

Oxidation of Mandelic Acid by N-Bromo-Iso-Nicotinamide in Acetic Medium : A Kinetics Study

Suman Vishwakarma^{1*}, Manisha Pradhan¹

¹Department of Chemistry, Govt. Girls P. G. College, Rewa, Madhya Pradesh, India

²Research Scholar, A. P. S. University, Rewa, Madhya Pradesh, India

Corresponding author: sumanvishwakarma825@gmail.com

ARTICLE INFO

Article History:

Accepted: 10 July 2023

Published: 30 July 2023

Publication Issue

Volume 8, Issue 4

July-August-2023

Page Number

30-37

ABSTRACT

Kinetics and mechanism of oxidation of Mandelic acid by N-Bromo-iso-nicotinamide have been investigated in an aqueous acetic acid medium, in the presence of perchloric acid as the source of [H⁺]. Mercuric acetate, a bromide ion scavenger, has been studied in the 350 C range. The rate is first-order concerning [NBIN] and fractional or zero order of the reaction concerning [substrate]. The influences of Hg(OAc)₂, HClO₄ ionic strength, and bromide ion rate was found to be insignificant. An intermediate complex formed an oxidant with the substrate. In a slow and rate-determining step complex to give the product. 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 and Activation parameters have been calculated.

Keywords : Kinetics, Mechanism, Mandelic Acid, NBIN, Acetic medium

I. INTRODUCTION

N-bromo-iso-nicotinamide (NBIN) has been as an oxidizing, halogenating species and in synthesis by several works [1]. Oxidation of mandelic acid was carried out under pseudo-first-order reaction conditions in an aqueous acetic acid medium by N-bromo-iso-nicotinamide (NBIN). The catalytic activity of picolinic acid (PA) for the oxidation of some α -hydroxy acids in A aqueous acetic acid medium by triethylammonium fluoro chromate (TriEAFC) [2], Pyridinium Fluorochromate [4], N-

Bromo-phthalimide (NBP) [3]. The kinetics of oxidation of alcohols at 328 K, in an aqueous acetic acid medium by N-bromo-iso-nicotinamide (NBIN) [5]. Kinetic investigation of organic compounds by N-Bromo-nicotinamide (NBN) [6-12] has been carried out in the temperature range 305-325K. Kinetics of the oxidation of α -hydroxy acid has been studied with some oxidizing agents [13-16].

Mandelic acid is antibacterial and effective in treating inflammation and exfoliating the skin.

N-bromo-iso-nicotinamide (NBIN) is moderate and shows antimicrobial activity. Its non-Hazardous consumes little time and easily isolates the final products when applied after oxidation. The activity of N-bromo-iso-nicotinamide (NBIN) oxidant is limited and scanty. Recently, this oxidant has been used in the oxidative study of unsaturated acid [17]. Due to this fact, a significant number of systematic kinetic results have been reported on the effect of perchloric acid [18], acetic acid, mercuric acetate, and potassium bromide on various organic reactions during the past few decades.

Hence, kinetic work has been no systematic documents attached on NBIN oxidant. This prompted a systematic kinetic study on the oxidation of mandelic acid with NBIN in an aqueous acetic acid medium to understand and illuminate the complicated kinetic chemical mechanism.

II. Materials and Method:

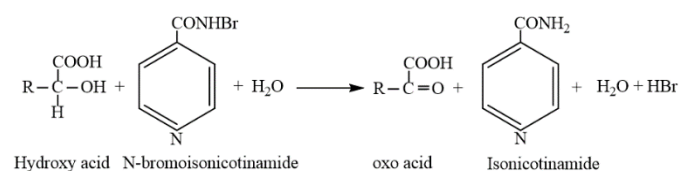
An aqueous solution of Mandelic acid (E. Merck), NBIN was prepared by the standard method by Hauser and Renfrow (1923), and its identified melting point then was found to be 210°C with soluble in water, acetic acid, and ethanol. Stock solutions of NBIN and NaClO₄(E. Merck) were prepared by dissolving weighed samples in double distilled water. All other reagents were of analytical grade. The reaction mixture was kept in a Black painted bottle to prevent interaction with light and photo-chemical decompositions.

