a Product obtained from lactic acid.

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