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

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ABSTRACT The oxidation of malic acid by N-chloronicotinamide in the presence of $HClO_4$ is studied. First order kinetics with respect to NCN is observed. The kinetics results indicate fractional order in hydroxy acid. Rate of the reaction increases with a decrease in the percentage of acetic acid. Inverse first order in $[H^+]$ and [nicotinamide] are noted. 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.

Keywords: *Malic acid, N-Chloronicotinamide, kinetics, oxidation, micelles*

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. The presence of micelles can have marked effects on thermodynamic favorability and reaction kinetics as well as on many physical properties[1]. 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 hydroxy acids by N-bromoacetamide. Chand Waqar[2] investigated the

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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-chloronicotinamide (NCN) could be compared with other N-haloimide such as N-bromosuccinimide (NBS) and N-bromosaccharin (NBSa). 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 NCN are yet to be explored. This prompted the micellar effect on the kinetics of the oxidation of the malic acid by NBN in the acidic medium.

RESULTS AND DISCUSSION

The kinetic results for the oxidation of malic acid by N-Chloronicotinamide (NCN) in the presence of surfactant (SDS) can be summarized as follows. The kinetic studies were carried out under pseudo-first order conditions with [malic acid] >> [NCN]. The kinetics of the oxidation of malic acid by NCN in presence of surfactant (SDS) and $HClO_4$ was investigated at several initial concentrations of the reactant. The reaction was of first order linearity of a plot of log [NCN] versus time for malic acid. The rate constants at different initial [NCN] are reported. Table 1 summarizes the pseudo first order rate constant's dependence on the NCN concentration. It was observed that, with the increase in initial NCN concentration, the value of rate constant decreased (Fig. 1).

At a constant value of NCN, surfactant (SDS) and $HClO_4$ the rate constant was determined at different initial concentrations of malic acid ranging from 5×10^{-3} to 50×10^{-3} mol dm^{-3}. Table 2 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 [malic acid] was linear with a slope of less than unity showing fractional order dependence on [malic acid] (Fig. 2).

Furthermore, a plot of log k versus malic acid was linear with an intercept on y axis, confirming the fractional order concentration dependence on substrate. The rate constant k decreased with increase in [$HClO_4$] from 5×10^{-3} to 50×10^{-3} mol dm^{-3} (Table 2) (Fig. 3).

Table 1. Effect of variation of [NCN] on reaction rate
[Malic acid]=0.03mol dm^{-3} [$HClO_4$]=0.01 mol dm^{-3}, [$NaClO_4$]=0.1mol dm^{-3},
AcOH:H_2O (1:4) Temp. =308 K [SDS]=0.01 mol dm^{-3}

[NCN] 10^4 moldm^{-3}	**10^5 k_{obs} sec^{-1}**
1.0	38.96
1.5	28.43
2.0	22.86
2.5	19.69
3.0	17.71
4.0	14.76
5.0	13.09

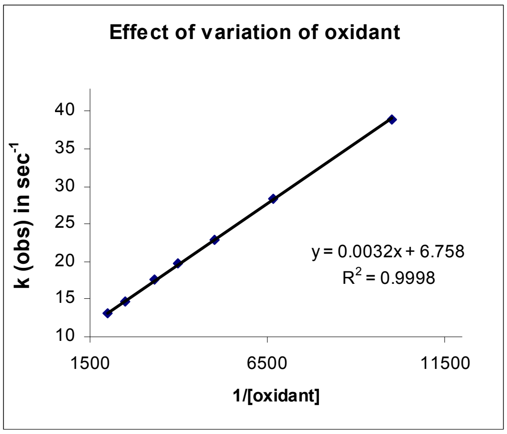


Figure 1. Effect of variation of [NCN] on reaction rate

This may be due to protonation of the substrate. The plot of log k versus log[$HClO_4$] is linear with negative slope. The slope being less than unity indicates inverse fractional order dependence on [$HClO_4$]. Successive addition of nicotinamide (as one of the oxidation products of NCN) 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 NCN was studied in aqueous acetic acid mixtures of various compositions (Table 2) (Fig.4). 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[11].

