Medical Science

MICELLES CATALYZED OXIDATION OF TARTONIC ACIDBY N-CHLOROSACCHRAIN

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ABSTRACT The Micelles catalyzed oxidation of tartonic acid has been carried out with N-Chlorosacchrain in acitic acid medium in the presence of H$^+$ ion. It is found that rate is a direct function of first power concentration of oxidant i.e. N-Chlorosacchrain and zero order with respect to substrate i.e aliphatic hydroxy acid. The reaction was found to increase with increase. concentration of acid.

KEYWORDS : Oxidimetric, Degradation, N-chlorosacchrain.

INTRODUCTION

N-Chlorosacchrain is a titrant for the oxidimetric determination of some typical aliphatic hyrodxy acid in acidic medium. This N-Chlorosacchrain is used as ion hollow oxident, soluble in organic solvent and used under anhydrous condition . It is a new oxidant, N-halogenocompounds is known for their halogenating property .that is stronger oxidizing agent as cpmpared to N–halaomides,the former being more acidic, loss halogen atom has haloniumion, which is an electrophile and further the resulting an ion is stabilized by the resonance.hence such compounds undergo hedterolitic fission to produce hallonium ion.

Saccharin is an imide of orthosulphobenzoic acid and is a stronger acid as compared to other imides of dicarbolic acid such as succinic acid.the an ion of saccharin gets extra stabilization as the acyl and sulphonyl group provides large orbital for the electron delocalization[1] .Saccharin form stable bromo and clhoro-derivativs, the former being successfully applied as oxidizing reagent and Chattaway[2]

Bacchawat[3] et al (1971) developed NCSA is a potential titrain for the oxidimetric determination of tartonic acid . it is carried out in aqueous acitic acid medium in the presence of HClO$_4$.

In the presence of H$^+$, protonation of NCSA and HOCl yields protonated NCSA (NCSA H$^+$).

While the oxidation of elephatic hydroxyl acid compounds by N-Chlorosacchrain is very rare and scanty and none of the researcher acclaimed the use of N-Chlorosacchrain ion probing the oxidation kinetics of elephaqtic hydroxyl compound with it, thus we have chosen NCSA for the first time as an oxidant for the kinetics study of tartonic acid in aqueous acitic acid medium.

Khan [4,5] et al. reported the oxidative kinetics of general hydroxyl acids (BIZ.mendelic, benzilic, glycolic and lactic acid)with NCSA in aqueous acitic acid medium.the reaction is found to be first –order with respect to oxidant, HClO4 and substrate at low concentration tending to zero at higher concentration of the substrate.Patil at al[6] (2007) studied the kinetic and mechanistis study on the oxidation of hydroxy acids, tartaric acid (TA) and malic acid (MA) by N-Bromophthalimide(NBP) in the presence of a cationic surfaceant , cetylerinethylammonium bromide (CTAB), in per chroric acid medium at 313K.The oxidation of TA & MAY NBP in the presence of CTAB is foster then in the absence of surfactant . the rate of oxidation of hydroxyl acid was found to be in the order : TA>MA

OBSERVATION AND ANALYSIS

Alaphatic Hydroxyl acid compounds employes are commercially available (E MERCH).all other chemicals used where analytical grade. The stock solution of the substrate was prepared in purified tartonic acid (S MERCK) aliphatic hydroxyl acid desolves in digiteled water directly.

NCSA was prepared by the method suggested by chattaway,and bacchawat.The kinetic measurementwere made under pseudo first order condition by meantaining (substrate) > (oxidant).The reaction was initiated by addind requsite amount of solution of substrate to the NCSA Solutioncontainingacetic acid and water.in a thermostatic bath.The unreacted NCSAwas estimated iodometrically.

RESULT AND DISCUSSION

The stoichiomeitric data established that for complete oxidation of one moles of each tartonic acid and one mole of NCSA is required . The product of the oxidation was ascertained by the formation of Glyoxalic, saccharin, CO2, HCl using glyoxylic acid, and fluorescene .The kinetic data have been collected for five fold concentration of oxidant (NCSA) at fixed concentration of other reactants and temperature. The linear plot of log a/(a-x) vs. time shows the first-order rate dependency with respect to NCSA.

The Stoichiometry of each reaction under study was determined under experimental condition..The oxidation products of the reaction were identified qualitatibaly by existing conventional methods chromatoghaphically[7] and by spot test qualitatively[8].The formation of free radicals was tested using acrylonitrile (monomer) by trapping method[9].

TYPICAL KINETIC RUN FOR THE EFFECT OF MICELLES CATALYSED OXIDATION OF N-CHLOROSACCHRAIN
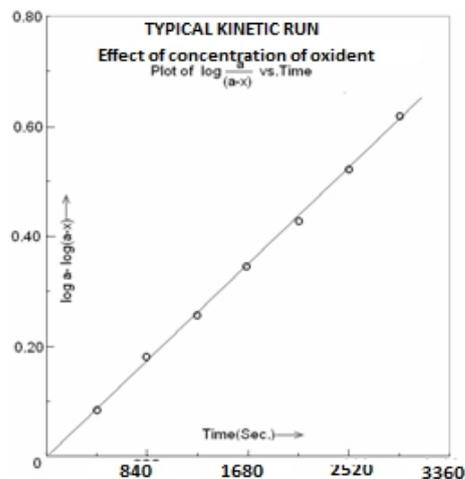

Fig. I : [T.A.] = 4.0 ×10^{-2} (mol.dm^{-3}), [NCSA] = 2.50 ×10^{-3} (mol.dm^{-3}), [H$^+$] = 0.05 ×10^{-3} (mol.dm^{-3}), HOAc-H$_2$O =20 % (v/V), Temp. = 308 K

