Kinetics of L-Tryptophan Oxidation in Acidic Medium using TMGCC: A Comprehensive Study

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ABSTRACT

Kinetics for the oxidation of L-tryptophan in a sulphuric acid medium by 1,1,3,3, -tetramethylguanidinium chlorochromate [TMGCC] has been investigated. The results of the experiment suggest that the intermediate complex formed between the protonated L-tryptophan and TMGCC, then decomposes in the rate-determining step to give the reaction products. The final oxidation products received were identified as indole-3-acetaldehyde, NH_4^+, and CO_2. First-order dependence on TMGCC, and a fractional order dependence on L-tryptophan have been found for the reaction. The thermodynamic parameters such as activation energy, entropy, and free energy were evaluated accordingly. A suitable mechanism has been proposed for the reaction.

Keywords: Tryptophan, Kinetics, Oxidation, Mechanisms.

INTRODUCTION

L-Tryptophan (L-Trp), an essential amino acid, plays a vital role in various biological processes, including protein synthesis and the production of neurotransmitters such as serotonin. Its oxidation is of considerable interest not only due to its physiological significance but also because it can lead to the formation of various bioactive compounds, some of which may have implications in human health and disease.

The study of L-Tryptophan oxidation is crucial for understanding its reactivity and the subsequent effects on biological systems [1-5]. In acidic media, L-Tryptophan undergoes oxidation through various pathways, leading to the formation of oxidized products that can impact its biological functions. The kinetics of this oxidation process are influenced by multiple factors, including pH, temperature, and the presence of catalysts. Understanding these kinetics is essential for both theoretical insights into amino acid reactivity and practical applications in pharmaceutical and biotechnological fields. The findings of this study will contribute to a deeper comprehension of L-Tryptophan's behaviour in oxidative environments, highlighting its significance in both health and disease contexts.

1,1,3,3, -tetramethylguanidinium chlorochromate (TMGCC) has garnered attention for its effectiveness in facilitating chemical reactions, including oxidation processes [6]. Their unique properties make them suitable for investigating the kinetics of L-Tryptophan oxidation under acidic conditions. This research article aims to explore the kinetics of L-Tryptophan oxidation in acidic media using TMGCC as a catalyst.

MATERIALS AND METHODS

Materials

The chemicals used in the research work are of high purity grade. TMGCC was freshly prepared before carrying out the experiment work in the laboratory as reported [6], and a check of purity was ascertained by an iodometric method [7]. L-tryptophan was used directly as received from Merck. Standard methods were used for the purification of solvents [8].

Product analysis:

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In the oxidation of L- tryptophan by TMGCC, the final product is the carbonyl compound, and it was tested by 2,4 DNP test [9] by the addition of 2,4- dinitrophenylhydrazine to the mixture, which gave a yellow precipitate, thus confirming quantitatively the presence of the carbonyl compound. The product mainly identified was indole-3acetaldehyde as tested by the spot test [10]. Cr (IV) was identified using the iodometric method. The by-products formed during the reaction were identified as carbon dioxide gas and ammonium ion, where the carbon dioxide gas was tested by limewater, and ammonium ion got tested using Nessler's reagent [11]. Other oxidation products having similarities with different experimental conditions have been received as mentioned in previous studies [12– 16].

Kinetic Measurements

The concerned investigations were performed on kinetics under the usual pseudo-first-order conditions by keeping the concentration of L-tryptophan at more than the concentration of TMGCC. The temperature of the reaction was controlled at 25^0C with an accuracy of $\pm 0.2^0$C. The TMGCC solution and a mixture having tryptophan and sulphuric acid, both were thermostated separately for almost 2 hours. The above-mentioned solutions were allowed to mix and then they were transferred to the cell and then subsequent 3 to 4 experimental readings were collected. The rate of consumption of Cr (VI) was checked by decrease in absorption using a spectrophotometer at its absorption maximum, k_{max} = 350 nm, where Cr (VI) absorbs to a noticeably greater value as compared to any other reactants and products, as the function of time and it was thus verified using UV-Vis spectrophotometer having cell at constant temperature. For pseudo-first order rate constant, the k_{obs} was assessed using a gradient between ln(A) and time from the following equation given below:

$$\log_e(A_t - A_\infty) = \log_e(A_0 - A_\infty) - K_{obs}.\, T \qquad (1)$$

{A_t is the absorbance of the reaction mixture measured at time t.

and A_∞ is the absorbance of the mixture measured at equilibrium.}

A_∞ was measured as soon as the reaction got completed. Then the k_2 (second order rate constant), was evaluated using the relation given below:

$$k_2 = k_{obs} / [\text{L- tryptophan}]$$

RESULTS AND DISCUSSION

Stoichiometry

Stoichiometry of reaction between the L- tryptophan and TMGCC in sulphuric acid medium was found in the ratio of 1:1. TMGCC underwent two-electron change and with the earlier observations it is in accord with structurally similar other halo-chromates.

