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CETYL TRIMETHYL AMMONIUM BROMIDE ASSISTED OXIDATION OF HYPOXANTHINE AND XANTHINE USING Mn(VII) IN AQUEOUS BRONSTED ACID MEDIA: A KINETIC AND MECHANISTIC STUDY

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ABSTRACT

Cetyl trimethyl ammonium bromide (CTAB) assisted Oxidation of hypoxanthine (HXAN), and xanthine (XAN) alkaloids by Mn(VII) occurred smoothly in presence of aqueous Bronsted acid ($HClO_4$, H_2SO_4) media. The rate of oxidation of HXAN, XAN by Mn(VII) was enhanced due to an increase in [$HClO_4$] / [H_2SO_4] in the presence of CTAB at a constant temperature. Reaction kinetics obeyed I-order in [Mn(VII)], [HXAN], or [XAN] at constant temperature and acid concentration in micellar (CTAB) conditions. In this present work, the acidity functions developed by Zucker-Hammett, Bunnett, and Bunnett-Olsen were used for analyzing rate enhancement, and the probable reaction mechanism that involves water moiety in the slow step has been proposed according to the criteria of Bunnett-Olsen.

Keywords: Mn (VII) Oxidation; Xanthine; Hypoxanthine; Cetyl Trimethyl Ammonium Bromide; Micellar Catalysis; Bronsted Acid Media

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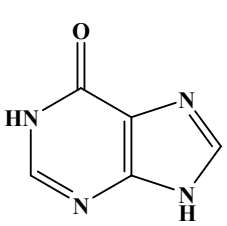
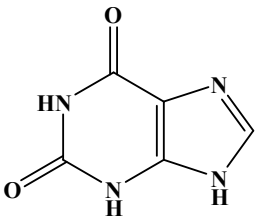
INTRODUCTION

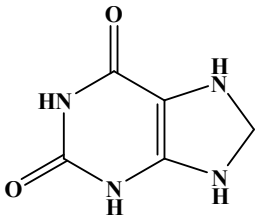
Hypoxanthine (I) is a purine group alkaloid, which has immense biological importance. It is used as a necessary additive in certain cells, bacteria, and parasite cultures, where it acts as a substrate and nitrogen source.[1] A perusal of the literature also shows that the conversion of adenosine monophosphate (AMP) to uric acid (III) involves xanthine (II), as an important intermediate that can also be produced by the oxidation of hypoxanthine, and it is catalyzed by xanthine oxidase (XOA). Additionally, uric acid is produced as an oxidation byproduct from the breakdown of purines obtained from food.[2-4]



(I) Hypoxanthine



(II) Xanthine



(III) Uric acid

Stimulated by these striking biological aspects, our research group has embarked on kinetic studies that involve the oxidation of alkaloids, containing purine rings, using different metal ion oxidizing agents.[5] Further, we attempted to investigate the kinetic study of hypoxanthine (HXAN) and xanthine (XAN) using Mn(VII), but the reaction did not proceed even in highly concentrated acid solutions at elevated temperatures.

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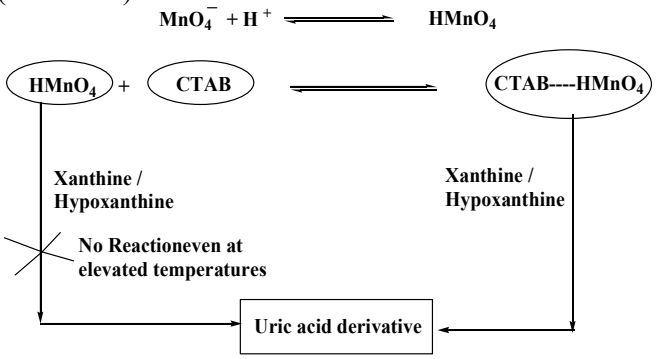
However, our preliminary studies in micellar media indicated smooth oxidation of xanthine and hypoxanthine by Mn(VII) in aqueous $HClO_4$ and H_2SO_4 media (Scheme-1). It is well documented in the literature that micro to nano-sized micelles was formed by surfactants in aqueous solutions, and such micelles can dissolve a wide range of reagents and catalysts on account of hydrophobic, hydrophilic, electrostatic, and ion pairing effects.[6-15] There were numerous attempts where micelles were explored to act as biocatalysts, and there has been close parallelism between micelles and enzymes. Inspired by the aforementioned remarkable characteristics of micelles and our initial kinetic findings, authors have started a thorough kinetic study on Mn(VII) catalyzed oxidation of Hypoxanthine/Xanthine in aqueous acidic (Bronsted acids) media (Scheme-1).