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

The mixture containing in stoichiometry reaction large excess of mandelic acid over oxidant (NBIN) in different ratios was allowed equilibrated for 24 hours at (308K). The calculation 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.



where R= C₆H₅ in Mandelic acid [MA]

Whose Oxidation product is phenyl glyoxalic acid was detected by measuring the melting point of its amide derivative as a fellow.

Product analysis

This is also identification confirmed by spot test, and 2-4 dinitro phenyl hydrazine method [7]. In a typical experiment, hydroxy acid (0.05 mol, MA=7.6g.), and NBIN (20.01g, 0.01mol) were dissolved in aqueous acetic acid and were allowed to stand in the dark for 24 h to the completion of 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 (phenyl glyoxalic acid.) in 85 to 89% yield, after recrystallization.

III. SPECTRAL STUDY

An infrared spectrum exhibited a carbonyl band at 1705 cm^{-1} and certain other bands below 900 cm^{-1} characteristics of the benzaldehyde group in studied in reactant compound. The IR spectrum of the other product sample has two sharp bands at 1662 and 1650 cm^{-1} indicating the presence of two carbonyl groups. Bands at 3323.01 cm^{-1} (OH stretching), 1249.9 cm^{-1} (C-O stretching), and 1156 cm^{-1} (OH bending) are characteristic of phenyl glyoxalic acid.

IV. RESULT AND DISCUSSION

The kinetic oxidation of Mandelic acid by the acetic solution of NBIN in the presence of solvent has been studied at a constant temperature of 308K (Table 1). Order of reaction concerning each reactant was determined by various concentrations of oxidant, substrate, $[\text{H}^+]$, and acetic acid one by one in different sets keeping the concentration of all other reactants constant at constant temperature (Table 1). In $[\text{NBIN}]$ kinetic run, the initial rate $(-dc/dt)$ of the reaction was determined. The first order of the reaction k_1 , for the variation of all reactions, was calculated as:

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

Where $[\text{NBIN}]^*$ denotes the $[\text{NBIN}]$ at which $(-dc/dt)$ was determined.

First-order kinetic was observed in a plot $(\log a/a-x)$ versus $[\text{Oxidant}]$ is linear, and Plot between $(-dc/dt) \times 10^5\text{ ML}^{-1}\text{ S}^{-1}$ and $[\text{NBIN}] \times 10^3\text{ M}$ (fig 1). The typical graph plot of $1/k$ vs. $1/[\text{S}]$ is linear(fig2). Thus, Michaelis- Mentan type kinetic are observed with respect to the Hydroxy acid [19]. The reaction rate decreases, increasing the concentration of acetic acid(fig.3). positive slop of $\log k_1$ vs. $1/D$ plot indication interaction of cation-dipole type reaction in the rate determining step [20]. investigation of various concentrations of $[\text{HClO}_4]$ (table 2) that indicate fractional order dependence on perchloric acid on the reaction rate. Ionic strength investigation in the presence of sodium perchlorate indicates 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 is every possibility for the formation of a complex between all different reactants of the reaction.

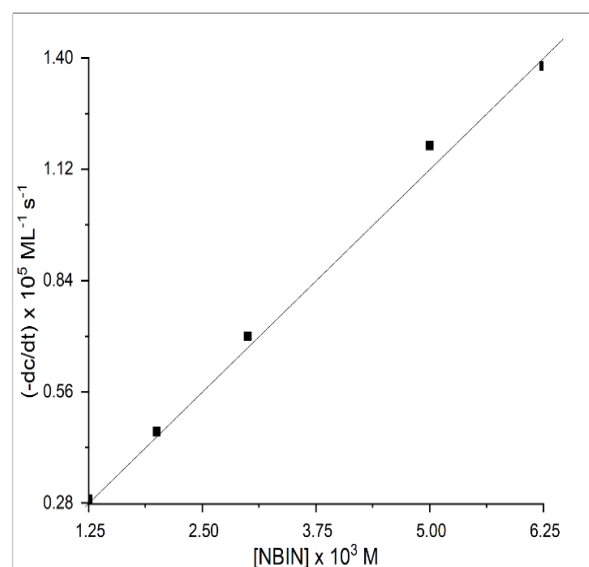


Fig. 1. Plot between $(-dc/dt) \times 10^5\text{ ML}^{-1}\text{ S}^{-1}$ and $[\text{NBIN}] \times 10$

Table: 1 Effect of Variation of Oxidant, Mandelic acid, and HClO₄ at 308K temp.