The overall equation for the L-tryptophan's oxidation by TMGCC in H_2SO_4 (acidic medium) can be represented as follows:

$$\text{L-tryptophan} + \text{TMGCC} \xrightarrow[H_2O]{H^+} \text{Indole-3- acetaldehyde} + \text{Cr(IV)} + NH_4^+ + CO_2 \qquad (2)$$

Order of Reaction

The reaction order(n) was calculated using the slope of the plots between logk_{obs} and log(concentration) by changing the concentrations(C) of substrate and acid, and making other conditions constant. The [TMGCC] was varied by keeping others at a fixed concentration. The pseudo-first-order rate constant, k_{obs}, was calculated using gradient from ln(A) versus time plots. It was confirmed from the above data that the reaction is of order first with respect to [TMGCC]. The k_{obs} was also calculated at diverse initial concentrations of the tryptophan by keeping

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concentrations of others constant. A linear plot of k_{obs} against [L-tryptophan] indicated that the reaction's order was less than one with respect to [L-tryptophan] and its intercept was positive.

Rate-laws:

A typical kinetic run proved that the reactions with respect to TMGCC are of first order Figure 1. The pseudo-firstorder rate constant, k_{obs} is not dependent on the initial concentration of TMGCC. A linear plot of $1/k_{obs}$ against 1/[L- tryptophan] obtained with the intercept on the y-axis, with $r > 0.995$ and to further prove this fact MichaelisMenten reaction was applied to the L- tryptophan (Trp), leading to the generalization of the following reaction mechanisms 3 & 4 obtained, where the depiction of the following rate law is shown by equation 5 as follows:

$$\text{Try} + \text{TMGCC} \underset{}{\overset{K,H^+}{\rightleftharpoons}} [\text{Complex}] \quad (3)$$

$$[\text{Complex}] \xrightarrow{\text{Slow}} \text{Products} \quad (4)$$

$$\text{Rate} = k_2 [\text{Try}] [\text{TMGCC}] / (1 + K [\text{Try}]) \quad (5)$$

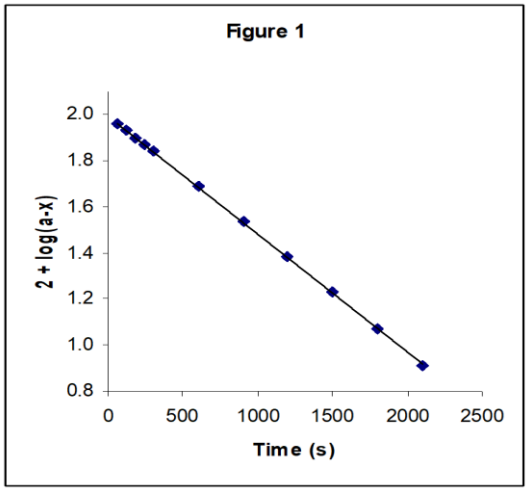

FIGURE 1: Oxidation of Tryptophan by TMGCC: A typical kinetic run

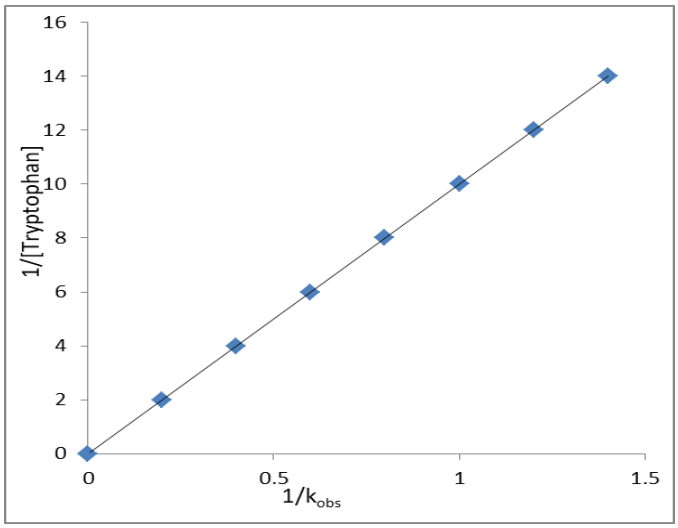

FIGURE 2: Oxidation of Tryptophan by TMGCC: A double reciprocal plot Test for free radicals:

The polymerization test was employed to check the presence of the free radical species formed during the reaction. It was performed by taking a known quantity of acrylonitrile with the mixture of the reaction and was thus kept for approximately 3 hours. Mixture's dilution using methanol did not resulted in any white precipitate, which supported the absence of free radicals in the reaction mixture. Further, it was reinforced by the fact that

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the reaction's rate does not change with the addition of acrylonitrile Table 1. This completely ruled out the prospect of oxidation of only a single electron giving rise to the involvement of free radicals.

TABLE 1: Effect of variation of [TMGCC)], [Trp], on the observed rate constant in the oxidation of L-tryptophan by TMGCC in sulphuric acid solutions at 298K.

