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Physical Study on Catalysed Oxidation of Some Aromatic Hydroxyl Acid by N-Chlorosuccinimide in Aqueous Acetic Acid Medium

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ABSTRACT

Kinetics study of phosphotungustic acid catalysed oxidation of aromatic hydroxy acids para hydroxyl acid by N-chlorosuccinimide have been studied in aqueous acetic acid medium. The order of [N-chlorosuccinimide] was found to be one and fractional-order with respect to catalyst [PTA]. However, the order of [hydroxy acids] changed from unity to a fractional one in presence of PTA. The insignificant change in rate was observed with [H+] and neutral salts. The basis of kinetics features, the probable and activation mechanism are discussed and individual rate parameters evaluated.

Keywords: Investigation, variation, measurement, activation, phosphotungustic acid.

INTRODUCTION

N-chlrosuccinimide (NCS) a halo oxidant has been utilised as a chlorinating and oxidizing agent in synthetic organic compounds as well as analytical reagent especially in acid medium.[1,2] In recent development NCS has been extensively employed as an oxidant for a variety of organic substrates,[3] chalcones,[4] 2-hydroxy propanoic acid[5] (in alkaline medium) 9-telluraheptadecanoic acid,[6] alcohols,[7] benzyl phenyl ether[8] etc. During the past few decades, there has been an upsurge in the designing of a variety of catalysts to explore their utility in synthetic organic chemistry. A number of transition and platinum group metal ions have been used as a catalysts under homogeneous and heterogeneous reaction conditions. Microconcentration of PTA with Keggin type structure has been found as an efficient catalyst in a number of redox systems such as in oxidation of amines[9] , aromatic alcohol[10], benzhydrol.[11] etc. hydroxy acids are bi-functional compounds containing carboxylic and hydroxyl groups exhibit different mechanistic paths when studied by several oxidants. However, there seems to be no report on phosphotungustic acid acid-mediated oxidation of aromatic hydroxyl acid by NCS. In view of the above, we studied the kinetics of few aromatic hydroxy acids by NCS in aqueous acetic acid solutions under conditions using micro concentration of PTA as catalyst.

EXPERIMENTAL

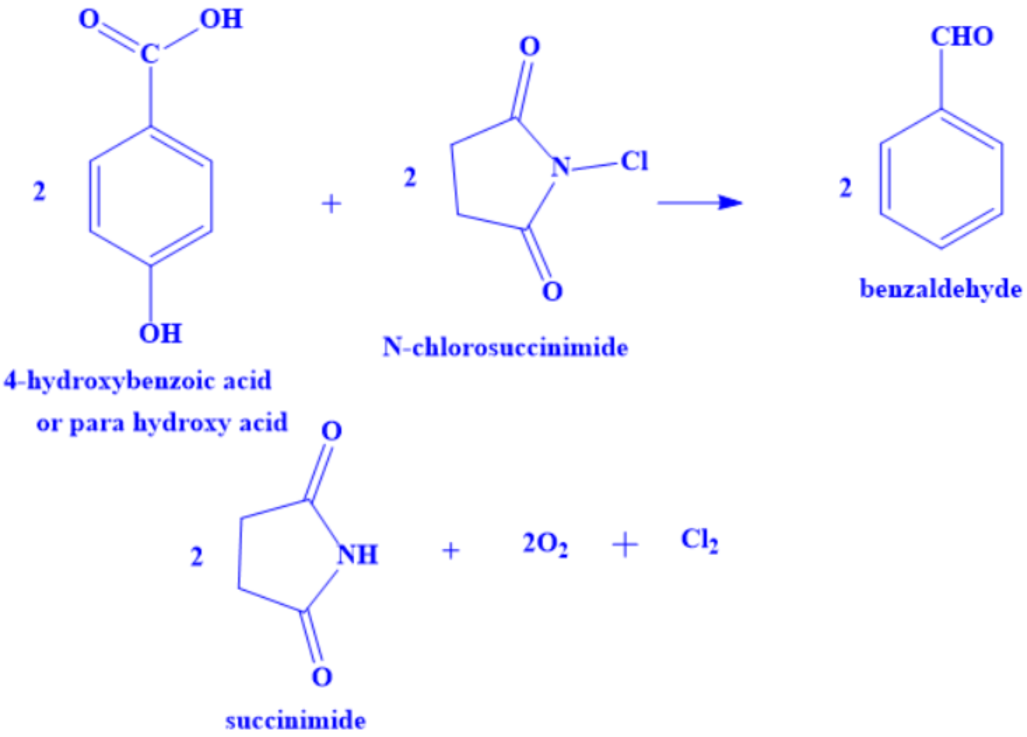
All chemicals and reagents used are of analytical grade. The solutions employed in the investigation were made by using fractionally distilled acetic acid and doubly distilled water. The solution of reagent phosphotungustic acid was prepared by evaporating a mixture of 10gm of sodium tungustate dissolved in 5gm of phosphoric acid and enough boiling water. The reaction mixture was cooled and resulting crystal of PTA is separated out.