$[NBIN] \times 10^3 \text{ mol (dm}^{-3}\text{)}$	$[\text{Substrate}] \times 10^3 \text{ mol (dm}^{-3}\text{)}$	$[H^+] \times 10^3 \text{ mol (dm}^{-3}\text{)}$	$(-dc/dt) \times 10^5 \text{ ML}^{-1} \text{ S}^{-1}$	$K_{obs} \times 10^4 \text{ sec}^{-1}$
1.25	3.25	1.0	0.29	2.30
2.0	3.25	1.0	0.46	2.43
3.0	3.25	1.0	0.70	2.44
5.0	3.25	1.0	1.18	2.46
6.25	3.25	1.0	1.38	2.07
2.0	2.0	1.0	-	3.55
2.0	3.25	1.0	-	4.18
2.0	5.0	1.0	-	4.50
2.0	6.25	1.0	-	4.77
2.0	8.0	1.0	-	4.84
2.0	3.25	1.0	-	4.49
2.0	3.25	1.25	-	5.11
2.0	3.25	2.25	-	5.57
2.0	3.25	2.5	-	3.42
2.0	3.25			3.17

Table:2 Effect of Variation AcOH-H₂O%(V/V), KBr, and Hg(OAc)₂ at 308K temp.

[AcOH]-H ₂ O% (v/v)	$[KBr] \times 10^3 \text{ mol (dm}^{-3}\text{)}$	$[Hg(OAc)_2] \times 10^3 \text{ mol (dm}^{-3}\text{)}$	$K_{obs} \times 10^4 \text{ sec}^{-1}$
15-85%	1.0	1.0	4.76
20-80%	1.0	1.0	3.96
25-75%	1.0	1.0	3.56
30-70%	1.0	1.0	3.33
40-60%	1.0	1.0	3.05
30-70%	1.0	1.0	4.32
30-70%	1.25	1.0	3.69
30-70%	2.25	1.0	3.68
30-70%	2.5	1.0	4.73
30-70%	5.0	1.0	4.67
30-70%	1.0	1.0	2.35
30-70%	1.0	1.25	3.15
30-70%	1.0	2.25	3.98
30-70%	1.0	2.5	3.60
30-70%	1.0	5.0	3.37

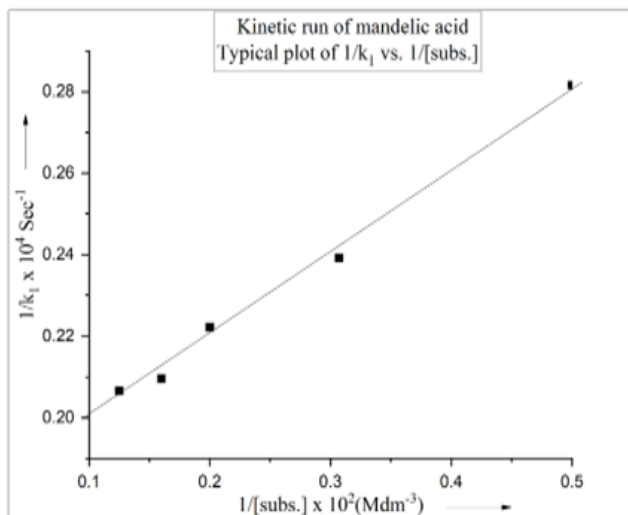


Fig. 2 Plot between $1/k_1$ and $1/[\text{Substrate}] \times 10^2 (\text{M dm}^{-3})$