[TMGCC] (mol/dm^3)	10^3 [Trp] (mol/dm^3)	[H^+] (mol/dm^3)	10_4 k_{obs} (1/s)
1.0	0.02	0.10	2.50
1.0	0.03	0.10	3.14
1.0	0.05	0.10	4.60
1.0	0.10	0.10	6.40
1.0	0.20	0.10	8.30
1.0	0.30	0.10	9.50
0.3	0.05	0.10	4.80
0.5	0.05	0.10	4.70
0.8	0.05	0.10	4.67
1.0	0.05	0.10	4.60
2.0	0.05	0.10	4.90
1.0	0.10	0.10	6.47*
*Contained Acrylonitrile (0.001 mol/dm^3)			

Effect of Temperature:

The influence of temperature on the reaction rate was examined at four different temperatures, namely 288, 298, 308, and 318 K**,** while maintaining constant conditions for all other variables except the concentration of sulfuric acid. The results indicated that the rate of reaction increases with rising temperature, demonstrating a direct relationship between temperature and reaction rate. The kinetic data obtained at these temperatures were used to calculate the values of formation constant (K) and rate constant (k_2).

Thermodynamic Parameters:

The thermodynamic parameters for the complex formation and the activation parameters of the decomposition of the Trp-TMGCC complexes had been calculated using K and k_2 values at various temperatures.

The data obtained for formation constant, thermodynamic parameters, rate constant, and activation parameters are depicted in Tables 2 and 5.

TABLE 2: Formation constant for the Trp-TMGCC complexes.

K (dm^3/mol)			
288 K	298 K	308 K	318 K
20.5	17.4	14.2	10.9

TABLE 3: Thermodynamic Parameters for formation of Trp -TMGCC complexes.

−ΔH (kJ/mol)	−ΔS (J/mol K)	−ΔG (kJ/mol
10.2 ± 0.3	± 8 ± 2	4.5 ± 0.3

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TABLE 4: Rate constants (k_2) for the decomposition of the Trp-TMGCC complexes.

10^4 k_2(dm^3/mol s) at			
288 K	298 K	308 K	318 K
4.81	10.2	21.8	48.5

TABLE 5: Activation Parameters for the oxidation of Tryptophan by TMGCC.

$\Delta H^{\#}$ (kJ/mol)	$-\Delta S^{\#}$ (J/mol K)	$\Delta G^{\#}$ (kJ/mol)
31.8 ± 0.8	44 ± 3	43.2 ± 0.8

Effect of Acidity:

As reported in the literature survey that the amino acid exists as zwitter ion at pH of 7 and predominantly tends to protonate at pH <7. The employment of a high concentration of hydrogen ions during the reaction and also the observed augmentation of reaction's rate on increasing acid's concentration recommended the protonation of Ltryptophan in the step before equilibrium, whereas the protonated form (Trp^+) appeared as reactive in the slow step.

Varying the concentration of acid and keeping others constant, found that the concentration of acid was seen to catalyze the rate of reaction. It was indicated by Table 6, that the process of oxidation was catalyzed by acid.

TABLE 6: Dependence of reaction rate on hydrogen ion concentration at 298K.

[TMGCC] (mol/dm^3)	10^3 [Trp] (mol/dm^3)	[H^+] (mol/dm^3)	10^4 k_{obs} (1/s)
1.0	0.10	0.02	1.25
1.0	0.10	0.03	1.90
1.0	0.10	0.04	2.58
1.0	0.10	0.06	3.70
1.0	0.10	0.10	6.46
1.0	0.10	0.20	12.3

Solvent Effect:

The effect of the solvent can be described in terms of solvation, as solvent plays an important role during reactions. Here, L-tryptophan's oxidation has been considered in various types of solvents. In all of the selected solvents, the same type of kinetics has been observed, and the values of second-order rate constants, k_2, have been presented in Table 7.

TABLE 7: Effect of solvent at 298K.

Solvents	K (dm^3/mol)	k_2 (1/s)
Chloroform	16.8	3.06
1,2-dichloroethane	17.2	3.62
DCM	16.6	3.52

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DMSO	17.4	10.8
Acetophenone	17.0	3.25
DMF	17.5	5.78
Butanone	16.7	2.38
Nitrobenzene	17.1	4.27
Benzene	16.5	1.20
Cyclohexane	17.3	0.13
Toluene	16.3	0.90
Acetophenone	17.6	5.02
Tetrahydrofuran	18.0	1.60
tert-Butyl alcohol	16.7	1.27
1,4-Dioxane	16.9	1.71
1,2-Dimethoxyethane	17.8	0.85
Acetic acid	16.6	0.60
Ethyl acetate	17.7	1.30
Carbon disulfide	17.5	0.45

Kamlet presented equation [17] for the rate constant in terms of linear solvation energy relationship, which has been given below Equation 6 where the π, α, β (solvatochromic parameters) are characteristic of various solvents.

