Kinetic and Mechanistic Study of The Oxidation of Malic Acid by N-Bromoisonicotinamide: in Aqueous Acetic Medium

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***Abstract*- The oxidation of Malic acid to the corresponding oxoacids with N-bromoisonicotinamide in aqueous acetic acid has been studied. The reaction is first-order concerning [NBIN] and Fractional or zero-order concerning the substrate. The reaction fractional- order exhibits fractional -order on H^+ ion dependence. The effect of solvent composition on the reaction rate was studied by different acetic acid concentrations. The oxidation of malic acid has been studied in two solvents and the solvent effect analysed also. A suitable mechanism for the reaction was informing which agrees with the measured kinetic and various thermodynamic parameters.**

***Keywords*: oxidation, mechanism, malic acid, N-bromoisonicotinamide, temperature.**

1. Introduction

The kinetics of organic compound oxidation in an aqua-organic solvent medium reveals the important role of specific and non-specific solvent effects on the reactivity [1]. Hydroxy acid may be oxidized either as alcohols yielding the corresponding oxoacid to yield an aldehyde or carbonyl compound [2].

N-bromoisonicotinamide (NBIN), is a halo-oxidant, low cost, easily handled, low toxicity, and mild nature with stability. Its widely used in the oxidative study of alcohols [3], amino acids [4], and unsaturated acids [5], two-alkanones[6][7]. Oxidation Study of Primary Alcohols (propanol and butanol) by N-chloro-iso-nicotinamide in Aqueous Acetic Acid Medium [8].

The study of the oxidation of organic compounds is of enormous importance both from mechanistic and oxidative points of view. A chemical reaction may have various aspects one of which being oxidation. Oxidation reactions are no less common in general chemistry and their importance has resulted in the collection of several empirical observations and conclusions. The study of such oxidation reactions through elucidation of their mechanisms and hence the investigation of reaction kinetics in chemical reactions are important aspects of chemistry. The kinetics deals with the study of change in concentration of the components of the reaction system in the liquid phase with the passage of time and the results are summarized in the form of rate expressions.

Malic acid is a dicarboxylic acid with the molecular formula $C_4H_6O_5$ it is a crystalline white solid that is soluble in water and polar organic solvents. It is very useful for various applied on the skin to treat acne and other skin problems, cosmetics, as a flavoring agent in food, treatment fibromyalgia, and drugs,

The survey of the literature reveals that there seem to be no reports available on the oxidation aspects using N-bromo-iso-nicotinamide [NBIN]. In continuation of our earlier work with halo-oxidant, we now report the kinetics and mechanism of oxidation of malic acid by NBIN in aqueous acetic acid medium. A suitable mechanism and thermodynamics activation parameter has also been proposed.

2. EXPERIMENTAL

Materials:

An aqueous solution of malic acid (E. Merck), NBIN was prepared by the standard method by Hauser and Renfrow (1923), and it is identified by melting point 210ºc with soluble in acetic acid, water. Its purity was checked iodometrically. All solutions were prepared in double distilled water and all stock solutions were kept in the dark until needed to prevent photo-chemical decompositions.

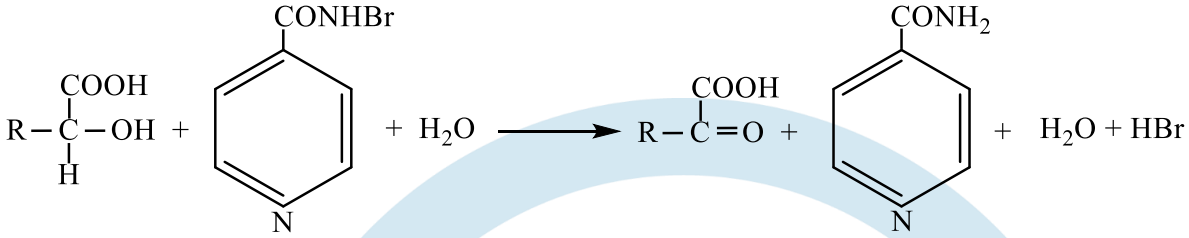
Kinetic Procedure:

The kinetic investigation was conducted at pseudo-first-order conditions [NBIN]<<[MLA] in a highly equipped thermo-stated to attain equilibrium at the temperature of the experiment with ±1ºK 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 color).