(i) Aq MeCN/H_2SO_4 (ii) Aq.MeCN/ $HClO_4$

Scheme 1: CTAB catalysed Mn(VII) oxidation of xanthine and hypoxanthine

EXPERIMENTAL

Chemical Reagents and Solvents

The required chemicals like Hypoxanthine (HXAN), Xanthine (XAN), CTAB, $KMnO_4$, and ACN (HPLC grade) were procured from Aldrich, SD fine chemicals, and E-Merck. Distilled water(doubly), and ACN were used as solvents.

Oxidation of Alkaloids: Stoichiometry and Oxidation Products

In order to determine the stoichiometry of xanthine/hypoxanthine (alkaloid) and potassium permanganate (Mn(VII)), Xanthine(10^{-2} mol), Mn(VII) ($1.5*10^{-2}$ mol), and millimolar CTAB have been taken in a 50 mL flask and made up the reaction mixture using acid solution (aqueous). The absorbance of the (Mn(VII)) content in the reaction mixture has been monitored at regular intervals until the reaction was completed. The change in absorbance of Mn(VII) suggests stoichiometry of oxidation reaction of alkaloid employing Manganese (VII) in CTAB, an aqueous acid medium at room temperature is 1:1. Following completion, the components were extracted with dichloromethane and washed with H_2O (50mL). The dichloromethane covering was removed and $MgSO_4$ was added for drying. After the solvent had been dispersed, the slag was cleaned with SiO_2, 1:2 ethyl acetate-hexane, and flash column chromatography to enable the final amount. With the aid of spectrum data from the mass, NMR, and IR spectroscopies, the majority of oxidation was expressed as a derivative of uric acid.

Reaction Kinetics

In a flask containing a suitable solvent, known concentration/volume of substrate (Xanthine/Hypoxanthine) along with Bronsted acid ($HClO_4$/H_2SO_4), CTAB, were suspended, and Potassium Permanganate (Mn (VII)) solution was taken in another flask, and until the temperature reached equilibrium, both flasks were fixed in a thermostatic bath. An appropriate quantity of Mn(VII) with known concentration was added instantaneously into the flask containing other contents with thorough mixing to initiate the reaction. A black coating was applied to the outside of the flask to inhibit photochemical effects. A small amount of the reaction mixture that had been deposited in the cuvette was added to the lab's visible spectrophotometer. A thermostatic liquid at a required temperature circulated through an inlet and outlet cell compartment of the spectrophotometer. To determine the amount of Mn(VII) contained in a reaction mixture, a calibration curve plotting absorbance vs. [Mn (VII)] had previously been developed. Absorbance measurements that were accurate to within ±3% of one another.

Order of Reaction, its Determination

In this kinetic study authors adopted a graphical method,[16-19] in determining the order of reaction with the help of the following rate equations;

$\ln [(A_0)/ (A_t)] = (k') t$ (1)(First order kinetic equation)

$\frac{1}{A_t} = \frac{k}{(\varepsilon)} t + \frac{1}{A_0}$ (or) $\frac{1}{A_t} = \frac{k[Mn(VII)]_0}{(A_0)} t + \frac{1}{A_0}$ (2)(Second order kinetic equation)

Where, A_0 = absorbance value at a time(t)= "0", A_t = absorbance values at a time(t)= "t", A_0 α ($[Mn (VII)]_0$), and A_t α ($[Mn (VII)]_t$), k'=first order rate constant, ε = $[Mn(VII)]_0 /A_0$, k =Second order rate constant =$[Mn(VII)]_0$* (slope/intercept).

In this work, however, k (second-order rate constant) was calculated from $\frac{k'}{[Substrate]}$.

Observation Table

Conditions	Plot	Figures	Observation	Conclusion
[Substrate] >> [Mn (VII)] (i.e., Pseudo first order conditions)	[ln (A_0/A_t)] vs time. (First-order plot)	1-2	The plots were found to be linear passing through the origin, which is a characteristic of first-order kinetics	I-order kinetics w.r.t [Mn (VII)]
[Mn (VII)] = [substrate], under constant acidity (i.e., second-order conditions)	[1/(A_t)] Vs time(t) (Second-order plot)	3	The plots were found to be linear with slope and intercept, which is a characteristic second-order kinetics	II-order kinetics w.r.t [Mn (VII)] and [Substrate]

It can be observed from the above that reaction follows First order kinetics w.r.t [substrate] since the reaction follows overall II-order kinetics, and w.r.t [Mn (VII)] first-order kinetics.