Table 2. Effect of variation of [Malic acid], [$HClO_4$] and the dielectric constant on reaction rate

10^3[MA]	$10^3[HClO_4]$	CH_3COOH %(v/v)	$10^5 k_{(obs)}$ sec^{-1}
5	10	20	9.76
10	10	20	15.39
20	10	20	24.12
25	10	20	28.15
30	10	20	31.30
40	10	20	38.29
50	10	20	44.58
30	5	20	46.38
30	10	20	28.87
30	20	20	18.11
30	25	20	15.73
30	30	20	13.86
30	40	20	11.21
30	50	20	9.72
30	10	20	27.89
30	10	25	25.15
30	10	30	22.18
30	10	40	16.17
30	10	50	10.66

[NCN]=0.00015 mol dm^{-3} [$NaClO_4$]=0.1mol dm^{-3}, Temp. =308K, [SDS]=0.01 mol dm^{-3}

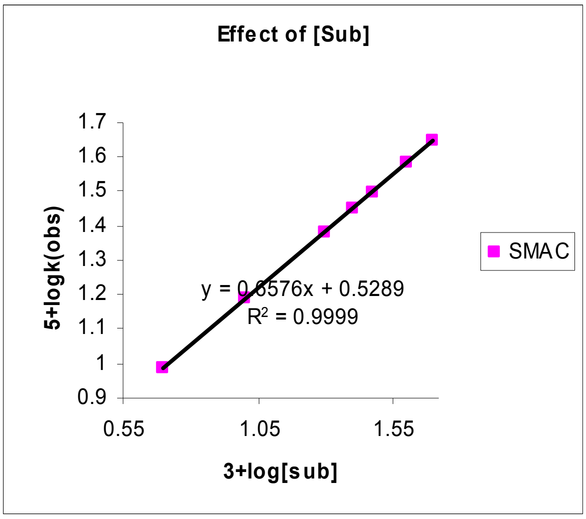


Figure 2. Effect of variation of [malic acid] on reaction rate

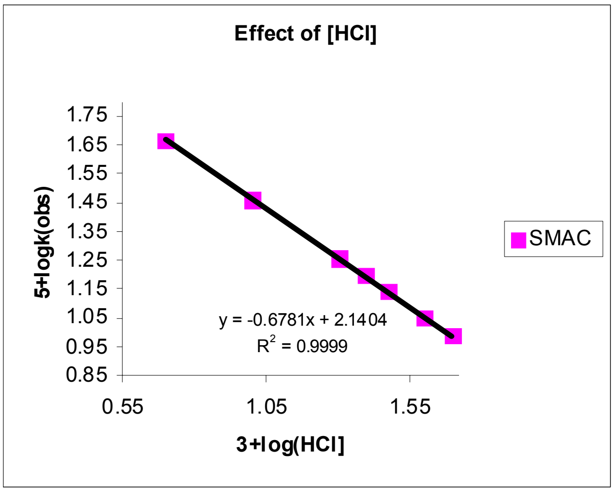


Figure 3. Effect of variation of [$HClO_4$] on reaction rate

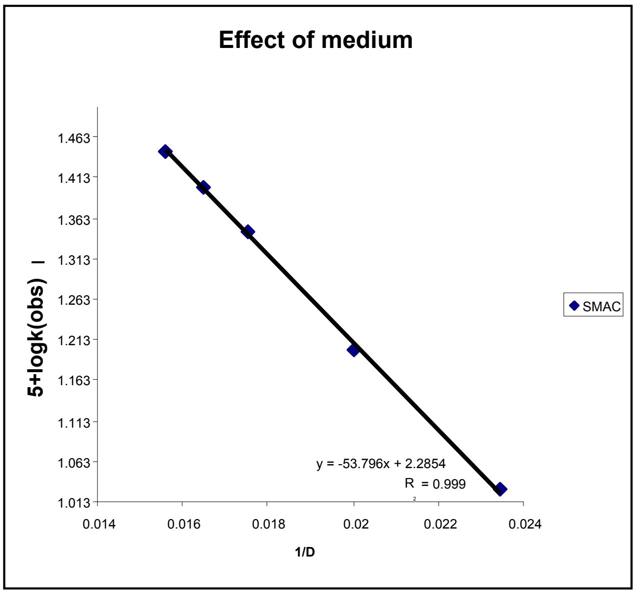


Figure 4. Effect of variation of medium on reaction rate

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, KBr has no effect whereas with the increasing concentration of KCl, 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.

