

Homogenous catalysis of Ru(III) for the oxidation of Thiamine by ChloramineT in acidic medium

Aftab Aslam Parwaz Khan^{1*}, Anish Khan¹, Abdullah M. Asiri,^{1,2} Ajaya Kumar Singh³

¹Chemistry Department, King Abdulaziz University, Jeddah-21589, Saudi Arabia

²Center of Excellence for Advanced Materials Research - King Abdulaziz University, Jeddah 21589, P.O. Box 80203, Saudi Arabia¹

³Department of Chemistry, Govt. V. Y .T. PG. Autonomous College, Durg (C.G.), India

*E-mail: draapk@gmail.com

Received: 10 September 2014 / Accepted: 24 November 2014 / Published: 2 December 2014

In this paper we report a nano concentration of ruthenium(III) used as a homogenous catalyst for the oxidation of thiamine (THM) by chloramine T(CAT) alongwith its mechanistic pathway, spectrophotometrically. Such studies are greatly helpful in gaining an insight into the interaction of metal ions through the study of the mechanistic pathway of THM in redox reactions. The reaction followed a pseudo first-order rate constant throughout the variation of CAT in the oxidation of THM. It was observed that the first-order kinetics with respect to [Ru(III)], [THM] and [H⁺]. It is clear from the experiential values of rate constant increase with increased concentration of each reactant. The investigators, thus, concluded that the variations of [p-toluene sulphonamide, PTS] and halide ions have an insignificant effect on the reaction rate. Protonated CAT, TsNHCl, and chloro complex of Ru(III), [RuCl₅(H₂O)]²⁻, have been suggested as the reactive species in acidic medium. The stoichiometry of the reaction is 1:1 in the presence of catalyst. The two main products, 4-amino-2-methyl-4,5-dihydropyrimidine-5-carbaldehyde and 2-(4-methyl-1,3-thiazol-5-yl)ethanol and 2-(4-methyl-1,3-thiazol-5-yl)ethanol were separated, and identified by column chromatography, TLC and FT-IR. Consequently, the interaction between the complex species and THM is supported kinetic orders of reaction by spectrophotometric verification, positive entropy of activation and the first-order rate constant increased with the decrease in the dielectric constant and increase ionic strength of the medium. The reaction constants involved in the mechanism were computed and the overall activation parameters were evaluated which lend support to the proposed mechanism.

Keywords: THM, Dielectric constant, Ionic strength, Polymerization, Catalysis and Activation parameters.

1. INTRODUCTION

This research paper describes a spectrophotometrical investigation of a nano concentration of Ru(III) used as homogenous catalysis oxidation of THM by CAT in acidic standard kinetics. The

mechanism of a chemical reaction cannot be completely described without the determination of its rate. The kinetic revision of a broad variety of chemical reaction is not only necessary for clean research but at all-time supplementary in industrial developed research with quality control. Investigations of analysis as well as methods of Kinetic have turned out to be a vital technique in enzyme, photo-chemistry and chemical catalysis, etc. The relevant study of oxidation of drugs is of immense significance both in mechanistic and synthetic point of view and it has approach's life also on the chemical system processes. Studies of the order of kinetics and mechanistic of redox reactions has been paying attention the notice of all chemists in the world and mechanistic of more than a few reactions have been undoubtedly delineated. Organic chemists used kinetic studies to find the mechanism of the organic reactions elsewhere and biochemists use kinetics to learn the rates of enzyme-catalyzed reactions. Chemical engineers used kinetics to calculate how quick the products will be formed and use thermodynamics to forecast the equilibrium work of art of the reaction mixtures. Polymer chemists used kinetics to explore the kinetics of the polymerization. Here in the present investigation we try to calculate the nano [Ru(III)] used as homogenous catalysis of the THM oxidation by CAT in acidic condition. Thiamine is sulfur-containing vitamin of the B complex and its chemical structure 2-[3-[(4 Amino,-methylpyrimidin-5-yl)methyl] 4methyl-thiazol-5-yl] ethanol (Fig.1) contains a thiazole ring with methyl, and aminopyrimidine with hydroxyethyl side chains linked by a methylene bridge.