The plot of $ln\left(\frac{A_0}{A_t}\right)$ Versus Time

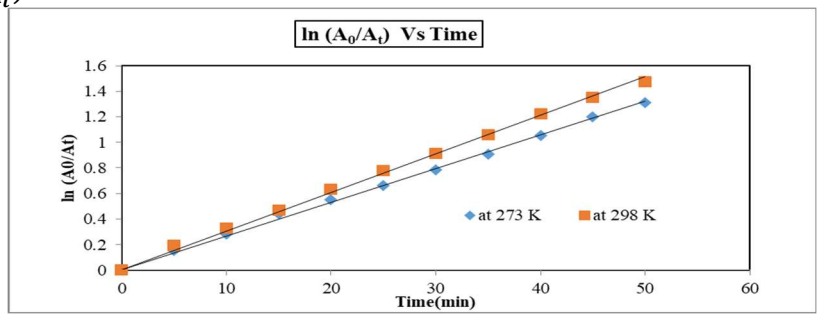


Fig.-1: Plot of $ln\left(\frac{A_0}{A_t}\right)$ versus Time for Oxidation of Xanthine under the following Conditions at 273 K and 298 K; [$KMnO_4$]= 0.0004, [Xanthine]=0.004, [$HClO_4$]= 0.2, [CTAB]= 0.0008, all the Concentrations were expressed in mol/dm^3

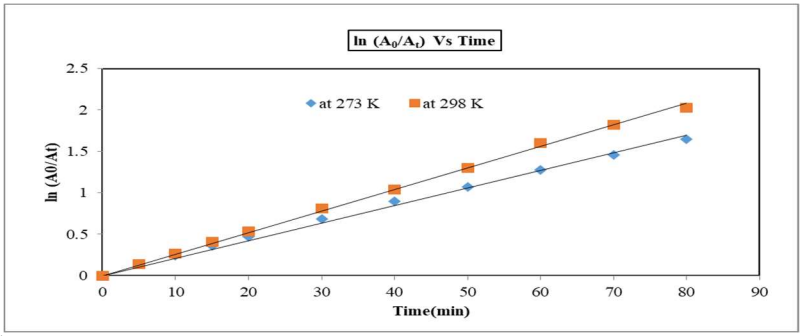


Fig.-2: Plot of $ln\left(\frac{A_0}{A_t}\right)$ versus Time for Oxidation of Hypoxanthine under the Following Conditions at 273 K and 298 K; [$KMnO_4$] = 0.0004, [Hypoxanthine] =0.004, [$HClO_4$] = 0.2, [CTAB] = 0.0008, all the Concentrations were expressed in mol/dm^3

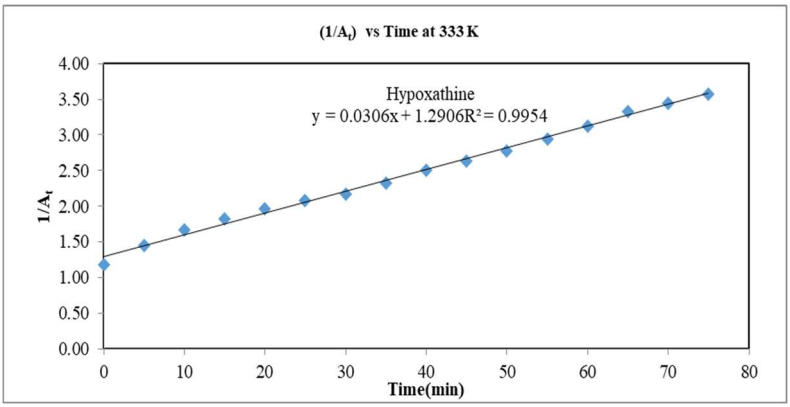


Fig.-3: Plot of $\left(\frac{1}{A_t}\right)$ versus Time for Oxidation of Hypoxanthine Under the Following Conditions at 333 K; [$KMnO_4$] = [Hypoxanthine] = 0.0005, [H_2SO_4] = 0.6, [CTAB] = 0.0005 all the Concentrations Were Expressed in mol/dm^3

Activation Parameter Computation

Authors took up kinetic studies of this work at different temperatures ranging from 273K to 333K to compute thermodynamic parameter ($\Delta G^{\#}$) by making use of Eyring's equation on the basis of the popular theory of reaction rates,

$\Delta G^{\#} = RT \ln\left(\frac{RT}{N\,h\,k}\right)$ (3)

$\Delta G^{\#} = (8.314) * T(23.7641) + ln\left(\frac{T}{k}\right)$ (4) is obtained after substituting the values from the below table appropriately.