Table: 1 Typical kinetic run for the effect of Concentration of oxidant (N-Chlorosaccharin)
Kinetics of oxidation reaction between TA with NCSA

S. No.	Time (sec.)	Vol. of N / 1000 hypo ml.	$10_4 k_1 (s^{-1})$
0	5.00	-
420	4.00	5.31
840	3.25	5.12
1260	2.60	5.19
1680	2.05	5.30
2100	1.65	5.28
2520	1.30	5.34
2940	1.05	5.30

Average $k_1 = 5.26 \times 10^{-4}(s^{-1})$

Graphical $k_1 = 5.19 \times 10^{-4}$ (s^{-1}) The reaction follows first-order kinetics with respect to substrate at lower concentration and tends toward zero-order at higher concentration. The evidence indicates the formation of complex during the reaction between each substrate and oxidant. The plot of k_1 vs. $[H_2SO_4]$ was linear with the positive unit slope and passing through origin which led to the conclusion that reaction is fully acid catalyzed and first-order with respect to acid concentration Fig. II.

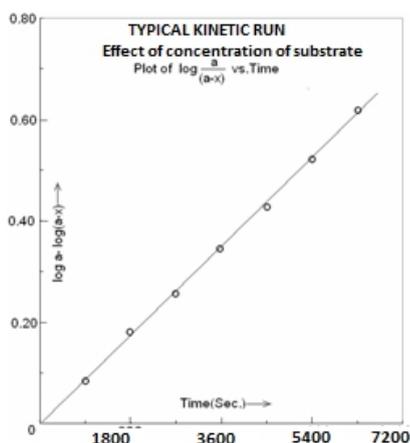**Typical kinetic run for the effect of Concentration of substrate (Tartronic Acid)**

TYPICAL KINETIC RUN
Effect of concentration of substrate
Plot of $\log \frac{a}{(a-x)}$ vs. Time

Table: 2 Typical kinetic run for the effect of Concentration of substrate (Tartronic Acid)

Fig. II: $[T.A.] = 2.50 \times 10^{-2}$ (mol.dm^{-3}), [NCSA] $= 2.50 \times 10^{-3}$ (mol.dm^{3}), $[H^+] = 0.05 \times 10^{-3}$ (mol.dm^{3}), HOAc-H$_2$O $= 20$ % (v/V), Temp. $= 308$ ^{0}k. (CTAB)$= 1.25 \times 10^{-3}$(mol.dm^{-3}),

| S.No.	Time (sec.)	Vol. of N / 1000 hypo ml.	$10_4 k_1 (s^{-1})$
0	5.00	-
900	3.85	2.90
1800	2.95	2.93
2700	2.25	2.95
3600	1.80	2.83
4500	1.35	2.91
5400	1.05	2.89
6300	0.80	2.90

Average $k_1 = 2.90 \times 10^{-4}(s^{-1})$,
Graphical $k_1 = 2.89 \times 10^{-4}$

The polarity of the medium was varied by using different percentage of acetic acid and water binary mixture. It was observed that the rate of oxidation of substrate increase with increase in the percentage composition i.e. content of acetic acid in the reaction mixture. Since the plot of $\log k_1$ vs. 1/D is linear with positive slop.

The addition of primary salts does not alter the rate of reaction. This shows that rate determining step involves either neutral species or an ion and a neutral molecule. All these aliphatic bi-functional hydroxyacid follow first order kinetics eith respects to NCSA under the condition [Substrate]>>[NCSA]

Micelles catalyzed study is mainly due to the reasons that its rate is proportional to the enzyme concentration10while equilibrium constant remains unaffected.

$$(NH2)2\,CO + H2O \rightarrow CO2 + 2\,NH$$
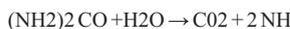
There are number of other types of oxidants which have been employed in the oxidation of hydroxyl acids such as Co(lll)[10,11] Cu(ll)[12] ammonical silver nitrate[13-16] Hg2+[17], fenton'reagent[18], and lead tetraacetate[19].

Oxidation Study by micelles Catalysts:- (Fig.)

Micelles providing the surface to reactants molecules
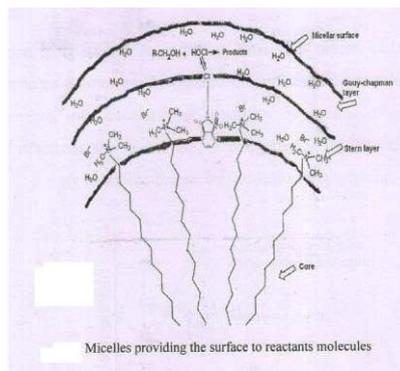
Mechanism

The oxidation of hydroxyl acids with NCSA in aqueous acetic medium can therefore be formulated as,
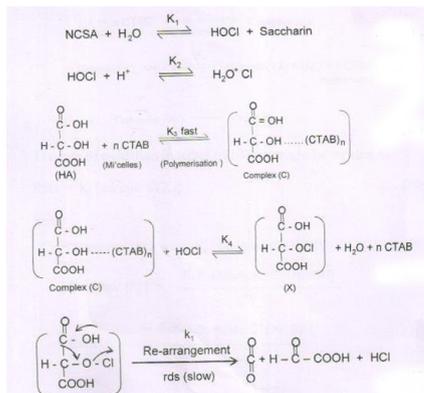
The above mechanism leads to the following rate law.

$$K_{Obs} = \frac{k_1\,K_1\,K_4\,[\text{Complex}]\,[CTAB]}{[S] + k_1 + K_1\,K_2\,[H^+] + K_1\,K_4\,[\text{Complex}]}$$

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