

Tungustophosphoric acid catalyzed oxidation of some α -amino acids by N-chlorosuccinimide

Anamika Singh^{1*}, H.P. Dwivedi¹

1. Department of Chemistry, Government S.G.S., Govt. P.G. College, Sidhi-486661 (M.P.) India.

Abstract: We describe the tungustophosphoric acid (Keggin anion type) catalyzed oxidation of a couple of *l*-alanine and *l*-leucine by N-chlorosuccinimide in aqueous acetic acid medium resulting to the formation of corresponding aldehydes. The reaction proceeds through formation of transient existence of ternary complex in equilibrium state. The ternary complex in equilibrium state. The stoichiometry $\frac{\Delta[\text{NCS}]}{[\alpha\text{-amino acid}]}$ (1:1) is in good agreement supported by rate law as first-order to [NCS] oxidant and fractional-order each to [TPA], $[\text{H}^+]$ and [*l*-amino acids]. The participation of Zwitter ion and postulated reacting species HOCl was involved in the proposed plausible mechanism. The role of activation parameters was discussed in favour of mechanism.

Key words: Tungustophosphoric acid, *l*-alanine, *l*-leucine, N-chlorosuccinimide, oxidation.

1. INTRODUCTION

N-chlorosuccinimide belong to N-halo compound and is a mild oxidant synthesized by chlorination of succinimide and produces hypohalous acids in aqueous solution.^[1] Recently NCS has been used successfully as an effective oxidizing agent halogenation dehydrogenation,^[2,3] and oxidations of chalcones,^[4] acid,^[5,6] alcohols,^[7] hydroxy acids etc. Amino acid contain non-polar groups, polar acidic or basic substituents exist as a capability of Zwitter ion forming intermediate with oxidant species.^[9] Although a related studies of α -amino acids have been earlier reported by different oxidants.^[10-13] Tungustophosphoric acid (Keggin^[14] type structure) (TPA) is the strongest heteropoly acid propel it as a catalyst of choice.^[15] The efficiency of catalyst TPA homogeneous and can be visualized from the reported oxidation studies of organic substrates involving it in amines,^[16] alcohol^[17-19] etc.

The surveyed literature reveals that no much reports are available or documented about the TPA catalysed oxidation of α -amino acids by N-chlorosuccinimide hence we thought noteworthy to reports the results of above entitled topic in context of kinetic investigation.

2. EXPERIMENTAL

All the chemicals used were of reagent grade. The solution of oxidant N-chlorosuccinimide (Aldrich sigma) was prepared in acetic acid (B.D.H.) and standardized daily by iodometric process as decomposition occurred on standing for a long time or exposure to light. This problem was minimized by storing the solution in brown flask. The solutions of *l*-alanine and *l*-leucine (CDH) were used as such received and prepared in distilled water and acetic acid. The TPA solution was prepared as mentioned in literature^[14] (loc. cit.).

Kinetic measurements

All kinetic studies were made under pseudo first-order condition by keeping large excess of [α -amino acid] over [NCS]. The reaction mixture containing known amounts of solutions of α -amino acid, TPA and mineral acid in definite composition of acetic acid water were equilibrated at their desired temperatures.

The reaction was initiated by mixing thermostated ($\pm 0.1\text{K}$) solution of the NCS. The reaction kinetics was monitored by the iodometric procedure followed with drawing aliquots of the reaction mixture at regular intervals of time. The replicate kinetic runs showed that rate constants k_{obs} were reproducible $\pm 3\%$.