R	N	h	T
8.314 Jmol^{-1}K	6.022*10^{23} mol^{-1}	6.626*10^{-34}Jsec	kelvin

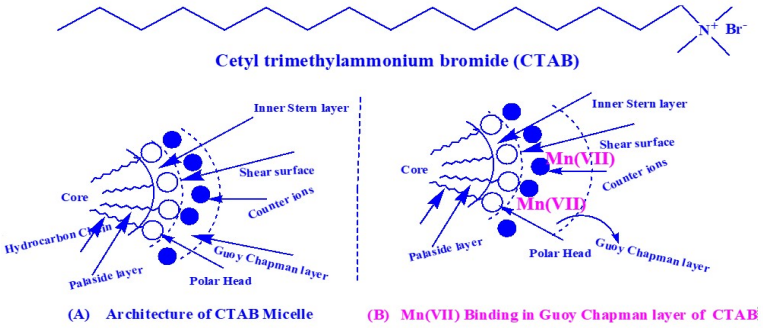
Gibbs–Helmholtz equation, [16-19] $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$ (5) a very popular equation, was used to compute $\Delta H^{\#}$, and $\Delta S^{\#}$ with the help of $\Delta G^{\#}$ Vs Temperature (T) plot. (Fig.-4 to 7).

Where $\Delta G^{\#}$, $\Delta H^{\#}$, $\Delta S^{\#}$, and T are free energy, enthalpy, the entropy of activation, and temperature respectively.

RESULTS AND DISCUSSION

Studies on the Binding of CTAB to Mn(VII) and Mn(VII) Reactive Species in CTAB Micellar Medium

In order for a chemical reaction to occur in micellar medium, a surfactant added must be higher in concentration than CMC, which is called as critical micelle concentration. This is likely on account of reactants in higher concentration in the environment of micelles, which could facilitate suitable alignment(orientation), and solvation of the species. On the other hand, the surfactant aggregate's micellar pseudo phase could experience rate increases. Micelles function as micro to nanoreactors, according to recent findings. The amphipathic nature of surfactants causes regions of hydrophilic, and hydrophobic which have polar and nonpolar natures respectively. The hydrophobic tail often has one or more hydrocarbon chains of various lengths, while the polar head group is typically neutral, cationic, anionic, or zwitterionic. A cationic surfactant called cetyltrimethylammonium bromide (CTAB) has a cetrimonium (hexadecyltrimethylammonium) cation bonded to a polar bromide group. At extremely low concentrations, ionic surfactants like CTAB are reasonably soluble in water. However, upon reaching CMC, surfactants form micelles, which are globular aggregates. The hydrophilic heads are attracted by aqueous media and are found to be near the surface of the globe, while the hydrophobic tails collectively form a core non-polar in nature. Further, CTAB being is a cationic surfactant, carries cationic polar head groups, and attracts negatively charged permanganate (MnO_4^-) ions to result in CTAB bound $CTAMnO_4$ [CTAMn(VII)] species[20-23], as shown in Scheme-2.



Scheme-2: Architecture of CTAB Micelle and Mn(VII) Binding in Guoy Chapman of CTAB

Acid Catalysis, Acidity Functions, and Mechanism of Oxidation

The reaction rate for oxidation of alkaloid substrates was enhanced with an increase in acid concentration as the data shown in Table-1.

