KINETICS AND MECHANISM OF OXIDATION OF MALIC ACID BY N-BROMONICOTINAMIDE (NBN) IN THE PRESENCE OF A MICELLAR SYSTEM

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ABSTRACT. The oxidation of malic acid by N-bromonicotinamide in the presence of micellar system is studied. First order kinetics with respect to NBN is observed. The kinetics results indicate that the first order kinetics in hydroxy acid at lower concentrations tends towards a zero order at its higher concentrations. Inverse fractional order in $[H^+]$ and [nicotinamide] are noted throughout its tenfold variation. Variation of $[Hg(OAc)_2]$ and ionic strength of the medium do not bring about any significant change in the rate of reaction. Rate of the reaction increases with a decrease in the percentage of acetic acid. Decrease in the rate constant was observed with the increase in [SDS]. The values of rate constants observed at four different temperatures were utilized to calculate the activation parameters. A suitable mechanism consistent with the experimental findings has been proposed.

Abbreviations

NBN N-Bromonicotinamide
MA Malic acid
NA Nicotinamide
SDS Sodium dodecyl sulphate

1. INTRODUCTION

The kinetics of the oxidation of hydroxy acids has been studied with a number of oxidizing agents like potassium bromate, hexamethylenetetraminebromine, sodium N-chlorobenzenesulfonamide, N-bromoacetamide, ditelluratocuprate(III), 2,2-bipyridium chlorochromate, benzo-dipteridine etc. Although hydroxy acids have been utilized for a number of catalyzed reactions, nobody has examined the role of catalysts in NBN oxidation of hydroxy acids. Malic acid is a key intermediate in the major biochemical energy-producing cycle in cells, known as the Krebs's cycle, it takes place in the cells mitochondria in most living organisms. The body synthesizes malic acid during the process of converting carbohydrates to energy. Preliminary evidence suggests that individuals with the disease fibromyalgia (a disorder that involves fatigue and pain in the muscles) might have difficulty in creating or utilizing malic acid. Such a deficiency could interfere with normal muscle function. The presence of micelles can have marked effects on thermodynamic favorability and reaction kinetics as well as on many physical properties¹. Organic reactions involving ionic, polar and neutral reactants in micellar solution are generally believed to occur in the stern layer of a micelle of an ionic surfactant. The catalysis and inhibition by ionic micelles is due to ionic micellar incorporation of both the reactants. Due to these facts a significant amount of systematic kinetic results have been reported on the effect of micelles on various organic reactions during past few decades.

A.K. Singh[1] studied the kinetics and mechanism of oxidation of some lactose by N-bromophthalimide.

Chand Waqar [2] investigated the mechanism of Ru(III)-catalysed oxidation of glycollic and mandelic acids with N-bromosuccinimide in acidic media.

Pradeep K. Sharma[3] reported the oxidation of some α -hydroxy acids by tetraethylammonium chlorochromate.

Ajaya Kumar Singh[4] followed the kinetic and mechanistic study on the oxidation of hydroxy acids by N-bromophthalimide in the presence of a micellar system.

E.V. Sundaram[5] explained the oxidation of α -hydroxy acids with Quinolinium Dichromate .

Asim K Das[6] studied the micellar effect on the reaction of Chromium(VI) oxidation of some representative alpha-hydroxy acids in the presence and absence of 2,2'-bipyridyl in aqueous acid media.

A perusal of literature shows that the reactivity of N-bromonicotinamide (NBN) could be compared with other *N*-bromoimide such as N-bromosuccinimide (NBS) and N-bromosaccharin (NBSa). Since NBN is more stable than the latter, it is extremely stable in solid state when kept out of light and moisture. Its standard solution has excellent keeping qualities. There are several reports available in the literature on the oxidation of alpha-hydroxy acids by oxidants such as N-bromosuccinimide, N-bromoacetamide, potassium bromate, N-bromobenzenesulphonamide, and iodate[7]. However, the details of oxidation of malic acid by N-bromonicotinamide are yet unknown. This prompted the micellar effect on the kinetics of the oxidation of the malic acid by NBN in the acidic medium.

