



Study on Catalysed Oxidation of Some Aliphatic Hydroxy Acids by N-chlorosuccinimide in Aqueous Acetic Acid Medium

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Abstract: The phosphotungstic acid catalysed oxidation of aliphatic hydroxy acids by halo-oxidant N-chlorosuccinimide (NCS) in aqueous acetic acid lead to the formation of corresponding acetone di-carboxylic acid and acetaldehyde. The reaction follows first to zero order kinetic with respect to [NCS] and rate unchanged by hydrogen ion. The rate of oxidation retards with decrease in dielectric constant of solvent. The study showed curvature due to of complex formation between substrates and postulated species HOCl of oxidant. The stoichiometric ratio 1:1 was determined for the reactions. The correlation between enthalpies and free energies of activation is reasonably linear. A suitable mechanism in conformity with kinetics results was proposed.

Keywords: Existence, conformity, excellent, symmetry, cage.

1. INTRODUCTION

Hydroxy acids are naturally occurring organic acids containing bi-functional groups. They are largely used in bio-chemical process in metabolism of all aerobic organisms. Hydroxy acids^[1] act as an antioxidant, by virtue of this property bio-chemically used as preservative in food industries, in purification of water, soaps, detergents and as material of biological tissue for imaging^[2] virus etc. Phosphotungstic acid ($H_3PW_{12}O_{40}$) a Keggin type catalyst easily releases proton and transform it to act as an outersphere oxidant. PTA is the strongest of heteropoly acids. Its conjugate base is the $[PW_{12}O_{40}]^{3-}$ anion^[3], has full tetrahedral symmetry and comprises a cage of twelve tungsten atoms linked by oxygen atoms with phosphorous atom at its centre. Its high acidity and thermal stability in acetic acid shows that the three protons dissociate independently rather than sequentially. The PTA catalysed^[4] oxidation of amines^[5], alcohols^[6,7], have already been acclaimed by few researchers.

Kinetic studies on the oxidation of α -hydroxy acids with several oxidizing agents such as Ag (II),^[8] Cr (VI)^[9], N-bromophthalimide^[10], N-bromosuccinimide^[11] in aqueous perchloric acid medium, alkaline hexacyanoferrate(III)^[12] and chloramines-T^[13] and $KBrO_3$ ^[14] in presence of Ru(III) in acidic medium have been reported. The literature studies revealed that the kinetic oxidation of citric acid and tartaric acid by N-bromoacetamide in perchloric acid and $IrCl_3$ as catalyst was reported.^[15] However the kinetics of oxidation of citric acid and malic acid by halo-oxidant N-chlorosuccinimide has not yet been probed. Hence this has initiated us to do the investigation in aqueous acetic acid medium using PTA as catalyst and also propose the reaction mechanism.

2. EXPERIMENTAL

All reagents and solvents used in this study were of analar grade. A fresh solution of N-chlorosuccinimide was prepared before installing the experiment. Other solutions of chemicals were prepared in doubly distilled water. The solution of phosphotungstic acid (PTA) was prepared by dissolving requisite amount of sodium tungstate in phosphoric acid. The kinetics and oxidation of citric acid and malic acid by NCS in aqueous acetic acid medium in presence of catalyst PTA was investigated under pseudo first-order conditions i.e., $[hydroxy\ acid] > [NCS]$ at their experimental temperature.

The kinetic study was performed by mixing the requisite amount of NCS, hydroxy acids acetic acid and PTA maintained at, desired temperature in a thermostat of sensitivity $\pm 0.1^\circ C$. The rate of reaction was determined from the concentration of the unconsumed [NCS] at different intervals of time by iodometry.

The rate constants were determined by integration and least square methods, from the linear plots of $\log [\text{NCS}]$ versus time. Replicate runs showed that rate constants were reproducible to within $\pm 3\%$.

The stoichiometry of the reaction was determined by allowing the reaction mixture containing varying amount of $[\text{NCS}]$ largely in excess over $[\text{hydroxy acid}]$. The estimation of unreacted NCS was carried out iodometrically. The observed stoichiometry of the reaction was calculated as $[\text{HA}]: [\text{NCS}] = 1:1$. The oxidative end-products were identified by existing conventional methods^[16] as acetone dicarboxylic acid and acetaldehyde.