Table-1: Influence of Acid Concentration on CTAB Assisted Mn(VII) Catalyzed Oxidation Reaction of Xanthine / Hypoxanthine

[Acid] mol/dm^3	(k'/min) in H_2SO_4 medium		(k'/min) in $HClO_4$ medium	
	(XAN)	(HXAN)	(XAN)	(HXAN)
0.200	0.0208	0.0318	0.0303	0.0206
0.400	0.0211	0.0141	0.0332	0.0318
0.800	0.0215	0.0152	0.0369	0.0382
1.20	0.0219	0.0159	0.0393	0.0427
1.60	0.0223	0.0163	0.0410	0.0486
2.00	0.0229	0.0167	0.0423	0.0537

Protonation of permanganate ion (MnO_4^-) that involves the following equilibrium was well documented in the literature.[24,25]

$$(MnO_4^-) + (H^+) \underset{}{\overset{K}{\rightleftharpoons}} HMnO_4 \, (K = 2.99 \times 10^{-3} \, dm^3/mol \text{ at } 25^oC)$$

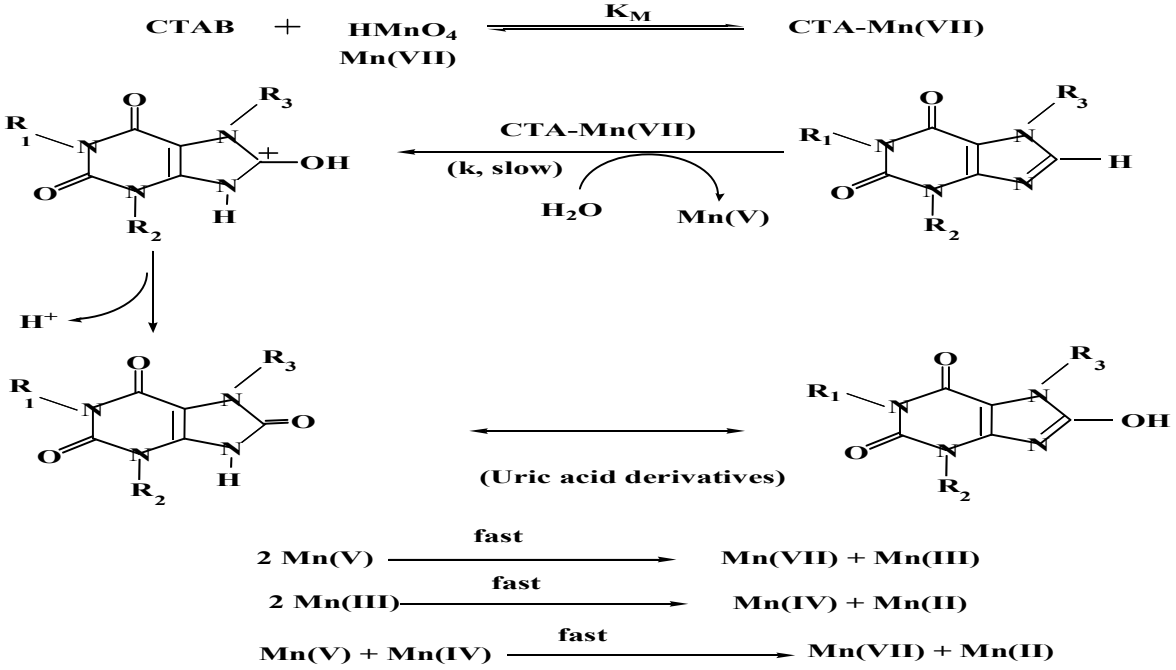
From the above equilibrium, it is clearly understood that HMnO4 (Permanganic acid) is produced upon protonation of MnO_4^- in the presence of acid media(aqueous). In this present work, authors took up the study of rate dependence on acidity (≥0.100) of reaction medium using various acidity functions reported in the literature.[26-33] Table-2 comprises well-known plots and their corresponding slopes pertaining to acidity functions used in this present study.

Table-2: Slopes and R^2 Values of Acidity Function Plots Under Different Acid Conditions

Substrate	Plot	Slope	H_2SO_4		$HClO_4$	
			Slope	R^2	Slope	R^2
Xanthine	log k Versus H_0 (Zucker-Hamett-i)	m	0.039	0.911	0.147	0.999
	log k Versus log [Acid] (Zucker-Hamett-ii)	m*	-0.034	0.985	-0.140	0.919
	log (k+H_0) Versus log a_w (Bunnett-i)	ω	15.4	0.977	9.83	0.977
	(log k - log [acid]) Versus log a_W (Bunnett-ii)	ω*	-13.5	0.919	-10.2	0.940
	log (k+H_0) Versus (H_0+ log [H^+]) (Bunnett-Olson-i)	ϕ	-1.20	0.947	-0.880	0.869
	log k Versus (H_0+ log [H^+]) (Bunnett-Olson- ii)	ϕ*	1.12	0.999	1.23	0.999

