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KINETICS OF OXIDATION OF SOME ORGANIC COMPOUNDS BY N-CHLORONICOTINAMIDE IN AQUEOUS ACETIC ACID MEDIUM

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ABSTRACT: Chemical kinetics is a branch of chemistry which deals with rate of reaction. Kinetics of oxidation of Cyclohexanol by N-Chloronicotinamide(NCN) in 50% V/V aqueous acetic acid mixture has been investigated in the presence of $HClO_4$ and NaCl. The observed rate of oxidation is first-order with respect to oxidation (NCN) and fractional-order with respect to cyclohexanol. A decrease in dielectric constant of the medium increases the rate. Addition of nicotinamide (NA), the reduction product of NCN, has a retarding effect an the rate of oxidation. Arrhenius and activation parameters are calculated. Kinetics of bromination[1] and oxidation[2,3] of saturated organic compounds by N-bromosuccinimide (NBS) have been received considerable attention. Kinetics and mechanism of oxidation of amino acids by NCN has been reported in aqueous acetic acid medium. A suitable mechanism consistent with the observed kinetics has been proposed.

KEYWORDS: Kinetics, Oxidation, N – chloronicotinamide.

INTRODUCTION

Chemical kinetics is a branch of chemistry which deals with rate of reaction. A detail study of chemical kinetic along with other non-kinetic study enables us to understand thoroughly mechanism of reactions. There are some reactions which takes place very fast, within fraction of second. Some reactions are extremely slow for example rusting of iron. In between these two extreme ends, there are reactions which take reasonable time for completion. These reactions can be studied conveniently with suitable methods. There are several researchers who contributed in the field of chemical kinetics. Ludwig Ferdinand Wilhelmy, Wilhelmy Ostward, C.F. Wenzel, Louis Jacques Thenard, Pierre Eugene Mareelin Berthelor, Leon Pean de Saint Gilles, Peter Waage and Harcourt etc. had made pioneering work in the field of chemical kinetics.

N - chloronicotinamide (NCN) has been extensively used in both chlorination and oxidation of many organic substrates. NCN [1] is one of the stable, mild, efficient and inexpensive N-halon compound [2] and is used as a source of electrophilic chlorine. Nicotinamide is a derivative of niacin (Vitamin B3) with similar vitamin activity and plays an important role in certain biochemical mechanisms in human cells. The study becomes more important from the biological point of view. An extensive literature survey reveals that kinetics and mechanism of oxidation of amino acids [3], alcohols [4, 5], aldehydes [6], s-phenylmercapto acetic acid [7], and benzyl ethers [8] have been carried out using NCN. Literature survey reveals that there are no kinetic and mechanistic studies involving this useful compound with chalcones.

Chalcones are of interest because they have a unique structural feature of having a >C=O functional group in conjugation with >C=C< and the whole molecule is in conjugation. Chalcones are oxidized by different oxidizing agents and in all these reactions either the >C=C< or >C=O group of the chalcone is attacked by the oxidant [9-18]. Chalcones are natural substance found in a number of plants or synthetically prepared. They display many biological activities [19] viz., antiviral, anti-inflammatory, antimicrobial, antimitotic, antitumor, cytotoxicity, analgesic and antipyretic properties. They also act as potential anti-ulcer, antifungal, anti-cancer [20] and antimalerial growth [21].

MATERIALS AND METHODS

Acetic acid was purified by standard method [22] and used. Chalcones were prepared in the laboratory [14]. Standard solution of NCN was prepared in water and its purity was checked iodometrically. Hydrochloric acid (AnalaR) was used as a source of [H+]. Conductivity water was used throughout the studies. Other chemicals used were of analytical grade.

Kinetic measurements

The kinetic runs were carried out under pseudo-first order conditions ([chalcones] >> [NCN]. Rate studies were carried out at the desired temperature with an accuracy of ±0.5°C. The reaction was initiated by the rapid addition of known amounts of oxidant to reaction mixtures containing the required amount of chalcone, HCl, NaClO4, acetic acid and water in glass stoppered pyrex boiling tubes; thermo-stated at 40°C. The progress of reaction was monitored by iodometric determination

of unconsumed [NCN] in known aliquots of the reaction mixtures at different time intervals.

RESULTS AND DISCUSSION

Kinetic Experiments :

Keeping excess of the hydroxy acid over PCC attained the pseudo first order conditions. The temperature was kept constant to ± 0.1 K. The reaction was followed by monitoring the optical density of the reaction mixture spectrophotometrically at 354 nm up to 70% of the reaction by using a digital UV/ visible spectrophotometer model. No other reactant or product had any significant absorption at this wavelength.