Stoichiometry and Product analysis

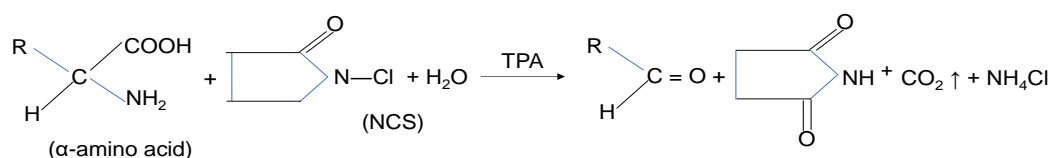
The stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing $15 \times [\text{NCS}]$ over [α -amino acid] in acetic acid and other reagents at their experimental temperatures. The estimation of unreacted [NCS] revealed 1:1 stoichiometric ratio $\frac{\Delta[\text{NCS}]}{[\alpha\text{-amino acid}]}$ as conformed by the equation.

where R = $-\text{CH}_3$ and $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ for alanine and leucine respectively.

The corresponding aldehydes were identified by chemical tests and by forming their 2:4-DNP derivatives. The one electron based free radicals mechanism is ruled out as the test in reaction mixture by added monomer polymer acrylonitrile was found negative.

3. RESULTS AND DISCUSSION

The variation of 5X concentrations of [NCS] was to be linear ($R^2 > 0.096$) made and Graphic plots of $\lg(a-x)$ against time found indicating first-order dependence of reaction rate as k_{obs} evaluated for all α -amino acids.



The double reciprocal plots $1/k_{\text{obs}}$ vs. $1/[\alpha\text{-amino acid}]$ is obtained line as intercepting on the ordinate (Table 1) indicating that order with respect to substrate is 1 to 0 verifying Michaelis-Menten equation for the reaction between Zwitter ion and HOCl reacting species of NCS. The addition of multi fold concentrations of mineral acid $[\text{H}^+]$ ion to the reaction did not bring out any meaningful change in rate. The oxidation was investigated in aqueous acetic acid medium and no reaction was seen with chosen solvent. The study reveals that k_{obs} retards by rising percentage content of acetic acid. The plots of $\log k$ vs. $D-1/(2D+1)$ (Fig. not shown) was yielded negative intercept proves the involvement of two dipoles in reaction kinetics.

Table 1: Dependence of rate on variation of $[\alpha\text{-amino acid}]$ at 303 K

$10^3 \times [\text{NCS}]$ (mol dm⁻³) = 3.33 (1, 2) ; $[\text{H}^+]$ (mol dm⁻³) = 0.666 (1-2) ;

$10^4 \times [\text{TPA}]$ (mol dm⁻³) = 4.0 (1-2) ; $\text{CH}_3\text{COOH-H}_2\text{O}$ %, (v/v) = 40 (1), 50 (2) ;

$10^2 \times [\alpha\text{-amino acid}]$ (mol dm ⁻³)	$10^4 k$ (s ⁻¹)	
	ℓ -alanine (1)	ℓ -leucine (2)
1.00	1.65	-
1.25	-	2.07
1.50	2.17	-
1.66	-	2.71
2.00	2.82	3.20
2.50	3.07	-
3.33	3.46	3.62
4.00	3.70	4.26
5.00	3.68	4.10

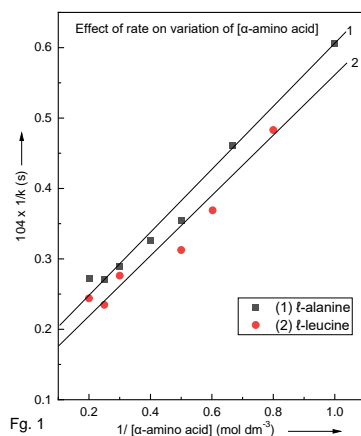


Fig. 1
Double reciprocal plot of k^{-1} vs. $[\alpha\text{-amino acid}]^{-1}$
 $10^3 \times [\text{NCS}] = 3.33$ (1-2) ; $[\text{H}^+]$ (mol dm⁻³) = 0.666 (1-2) ;
 $10^4 \times [\text{TPA}]$ (mol dm⁻³) = 4.0 (1-2) ;
 $\text{CH}_3\text{COOH-H}_2\text{O}$ %, (v/v) = 40(1), 50 (2)