3. RESULTS AND DISCUSSION

The rate and other experimental data were obtained for two aliphatic hydroxy acids viz. citric acid and malic acid. The kinetics study was carried out at several initial concentrations of the reactants in aqueous acetic acid medium in presence of catalyst PTA at constant temperature. The study showed first-order dependence on $[\text{oxidant}]$. The observed order with respect to varying $[\text{substrate}]$ was found 1 to 0 at their higher concentrations (Table 1). The values of second order $k_2 = k_1/[\text{HA}]$ do not show constancy. The double reciprocal plot between k^{-1} and $[\text{substrate}]^{-1}$ is also linear with positive intercept on Y-axis (Fig.1) provides an evidence for the formation of complex in a pre-equilibrium at transition state. The study shows unchanged rate on four to five fold varying $[\text{H}^+]$.

The increase in percent of acetic acid in the reaction mixture decreases the rate (Table 2). Plot of $\log k$ versus $1/D$ (D is the dielectric constant of the medium) is found to be linear with negative slope (Fig. 2) indicating the involvement of two dipoles are negative ions in reaction.

The reaction is catalysed within a certain limit of $[\text{PTA}]$ and indicate fractional order dependency of rate on higher concentration of PTA. It has ability to form complex with substrate, and act as an chelating agent in metal binding. The protons released during the reaction by PTA are responsible for protonation of NCS. The catalyst $[\text{PW}_{12}\text{O}_{40}]^{3-}$ Keggin on gets converted into oxidised form in formation of complex by the replacement of one of the water molecule of hydration, which is more probable transition state. Oxidation of substrate by heteropoly anions occurred is a overlap of with tungstate frame work.

The influence of NaCl and KCl almost found negligible effect on rate of oxidation. It is evident that inhibition in rate of oxidation occurs with increase in $[\text{succinimide}]$, a reductant product of NCS in all the hydroxy acids under investigation. Various thermodynamic parameters were evaluated at four different temperatures for the system.

Table1. Effect of variation of concentration of substrate

$10^3 [\text{NCS}] (\text{mol}^{-1} \text{ dm}^3) = 2.50 (1,2) ;$

$10^4 [\text{PTA}] (\text{mol}^{-1} \text{ dm}^3) = 4.0 (1,2) ;$

$\text{HOAc-H}_2\text{O}, \% (\text{V/V}) = 50 (1), 20 (2) ;$

Temperature $K = 303 (1), 313 (2)$

S. No.	[Substrate] $\times 10^2$ (mol dm^{-3})	Citric acid	Malic acid
		(1)	(2)
		$\leftarrow 10^4 k_1 (\text{s}^{-1}) \rightarrow$	
1	1.0	-	1.63
2	1.25	1.43	-
3	2.0	1.96	2.40
4	2.50	2.32	2.74
5	3.33	2.85	3.17
6	4.00	3.05	4.53
7	5.00	3.48	3.82
8	6.66	3.73	3.95
9	10.0	4.15	-

1. Citric acid (CA); 2. Malic acid (MA)

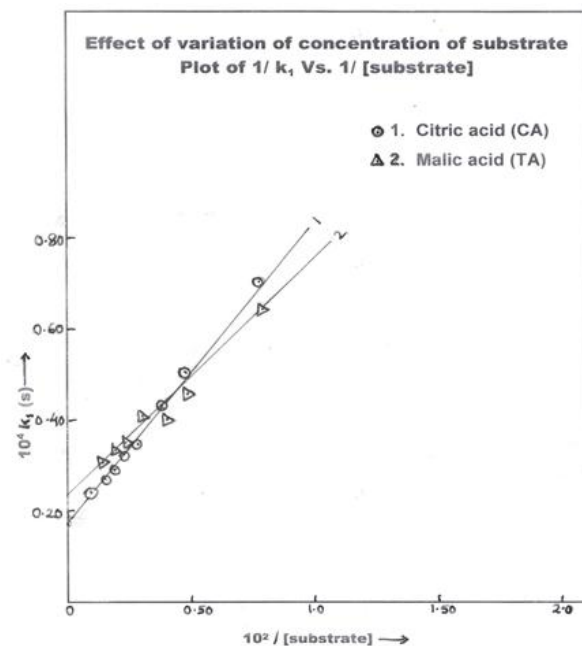


Fig1. $10^3 [\text{NCmol}^{-1} \text{dm}^3] = 2.50 (1,2)$; $10^4 [\text{PTA}] (\text{mol}^{-1} \text{dm}^3) = 4.0(1,2)$; $\text{HOAc-H}_2\text{O. \% (V/V)} = 50 (1), 2.0(2)$;