$$\log k_2 = A_0 + p\pi + a\alpha + b\beta \quad (6)$$

Here π indicates the polarity of solvent (a measure of the ability of solvent to stabilize a charge or dipole due to its dielectric effect), β indicates the hydrogen bond acceptor basicity (the ability of solvent to donate an electron pair or in a hydrogen bond to accept a proton) and α indicates the hydrogen bond donor acidity (where solvent either donate a proton or accept electron pair in hydrogen bond which is in between solute to solvent) and A_0 is the term of intercept. Here the coefficient of determination (r^2), standard deviation (SD), and Exner's statistical parameter [18], (ψ) has been used to correlate analyses. Results thus obtained from biparametric equation 6 has been given by the following equations 7-10:

$$\log k_2 = -4.81 + (1.62 \pm 0.19)\,\pi - (0.13 \pm 0.14)\,\alpha + (0.18 \pm 0.14)\,ß \quad (7)$$
$$r^2 = 0.8652,\ SD = 0.17,\ n = 18,\ \psi = 0.40$$

$$\log k_2 = -4.54 + (1.70 \pm 0.18)\,\pi - (0.13 \pm 0.16)\,ß \quad (8)$$
$$r^2 = 0.8474,\ SD = 0.18,\ n = 18,\ \psi = 0.41$$

$$\log k_2 = -4.50 + (1.70 \pm 0.17)\,\pi \quad (9)$$
$$r^2 = 0.8474,\ SD = 0.18,\ n = 18,\ \psi = 0.41$$

$$\log k_2 = -4.38 + (0.43 \pm 0.35)\,ß \quad (10)$$
$$r^2 = 0.0840,\ SD = 0.45,\ n = 18,\ \psi = 0.98$$

here, the number of data points considered in the analysis has been represented by 'n'.

The Swain equation has also been used for the solvent effect examination. Swain equation [19] has given following data on concept of cation-anion solvation:

$$\log k_2 = aA + bB + C \quad (11)$$

In equation (11), the anion-solvating power of solvent A has been indicated by 'A', the cation-solvating power indicated by 'B', and 'C' is the term of intercept. Solvent polarity is indicated by (A+B). Equation 11 has been used to analysis rates in various solvents.

$$\log k_2 = (0.63 \pm 0.02)\, A + (1.72 \pm 0.01)\, B - 4.74 \quad (12)$$
$$r^2 = 0.9997,\ SD = 0.01,\ n = 19,\ \psi = 0.01.$$

$$\log k_2 = (0.38 \pm 0.58)\, A - 3.54 \quad (13)$$
$$r^2 = 0.0274,\ SD = 0.47,\ n = 19,\ \psi = 1.00$$

$$\log k_2 = (1.67 \pm 0.12)\, B - 4.50 \quad (14)$$
$$r^2 = 0.9279,\ SD = 0.12,\ n = 19,\ \psi = 0.26$$

$$\log k_2 = 1.36 \pm 0.16\, (A + B) - 4.70 \quad (15)$$
$$r^2 = 0.8458,\ SD = 0.18,\ n = 19,\ \psi = 0.41$$

Swain's equation 12 correlation for rates of oxidation of tryptophan in diverse solvents has given brilliant results. In equation 14 only 'B' parameter gives a major contribution. In equation 15 the term (A+B) shows the solvent polarity parameter and also contributed for about 84% of the data.

Reaction Mechanism:

We investigated the mechanism of L-tryptophan oxidation by chlorochromate (CrO_3Cl^-) using density functional theory (DFT).

All quantum chemical calculations were performed with the ORCA program package. Geometry optimizations and harmonic frequency calculations were carried out at the B3LYP-D3(BJ)/def2-TZVP level with the corresponding def2/J auxiliary basis set. Solvent effects were included via the CPCM (water) continuum model. Dispersion was accounted for using Grimme's D3(BJ) correction. For each optimized structure, vibrational frequency analysis was used to confirm minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency). Thermal corrections to 298.15 K were extracted from the frequency calculations and added to electronic energies to obtain Gibbs free energies (G).

Protonation at the amino group (Trp-NH_3^+) is predicted to be energetically favoured, relative to the neutral form under CPCM (water), consistent with the strongly acidic experimental conditions. We find that protonation of Ltryptophan (Trp^+) and explicit acid stabilization produces a strongly bound reactant complex (ΔG_bind = [~-159 kJ·mol^{-1}]; and that the computed transition state for the crucial electron/proton transfer lies at $\Delta G‡$ = [34 kJ·mol^{-1}] above the reactants. Coordinates, ORCA input files and vibrational data are provided in the Supporting Information.

TABLE 8: Gibbs free energies of different systems at B3LYP/def2-TZVP level.

System	G_Hartree	G_kJ/mol
Trp+	-686.5792617	-1802613.591

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Oxidant	-1730.542348	-4543538.278
Intermediate complex	-2417.182253	-6346311.088
TS	-2417.10879	-6346118.209
Iminium Cation	-496.8138325	-1304384.528
CO_2	-188.5979943	-495163.9625
$CrO(OH)_2$	-1271.334364	-3337887.89
HCl	-460.7780322	-1209772.548
NH_{4+}	-56.98969338	-149626.4183
H_2O	-76.42312664	-200648.89
Indole-3- acetaldehyde	-516.2655171	-1355454.919