The rate and other experimental data were obtained for both the hydroxy acids studied and similar results were obtained. The oxidation of hydroxy acids resulted in the formation of the corresponding oxoacids.

PCC undergoes a two electron change.

Effect of substrate concentration :

The reaction increases linearly with an increase in the [hydroxy acids] (Table 1). The plot of $1/k_{obs}$ *versus* 1/[subsrate] gave linear line passing through origin suggests that the rate does not obey Michaelis-Menten type kinetics. The hydroxy acids also show first order dependence over substrate in quinolinium bromochromate (QBC) and pyridinium hydrobromide perbromide .

Test for polymerization :

The oxidation of hydroxy acids by PCC in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile.

Effect of ionic strength : There was no effect of SO_4^{2-} and CH_3COO^- observed on the reaction rate in the Debye Huckle limit. It proves that interaction in rate determining step is not ion-ion type and one of the reactant molecules is neutral.

Effect of solvent composition : The rate of oxidation of lactic and mandelic acid was determined in different solvent composition [1,4-dioxane]. The kinetics is similar for both the acids in the solvent. According to Scatchard the plot of log k_{obs} *versus* 1/D was liner and indicates ion dipole type of interaction (Table 2) in rate determining step.

The rate of oxidation increased on increasing the concentration of hydroxy acid (HA). Plot of $1/k_{obs}$ *versus* 1/[HA] is linear and passing through origin means no Michaelis-Menten type kinetics were observed and no reversible complex formation between acids and PCC. The rate of reaction increases with increasing H^+ concentration. Plot of log k_{obs} *Vs* log $[H^+]$ is straight line with slope ≈ 1 supports the idea that may be protonated PCC enhance the rate of oxidation.

There is no effect of ionic strength proves that in rate determining step ions are not involved. Increase in the percentage of 1,4-dioxane increase the rate, suggest that medium of low dielectric constant favors the reaction. Linear plots of log k_{obs} versus 1/D for both the acids confirm the ion-dipole type of interaction in rate determining step. Log k *versus* (D-1)/(2D+1) is a straight line (Laidler 1940), with negative slope indicates that activated state is less polar, while positive slope indicates more polar activated state. In our study we get negative slope indicate that activated state is less polar. Therefore, by increasing percentage of dioxane should increase which we have observed in both the acids. Rate of reaction was increased by increasing temperature. Various thermodynamic parameters are evaluated. Energy of activation and large and negative value of entropy suggest that α-C-H bond and formation of corresponding oxoacids as product. This fits in the criterion suggested by Narain and Bakore . The energy of activation ranges between 37 and 57 kJ mol^{-1}. Energy of activation does not correspond to carbon-carbon bond fission in the decomposition of organic substrates by Cr(VI) in rate-determining step. Calculation of activation parameters showed that these reactions are not enthalpy controlled. Lowest energy of activation is not associated with highest rate or vice versa.

Table 1. Variation of rate with substrate concentration

[PCC] = 2×10^{-3} M; Temp = 303 K

[Substrate] x 10^2 M	Lactic acid, K_1 x 10^4, sec^{-1} at $[H^+]$ = 0.5M	Mandelic acid, k_1 x 10^4, sec^{-1} at $[H^+]$ = 0.2M
1.0	4.03	4.61
1.5	5.77	6.39
2.0	7.81	8.27
2.5	9.83	10.41
3.0	11.44	12.28
4.0	15.91	14.62
5.0	20.02	18.35

Table 2. Variation of rate with solvent composition.
[PCC] = 2×10^{-3} M; Temp = 303 K; [HA] = 2×10^{-2} M

[Substrate] x 10^2 M	Lactic acid, K_1 x 10^4, sec^{-1} at $[H^+]$ = 0.5M	Mandelic acid, k_1 x 10^4, sec^{-1} at $[H^+]$ = 0.2M
0	7.87	8.27
10	10.9	7.94
20	13.12	13.18
30	14.62	13.72
40	19.5	17.42
50	33.20	26.02

CONCLUSION

Kinetic studies demonstrate that the intermediate unstable complex decomposes in the slow rate determining step to give the corresponding benzoic acid and phenyl acetaldehyde as the products. High dielectric constant of the medium facilitates the reactivity. The mechanism is further supported by the value of energy of activation and other thermodynamic parameters. The fairly high positive values of free energy of activation and enthalpy of activation indicates that the transition state is highly solvated, while the negative entropy of activation suggests the formation of the compact activated complex with fewer degrees of freedom.

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