Mechanism

It has been reported [11-16] earlier that NCN is a stable oxidizing and chlorinating agent because of the large polarity of the N–Cl bond. NCN, like other similar N-haloimides, may exist in various forms in an acidic medium, that is, free NCN, protonated NCN, Cl^+, HOClr, $(H_2OCl)^+$ according to the following equilibria[17-22].

$$\text{NCN} + H_2O \rightleftarrows \text{HOCl} + \text{NA} \qquad (1)$$

$$\text{NCN} + H^+ \rightleftarrows \text{NA} + Cl^+ \qquad (2)$$

$$\text{NCN} + H^+ \leftrightarrows [\text{NCNH}]^+ \qquad (3)$$

$$\text{HOCl} + H^+ \rightleftarrows [H_2OCl]^+ \qquad (4)$$

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 NCN or $(NCNH)^+$ 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 $(H_2OCl)^+$ 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 chlorine (Cl^+) as a reactive species is also ruled out. Thus, the only choice left is HOCl, which, when considered as the reactive species of NCN, leads to a rate law capable of explaining all the kinetics observations and other effects. Hence, in the light of kinetic observations, HOCl can safely be assumed to be the main reactive species of NCN for the present reaction. On the basis of the above experimental findings and taking HOCl to be the most reactive species of NCN, the following scheme can be proposed for the kinetics of oxidation of malic acid by NCN in acidic medium.

$$\text{NCN} + H_2O \overset{K_1}{\rightleftarrows} \text{HOCl} + \text{NA} \qquad (5)$$

$$HOCl + NA \underset{k}{\overset{K_2}{\rightleftarrows}} X^- + (H_3O)^+ \qquad (6)$$

$$X^- \xrightarrow[\text{Rate controlling step}]{} (HO)CH\,(CH_2COOH) + NA + CO_2 + HCl \qquad (7)$$

The rate of disappearance of NCN is given as

$$-\frac{d[NCN]}{dT} = \frac{kK_1K_2[MA][NCN]_{TOTAL}}{[NA][HCl]+K_1K_2[MA]}$$

where

$[NCN]_{TOTAL} = [NCN] + [NA] + [X^-]$

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

Influence of SDS on k_{obs}

A continuous decrease in the rate constant was observed with the increase in [SDS] at constant [MA] and [NCN] (Table 4). The inhibition effect is due to the fact that N-chloronicotinamide has N -Cl 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.

$$nD + S \Longleftrightarrow D_nS$$

$$D_nS \xrightarrow{K_m} \text{Products}$$

$$S \xrightarrow{k_w} \text{Products}$$

Piszkiewicz[23] 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:

$$k(obs) = \frac{k_m[D]^n + k_wK_D}{K_D + [D]^n}$$

$$\log\frac{k(obs)-k_w}{k_m - k(obs)} = n\log[D] - \log K_D$$

Table 3. Effect of [SDS] on reaction rate

10^3 **SDS**	**10^5 $k_{(obs)}$ sec^{-1}**
0	25.65
2	22.32
2.5	20.01
4	18.28
5	16.83
6	14.59
8	13.48
10	12.59
20	-
30	-
40	-
50	-
60	-
70	-
80	-
100	-
110	-
120	-
130	-

[Malic acid]=0.03 mol dm^{-3} [$HClO_4$]=0.01mol dm^{-3},[NCN]=0.0015 mol dm^{-3}
[$NaClO_4$]=0.1mol dm^{-3},AcOH:H_2O (1:4) Temp. =308K

Effect of temperature

Increase in temperature increases the rate of oxidation and plot of log k_{obs} Vs reciprocal of temperature is linear. The oxidation of malic acid by NCN was studied at different temperatures in the presence and absence of SDS (308 to 323K) (Table 4) (Fig.5) and the activation parameters were evaluated (Table 5) (Fig.6). Activation parameters are believed to provide useful information regarding the environment in which chemical reactions take place.

Table 4. Effect of Temperature on reaction rate

Temperature K	**10^5 k_{obs} sec^{-1}**
308	27.98
313	31.65
318	35.67
323	40.04

[Malic acid]=0.03 mol dm^{-3} [$HClO_4$]=0.01mol dm^{-3},
[NCN]=0.0015 mol dm^{-3} [$NaClO_4$]=0.1mol dm^{-3}, AcOH:H_2O (1:4)