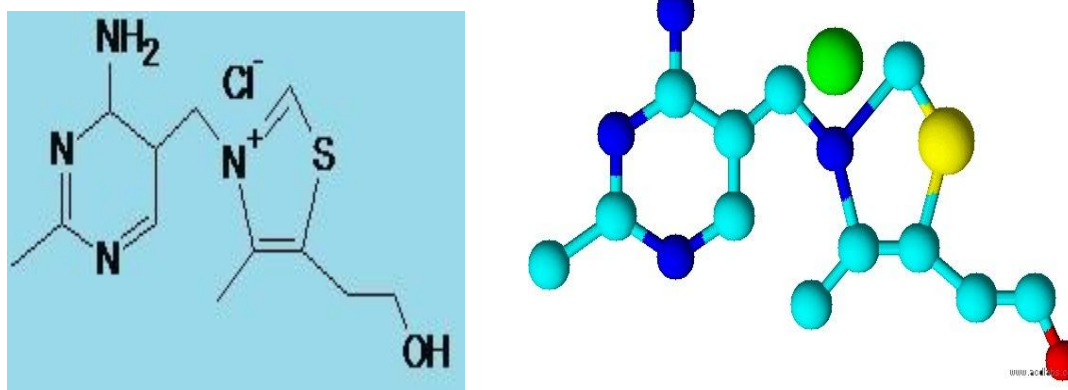


Figure 1. Chemical Structure of THM with 3D view

It is a biologically and pharmaceutically important vitamin, used in the biosynthesis in gamma aminobutyric acid (GABA) and neurotransmitter acetylcholine. It has also been used for the management of beri beri disease and cured. Since the discovery and isolation of THM, a number of protocols have been used in its determination, including spectrophotometry[1-5], microbial[6-7], spectrofluometry[8-16], chemiluminescence[17], potentiometric[18-20], rate of reaction[21] and UV photo degradation [4-5]. Most often, the methods focus on some extraction, expensive and intensive solvent and device are being used and most of the methods are time consuming. Spectrofluometry methods are frequently additional sensitive and selective than this methods applicable. CAT a well-known part of this group, (*p*-Me-C₆H₄SO₂NCINa.3H₂O or CAT), is a well-recognized analytical reagent, and the mechanism catalyzed aspects in numerous reactions have been done [22-27]. The

redox reaction of CAT decrease with an increase of the pH of the medium and the reaction conditions[28].

The CAT is a resource of +halogen and the most effective oxidant in both condition [29-30] and all the possible reaction for CAT had been well illustrated [25-27 and 31]. To our knowledge, this is the first report that aimed at the novel, and efficient procedure on the nano concentration of Ru(III) developed as homogenous catalysis for the oxidation of THM by CAT and their mechanistic pathway. Literature survey has revealed that no attention has been paid towards the oxidation of THM with oxidant CAT from the mechanistic point of view. The objectives of the work presented in this paper elucidate the plausible reaction mechanism, the formation of a complex which later decomposes at slow step, the obtainment and identification of the products, the efficiency of catalysis and also the evaluation of the reaction at different temperatures which allowed determining the activation parameter.

2. MATERIALS AND METHODS

2.1. Materials and Reagents

Appropriate amounts of Thiamine (Himedia), was prepared by dissolving a known amount in double distilled water. Chloramine-T (E. Merck) was purified by the method of Morris et al. [32]. An aqueous solution of CAT was prepared, standardized periodically by the iodometric titration, and stored in brown bottles to prevent its photochemical deterioration. The catalyst, ruthenium(III) chloride (Sigma) solution was prepared in HCl and standardized against EDTA [33]. Acetonitrile (Sigma) and acrylonitrile (Sigma) were used directly as received to study on the effect of solvent polarity in varying proportions (v/v) of water-acetonitrile mixtures on the reaction medium and free radical formation, respectively. All the other reagents were of analytical grade, and their solutions were prepared by dissolving the requisite amounts in doubly distilled water. HCl and NaClO₄ were employed to maintain the pH and ionic strength respectively.

2.2. Kinetic procedure

All the measurements were completed in glass Stoppard Pyrex boiling tubes coated black to do away with photochemical deterioration. The reaction was initiated by mixing previously thermo stated solutions of CAT and THM, which also contained requisite amounts of ruthenium(III) chloride, HCl, at constant ionic strength NaClO₄ ($I = 1.0 \text{ mol dm}^{-3}$) adjusted by Bronsted and Bjerrum Theory and the total volume constant of 50 ml keep with water. All the kinetic runs were equilibrated at 298K for 30 min. The progress of the reaction was monitored by estimating the amount of unreacted CATs iodometrically through a UVD-2960 double beam PC connected UV-vis spectrophotometer. All the potentiometric measurements were done with EL20 Education Line pH meter from Mettler Toledo Inc. The course of reaction was studied for at least two half-lives. The first-order rate constant was evaluated from a plot of $\log [\text{CAT}]$ versus time (Fig.2) and was reproducible within $\pm 5\%$. Regression

analysis of the experimental data to obtain the regression co-efficient, r was performed by using Microsoft 2010.