Hypoxanthine	log k Versus H_0 (Zucker-Hamett-i)	m	0.087	0.971	0.305	0.990
	log k Versus log [Acid] (Zucker-Hamett-ii)	m*	-0.073	0.956	0.298	0.952
	log (k+H_0) Versus log a_w (Bunnett-i)	ω	14.8	0.976	8.01	0.966
	(log k - log [acid]) Versus log a_W (Bunnett-ii)	ω*	-14.1	0.919	-10.2	0.940
	log (k+H_0) Versus (H_0+ log [H^+]) (Bunnett-Olson-i)	ϕ	-1.15	0.941	-0.707	0.838
	log k Versus (H_0+ log [H^+]) (Bunnett-Olson- ii)	ϕ*	1.17	0.999	1.42	0.998

According to the aforementioned kinetic characteristics, the most likely process might be described as [CTA-Mn(VII)] being formed in the first step, which then reacts with alkaloid in the slow step to produce products, as illustrated in Scheme-3.



Scheme- 3: CTAB catalysed Mn(VII) oxidation of Xanthine alkaloids

The rate law for Scheme-3 could be derived by considering the overall concentration of ($C_{Mn(VII)}$) is equal to the concentration of free Mn(VII) species plus [CTA-Mn (VII)] species, at constant acidity.

$$C_{Mn(VII)} = [Mn(VII)] + [CTA\text{-}Mn(VII)] \quad (7)$$

From Micelle-Mn(VII) binding equilibrium,

$$K_M = [CTA\text{-}Mn(VII)]/[CTAB]\,[Mn(VII)] \text{ or } [Mn(VII)] = [CTA\text{-}Mn(VII)]/\,K_M\,[CTAB]$$

Substitution in eq.(7) gives

$$C_{Mn(VII)} = [CTA\text{-}Mn(VII)] + [CTA\text{-}Mn(VII)]/\,K_M\,[CTAB]$$

$$\Rightarrow C_{Mn(VII)} = \{K_M\,[CTA\text{-}Mn(VII)]\,[CTAB] + [CTA\text{-}Mn(VII)]\}/\,K_M\,[CTAB]$$

$$\Rightarrow C_{Mn(VII)} = [CTA\text{-}Mn(VII)](1+K_M\,[CTAB])/\,K_M\,[CTAB]$$

$$\Rightarrow [CTA\text{-}Mn(VII)] = K_M\,[CTAB]\,C_{Mn(VII)}/\,(1+K_M\,[CTAB]) \quad (8)$$

But the rate of the reaction (V) at constant acidity is written as,

Rate (V) = k [S] [CTA-Mn(VII)]

(Here, S= Xanthine or hypoxanthine) Substituting for [CTA-Mn(VII)], rate-law comes out as,

$V = k K_M [S] [CTAB] C_{Mn(VII)} / (1+ K_M [CTAB]$ (9)

$V/ C_{Mn(VII)} = k' = k K_M [S] [CTAB] / (1+ K_M [CTAB])$ (10)

This rate law is similar to the rate law of the Michaelis-Menten type employed in enzyme kinetics and Menger Portnoy's equation in micellar catalysis.[34,35] Binding constants (K_M) for Mn(VII) and CTAB micellar interactions have been evaluated spectrophotometrically using Benesi - Hildebrand equation as applied to molecular/charge-transfer interactions[36-38] and presented in Table-4. Binding constant (K_M) data presented in Table-4 indicated a marginally higher values in sulfuric acid than those observed in perchloric acid medium. An increase in temperature (from 303 to 333K) indicated a slight decrease in binding constants in both the acid media.

Table-3: Mn (VII) - CTAB Interactions in Different Acidic Media

Medium	Temp(K)	Binding constant (K_M)	ε (molar absorptivity)
H_2SO_4	303	7.9848	21.7391
	313	7.6016	20.3252
	323	7.4980	19.6078
	333	7.3648	18.9036
$HClO_4$	303	7.8662	21.9298
	313	7.4979	20.7469
	323	7.4036	20.0803
	333	7.1877	19.1571

Further insight into rate equation (9) clearly depicts that the value of $K_M[CTAB] << 1$. It is possible to ignore ($K_M[CTAB]$) in the denominator. Therefore, at a given constant acid concentration, and [CTAB], the rate law reduces to the second-order rate law. Table-4 contains a compilation of binding constants (K_M).

