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Kinetics and Mechanism of Oxidation of Tartaric Acid by N-Chloronicotinamide (NCN)

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ABSTRACT

The oxidation of tartaric acid by N-chloronicotinamide in the presence of H_2SO_4 is studied. First order kinetics with respect to NCN is observed. The kinetics results indicate fractional order dependence about [tartaric acid]. Inverse first order in [nicotinamide] and inverse fractional order about [H^+] are noted. Rate of the reaction increases with a decrease in the percentage of acetic acid. 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: Tartaric acid, N-Chloronicotinamide, oxidation, mechanism

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 Kreb'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. A.K. Singh [1] studied the kinetics and mechanism of oxidation of some hydroxy acids by N-bromoacetamide. 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 tetraethyl ammonium 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-bromobenzenesuphonamide , and iodate[7] However, the details of oxidation of tartaric acid by N-chloronicotinamide are yet to be explored. This encouraged the systematic kinetic study on the oxidation of tartaric acid by NCN in aqueous acetic acid medium.

Materials and methods

Abbreviations

NCN N-Chloronicotinamide

TA Tartaric acid

NA Nicotinamide

Preparation and standardisation

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. Tartaric acid ((Merck) was used. $HClO_4$ (A.R. grade) 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.

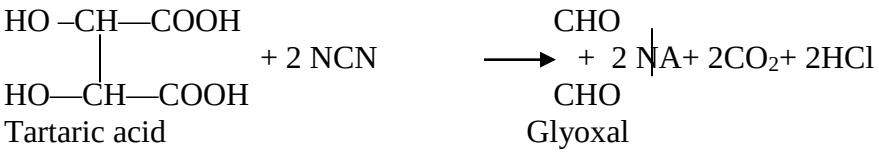
Kinetic Measurements

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

Stoichiometry

The reaction mixture containing a known excess of [NCN] >> [tartaric acid] was kept in the presence of H_2SO_4 and $Hg(OAc)_2$ 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 tartaric acid.



Product Analysis

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

Results

The kinetic results for the oxidation of tartaric acid by
N-Chloronicotinamide (NCN) can be summarized as follows. The kinetic studies were carried out under pseudo-first order conditions with [tartaric acid] >> [NCN].

The kinetics of the oxidation of tartaric acid by NCN in presence of $HClO_4$ 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 tartaric acid. The rate constants at different initial [NCN] are reported.

Table 1- Effect of variation of [NCN] on reaction rate

[Tartaric acid]=0.03mol dm^{-3}, [H_2SO_4]=0. 1mol dm^{-3},

AcOH:H_2O (1:4), $[NaClO_4]$=0.1mol dm^{-3}, Temp. =308 K

[NCN] 10^4 moldm^{-3}	**10^5 k_{obs} sec^{-1}**
1.0	35.01
1.5	23.45
2.0	17.43
2.5	14.05
3.0	11.84
4.0	9.06
5.0	7.14

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 . At a constant value of NBN, H_2SO_4, the rate constant was determined at different initial concentrations of tartaric 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 tartaric acid concentration. The rate constant, increased with increasing [tartaric acid]. The plot of log k versus log [tartaric acid] was linear with a slope of less than unity showing fractional order dependence on [tartaric acid]. Furthermore, a plot of log k versus [tartaric acid] was linear with an intercept on y axis, confirming the fractional order dependence on substrate. The rate constant k decreased with increase in $[H_2SO_4]$ from 5×10^{-3} to 50×10^{-3} mol dm^{-3} (Table 2) . This may be due to protonation of the substrate. The plot of log k versus log$[H_2SO_4]$ is linear with negative slope. The slope being less than unity indicates inverse fractional order dependence on $[H_2SO_4]$. 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 tartaric 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 tartaric acid by NCN 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 [11].

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

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

10^3[TA]	10^3[H_2SO_4]	CH_3COOH %(v/v)	10^5 $k_{(obs)}$ sec^{-1}
5	10	20	5.56
10	10	20	9.74
20	10	20	16.75
25	10	20	19.91
30	10	20	23.55
40	10	20	29.01
50	10	20	34.74
30	5	20	34.41
30	10	20	23.52
30	20	20	16.49
30	25	20	14.68
30	30	20	13.25
30	40	20	11.35
30	50	20	10.01
30	10	20	23.55
30	10	25	20.90
30	10	30	18.11
30	10	40	13.14
30	10	50	8.56

In the present case, KBr has no effect on the reaction rate where as the rate of reaction increased with an increasing concentration of KCl.

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 tartaric acid by NCN was studied at different temperatures (303K to 323K) (Table 3) and the activation parameters were evaluated (Table 4). Activation parameters are believed to provide useful information regarding the environment in which chemical reactions take place.

Table 3-Effect of Temperature on reaction rate

[Tartaric acid]=0.03 mol dm^{-3} $[H_2SO_4]$=0.01mol dm^{-3},
[NCN]=0.0015 mol dm^{-3} $[NaClO_4]$=0.1mol dm^{-3},
AcOH:H_2O (1:4)

Temperature K	**10^5 k_{obs} sec^{-1}**
303	18.85
308	23.31
313	28.52
318	34.96
323	42.61

Substrate	**E_a kJmol^{-1}**	**$\Delta H^{\#}$ kJmol^{-1}**	**$\Delta S^{\#}$ J K^{-1}mol^{-1}**	**$\Delta G^{\#}$kJmol^{-1}**
Tartaric acid	14.32	16.88	– 168.7	66.22

Table 5- Activation Parameters

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 [12] 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^+, HOCl, $(H_2OCl)^+$ according to the following equilibria.

$$NCN + H_2O \rightleftharpoons HOCl + NA \quad (1)$$

$$NCN + H^+ \rightleftharpoons NA + Cl^+ \quad (2)$$

$$NCN + H^+ \rightleftharpoons [NCNH]^+ \quad (3)$$

$$HOCl + H^+ \rightleftharpoons [H_2OCl]^+ \quad (4)$$

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 H_2SO_4, although it fully explains the negative effect of nicotinamide. Therefore, the possibility of cationic bromine (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 NBN, the following scheme can be proposed for the kinetics of oxidation of tartaric acid by NCN in acidic medium.

$$NCN + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} HOCl + NA \quad (5)$$

$$HOCl + TA \overset{K_2}{\rightleftharpoons} X^- + (H_3O)^+ \quad (6)$$

$$X^- \xrightarrow[\text{Rate controlling step}]{k} \text{Products} \quad (7)$$

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

$$-\frac{d[NBN]}{dT} = \frac{kK1K2[TA][NBN]TOTAL}{[NA][H+]+K1K2[TA]}$$

where

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

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

Conclusion

At the end of this study, it is evident that the reaction rates are enhanced by increase in [tartaric acid] and temperature. Added nicotinamide retards the rate. HOCl is the reactive intermediate leading to product. Glyoxal is the product of oxidation. Suitable mechanism in compliance with experimental observations was proposed and the rate law was derived.

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