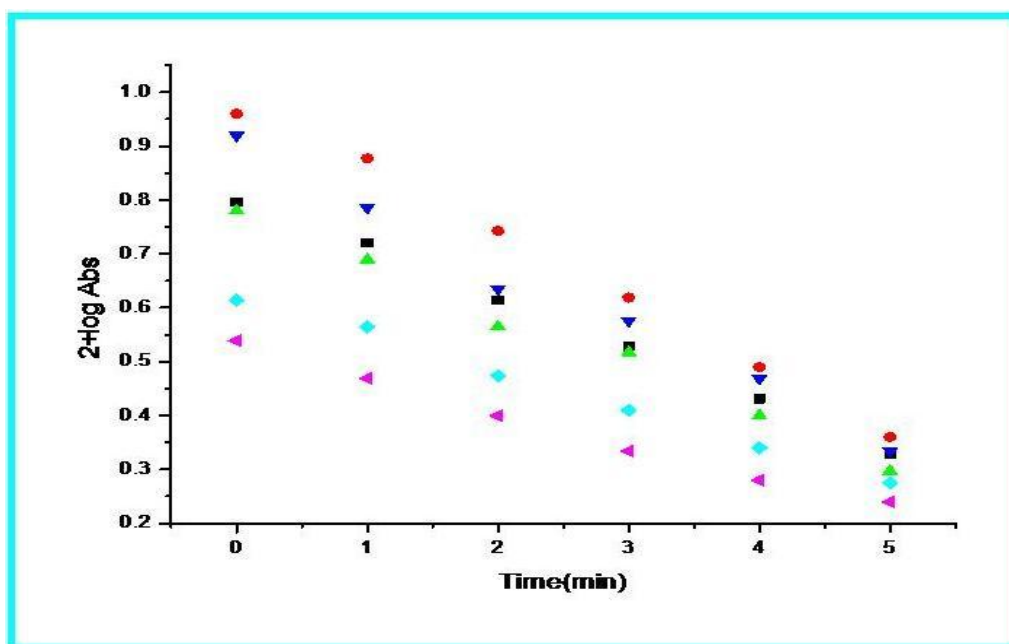
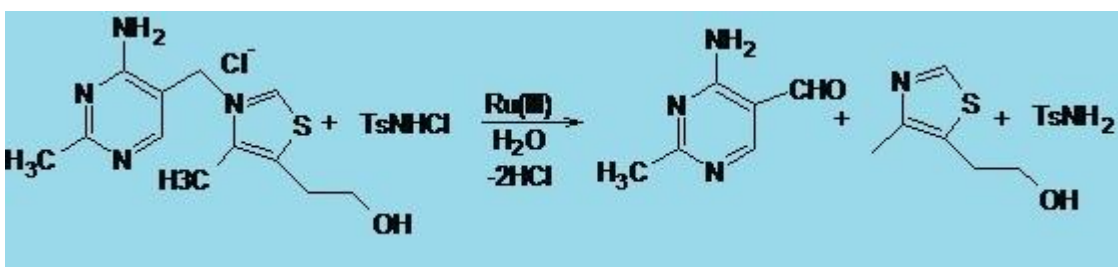


Figure 2. First order plots of Ru(III) catalyzed oxidation of THM by CAT in acidic medium.

3. RESULTS AND DISCUSSION

3.1. Stoichiometry and Product Analysis

Varying ratios of CAT to THM were equilibrated for 48 h in an inert atmosphere at 25°C in presence of catalyst. The unreacted concentration of oxidant was determined spectrophotometrically. The stoichiometry of the reaction was calculated by the limiting logarithmic method [34] and the results showed that one mole of THM consumed per mole of CAT in the presence of catalysts was 1:1. Scheme 1 represented the stoichiometric results in an acidic medium.



Scheme.1. A schematic representation of a stoichiometric ratio of the reaction mechanism for Ru(III) catalyzed oxidation of THM by CAT.

The product of THM-Ru-CAT mixture in the form of a stoichiometric ratio under stirred condition was satisfactory to run for 48 h in an inert atmosphere at 25°C. After completion of the stirring, the reaction products were separated, isolated and identified by column chromatography, TLC and FT-IR.