2. EXPERIMENTAL

2.1. Materials

N-Bromonicotinamide (NBN) was prepared by the reported method[8]. The melting point of the sample was found to be 483 K. Solutions of NBN were prepared in 80% acetic acid and stored in a black-coated flask to prevent photochemical deterioration. The prepared solution was then standardized iodometrically against standard sodium thiosulphate using starch as indicator. Standard solutions of SDS (GR) and malic acid (Merck) were prepared using double distilled water. The standard solution of mercuric acetate (Merck) was acidified with 20% acetic acid. HClO_4 (A.R. grade) diluted with double distilled water was standardized via acid-base titration. All other standard solutions of NaClO_4 , KCl, KBr and nicotinamide were prepared using double distilled water. Double distilled water was distilled over KMnO_4 in an all glass (Pyrex) distillation set up. Distilled acetic acid was used throughout the experiment.

2.2. Kinetic Measurements

The solution of malic acid and oxidant were kept in black coated bottles separately. These solutions were kept in the thermostat to attain the thermostatic temperature. The appropriate quantity of oxidant was added to the substrate containing surfactant and other reagents and the reaction bottle was shaken well. The reaction was followed potentiometrically by setting up a cell made up of the reaction mixture into which the platinum electrode and reference electrode(SCE) were dipped. The e.m.f of the cell was measured periodically using a Equip-Tronics (EQ-DGD) potentiometer. The reactions were studied at constant temperature 35°C. Different studies such as variation of malic acid, oxidant (NBN), perchloric acid, sodium perchlorate, nicotinamide, surfactant and temperature were carried out. The reaction was carried out under pseudo-first order condition ($[\text{malic acid}] \gg [\text{NBN}]$). The pseudo-first order rate constants computed from the linear ($r^2 > 0.9990$) plots of $\log(E_t - E_\infty)$ against time. Duplicate kinetic runs showed that the rate constants were reproducible within $\pm 3\%$. The course of the reaction was studied for more than two half-lives.

2.3. STOICHIOMETRY

The reaction mixture containing a known excess of $[\text{NBN}] \gg [\text{MA}]$ was kept in presence of HClO_4 , $\text{Hg}(\text{OAc})_2$ and surfactant at 35°C for 72 h. After completion of the reaction, the unconsumed NBN was calculated iodometrically. It was found that nearly 1 mole of NBN was consumed for each mole of malic acid.

2.4. PRODUCT ANALYSIS

The presence of 2-aldoethanoic acid as the main oxidation products was detected by the spot test [9] and the 2,4-dinitrophenylhydrazine method [10].

2.5. CMC DETERMINATION

Surfactants spontaneously aggregate above a certain concentration called critical micelle concentration (CMC) to form micelle, whose determination has considerable practical importance, normally to understand the self-organizing behavior of surfactants in exact ways. Micelles act as microreactors, which both speed or inhibit the rate of uni- and bimolecular reactions. Micelle aggregates affect chemical reactivity primarily by binding or excluding reactants and only secondarily by changing the free energy of activation. The critical micelle concentration values of the surfactant (SDS) was determined conductometrically (Digital conductivitymeter, model 611E, Electronic India Company) in the presence and absence of reactants at 40°C . The CMC value was determined from plot of the specific conductivity versus surfactant concentration. The breakpoints of nearly straight-line portions in the plot are taken as an indication of micelle formation, and this correspond to the CMC of surfactant. The CMC values of SDS in different experimental conditions at 40°C are summarized in Table 1. The CMC value is lower than that given in the literature for aqueous solutions of SDS without added electrolyte, which was found to be approximately about $3.18 \times 10^{-3} \text{ mol dm}^{-3}$ in reaction mixture for malic acid.