Stoichiometry:

The mixture containing in stoichiometry reaction large excess of malic acid over oxidant (NBIN) in different ratios was allowed equilibrated for 24 hours at (313K). The estimation of unconsumed NBIN in experiment sets showed that one mole of hydroxy acid was consumed on one NBIN. In case the determined stoichiometry can be expressed according to the equation. Whose Oxidation product is Oxaloacetic acid was detected by measuring the melting point and spot test of its amide derivative as a fellow.



Hydroxy acid N-bromoisonicotinamide oxo acid Isonicotinamide

Where, R=CH_2COOH in malic acid

Product analysis:

This is also identification confirmed by spot test, and 2 -4 dinitro phenyl hydrazine method [9]. In a typical experiment, malic acid 0.05 mol, 6.7g., and NBIN (20.01g, 0.01mol) were dissolved in aqueous acetic acid and allowed to stand in the dark for 24 h to complete the reaction. It was then treated with an excess(250ml) of freshly prepared solution of 2, -4 dinitrophenylhydrazine in 100 ml HCl(2N) acid and kept overnight in the refrigerator. The Precipitation of DNP was filtered off, dried, weight, and recrystallization from ethanol and again weighed. The product was identified (m.p. and mixed m.p.) to an authentic sample of DNP of the corresponding oxo acid (Oxaloacetic acid) in 86 to 90% yield, after recrystallization.

Spectral analysis:

FT-IR is one of the most important to the identification of the functional groups has been observed and the studied product compound contains Four carbon atoms. The IR stretching vibration of v-OH observes at 3323 cm-1. The experiment. The C=O stretching vibration sharp bands at 1755 cm-1 indicate the presence of carbonyl groups. The C-C stre. Vibration appears at 1010 cm-1. The C-H stre. Vibration at 2926 cm-1 is characteristic of Oxaloacetic acid.

Result and discussion:

The kinetic oxidation of Malic acid by the acetic solution of NBIN in the presence of solvent has been studied at a constant temperature of 313K (Table 1). Order of reaction concerning each reactant was determined by various concentrations of oxidant [NBIN], substrate [MLA], [H^+], and acetic acid one by one in different sets keeping the concentration of all other reactants constant at constant temperature (table:1). In [NBIN] kinetic run, the initial rate (-dc/dt) of the reaction was determined. The first order of the reaction k1, for the variation of all reactions, was calculated as

$$\text{Rate} = \frac{(-dc/dt)}{[NBIN]}$$

Where [NBIN]* denotes the [NBIN] at which (-dc/dt) was determined.

First-order kinetic was observed in a plot (log a/a-x) versus [Oxidant] is linear, and Plot between (-dc/dt) x 10^5 ML^{-1} S^{-1} and [NBIN] x 10^3 M (fig 1). The typical graph plot of 1/k vs. 1/[S] is linear(fig2). The reaction rate decreases, increasing the concentration of acetic acid (fig.3). The plot of log k_1 versus 1/D is linear with a positive slope[10]. The ionic strength investigation in the presence of various concentrations of sodium perchlorate (table 2) that negligible effect on the reaction rate. The reaction was studied at six different temperatures i.e.,303K to 328K (Table 3) (fig4). The activation parameters are recorded (Table 4).

The kinetic observations show that the investigation is a complex reaction. In such a reaction are possibilities for the formation of a complex between all different reactants of the reaction.

Table: 1 Effect of Variation of Oxidant, Malic acid, and HClO4 at 313 K temp.