The effected of tungstophosphoric acid was varied at fixed $[\alpha\text{-amino acid}]$ alongwith taking part reagent in reactions at fixed temperature (Table 2). The kegging anion type catalyst accorded a kinetic evidence for the formation of ternary complex with α -amino acid and active species of NCS is more probable in the transition state. The plot of $[\text{TPA}] \times \frac{1}{k_{\text{obs}}}$ vs. $\frac{1}{[\alpha\text{-amino acid}]}$ giverise slope less then unity indicating fractional-order dependence of rate on [PTA] at its higher concentration. The influence of salt effect and succinimide had exhibited almost negligible effect on rate. This study reveals that succinimide a reductant product of oxidant does not act as reacting species.

Table 2: Dependence of rate on [TPA] catalyst at 303 K

$10^3 \times [\text{NCS}]$ (mol dm⁻³) = 3.33 (1-2) ; $[\text{H}^+]$ (mol dm⁻³) = 0.666 (1-2) ;

$10^4 \times [\text{TPA}] (\text{mol dm}^{-3}) = 6.25$ (1-2); $\text{CH}_3\text{COOH-H}_2\text{O} \%$, (v/v) = 40 (1), 50 (2);

$10^2 \times$ [α -amino acid] (mol dm^{-3})	10^2 [α -amino acid] (mol dm^{-3})	$10^4 k (\text{s}^{-1})$	
		ℓ -alanine	ℓ -leucine
1.25	0.8000	2.75	-
1.50	0.6666	2.53	2.39
1.66	0.6024	-	2.03
2.00	0.5000	-	1.83
2.50	0.4000	1.82	-
3.33	0.3003	1.65	1.49
4.00	0.2500	1.50	1.38
5.00	0.2000	1.41	1.26

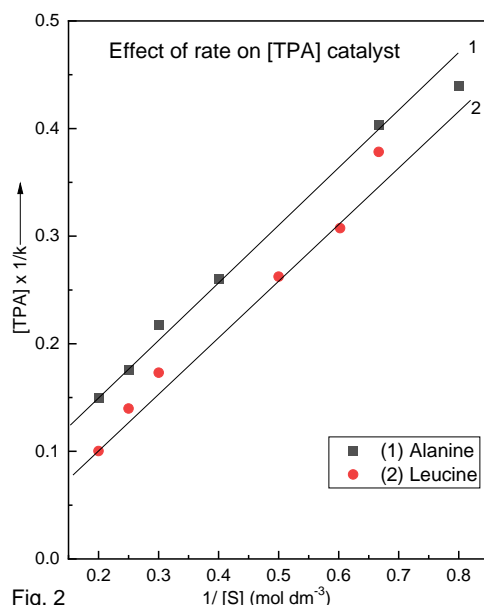


Fig. 2

Plot of $[\text{TPA}] / k$ vs. $1/[\text{S}]$

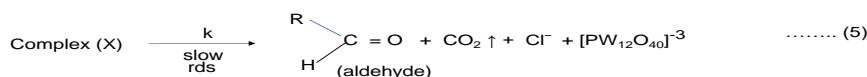
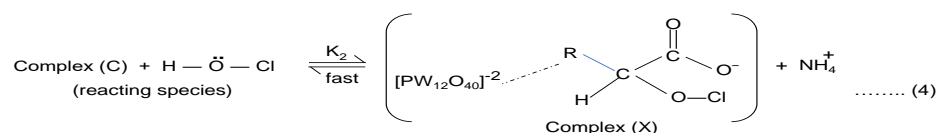
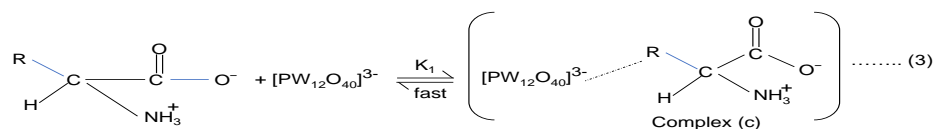
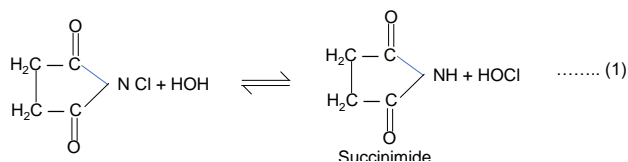
$10^3 \times [\text{NCS}] = 3.33$ (1-2); $[\text{H}^+] (\text{mol dm}^{-3}) = 0.666$ (1-2);