KINETIC MEASUREMENTS

These were performed under pseudo first-order conditions with [hydroxy acids] at least ten times excess over [NCS] at constant ionic strength (μ) and desired temperature. The reaction was initiated previously thermostated solutions of NCS and hydroxy acid. The progress of the reaction was followed by iodometric [12] determination of the unreacted [NCS] for 80% of the reactions. The initial rates were evaluated from the tangential slopes of the plots of [NCS] versus time, which are reproducible within + 3%.

The study rules out the presence of free radicals in the system when tested by trapping method.

STOICHIOMETRY; of the reaction was determined by taking known excess of NCS over [HA] in aqueous acetic acid medium at experimental temperature. Final analysis indicated that one mole of HA consumed one mole of NCS for each substrate as is obvious from an exemplary empirical stoichiometric equation of lactic acid. The selective oxidations of hydroxy acids to their para hydroxyl acid to product aromatic aldehyde,succinimide were identified by U.V.[13] and chromatographic method.[14]

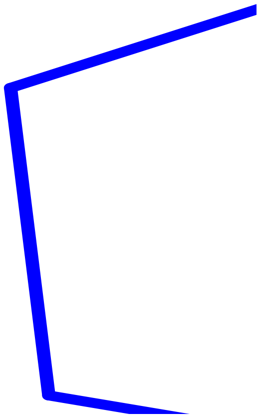


RESULTS AND DISCUSSION

The increase in [NCS] did not \affect the pseudo first-order dependence of the rate in all cases. The rate of oxidation initially accelerated with an increase in [substrate] and a first-order dependence of rate was observed. However, in the presence of phosphotungustic acid (PTA), the order with respect to [substrate] changed from 1 to a fraction at higher concentration of hydroxy acids. The double reciprocal plot of (k-1 versus 1/[substrate] (in PTA catalysed, NCS reaction) is linear with excellent corelationship. This observation confirms the formation of intermediate complex between active species of NCS and [PTA substrate]. No significant change in reaction rates, was observed with the variation of five fold variation of acidity. The Keggin type catalyst PTA indicated fraction-order rate and provide a kinetic evidence for complex formation with hydroxy acids. The proton released by PTA, get converted Keggin anion into oxidised form and acts as an outer sphere reagent is more probable transitions state. The reaction rates were found to decrease with an increase in the percentage composition of acetic acid decrease in dielectric constant of the solvent indicating ion-dipole inter action as compiled .The plot of log kobs versus the inverse of the relative permittivity (dielectric constant, D) is linear for all hydroxy acids with negative slope. A four-fold change in the concentration of KCl did not affect the rate of oxidation reaction to an any considerable extent, whereas the rate diminishes gradually by the [succinimide] of a reductant product added to the reaction. The plot of k-1 versus [succinimide] was obtained linear in each hydroxy acids.