Influence of Structure on Entropy and Enthalpy Changes

The thermodynamic parameter $\Delta S^{\#}$ is very significant for understanding whether the reaction follows an associative or dissociative mechanism which depends on molecularity of the reaction in rate determining step. Positive and negative $\Delta S^{\#}$ values reveals that the reaction is associated with dissociative and associative mechanism respectively. The $\Delta S^{\#}$ values for the present study shown here in Table-5 were negative, and suggest that reaction follows associative mechanism due to interaction of Mn(VII) and CTAB to afford CTAB-bound Mn(VII).

$\Delta G^{\#}$ Versus Time plots

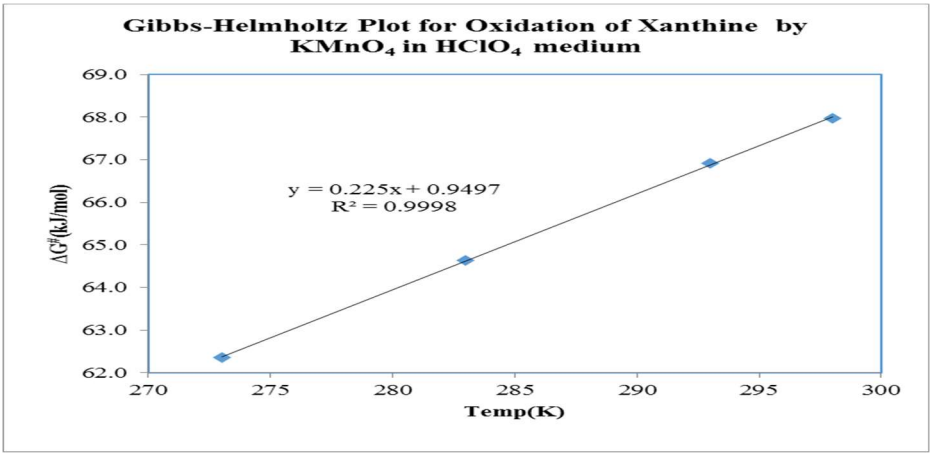


Fig.-4: Gibbs-Helmholtz Plot for Oxidation of Xanthine by $KMnO_4$ in $HClO_4$ Medium

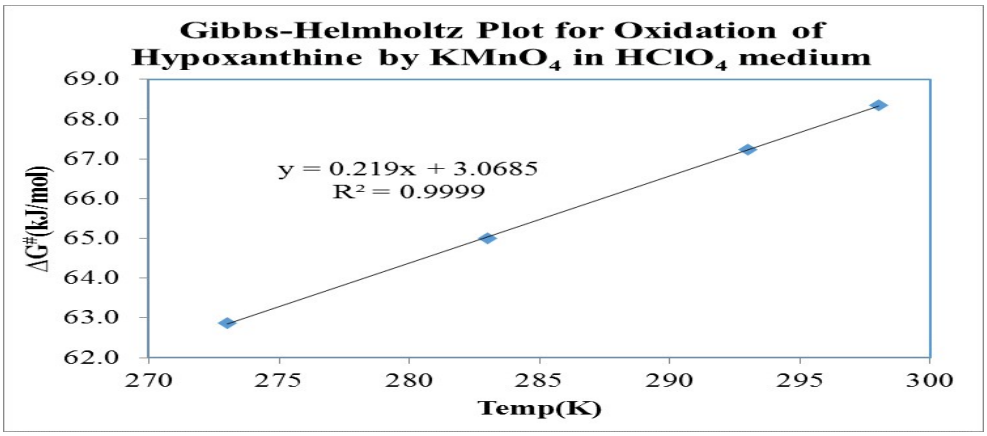


Fig.-5: Gibbs-Helmholtz Plot for Oxidation of Hypoxanthine by $KMnO_4$ in $HClO_4$ Medium