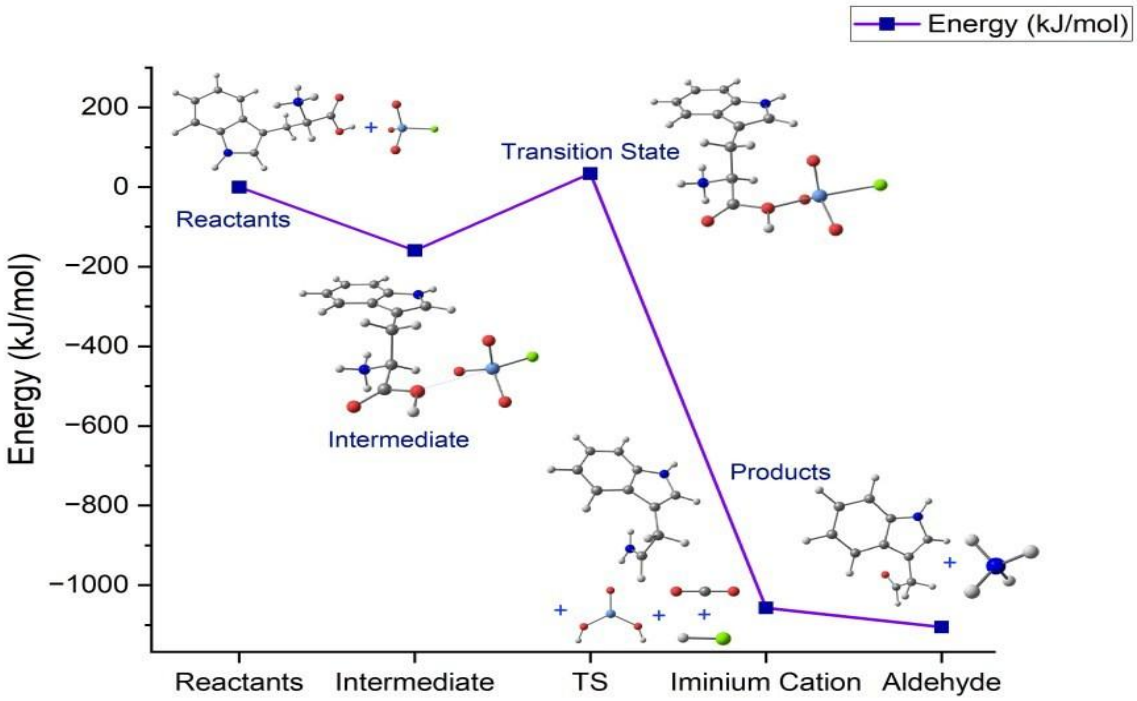

FIGURE 3: Free energy profile for the oxidation of *L*-tryptophan to indole-3-acetaldehyde, showing calculated relative gibbs free energies (ΔG, in kJ·mol^{-1}) of intermediates and transition states along the reaction pathway. All energies were obtained at the DFT level using the B3LYP functional with the def2TZVP basis set. Atom color scheme: carbon = grey, nitrogen = blue, chromium = sky blue, oxygen = red, hydrogen = white, chlorine = green.

FIGURE 4: Optimized structures of (A) reactants (trp+ and oxidant), (B) transition state and (C) iminium cation. All energies were obtained at the DFT level using the B3LYP functional with the def2-TZVP basis set. Atom colour scheme: carbon = grey, nitrogen = blue, chromium = sky blue, oxygen = red, hydrogen = white, chlorine = green.

TABLE 9: Selected structural parameters of the reactant (R), transition state (TS), and product (P) for the oxidation of *L*-tryptophan. Bond lengths are given in Å and bond angles in degrees (°).