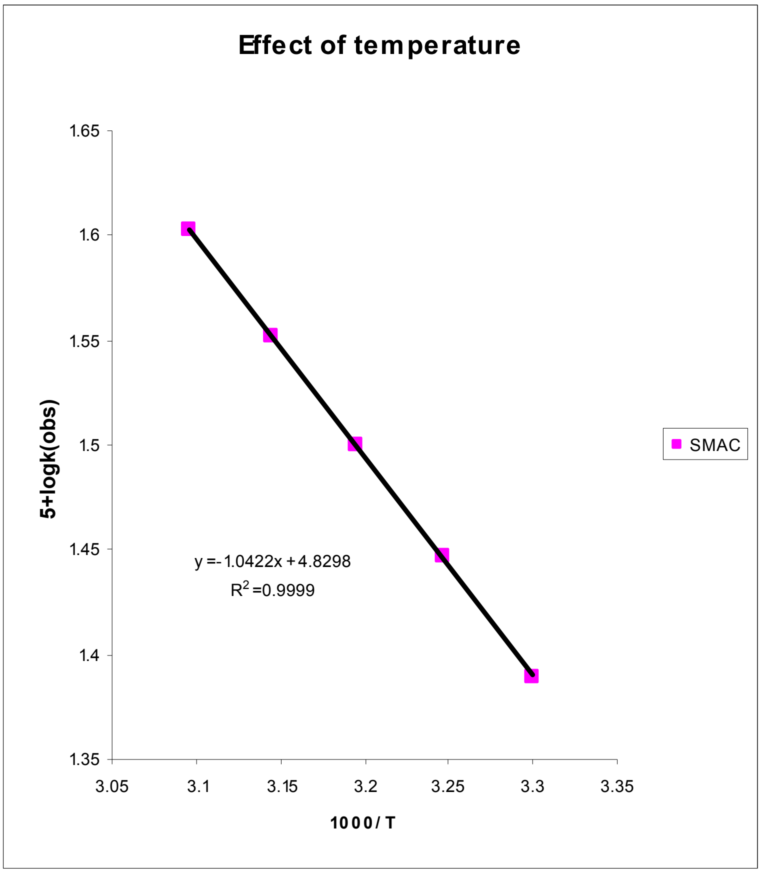


Figure 5. Effect of Temperature on reaction rate

Table 5. Effect of Temperature on reaction rate in the presence of SDS

Temperature K	**10^5 k_{obs} sec^{-1}**
308	25.75
313	30.02
318	34.58
323	39.79

[SDS]=0.01 mol dm^{-3}

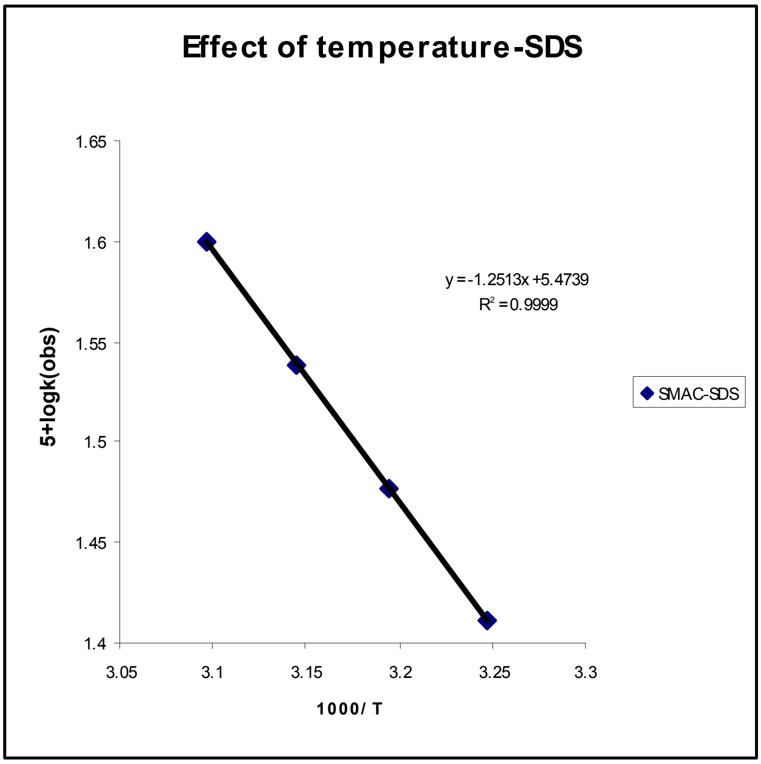


Figure 6. Effect of Temperature on reaction rate in presence of SDS

Table 6. Activation Parameters

Substrate	**E_a kJmol^{-1}**	**$\Delta H^{\#}$ kJmol^{-1}**	**$\Delta S^{\#}$ J K^{-1}mol^{-1}**	**$\Delta G^{\#}$kJmol^{-1}**
Malic acid	11.14	8.58	– 186.5	66.04
Malic acid+SDS	12.95	10.39	–180.9	66.14