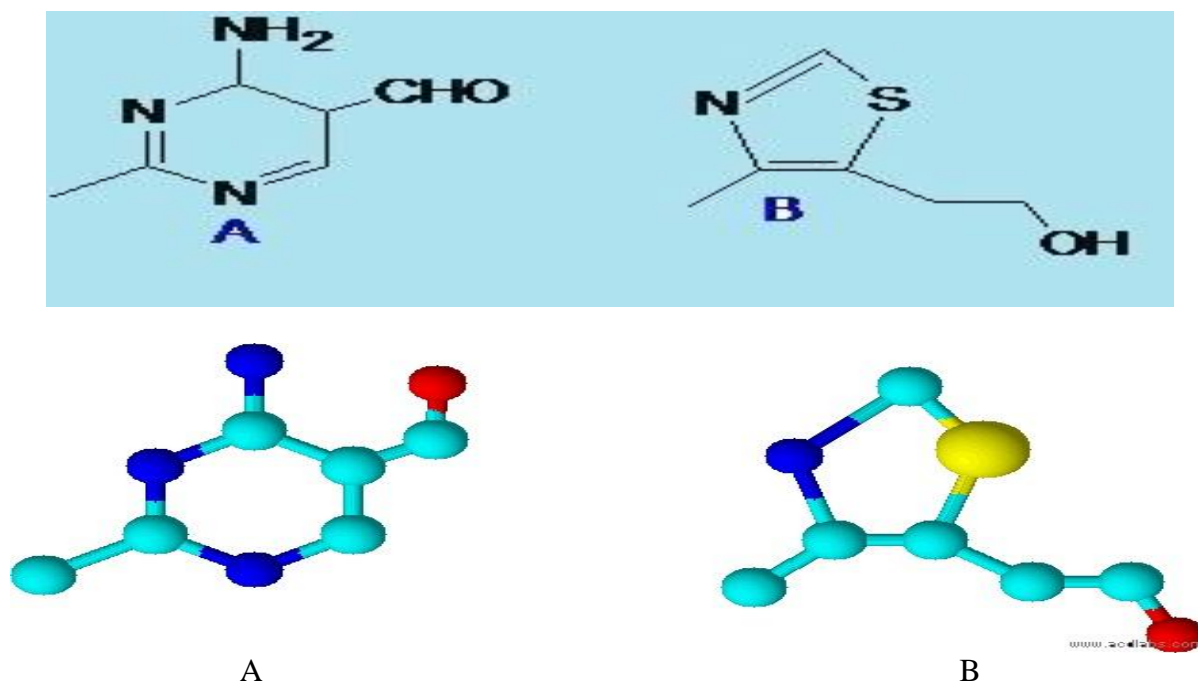


Figure 3. Chemical structure of the products of THM with balls & sticks 3D view(A)(B)

The two main products, FT-IR spectrum of first product 4-amino-2-methyl-4,5-dihydropyrimidine-5-carbaldehyde and 2-(4-methyl-1,3-thiazol-5-yl)ethanol (Fig.3) shows a peak at, 1652 cm^{-1} due to $\nu(\text{C}=\text{O})$ stretching of aldehyde; 3312 to 3395 cm^{-1} due to NH stretching absorption respectively. The IR spectrum of second product 2-(4-methyl-1,3-thiazol-5-yl)ethanol (Fig.3) showed an absorption band at $3110, 1518, 1484$ and 1252 cm^{-1} indicating the presence of $\text{CH}_3, \text{C}=\text{C}, \text{C}=\text{N}$ and $\text{C}-\text{S}-\text{C}$ respectively and a broad peak at 3325 cm^{-1} due to $\nu(\text{OH})$ stretching. The p-Toluenesulfonamide was extracted with ethyl acetate and identified by paper chromatography ($R_f = 0.905$). This method is supported by the literature [35-36].

3.2. Influence of varying catalyst concentrations on the rate

The concentration of catalyst was varied from 5.0×10^{-9} to $1.0 \times 10^{-8}\text{ mol dm}^{-3}$ keeping constant of other reaction ingredients. Pseudo-first-order rate constants were evaluated in view of concentrations of peracid and substrate (Fig.4). A plot of first-order rate constant against the concentration at the catalyst was made with straight line indicating first-order reaction in view of concentrations of catalyst.

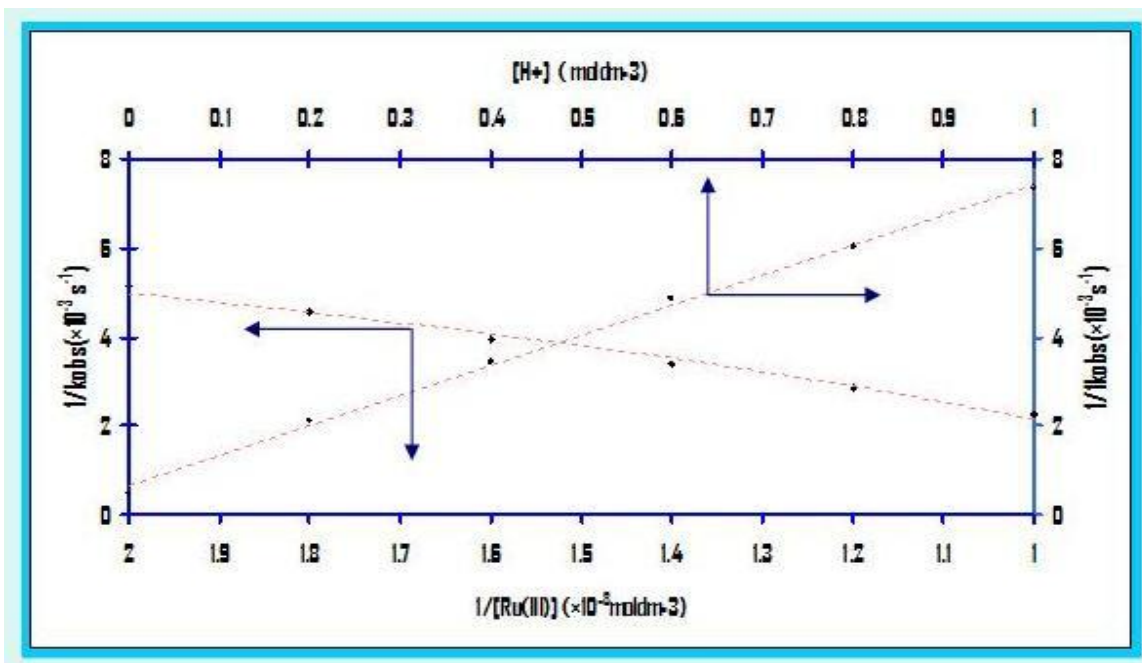


Figure 4.Confirmation of rate law (5) of Ru(III) catalysed oxidation of THM by CAT in the form of Eq. 6

3.3. Influence of varying oxidizing concentrations on the rate

The concentration of oxidizing was varied at fixed concentrations of other ingredients in an inert atmosphere at 25°C were calculated from the plot of rate constant against the concentration of CAT with straight line confirming first order with respect to oxidizing concentrations (Table 1).