$10^4 \times [\text{TPA}] (\text{mol dm}^{-3}) = 6.25$ (1-2);

$\text{CH}_3\text{COOH-H}_2\text{O} \%$, (v/v) = 40(1), 50 (2)

Mechanism

The TPA catalysed oxidation mechanism of the reaction between pre-dominant species of α -amino acid and NCS may be synchronised as :



Based the above steps involved in mechanism and execution of study state condition the rate expression can be obtained as :

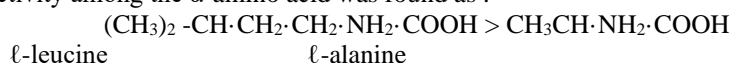
$$k_{obs} = \frac{k K_1 K_2 [TPA] [S]}{1 + K_1 [S] + K_1 K_2 [S]} \dots\dots (6)$$

The equation (6) be transformed in to the rearrange equation (7) at fixed [substrates].

$$[TPA]x \frac{1}{k_{obs}} = \frac{1}{k K_1 K_2 [S]} + \frac{1}{k K_2} \dots\dots (7)$$

The reciprocal of equation (6), satisfied Michaelis-Menten type kinetics and equation (7) strongly favoured the formation of ternary complex of transient time.

The observed order of reactivity among the α -amino acid was found as :



The structural domaincy of reactivity was supported by inductive effect that causes the fission of bond expelling protons, deamination, total electron density on carbonation ad the replacement of group by the group of higher degree of branching responsible for enhancement of the above order.

The value of activation energy (Ea) is lowest for fastest reaction (Table 3) and vice versa. The observed ΔS^\ddagger values are large negative interpreted that fraction of collisions becomes more stringent and decomposition of activated complex is a quite. Slow process. The polar nature of complex is due to loss of transitional energy that occur. The close values of ΔG^\ddagger indicate that similar mechanism prevail in them.

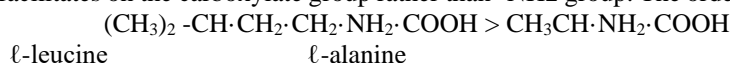
Table 3: Thermodynamic and activation parameters for the TPA catalysed reaction between ℓ -amino acid and N-chlorosuccinimide

ℓ -amino acid	Ea (kJ mol ⁻¹)	A (s ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)
ℓ -alanine	37.57	4.71×10^2	33.02	85.47	171.67
ℓ -leucine	34.73	2.84×10^2	31.02	85.14	177.16

Summing up of al ΔH^\ddagger and ΔS^\ddagger values of above order in the present study, this is not unjustified that reactions are both enthalpy and entropy controlled.

Conclusions

The kinetic results reveals that transient existence of ternary complex disproportionates in a slow rate determining step process to yield acetaldehyde and iso-veraldehyde as the main products. HOCl was postulated in as a prime active species of oxidant NCS. The attack of electrophile facilitates on the carboxylate group rather than -NH₂ group. The order of reactivity follows the sequence:



The derived rate law is in well consistence with the first-order to [NCS] and [α -amino acids] and energy of activation. The polar intermediate complex leads to the immobilization of solvent molecules around the charged ends which results in to the loss of entropy as noticed in the present case.

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Conflict of Interest

The authors declare conflict of no interest whatsoever.

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