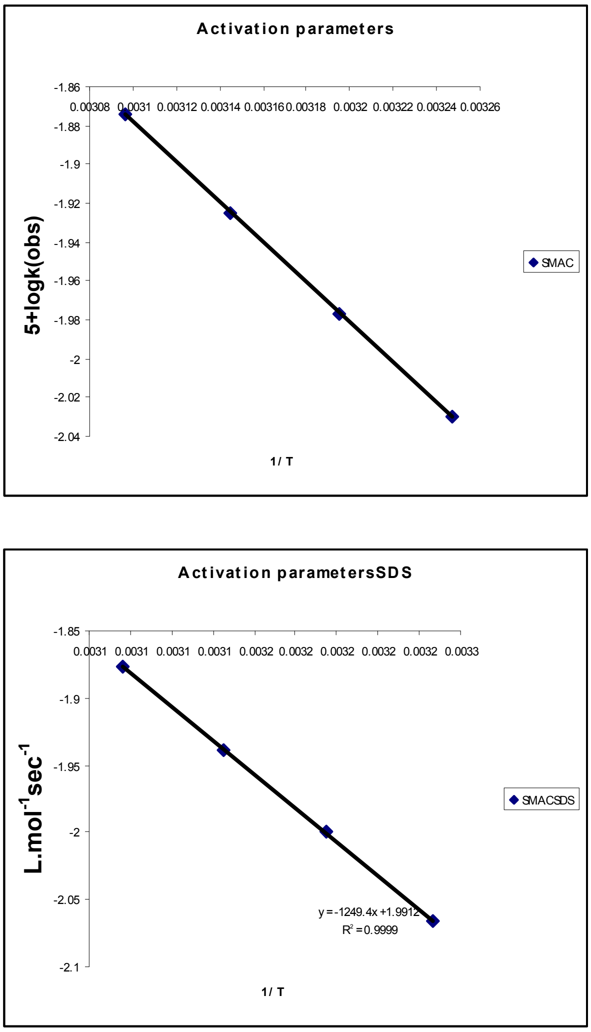


Figure 7. Activation parameters

EXPERIMENTAL

Materials and methods

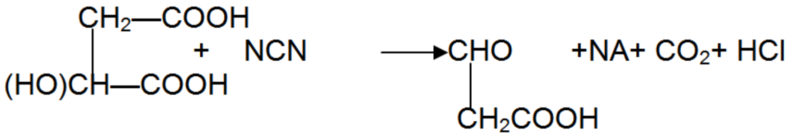
N-Chloronicotinamide (NCN) was prepared by the reported method[8]. Standard solution of NCN was prepared afresh in water and its purity was checked iodometrically. Standard solutions of SDS (GR) and malic acid (Merck) were prepared using double distilled water. $HClO_4$ (A.R. grade) was diluted with double distilled water and 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 (Table 1).

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 (NCN), perchloric acid, sodium perchlorate, nicotinamide, surfactant and temperature were carried out. The reaction was carried out under pseudo-first order condition ([malic acid] >>[NCN]). The pseudo-first order rate constants were 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 ±3%. The course of the reaction was studied for more than two half-lives.

Stoichiometry

The reaction mixture containing a known excess of [NCN] >> [malic acid] was kept in the presence of $HClO_4$ and at 40°C for 72 h. After completion of the reaction, the unconsumed NCN was calculated iodometrically. It was found that nearly 2 moles of NCN were consumed for each mole of malic acid.



$$\mathrm{CH_2{-}COOH \,/\, (HO)CH{-}COOH} + \mathrm{NCN} \longrightarrow \mathrm{CHO \,/\, CH_2COOH} + \mathrm{NA} + \mathrm{CO_2} + \mathrm{HCl}$$

Malic acid 2-Aldoethanoic acid

Product analysis

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

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 can 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 these correspond to the CMC of surfactant. The CMC values of SDS in different experimental conditions at 40°C are summarized in Table 8. 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 3.21×10^{-3} mol dm^{-3} in reaction mixture for malic acid.

Table 8. Critical micelle concentration (CMC values of SDS in different experimental conditions)
[Malic acid]=0.03mol dm^{-3} [$HClO_4$] = 0.01 mol dm^{-3}, [$NaClO_4$]=0.1mol dm^{-3}, AcOH:H_2O (1:4) Temp. =308 K

Solutions	10^3 CMC mol dm^{-3}**SDS**
Water	7.9
Water+NCN	7.1
Water+malic acid	4.2
Water+malic acid+NCN+ $HClO_4$+20% v/v AcOH	2.8

CONCLUSIONS

In the light of kinetic observations for the micellar effect on the kinetics of oxidation of malic acid by N-chloronicotinamide in the presence of perchloric acid, the following conclusions can be easily drawn: the reactive species of oxidant NCN is HOCl not NCN 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 is much lower than values 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 NCN as oxidant in organic synthesis.

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