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Reactants (trp+ and Oxidant)				**TS**		**Product**	
N1-C2	1.494	Cr2-O1	1.595	N1-C2	1.494	C14-C16	1.408
N1-H24	1.024	Cr2-O3	1.596	N1-H24	1.024	C14-C12	1.385
N1-H25	1.024	Cr2-O4	1.595	N1-H25	1.024	C14-H15	1.083
N1-H28	1.022	**Cr2-Cl5**	**2.215**	N1-H28	1.024	C16-C18	1.386
C2-C3	1.517	O1-Cr2-O3	111.4	C2-C3	1.507	C16-H17	1.083
C2-C6	1.542	O1-Cr2-O4	111.4	C2-C6	1.546	C10-C18	1.394
C2-H26	1.089	O1-Cr2-Cl5	107.2	C2-H26	1.088	C18-H19	1.083
C3-O4	1.207	O3-Cr2-O4	111.3	**C3-O4**	**1.197**	C10-C11	1.42
C3-O5	1.33	O3-Cr2-O5	108	**C3-O5**	**1.367**	C10-N8	1.376
O5-H27	0.974	O4-Cr2-Cl5	107.4	**O5-H27**	**0.978**	C11-C12	1.402
C6-H7	1.089			**O5-Cr31**	**1.769**	C11-C6	1.439
C6-H8	1.093			C6-H7	1.089	C12-H13	1.083
C6-C9	1.495			C6-H8	1.093	C6-C7	1.373
C9-C10	1.374			C6-C9	1.493	C6-C3	1.491
C9-C14	1.44			C9-C10	1.373	C7-N8	1.371
C10-N11	1.372			C9-C14	1.439	C7-H20	1.078
C10-H23	1.078			C10-N11	1.372	N8-H9	1.007
N11-H12	1.007			C10-H23	1.078	C3-C2	1.479
N11-C13	1.374			N11-H12	1.007	C3-H5	1.098
C13-C14	1.422			N11-C13	1.374	C3-H4	1.097
C13-C21	1.394			C13-C14	1.422	C2-N1	1.275
C14-C15	1.403			C13-C21	1.394	C2-H23	1.085
C15-H16	1.084			C14-C15	1.403	N1-H21	1.018
C15-C17	1.385			C15-H16	1.084	N1-H22	1.014
C17-H18	1.083			C15-C17	1.385	C16-C14-C12	121.2
C17-C19	1.407			C17-H18	1.083	C16-C14-H15	119.2
C19-H20	1.083			C17-C19	1.407	C14-C16-C18	121.3
C19-C21	1.386			C19-H20	1.083	C14-C16-H17	119.3
C21-H22	1.083			C19-C21	1.386	C12-C14-H15	119.7
C2-N1-H24	110.1			C21-H22	1.083	C14-C12-C11	118.8
C2-N1-H25	111.2			Cr31-O29	1.605	C14-C12-H13	120.6
C2-N1-H28	111.8			Cr31-O30	1.604	C18-C16-H17	119.4
N1-C2-C3	107.9			**Cr31-Cl32**	**2.61**	C16-C18-C10	117.4
N1-C2-C6	110.6			Cr31-O33	1.626	C16-C18-H19	121.4
N1-C2-H26	107			C2-N1-H24	110.2	C10-C18-H19	121.1
H24-N1-H25	108.2			C2-N1-H25	111.6	C18-C10-C11	122.1
H24-N1-H28	107.8			C2-N1-H28	112.1	C18-C10-N8	130.6
H25-N1-H28	107.5			N1-C2-C3	107.8	C11-C10-N8	107.3

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C3-C2-C6	112			N1-C2-C6	110.8	C10-C11-C12	119.1
C3-C2-H26	109.5			N1-C2-H26	107.3	C10-C11-C6	106.7
C2-C3-O4	123.8			H24-N1-H25	108	C10-N8-C7	109.5
C2-C3-O5	111			H24-N1-H28	107.2	C10-N8-H9	125.5
C6-C2-H26	109.7			H25-N1-H28	107.7	C12-C11-C6	134.1
C2-C6-H7	106.5			C3-C2-C6	111.9	C11-C12-H13	120.6
C2-C6-H8	108.7			C3-C2-H26	108.9	C11-C6-C7	106.7
C2-C6-C9	112.5			C2-C3-O4	125.6	C11-C6-C3	126.6
O4-C3-O5	**125.2**			C2-C3-O5	112.8	C7-C6-C3	126.7
C3-O5-H27	109.5			C6-C2-H26	110	C6-C7-N8	109.7
H7-C6-H8	107.4			C2-C6-H7	107.1	C6-C7-H20	129.4
H7-C6-C9	110.9			C2-C6-H8	108.4	C6-C3-C2	115.8
H8-C6-C9	110.7			C2-C6-C9	111.9	C6-C3-H5	112.3
C6-C9-C10	126.6			**O4-C3-O5**	**121.6**	C6-C3-H4	112
C6-C9-C14	126.9			**C3-O5-H27**	**109.1**	N8-C7-H20	120.9
C10-C9-C14	106.5			**C3-O5-Cr31**	**138.2**	C7-N8-H9	124.9
C9-C10-N11	109.9			**H27-O5-Cr31**	110.7	C2-C3-H5	105.8
C9-C10-H23	129.5			O5-Cr31-O29	97.7	C2-C3-H4	105.7
C9-C14-C13	106.9			O5-Cr31-O30	97	C3-C2-N1	123.4
C9-C14-C15	134.2			O5-Cr31-Cl32	174.8	C3-C2-H23	119.3
N11-C10-H23	120.7			O5-Cr31-O33	90.2	H5-C3-H4	104.3
C10-N11-H12	124.9			H7-C6-H8	107.5	N1-C2-H23	117.3
				H7-C6-C9	110.1	C2-N1-H21	120.6
				H8-C6-C9	111.6	C2-N1-H22	121.7
				C6-C9-C10	125.7	H21-N1-H22	117.8
				C6-C9-C14	127.6		
				C10-C9-C14	106.7		
				C9-C10-N11	109.8		
				C9-C10-H23	129.2		
				C9-C14-C13	106.8		
				C9-C14-C15	134.4		
				N11-C10-H23	121		
				C10-N11-H12	125		

A possible mechanism for the oxidation of L-tryptophan with TMGCC in sulphuric acid media can be given on the basis of other previously reported mechanisms [20]. The absence of free radical in the respective test ruled out any possibility of intermediate Cr (V) species in the concerned reaction involving Cr (VI) as an oxidant, which involved one-electron transfer.