Table2. Effect of solvent composition

$10^2 [\text{substrate}] (\text{mol}^{-1} \text{dm}^3) = 5.0 (1), 4.0 (2)$; $10^3 [\text{NCS}] (\text{mol}^{-1} \text{dm}^3) = 2.50 (1,2)$;

$10^4 [\text{PTA}] (\text{mol}^{-1} \text{dm}^3) = 4.0 (1,2)$; Temperature K = 303 (1), 313 (2)

S. No.	HOAcH ₂ O, % (v/v)	$\frac{10^3}{D^{\text{eff}}}$	Citric acid (1)	Malic acid (2)
			$\longleftarrow 10^4 k_1 (\text{s}^{-1}) \longrightarrow$	
1	10	15.50	-	4.65
2	20	17.18	4.68	4.53
3	30	19.16	4.41	4.17
4	40	21.98	3.95	3.81
5	50	30.86	3.48	2.96

1. Citric acid (CA); 2. Malic acid (MA)

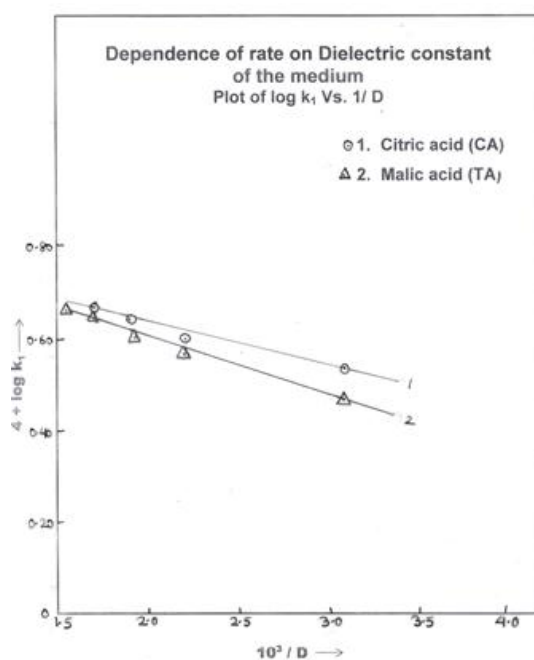
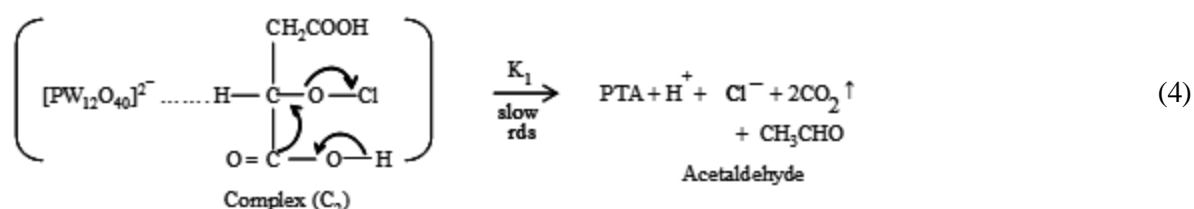
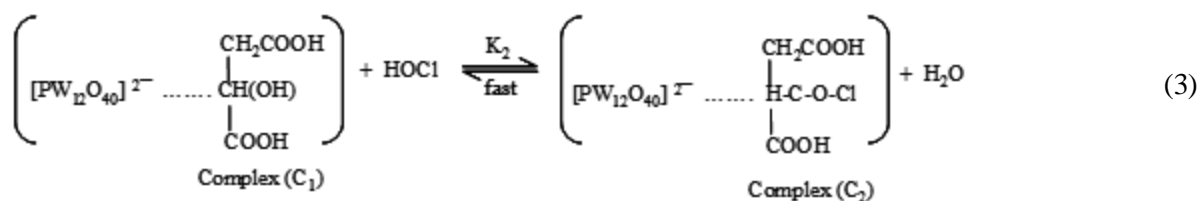
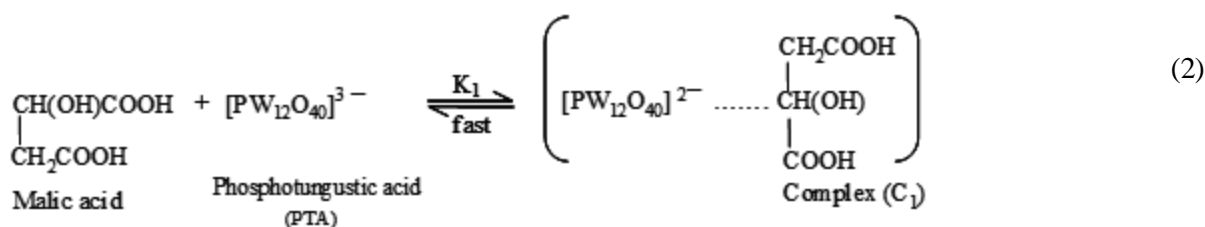
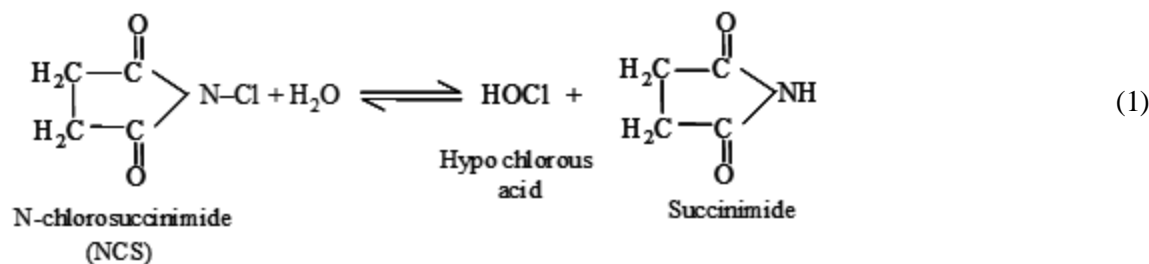