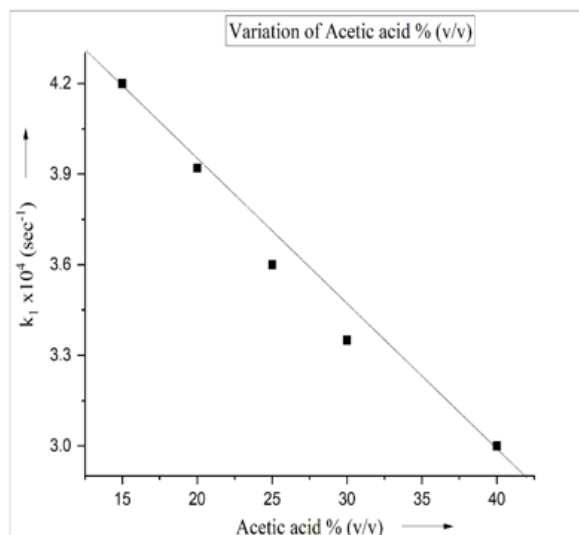


Fig 3 Plot between k_1 vs. Acetic acid % (v/v)

Table 3- Effect of the temperature on the reaction rate constant

Temp. K	Kr x 10 ⁴
303	1.68
308	2.04
313	2.49
318	3.11
323	3.51
328	3.70

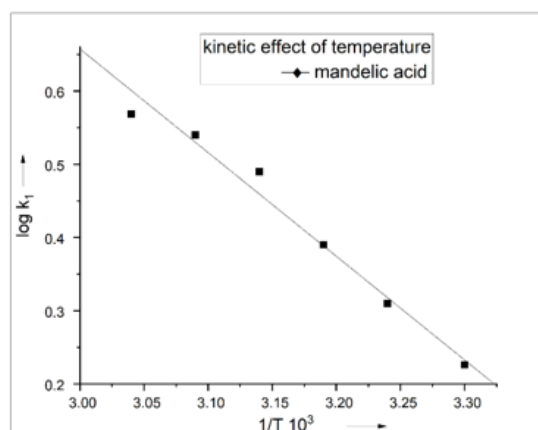


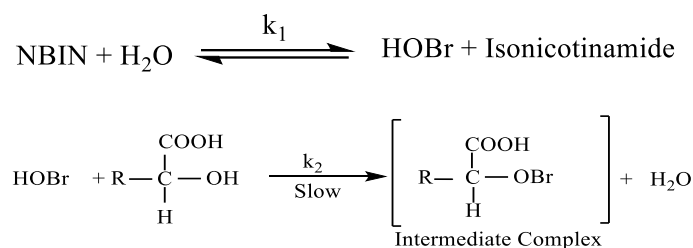
Fig 4 Plot between $\log k_1$ vs. $1/T \times 10^3$ for Mandelic acid

Table 4 Values of Activation Parameters

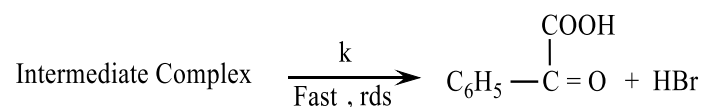
Substrate	Temperature Coeff.	$[\Delta E_a]$ KJ Mol ⁻¹	Arrhenius Factor [Log A]	$[\Delta S^\ddagger]$ JK ⁻¹ Mol ⁻¹	$[\Delta H^\ddagger]$ KJ Mol ⁻¹	$[\Delta G^\ddagger]$ KJ Mol ⁻¹
Mandelic acid	1.2893	30.87	3.01	-180.40	28.30	91.12

Reaction Mechanism

A common mechanism for the oxidation of mandelic acid obtained from free energy value (ΔG°). The pseudo-first-order rate constant against the hydroxy acid concentration was linear. The linear plot of $1/k_{\text{obs}}$ 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 unprotonated species are involved in the formation of the active oxidant. In the steps following as well as :



Where $R = \text{C}_6\text{H}_5$ -----(3)