Table 1. Effect of variations of CAT concentrations on the ruthenium(III) mediated oxidation of THM by CAT in acid medium at 25 °C

Variation of [CAT] × 10 ⁴ (mol.dm ⁻³)	k _{obs} × 10 ⁴ (s ⁻¹)	
	Observed	Calculated
1.0	7.51	7.51
2.5	7.57	7.51
5.0	7.56	7.51
7.5	7.55	7.51
10.0	7.55	7.51

3.4. Influence of varying substrate concentrations on the rate

In order to find out the Influence of rate on the concentration of substrate, the substrate was varied at constant concentration of other ingredients. The pseudo first-order rate constants (Table 2) were found to be increased with the increase in substrate concentrations. Further, the plot of first-order rate constant against the substrate concentrations is good with unity. At lower concentration of

substrate, the reaction was first order, and at higher concentration of substrate the reaction was independent.

Table 2. Effect of variations of THM concentrations on the ruthenium(III)mediated oxidation of THM by CAT in acid medium at 25 °C

Variation of [THM] $\times 10^3$ (mol.dm ⁻³)	$k_{\text{obs}} \times 10^4$ (s ⁻¹)	
	Observed	Calculated
1.0	6.20	6.18
2.0	6.44	6.45
4.0	7.25	7.28
6.0	7.48	7.51
8.0	7.64	7.77

3.5. Influence of varying acidity concentrations on the rate

The change in the kinetic rate of reaction with the change as the concentration of acidity is observed in present investigation. The first-order rate constants' decreases with the increase in acidity concentration (Table.3). The plot of $1/k_{\text{obs}}$ versus $\log [H^+]$ is linear and yields a fractional slope (Fig.4).

Table 3. Effect of variations of H^+ concentrations on the ruthenium(III) mediated oxidation of THM by CAT in acid medium at 25 °C

Variation of $[H^+]$	$k_{\text{obs}} \times 10^3$ (s ⁻¹)	
	Observed	Calculated
0.50	7.45	7.46
1.50	7.38	7.31
2.00	7.25	7.26
2.50	7.09	7.11
3.00	6.91	6.90

3.6. Influence of varying ionic strength and relative permittivity of the medium

The effect of ionic strength on the rate of the reaction was studied by varying the $NaClO_4$ from 0.1 to 2.0 mol dm⁻³, and keeping all other ingredients constant. It was found that the rate of the reaction is increased with increase ionic strength of the medium (Table 4).

Table 4. Effect of variations of ionic Strength and dielectric constant on the ruthenium(III) mediated oxidation of THM by CAT in acid medium at 25 °C

Ionic strength I (D) 35		dielectric constant D(I) 1.0 mol dm ⁻³	
I	k _{obs} × 10 ³	D	k _{obs} × 10 ³
0.1 mol dm ⁻³	2.35	60	4.36
0.5 mol dm ⁻³	3.22	55	4.44
1.0mol dm ⁻³	4.35	50	5.22
1.5mol dm ⁻³	4.38	45	6.41
2.0mol dm ⁻³	4.39	40	7.19
2.5mol dm ⁻³	4.45	35	7.63

The influence of the relative permittivity of the medium (*D*) was calculated by varying the CH₃CN-H₂O content (v/v) and keeping all other ingredients constant. The rate of reaction increases with decreasing CH₃CN content (Table 4).. The plot of log *k_{obs}* versus 1/*D* was linear (Fig 5) with a negative slope.