The existence of Amino acids in the form of zwitter ions is known [21, 22]. Mainly, they tend to protonate in acidic medium which is in accordance with below equilibria:

$$Try + H^{+} \rightleftharpoons Try^{+} \quad (16)$$

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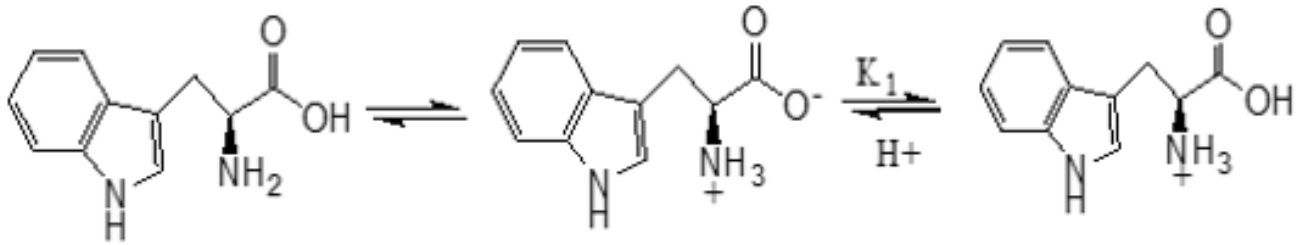
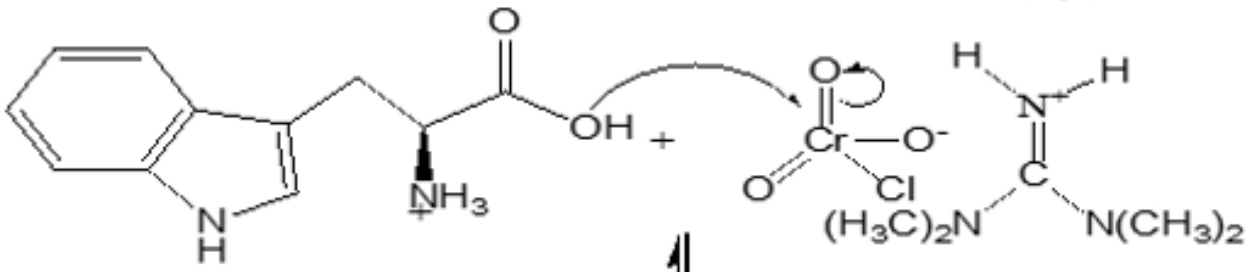
Also, the fractional-second order rate constant for the concentration of hydrogen ions was elucidated on basis of polar nature of both TMGCC and Trptophan in acidic media as they are more reactive species which have a major impact in the kinetics of redox reactions.

The 1:1 stoichiometry for TMGCC and L-tryptophan reaction in H_2SO_4 media, i.e., 1 Trp:1 TMGCC, with a fractional-first order dependence on [Trp] and a first order dependence on [TMGCC)]. The formation of complex before the slow step supported fractional order dependence of tryptophan concentration.

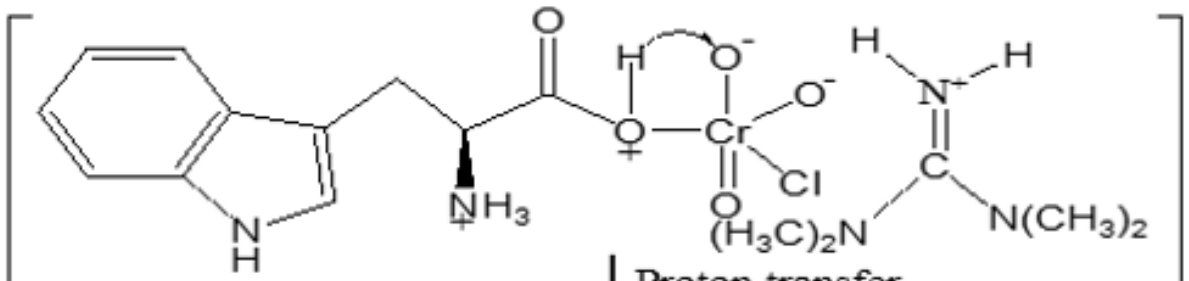
The mechanism for the oxidation of Tryptophan by TMGCC in H_2SO_4 medium may be suggested by Scheme 1, which involves a complex formation with a fast step between the protonated Tryptophan and TMGCC, leading to the formation of an intermediate complex. Further decomposition of the intermediate complex during the slow step, with successive fast steps, gave the final products of oxidation.

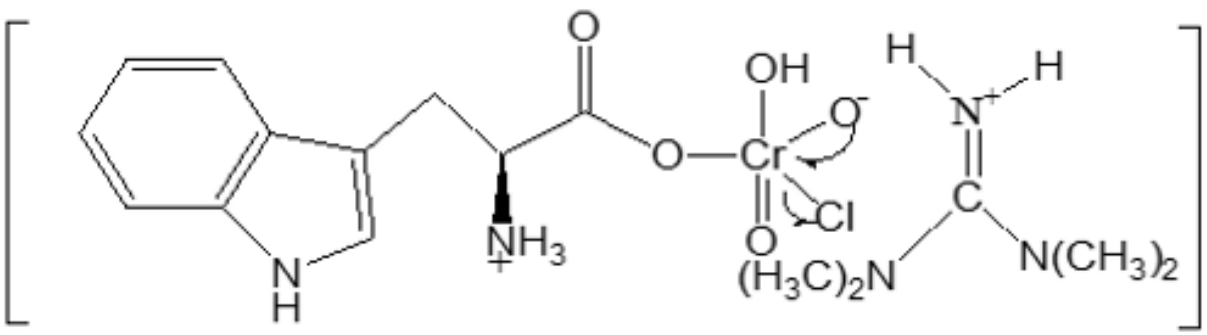


Tryptophan (Trp) Zwitter ion Protonated Tryptophan (Trp^+)