Phenyl glyoxalic Acid (Product)

The rate law was derived as:

$$K_{\text{obs}} = \frac{k k_1 k_2 [S]}{[\text{INA}] + k_1 + k_1 k_2 [S]} \text{ -----(4)}$$

The reciprocal of equation (4) gives

$$\frac{1}{K_{\text{obs}}} = \frac{1}{[S]} \left[\frac{\text{INA}}{k k_1 k_2} + \frac{1}{k_2} \right] + \frac{1}{K} \text{ -----(5)}$$

The above equation (5) explains the complex behaviour of reaction between oxidant, substrate, and other kinetic facts. The rate law also validities Michaelis- Menten equation follow as.

The rate law showed that the reaction follows first order kinetics with respect to $[\text{NBIN}]$ and inverse fractional order kinetics with respect to $[\text{H}^+]$. This may be clarified by looking balance among protonated and unprotonated oxidant.

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

$$\text{Rate} = k_1 [\text{NBIN}] [\text{H}_2\text{O}] \text{ -----(6)}$$

The rate law shows that the response pursues the first request energy regarding $[\text{NBIN}]$.

V. ACKNOWLEDGMENT

The author is grateful to the Principal, Head, department of chemistry, and my supervisor Professor Dr. Manish Pradhan, of the Government Girls P.G. College in Rewa, Madhya Pradesh, India, for his discussion, support, and insightful advice on my doctoral thesis.

VI. CONFLICT OF INTEREST

the authors declare a conflict of no interest whatsoever.

VII. CONCLUSION

From observed kinetic data the following conclusion can be drawn:

- i). HOBr and Protonated H_2OBr is reactive oxidizing species of NBIN in aqueous acetic acid medium, Stoichiometrically (1:1) and order of reactivity was discussed.
- ii). The reaction was observed of first-order with respect to $[\text{oxidant}]$ and fractional-order each with $[\text{mandelic acid}]$ and $[\text{H}^+]$. The oxidation rate of mandelic 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 mandelic acid support the formation of a rigid activated complex as proposed in equation (2) of the mechanism.
- v). The reactions provide test for mi
- vi). The following chemical reaction, phenyl glyoxalic acid was a Product in fast process obtained from mandelic acid.

VIII. REFERENCES

- [1]. M. Balasubramanian, and N. Mathiyalagan, "N-Bromo-iso-nicotinamide: New Mild, Stable, Effective and Efficient Oxidant for Organic Compound" *Oriental J. Chem.* (2010). Vol. 26(4), 1541-1544.
- [2]. A. Subash, V. S. Malik, S. Syed Shafi, and S. Sheik Mansoor "Kinetics and Mechanism Oxidation of some alpha-Hydroxy acids by Tri-EAFC in Presence of Picolinic Acid Catalyst in Aqueous Acetic Acid Media" *Der Pharma Chemica*, (2015), 7(11): 299-306.
- [3]. Sangeeta Patil, Y. R. Katre and Ajaya Kumar Singh "A Kinetic and Mechanistic Study on the Oxidation of Hydroxy Acids by N-Bromo-phthalimide in the Presence of a Micellar System" *Journal of Surfactants and Detergents*, (2007) volume 10, pages175–184.
- [4]. Devi, R.A., Easwaramoorthy, D., and Ravichandran, C. "Oxidation of 3-carboxy-3-hydroxy pentane dioic acid by N-chloro-succinimide in alkaline medium-kinetics and mechanism, *International Journal of Chem Tech Research* Volume 8, Issue 5, (2015), Pages 175-182
- [5]. M. Balasubramanian, V. Priya and N. Mathiyalagan, "Mechanistic study of oxidation of alcohols by N-bromo-iso-nicotinamide in aqueous acetic acid medium" *Int. J. Chem. Tech research*, (2011) Vol. 3, 1096-1101.
- [6]. Jagdish Bharad*, Balaji Madje and Milind Ubale, *Kinetic Study of Oxidation of Substituted Benzyl Alcohols by N-Bromo-phthalimide in Aqueous Acetic acid International Journal of Emerging Technologies in Computational and Applied Sciences*, (2013), 4(4), pp.334-337
- [7]. L. Pushpalatha, K. Vivekanandan: Oxidation of Acidic Amino Acids by N-bromo-nicotinamide – a Kinetic Study. *Oxid Commun.*, (2008), 31 (3), 598.
- [8]. L. Pushpalatha, K. Vivekanandan: N-bromo-nicotinamide Oxidation of Essential Amino Acids – a Kinetic Study. *Oxid Commun*, (2009), 32 (1), 85.
- [9]. L. Pushpalatha, K. Vivekanandan: Kinetics of Oxidative Cleavage of Non-essential Amino Acids by N-bromo-nicotinamide in Aqueous Acetic Acid Medium. *Oxid Commun*, (2010), 33 (4), 851.
- [10]. L. Pushpalatha, K. Vivekanandan: Mechanistic Investigation of Oxidation of Cystine by N-bromo-nicotinamide in Acid Medium. A Kinetic Study. *Oxid Commun*, (2013), 36 (4), 926.
- [11]. L. Pushpalatha: Mechanistic Investigation of Oxidation of Tryptophan by N-bromo-nicotinamide in Acid Medium. A Kinetic Approach. *Oxid Commun*, (2013), 36 (4), 938.
- [12]. 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
- [13]. Shanthi, Shanmugam, Asghar, Basim Hussain, Mansoor, and Syed Sheik "The Kinetics of Tri-propylammonium fluorochromate Oxidation of Mandelic Acids", *Iran. J. Chem. Chem. Eng.*, 2018, Vol. 37, No. 3.,