[NBIN] x 10^3mol (dm^{-3})	[MLA]x 10^2mol (dm^{-3})	[H^+]x10^3 mol(dm^{-3})	(-dc/dt) x 10^5 ML^{-1} S^{-1}	K_{obs} x 10^4 sec^{-1}
1.25	3.25	1.0	0.30	2.38
2.0	3.25	1.0	0.48	2.41
3.0	3.25	1.0	0.74	2.45
5.0	3.25	1.0	1.23	2.47

6.25	3.25	1.0	1.44	2.28
2.0	2.0	1.0	-	3.52
2.0	3.25	1.0	-	4.10
2.0	5.0	1.0	-	4.54
2.0	6.25	1.0	-	4.80
2.0	8.0	1.0	-	4.86
2.0	3.25	1.0	-	4.52
2.0	3.25	1.25	-	3.81
2.0	3.25	2.25	-	3.63
2.0	3.25	2.5	-	2.52
2.0	3.25	5.0		1.97

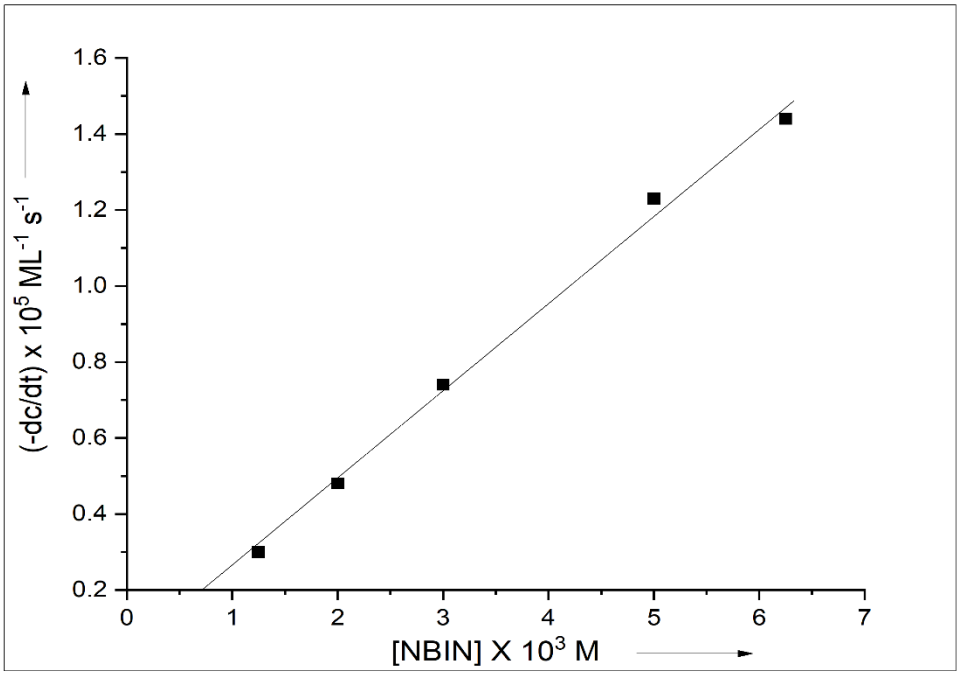


Fig.1 Plot between (-dc/dt) x 10^5 ML^{-1} S^{-1} and [NBIN] x 10^3 mol (dm^{-3})