MECHANISM

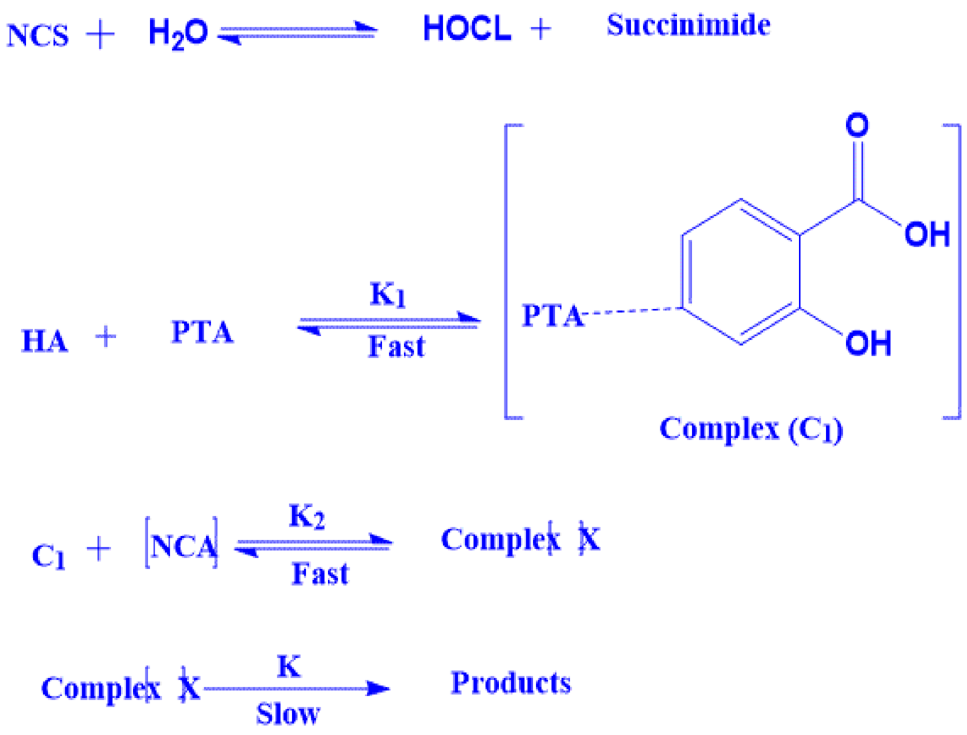
In order to gain an insight into the mechanistic path, it is essential to know the nature of the reactive species. NCS is known to exist in many forms in acid media namely, NCS itself, NCSH+ (protonated NCS), chloronium ion (Cl+) and HOCl.



The effect of variation of temperature has been studied to compute activation and thermodynamic parameters pertaining to the formation constant from known process Enthalpy of activation (ΔH#) is computed from Eyring plots while energy of activation is, obtained from Arrhenius equation. Entropy of complex formation has been obtained from Van't Hoff's equation, while free energy of formation obtained from Van't Hoff's relation isotherm protonated to yield oxonium salts. This discussion together with observed kinetics, and involvement of prime reacting species HOCl, substantiate a mechanism comprising slowest step.

The absence of free radicals, one to zero-order dependence on [substrate] is changed to PTA-catalysed system usually points out the intermediate complex formation with reacting species. One can visualize the complex formation of hydroxy acid with PTA. The PTA employed in study are known to form adduct with organic compounds due to partially filled d-orbitals. However, the solvent studies point out the rate is slow thus indicating the participation of ionic species in the rate limiting step. The most probable mechanism in PTA-catalysed system can be traced by taking para hydroxyl acid as a typical substrate.The reciprocals of (5) demand that plot of (1/k versus 1/[substrate]) should be linear with positive slope intercept on ordinate showing the validity of proposed mechanism. .The present study fit well with the one reported in oxidation of hydroxy acids by NBSA[16], NCSA[17] etc., which depicts the validity of a similar mechanism being operative in the probed system as their ΔG# values are quite high By and large ΔH# .values also show a similar trend. According to Hinshel-wood's classification of reaction series, it appears that ΔH# and ΔS # is important in controlling the reaction rate of above order in the present study.

RATE LAW; Based on kinetic results and the mechanis proposed, the following rate expression can be derived as:



In order to explain reactivity in terms of thermodynamic and activation parameters, we know that Ea (activation of energy) is the measure of reactivity of compound. The more reactive compound is expected to have lower value of Ea and vice-versa. The values of Ea obtained are well in accordance with the reactivity trends, supported by Arrhenius and Eyring plots made between log k versus 1/T and log $k_r h/k_B T$ versus 1/T The Gibb's free energy ($\Delta G^{\#}$) values are lying in the approximity between 87.25 to 88.81 kJ $mole^{-1}$ indicates that identical mechanism exists in between the reactions which is further confirmed by Exner's isokinetic plot[2] made between $\Delta H^{\#}$ and $-\Delta S^{\#}$ .The complex formed at the top of barrier of the transition state is governed by values of entropy of activation. The randomness, and rigidity are measured by entropy ($\Delta S^{\#}$) which is truely noticed in the reaction.The complex[3] formed is momentary, transient and unstable in nature and soon after decompose into the products. Overall in light of measured thermodynamic parameters, the reactions are enthalpy controlled.

CONCLUSION

The PTA catalysed oxidation of aliiphatic hydroxy acids have been reported with N-chlorosuccinimide. The cleavage of C-C of acids take place. HOCl was postulated as reacting species involved in the mechanism. The thermodynamic parameters suggested that reactions are both enthalpy and entropy controlled.

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