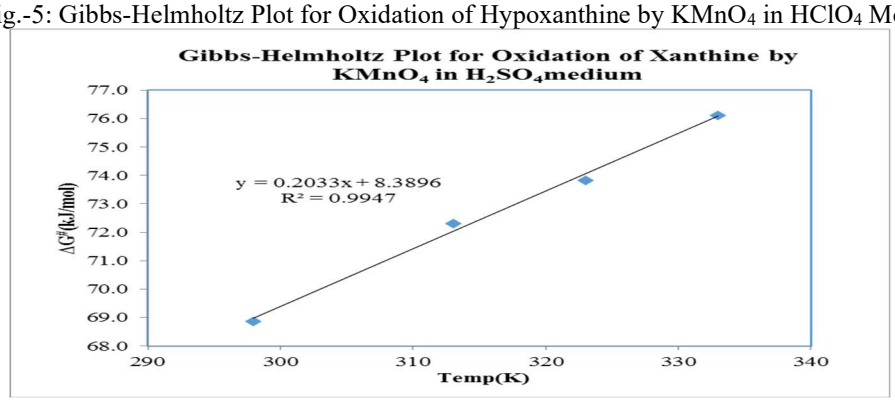


Fig.-6: Gibbs-Helmholtz Plot for Oxidation of Xanthine by $KMnO_4$ in H_2SO_4 Medium

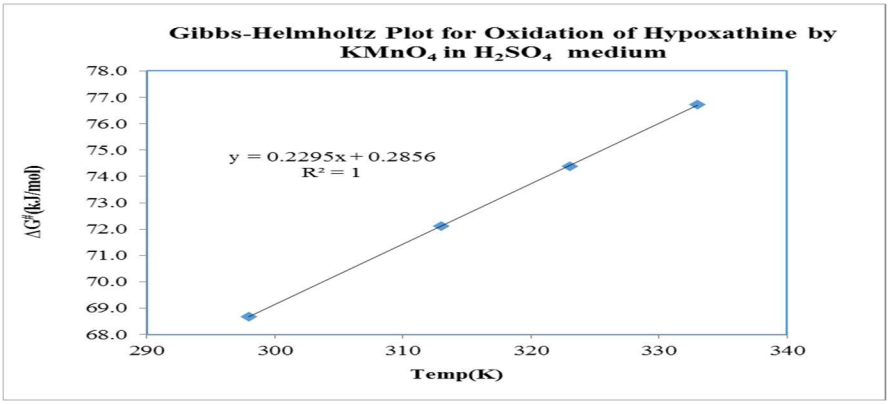


Fig.-7: Gibbs-Helmholtz Plot for Oxidation of Hypoxanthine by KMnO4 in H_2SO_4 Medium

Table-4: Activation Parameters $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$

Compound (Substrate)	T (in Kelvin)	k_m ($dm^3mol^{-1}min^{-1}$)	$\Delta G^{\#}$ ($kJmol^{-1}$)	G-H Equation ($\Delta G^{\#}=\Delta H^{\#}-T\Delta S^{\#}$)	$\Delta H^{\#}$ ($kJmol^{-1}$)	$(-\Delta S^{\#})$ ($JK^{-1}mol^{-1}$)
In the presence of Sulfuric Acid(H_2SO_4) medium						
Xanthine	298	5.30	69.0	y = 0.2033x + 8.3896	8.39	203
	313	5.60	72.0			
	323	7.80	74.0			
	333	8.00	76.0			
	298	5.70	69.0			

Hypoxanthine	313	6.00	72.0	y = 0.2295x + 0.2856	28.5	230
	323	6.30	75.0			
	333	6.40	77.0			
In the presence of Perchloric Acid medium ($HClO_4$)						
Xanthine	273	6.65	62.4	y = 0.225x + 0.9497	95.0	225
	283	6.90	64.6			
	293	7.18	66.9			
	298	7.58	68.0			
Hypoxanthine	273	5.30	62.9	y = 0.219x + 3.0685	31.0	219
	283	5.90	65.0			
	293	6.30	67.2			
	298	6.50	68.3			

CONCLUSION

By using the versatile chemical reagent $KMnO_4$ in catalytic concentrations, we have explored the oxidation of Xanthine alkaloids such as Xanthine (XAN) and Hypoxanthine (HXAN). Uric acid derivatives were produced by oxidizing xanthine derivatives. Even at high temperatures, the reaction is too slow in acetonitrile media, however, it proceeded without any problems when CTAB surfactant was included. First-order kinetics were used in both the [$KMnO_4$] and [Xanthine alkaloid] reactions. A linear rise in [CTAB] accelerates the rate of oxidation. The slow step reaction between CTAB-bound Mn(VII) and substrate could be used to explain the mechanism of oxidation. The found negative entropies of activation in the current study could potentially be used to support this claim.

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CONFLICT OF INTERESTS

We, the authors, truly state that we have no competing interests, which could have influenced the work embodied in this manuscript.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The ORCID ids of all the authors are given below:

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