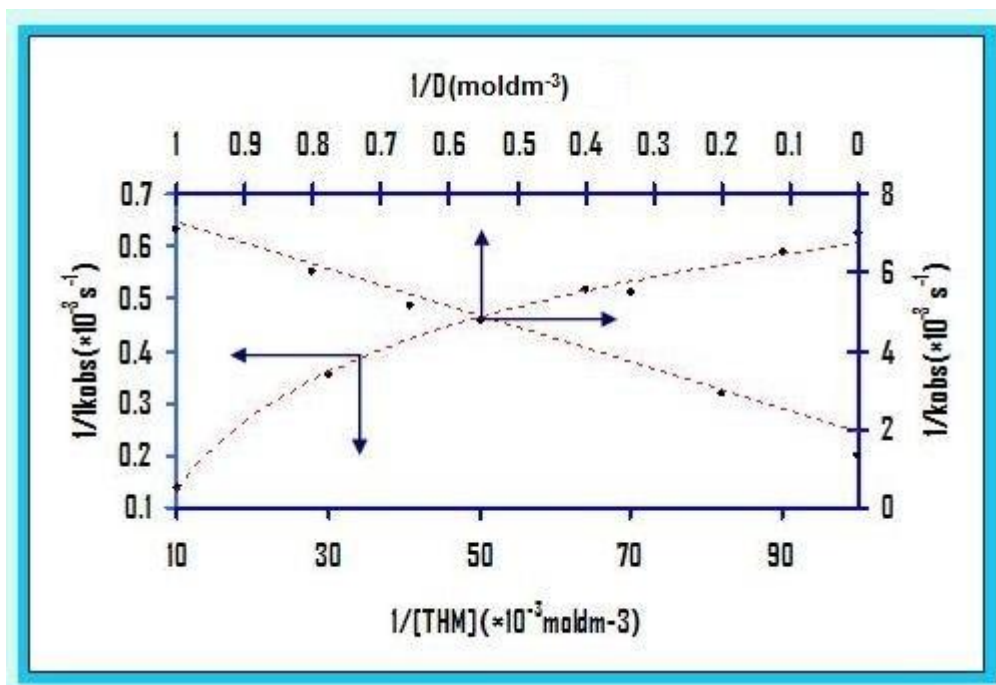


Figure 5. Effect of relative permittivity and substrate on the medium of Ru(III) catalysed oxidation of THM by CAT in acidic medium.

The values of *D* for CH₃CN-H₂O content (v/v) was calculated from the following equation
 $D = D_W V_W + D_A V_A$

where D_W and D_A are the dielectric permittivities of H_2O and CH_3CN and V_W and V_A are the volume fractions of H_2O and CH_3CN . The blank experiments of reacting with CAT and THM with alone CH_3CN did not affect on the rate of the reaction.

3.7. Influence of acrylonitrile study for the free radicals

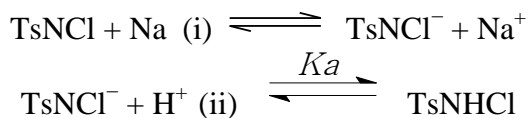
The test for free radicals was carried out by taking THM, CAT and Ru(III) in a round bottom with screw cap and rubber liner test tube and the acrylonitrile solution in another test tube. After equilibrated the system, the solutions were mixed and the reaction mixture was left for 24 h. A white precipitate of the THM product formed. This indicates that the reaction was routed through a free-radical path. It is also ascertained by the decrease in rate with initial addition of monomer.

3.8. Influence of varying temperature on the rate

The effect of temperature on the reaction rate was studied for all the kinetic runs at four different temperatures (20-37°C), keeping other ingredients conditions constant. The pseudo first-order rate constants thus obtained values are listed in Table 2. The activation parameters (E_a , ΔH^\ddagger and ΔS^\ddagger) have been evaluated using Arrhenius and Eyring equations from the linear Arrhenius plot of $\log k_{obs}$ versus $1/T$.

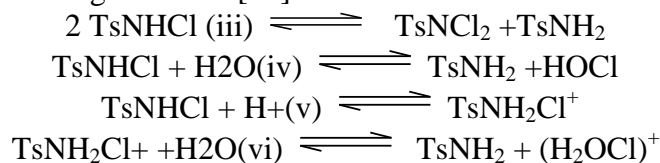
3.9. Reactive variety of CAT

In general, CAT undergoes a two-electron change in its reactions forming the reduction products, $TsNH_2$ and sodium chloride. The oxidation potential of $CAT-TsNH_2$ varies with the medium of the pH [37]. CAT behaves different types of reactive species in solution [38-39].

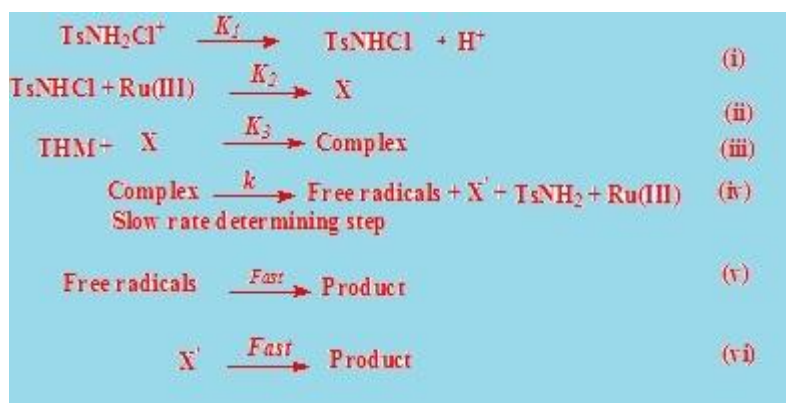


(CAT) (where, Ts represents $CH_3C_6H_4SO_2$ -group).