Table 1.- Critical micelle concentration (CMC values of SDS in different experimental conditions)

Solutions	10^3 CMC $\text{mol dm}^{-3} \text{ SDS}$
Water	8.3
Water+NBN	7.6
Water+malic acid	4.9
Water+malic acid+NBN+ $\text{Hg}(\text{OAc})_2 + \text{HClO}_4 + 20\% \text{ v/v AcOH}$	3.5

$[\text{Malic acid}] = 0.03 \text{ mol dm}^{-3}$ $[\text{HClO}_4] = 0.01 \text{ mol dm}^{-3}$,
 $[\text{NaClO}_4] = 0.1 \text{ mol dm}^{-3}$, $\text{Hg}(\text{CH}_3\text{COO})_2 = 0.001 \text{ mol dm}^{-3}$, $\text{AcOH:H}_2\text{O} (1:4)$ $\text{Temp.} = 308 \text{ K}$

3. RESULTS

The kinetic results for the oxidation of malic acid by N-Bromonicotinamide (NBN) in the presence of surfactant (SDS) can be summarized as follows. The kinetic studies were carried out under pseudo-first order conditions with $[\text{malic acid}] \gg [\text{NBN}]$.

All the investigations were carried out under the conditions where $[\text{Hg}(\text{OAc})_2]$ to eliminate bromide ions as $[\text{HgBr}_4]^{2-}$, which could have been produced and might set another parallel oxidation[11]. The kinetics of the oxidation of malic acid by NBN in presence of surfactant (SDS), HClO_4 and $\text{Hg}(\text{OAc})_2$ was investigated at several initial concentrations of the reactant. The reaction was of first order linearity of a plot of $\log [\text{NBN}]$ versus time for malic acid. The rate constants at different initial $[\text{NBN}]$ are reported.

Table 2 summarizes the pseudo first order rate constant's dependence on the NBN concentration. It was observed that, with the increase in initial NBN concentration, the value of rate constant decreased. At a constant value of NBN, surfactant(SDS), $\text{Hg}(\text{OAc})_2$, HClO_4 the rate constant was determined at different initial concentrations of malic acid ranging from 5×10^{-3} to $50 \times 10^{-3} \text{ mol dm}^{-3}$. Table 3 summarizes the pseudo first order rate constant's dependence on malic acid concentration. The rate constant, increased with increasing [malic acid]. The plot of $\log k$ versus $\log [\text{malic acid}]$ was linear with a slope of less than unity showing fractional order dependence on [malic acid]. Furthermore, a plot of $\log k$ versus malic acid was linear with an intercept on y axis, confirming the fractional order dependence on substrate. The rate constant k decreased with increase in $[\text{HClO}_4]$ from 5×10^{-3} to $50 \times 10^{-3} \text{ mol dm}^{-3}$ (Table 2). This may be due to protonation of the substrate. The plot of $\log k$ versus $\log [\text{HClO}_4]$ is linear with negative slope. The slope being less than unity indicates inverse fractional order dependence on $[\text{HClO}_4]$. Addition of mercuric acetate to the reaction mixture showed an insignificant effect on the rate of reaction, suggesting that mercuric acetate act as a bromide ion scavenger only in the form of $[\text{HgBr}_4]^{2-}$. Successive addition of nicotinamide (as one of the oxidation products of NBN) to the reaction mixture showed a decreasing effect on the rate of oxidation of malic acid. Addition of NaClO_4 (to study the effect of ionic strength) in the reaction mixture showed an insignificant effect on the rate of oxidation. In order to find the effect of dielectric constant (polarity) of the medium on the rate, the oxidation of malic acid by NBN was studied in aqueous acetic acid mixtures of various compositions (Table 2). The data clearly reveal that the rate of reaction increases with a decrease in the percentage of acetic acid, i.e., increasing dielectric constant or polarity of the medium leads to the inference that there is a charge development in the transition state involving a more polar activated complex than the reactants[12].

Table 2- Effect of variation of [NBN] on reaction rate

[Malic acid]= 0.03 mol dm^{-3} $[\text{HClO}_4]=0.01 \text{ mol dm}^{-3}$,
 $[\text{NaClO}_4]=0.1 \text{ mol dm}^{-3}$, $\text{Hg}(\text{CH}_3\text{COO})_2=0.001 \text{ mol dm}^{-3}$,
 AcOH:H₂O (1:4) Temp. =308 K [SDS] = $0.004 \text{ mol dm}^{-3}$