- [14]. Madhu S, Gupta R, Singh A, Singh B, Singh AK (1991), "Kinetics and mechanism of oxidation of some hydroxy acid by N-bromoacetate" J. Mol. Cata. (1991) 65:317.
- [15]. Deepak S. Rajmane and Gavididappa S. Gokavi "Kinetics and mechanism of oxidation of benzyl alcohol by Oxone-catalyzed by Keggin type 12-tungsto-cobaltate (II)" Arch. Appl. Sci. Res., 2014, 6 (3):133-137
- [16]. Ogata, Y., and Sawaki, Y.: Organic synthesis by oxidation with metal compounds edited by W.J. Mijs, Plenum, Newyork, 1986, 839-876.
- [17]. Aparna Prajapati, Arvind Prasad Dwivedi, Surendra Singh Parihar, "Enzyme Catalysed Study of Some Unsaturated Acids by N-Bromo-iso-nicotinamide- A Kinetic Approach", Int. J. Advanced Research Chem. Sci., (2019), Vol. 6, 1-5.
- [18]. Chandra Singh, Rajesh Sharma, and Dharmendra Dwivedi, "Kinetic and Mechanistic Aspect of The Perchloric Acid Catalysed Oxidation of Mandelic acid", International Journal of Applied and Universal Research, (2016), Vol. 3, Issue IV.
- [19]. D. Baghmar, P. Purohit, M. Baghmar, I. K. Sharma and Vinita sharma, "Kinetics and Mechanism of the oxidation of Some Alpha-hydroxy acids by Imidazolium fluorochromate" Int. J. Chem. Sci., (2011), 9(3), 1247-1260.
- [20]. Amis, E. S., "Solvent Effect on Reaction Rates and Mechanisms" Academic Press Newyork, 1967, p. 42.

Suggested Citation :

Suman Vishwakarma, Manisha Pradhan, "Oxidation of Mandelic Acid by N-Bromo-Iso-Nicotinamide in Acetic Medium : A Kinetics Study", International Journal of Scientific Research in Chemistry (IJSRCH), ISSN : 2456-8457, Volume 8 Issue 4, pp. 30-37, July-August 2023.
 URL : <https://ijsrch.com/IJSRCH12315>

Abbreviation

Abbreviation	Denotation
NBIN	N-Bromo-iso-nicotinamide
MA	Mandelic acid
Ac-OH	Acetic acid
KBr	Potassium bromate