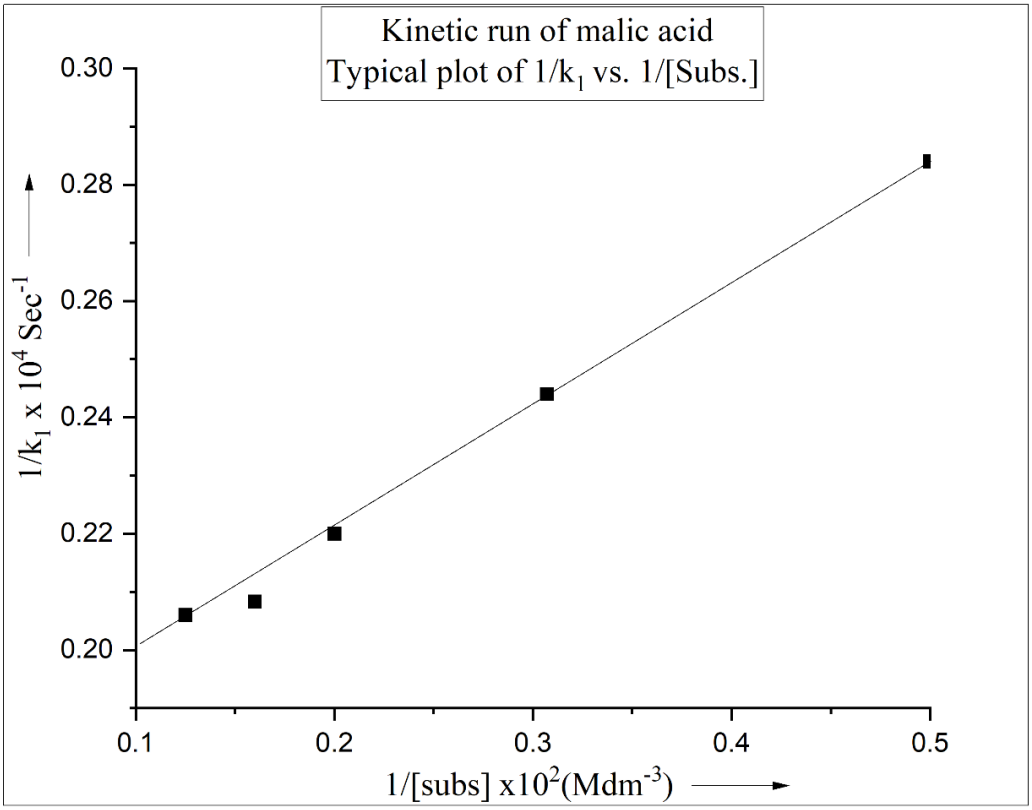


Fig. 2 Plot between 1/k1 and 1/[Substrate] x 10^2 mol (dm^{-3})

Table:2 Effect of Variation AcOH-H2O%(V/V), KBr, and Hg(OAc)2 at 313 K temp.

[AcOH]-H_2O% (v/v)	**[KBr]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	4.03
20-80%	1.0	1.0	3.65
25-75%	1.0	1.0	3.35
30-70%	1.0	1.0	3.05
40-60%	1.0	1.0	2.45
30-70%	1.0	1.0	2.78
30-70%	1.25	1.0	3.05
30-70%	2.25	1.0	5.55
30-70%	2.5	1.0	3.98
30-70%	5.0	1.0	3.32
30-70%	1.0	1.0	4.04
30-70%	1.0	1.25	4.76
30-70%	1.0	2.25	5.48
30-70%	1.0	2.5	5.16
30-70%	1.0	5.0	4.98

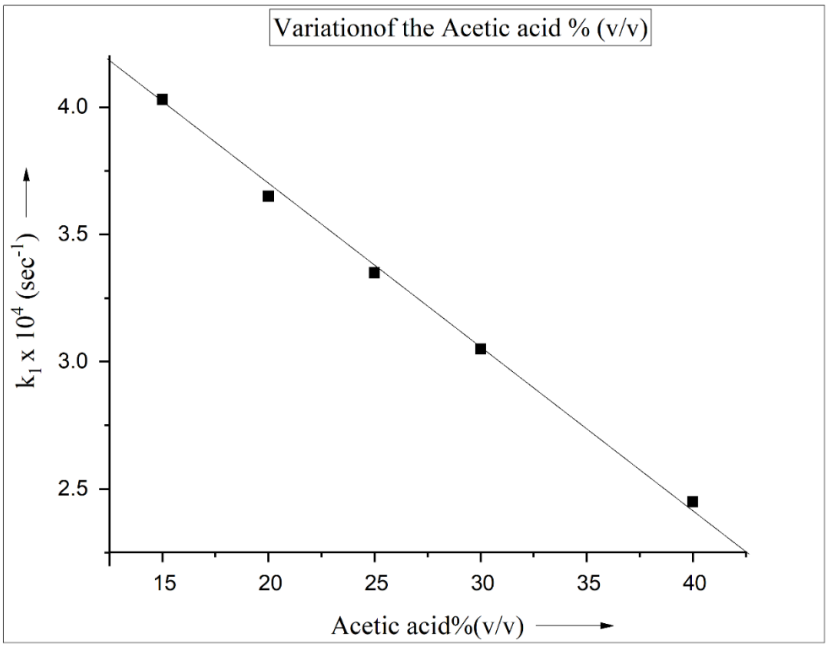


Fig 3 Plot between k_1 vs. Acetic acid %(v/v)