[NBN] 10^4 mol dm^{-3}	$10^5 k_{\text{obs}} \text{ sec}^{-1}$
1.0	41.96
1.5	31.69
2.0	26.97
2.5	24.01
3.0	21.97
4.0	19.54
5.0	17.95

Table 3- Effect of variation of [Malic acid], $[\text{HClO}_4]$ and the dielectric constant on reaction rate

$[\text{NBN}]=0.00015 \text{ mol dm}^{-3}$ $[\text{NaClO}_4]=0.1 \text{ mol dm}^{-3}$,
 $\text{Hg}(\text{CH}_3\text{COO})_2=0.001 \text{ mol dm}^{-3}$, Temp. =308K [SDS] = $0.004 \text{ mol dm}^{-3}$

$10^3 [\text{MA}]$	$10^3 [\text{HClO}_4]$	CH_3COOH %(v/v)	$10^5 k_{(\text{obs})} \text{ sec}^{-1}$
5	10	20	11.52
10	10	20	17.95
20	10	20	27.58
25	10	20	31.74
30	10	20	36.19
40	10	20	42.95
50	10	20	48.97
30	5	20	50.59
30	10	20	31.92
30	20	20	20.62

30	25	20	17.65
30	30	20	15.59
30	40	20	12.86
30	50	20	11.12
30	10	20	30.97
30	10	25	28.11
30	10	30	24.92
30	10	40	18.57
30	10	50	12.51

The effect of added salts on the rate of reaction was also explored because salts as additives, in micellar systems, acquire a special ability to induce structural changes which may, in turn, modify the substrate–surfactant interaction. In the present case, KCl has no effect whereas with the increasing concentration of KBr, rate of reaction increased.

Test for Free Radicals

To test for the presence of free radicals in the reaction, the reaction mixture containing acrylamide was kept for 24 h in an inert atmosphere. When the reaction mixture was diluted with methanol, the formation of a precipitate was not seen. This suggests that there is no possibility of formation of free radicals in the reaction.

Influence of SDS on k_{obs}

A continuous decrease in the rate constant was observed with the increase in [SDS] at constant [MA] and [NBN] (Table 4). The inhibition effect is due to the fact that N-bromonicotinamide has N-Br bond which it binds to SDS micelles in Stern layer, while ionized malic acid, bearing negative charge is repelled by the head group of negatively charged SDS micelles.

Table 4-Effect of [SDS] on reaction rate

[Malic acid]=0.03 mol dm⁻³ [HClO₄]=0.01mol dm⁻³,
 [NBN]=0.0015 mol dm⁻³ [NaClO₄]=0.1mol dm⁻³,
 AcOH:H₂O (1:4) Hg(CH₃COO)₂=0.005 mol dm⁻³
 Temp. =308K

10 ³ SDS	10 ⁵ $k_{\text{(obs)}}$ sec ⁻¹
0	28.75
2	25.42
2.5	23.11
4	21.08
5	19.33
6	17.65
8	16.78
10	15.39
20	-
30	-
40	-
50	-
60	-
70	-
80	-
100	-
110	-
120	-
130	-

Effect of temperature

Increase in temperature increases the rate of oxidation and plot of $\log k_{\text{obs}}$ Vs reciprocal of temperature is linear. The oxidation of malic acid by NBN was studied at different temperatures in the presence and absence of SDS (308 to 323K) (Table 5) and the activation parameters were evaluated (Table 6). Activation parameters are believed to provide useful information regarding the environment in which chemical reactions take place.

Table 5. Effect of Temperature on reaction rate

[Malic acid]=0.03 mol dm⁻³ [HClO₄]=0.01 mol dm⁻³,
[NBN]=0.0015 mol dm⁻³ [NaClO₄]=0.1 mol dm⁻³,
AcOH:H₂O (1:4) Hg(CH₃COO)₂=0.005 mol dm⁻³

Temperature K	10 ⁵ k _{obs} sec ⁻¹
308	30.93
313	35.50
318	40.31
323	45.87

Effect of Temperature on reaction rate in the presence of SDS

[SDS] = 0.004 mol dm⁻³

Substrate	E _a kJmol ⁻¹	ΔH [#] kJmol ⁻¹	ΔS [#] J K ⁻¹ mol ⁻¹	ΔG [#] kJmol ⁻¹
Malic acid	11.90	9.34	-183.7	65.93
Malic acid+SDS	12.86	10.30	-180.6	65.93