Protonated Tryptophan (Trp^+) TMGCC





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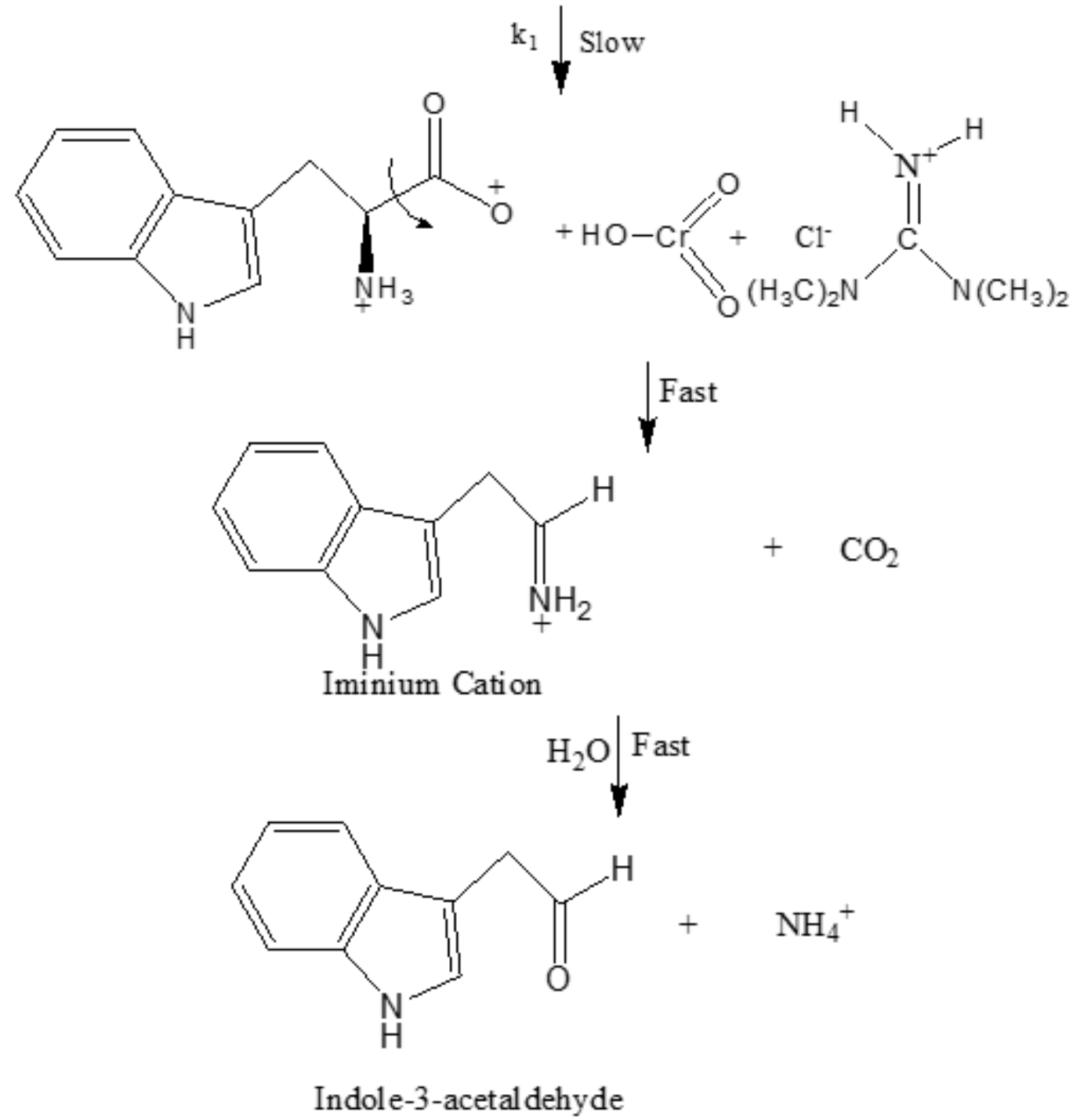

Scheme 1: Mechanism for L-tryptophan's oxidation by TMGCC in H_2SO_4 medium.

CONCLUSION

The kinetics of the L- tryptophan's oxidation by TMGCC was studied in H_2SO_4 medium, which proceeded through a complex formation. It showed a stoichiometry of 1:1, i.e. a single mole of tryptophan was used with one mole of TMGCC. The reaction is of first order with respect to TMGCC, fractional order with respect to tryptophan, and fractional second order with respect to acid. The final products of the oxidation of tryptophan were recognized as indole-3- acetaldehyde, NH_4^+ ion with CO_2.

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