Table 3 Effect of the temperature on the reaction rate constant

Temp. K	Kr x 10^4
303	1.56
308	1.60
313	1.98
318	2.42
323	2.73
328	3.46

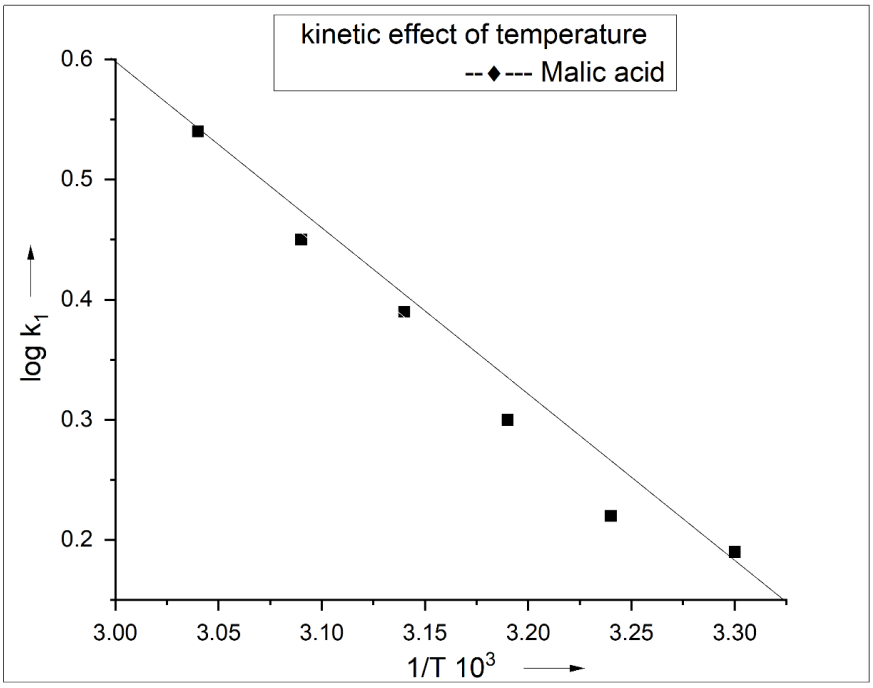


Fig 4 Plot between log k_1 vs. 1/T 10^3 for Malic acid

Table 4 Values of Activation Parameters

Substrate	Temperature Coeff.	[ΔEa] $KJMol^{-1}$	Arrhenius Factor [Log A]	[ΔS^*] $JK^{-1}Mol^{-1}$	[ΔH^*] $KJMol^{-1}$	[ΔG^*] $KJMol^{-1}$
Malic acid	1.2500	18.16	2.76	-173.66	15.50	94.51

Reaction Mechanism:

A common mechanism for the oxidation of malic acid obtained from free energy value (ΔG^*). The pseudo-first-order rate constant against the hydroxy acid concentration was linear. The linear plot of $1/k_{obs}$ against 1/[S] is also 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 steps following as well as :

$$NBIN^+ \underset{}{\overset{K}{\rightleftharpoons}} NBIN + H^+ \qquad \text{----------(1)}$$

$$NBIN + H_2O \overset{K_1}{\rightleftharpoons} HOBr + \text{Isonicotinamide} \qquad \text{----------(2)}$$

$$HOBr + R{-}\underset{H}{\overset{|}{\overset{COOH}{\overset{|}{C}}}}{-}OH \overset{k_2}{\underset{\text{Slow}}{\rightleftharpoons}} \left[R{-}\underset{H}{\overset{|}{\overset{COOH}{\overset{|}{C}}}}{-}OBr \right] + H_2O$$

Intermediate Complex ----------(3)