Table 6- Activation Parameters

Temperature K	10 ⁵ k _{obs} sec ⁻¹
308	29.98
313	33.66
318	37.39
323	41.61

Mechanism

It has been reported [13] earlier that NBN is a stable oxidizing and brominating agent because of the large polarity of the N-Br bond. NBN, like other similar N-haloimides, may exist in various forms in an acidic medium, that is, free NBN, protonated NBN, Br⁺, HOBr, (H₂OBr)⁺ according to the following equilibria [13].

Addition of nicotinamide to the reaction mixture decreases the rate of oxidation in acidic media suggesting that the pre-equilibrium step involves a process in which nicotinamide is one of the products. When NBN or $(\text{NBNH})^+$ is assumed as the reactive species, the derived rate laws fail to explain the negative effect of nicotinamide, hence neither of these species can be considered as reactive species. When $(\text{H}_2\text{OBr})^+$ is taken as the reactive species, the rate law obtained shows first order kinetics with respect to hydrogen ion concentrations contrary to the observed negative fractional order in HClO_4 ; although it fully explains the negative effect of nicotinamide. Therefore, the possibility of cationic bromine (Br^+) as a reactive species is also ruled out. Thus, the only choice left is HOBr, which, when considered as the reactive species of NBN, leads to a rate law capable of explaining all the kinetics observations and other effects. Hence, in the light of kinetic observations, HOBr can safely be assumed to be the main reactive species of NBN for the present reaction. On the basis of the above experimental findings and taking HOBr to be the most reactive species of NBN, the following scheme can be proposed for the kinetics of oxidation of tartaric acid by NBN in acidic medium.

According to above scheme, the rate of disappearance of NBN is given as

$$-\frac{d[\text{NBN}]}{dT} = \frac{kK_1K_2[\text{MA}][\text{NBN}]_{\text{TOTAL}}}{[\text{NA}][\text{H}^+] + K_1K_2[\text{MA}]}$$

where

$$[\text{NBN}]_{\text{TOTAL}} = [\text{NBN}] + [\text{NA}] + [\text{X}^-]$$

The above rate law is in good agreement with the experimental results.

Influence of SDS on k_{obs}

The inhibition effect is due to the fact that N-bromonicotinamide has N-Br bond which it binds to SDS micelles in Stern layer, while ionized malic acid, bearing negative charge is repelled by the head group of negatively charged SDS micelles.

Piszkiewicz[14] model assumes that 'n' number of surfactant molecules (D) and substrate (S) aggregate to yield the catalysis aggregate D_nS which then reacts to yield the product (P). This is represented by the above scheme where K_D is the dissociation constant of micelle back to its free components and K_m is the rate of reaction within the micelle. As per the above scheme the observed rate constant (k_{obs}) is expressed as a function of surfactant concentration D, by the equation:

$$k(\text{obs}) = \frac{K_m[D]n + kwK_D}{K_D + [D]n}$$

$$\log \frac{k(\text{obs}) - kw}{K_m - k(\text{obs})} = n \log [D] - \log K_D$$

4. CONCLUSIONS

In the light of kinetic observations for the micellar effect on the kinetics of oxidation of malic acid by N-bromonicotinamide in the presence of perchloric acid, the following conclusions can be easily drawn: the reactive species of oxidant NBN is HOBr not NBN itself, the reaction rates are enhanced by increase in [malic acid] and temperature. Added nicotinamide retards the rate. 2-Aldoethanoic acid is the product of oxidation. Activation parameters were evaluated for both catalyzed and unanalyzed reactions. The critical micelle concentration value is much lower than that given in the literature for aqueous solutions of SDS without added electrolyte. The rate of oxidation slightly decreases with increasing concentration of SDS. The micellar effect can be correlated with the nature of the reducing substrates and the reactions conditions. These micellar effects are quite important to understand and to substantiate the proposed mechanistic pathways. This may widen the applicability of NBN as oxidant in organic synthesis.

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