Fig2. $10^2 [\text{substrate}] (\text{mol}^{-1} \text{dm}^3) = 5.0(1), 4.0 (2)$; $10^3 [\text{NCS}] (\text{mol}^{-1} \text{dm}^3) = 2.50 (1,2)$; $10^4 [\text{PTA}] (\text{mol}^{-1} \text{dm}^3) = 4.0 (1,2)$; Temp.K = 303 (1), 313 (2)

3.1. Mechanism and Rate Law

Under the experimental conditions, the possible active species^[17] are Cl_2 , HOCl , $\text{H}_2\text{O}^+\text{Cl}$ and NCSH^+ in aqueous solution. On the basis of observed facts, HOCl was assumed to act as the effective oxidizing species

The reaction mixture fails to initiate polymerization of aqueous acrylonitrile solution indicating that the free radicals is unlikely in the present reaction. The following an exemplary of mechanism of malic acid is proposed:



Considering various steps involved in the mechanism and applying steady state approximation, the rate law is deduced:

$$\text{Rate} = \frac{k K_1 K_2 [\text{PTA}] [\text{HA}]}{1 + K_1 [\text{HA}] + K_1 K_2 [\text{HA}]} \quad (5)$$

The above rate law accounts for the first-order rate on oxidant and first to zero order dependence on [substrate] at assumed different conditions of it explains fully the involved complex mechanism.

The observed order of reactivity was found in sequence:

Malic acid > Citric acid

The solvent rate of citric acid is due to the more branching and bulky dormancy of weak steric effect which suppress the rate of oxidation. Similar pattern of reactivity has also been reported by a couple of authors.^[18]

4. CONCLUSION

Kinetic studies demonstrate that the intermediate complex was formed whose existence was momentary, unstable, decomposes (of C-C bond) in the slow rate determining step to give the

corresponding acetone dicarboxylic acid and acetaldehyde as the end-products. High dielectric constant of the medium facilitates the reactivity. The mechanism is supported by the thermodynamic parameters. The fairly high positive values of free energy of activation (ΔG^\ddagger) (86.45 to 88.58 kJ mol⁻¹) indicates that the transition is highly solvated and a similar mechanism, prevail in them. While the large negative entropy of activation ($-\Delta S^\ddagger = 122.06$ to 124.95 JK⁻¹ mol⁻¹) suggests the formation of the compact activated complex capability of HA with HOCl with fewer degrees of C–C bond fission freedom. Energy of activation (E_a) 60.18 kJ mol⁻¹ of malic acid is less than E_a (61.09 kJ mol⁻¹) of citric acid. Hence explains the proposed order of reactivity and indicate that reactions are enthalpy controlled.

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