Where R= CH_2COOH,

$$\text{Intermediate Complex} \xrightarrow[\text{Fast , rds}]{k} CH_2COOH{-}\overset{COOH}{\overset{|}{C}}{=}O + HBr \qquad \text{----------(4)}$$

(Product)

The rate law was derived as:

$$K_{obs} = \frac{k\, k_1 k_2 [S]}{[INA] + k_1 + k_1\, k_2 [S]} \qquad \text{----------(5)}$$

The reciprocal of equation (5) gives

$$\frac{1}{K_{obs}} = \frac{1}{[S]} \left[\frac{INA}{k\, k_1 k_2} + \frac{1}{k_2} \right] + \frac{1}{K} \qquad \text{----------(6)}$$

The above equation explains the complex behavior of the reaction between oxidant, substrate, and other kinetic facts. The rate law also validities Michaelis- Menten equation follow as.

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

$$\text{Rate} = k_1 [NBIN] [H_2O] \qquad \text{----------(7)}$$

The rate law shows that the response pursues the first request energy regarding [NBIN].

Conclusion

The study reveals First-order kinetic concerning N-bromoisonicotinamide and explains complex formation that follows stoichiometry 1:1. Oxaloacetic acid was isolated as reaction products. HOBr is the reactive species of oxidant. A mechanism consistent with observed parameters has been proposed and rate law is derived. The thermodynamics parameters, Ea, ΔH^*, ΔS^*, and ΔG^*, have been computed from Arrhenius plots.

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Conflict of Interest
The authors declare a conflict of no interest whatsoever

REFERENCES:
[1]. Bhuvaneshwari D.S., Elango K.P., Correlation Analysis of Reactivity in the Oxidation of Anilines by Nicotinium Dichromate in Nonaqueous Media, Int. J. Chem. Kinet., 38: 657–665 (2006).
[2]. Garg D., Kothari S., Kinetics and Mechanism of the Oxidation of Some α-hydroxy Acids by Hexamethylene Tetramine-Bromine, J. Chem. Sci., 26: 333-338 (2004).
[3]. M. Balasubramaniyan and N. Mathiyalagan, Mechanistic study of oxidation of alcohols by N-bromoisonicotinamide in aqueous acetic acid medium "Int. J. Chem Tech Research" (2011), vol. 3, 1096-1101.
[4]. Mathiyalagan, N. and Balasubramanian, M. "N-Bromoisonicotinamide" -Oriental J. Chem., 2014, 26, 1541
[5]. Aparna Prajapati, Arvind Prasad Dwivedi, Surendra Singh Parihar, Enzyme Catalyzed Study of Some Unsaturated Acids by N-Bromo-iso-nicotinamide- A Kinetic Approach, "Int. J. Advanced Research Chem. Sci." 2019), Vol. 6, 1-5.
[6]. Shahina Khan and K. N. Sharma, Study of Catalysed Oxidation of Some 2-alkenones by N-bromoisonicotinamide in aqueous acetic acid, International Journal for Research Trends, and Innovation,2023, Volume 8, Issue 5
[7]. Mamta Tiwari, S. S. Parihar, Vivek Verma H. P. Dwivedi, and S. S. Saket, "Kinetic Study on Micelles Catalysed Oxidation of some Aldehydes by N-Bromoisonicotinamide in Aqueous Acetic Acid Medium" J. ChemTracks 21(1&2), 2019, 119-124.
[8]. Priyanka Singh, and Sanjay Kumar Singh, Catalysed Oxidation Study of Primary Alcohols (propanol and butanol) by N-chloro-iso-nicotinamide in Aqueous Acetic Acid Medium, int. J. Scientific Development and Research 2023, Vol.8 Issue 1 ISSN: 2455-2631
[9]. Mitchell J. (Jr.), "Organic analysis" Vol. 1, Interscience Publisher, Inc., New York, (1953), 279.
[10]. Amis, E. S., "Solvent Effect on Reaction Rates and Mechanisms" Academic Press Newyork, 1967, p. 42

Abbreviation

NBIN	N-Bromoisonicotinamide
MLA	Malic acid
KBr	Potassium bromide
Ac-OH	Acetic acid