Thus, CAT exists as a free acid ($TsNHCl$) in acidic media. The dissociation constant of free acid at a pH ca. 4.5 is 2.8×10^{-5} by Morris et al. Further, free acid can undergo disproportionate or hydrolysis according to following reactions [40]:



It appears from the equilibrium (i)–(vi), that various probable oxidizing species of CAT exists in acidic media such as $TsNHCl$, $TsNCl_2$, $TsNH_2Cl$, $TsNH_2$, $HOCl$ and H_2OCl^+ . In the present work, the rate dependence on $[H^+]$ that the deprotonation of $TsNH_2Cl^+$ results for the formation of $TsNHCl$, which is a probable oxidizing species involved in the oxidation of LF in acid medium (Scheme 2).



Scheme 2. A general reaction mechanism for Ru(III) catalyzed oxidation of THM by CAT in acidic medium.

3.10. Catalytic activity

It has been pointed out by Moelwyn-Hughes [41] that, even in presence of the catalyst, the uncatalyzed reactions also proceed simultaneously, so that

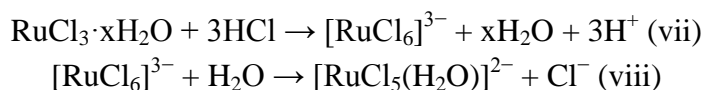
$$k_{\text{obs}} = k_0 + k_c [\text{catalyst}]^x$$

Here, k_{obs} is the observed pseudo first-order rate constant obtained in the presence of Ru(III) catalyst, k_0 is the pseudo first-order rate constant for the uncatalyzed reaction, k_c is the catalytic constant and x is the order of the reaction with respect to [Ru(III)]. In the present investigations, 'x' value was found to be unity. Thus, the value of k_c is calculated using the following Eq.

$$k_{\text{obs}} = k_0 + k_c / [\text{Ru(III)}]$$

3.11. Reactive species of Ruthenium (III) chloride

Ruthenium (III) chloride catalysis is very complex as a result of the formation of different intermediate complexes, free radicals and oxidizing states. A small number of investigation have been reported as Ru(III) complex in aqueous condition by the ion exchange and spectrophotometric method [42-44]. They obtained a number of octahedral complexes in the hydrated form as $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$, $[\text{RuCl}_4(\text{H}_2\text{O})_2]^{-}$, $[\text{RuCl}_3(\text{H}_2\text{O})_3]$, $[\text{RuCl}_2(\text{H}_2\text{O})_4]^{+}$ and $[\text{RuCl}(\text{H}_2\text{O})_5]^{2+}$. However, in other studies Ru(III) behaves different reactive variety in acid solution [45-47], the following equations can exist as:

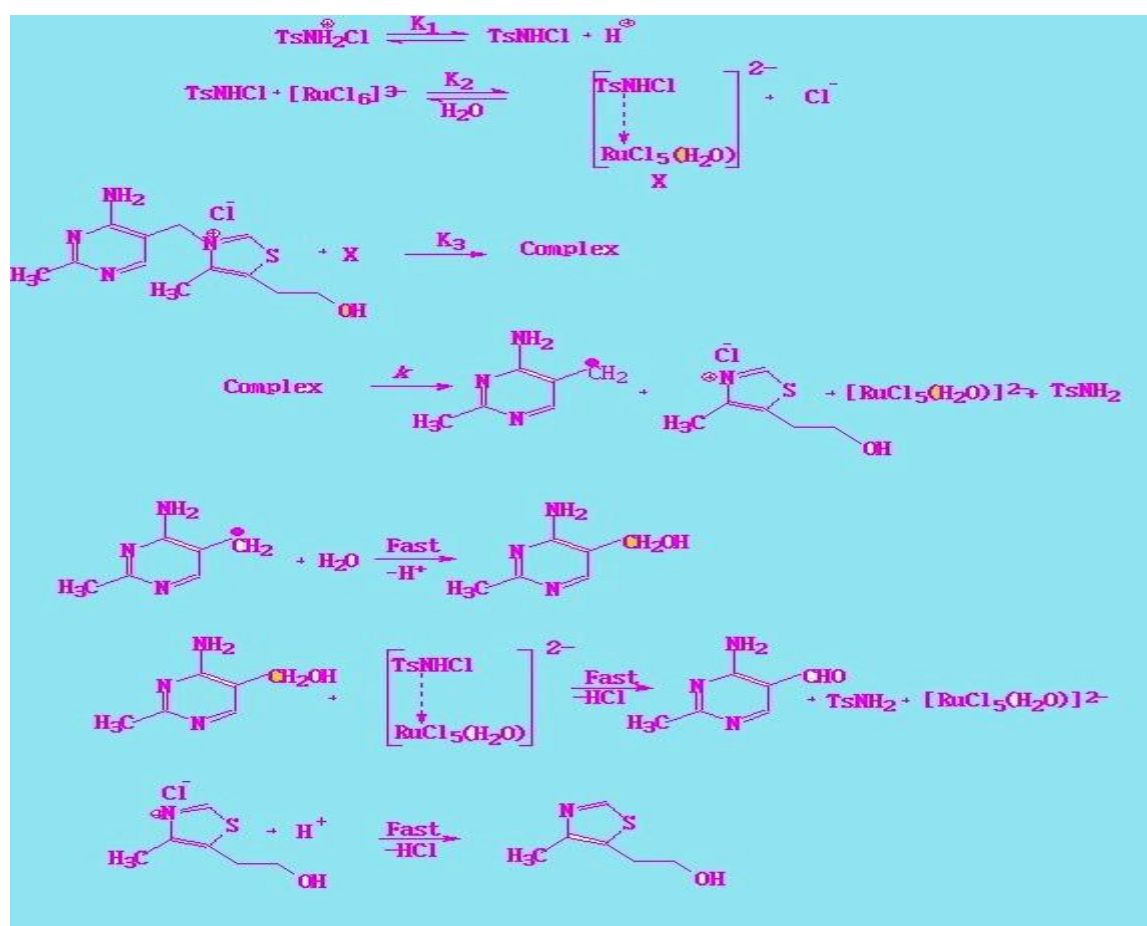


In the present study, chloride ion does not play any role in any circumstances in the reaction form on the rate and hence the reactive species, $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$, is assumed to be the homogenous catalyst.

The reaction between CAT and THM in the presence of Ru(III) catalyst has a stoichiometry of 1:1 with a first order dependence both on the [CAT] and on the [Ru(III)], and less than a unit-order dependence on both the per acid and substrate concentrations. No effect of added products such as, p-

toluenesulfonamide (PTS), and the addition of halides ions NaCl and NaBr did not affect the rate of the reaction. These results indicate that the halide ions play no role in the reactions. Similarly, the reaction was studied for the effect of [HCl], keeping other ingredients constant, the rate of reaction decreased with the increase in [HCl] (Table 3). The plot of $\log k$ versus $\log [\text{HCl}]$ was linear ($r = 0.9951$) with a negative slope of 0.41, showing an inverse fractional-order dependence of rate on [HCl]. Hence, the dependence of rate on [HCl] confirms the effect of $[\text{H}^+]$ only.

A mechanism and derivation of rate law according to the reaction (Scheme 2) a detailed plausible mechanism of oxidation of THM by CAT in acidic medium using Ru(III) as homogeneous catalyst may be well accommodated (Scheme 3).

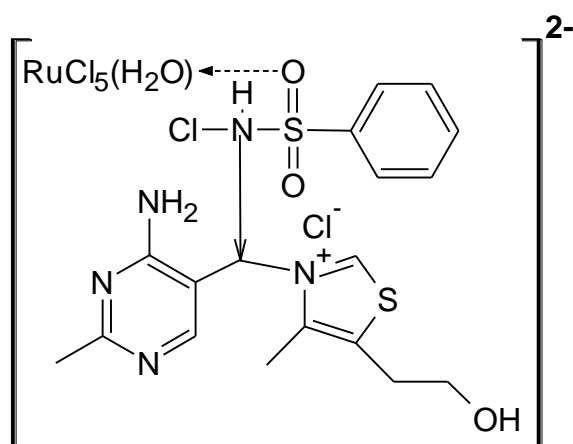


Scheme 3. A schematic representation of composite rate constant reaction mechanism for Ru(III) catalyzed oxidation of THM by CAT in acidic medium.

Oxidation of THM by CAT in presence of Ru(III) catalyst is a non-complementary reaction through six equivalent changes. In the light of these considerations, a plausible form of this reaction scheme and structures of the complex intermediate species are depicted in Scheme 2. A plausible mechanism is explained in Scheme 3, it appears that the TsNH_2Cl^+ deprotonate in an initial equilibrium to form the conjugate free acid TsNHCl . In the second step, the donor nitrogen atom of the TsNHCl combines with metal centre of the Ru(III) catalyst to form an intermediate complex. Further,

intermediate complex reacts with substrate forming a complex, which is reduced in a slow step to give the product TsNH₂, a free radical and an unstable complex derived from THM with regenerating the catalyst, Ru(III). This free radical undergoes hydrolysis to give another intermediate product, (2,4-Dimethyl-pyrimidin-5-yl)-methanol. This intermediate product, (2,4-Dimethyl-pyrimidin-5-yl)-methanol reacts with X in a fast step to give the final product 4-amino-2-methylpyrimidine-5-carbaldehyde. The unstable complex formed in the rate determining step react with H⁺ to give another final product, 2-(4-methylthiazol-5-yl)-ethanol. The effect of the dielectric constant in presence of 1.0 mol dm⁻³ NaClO₄ solution, keeping other ingredients constant. It was found that the rate constant increases with decreasing dielectric constant as the ionic species are involved in the reaction medium. This means reactants are more solvated at low dielectric constant rather than that at higher values [48].

A plot of 1/k_{obs} versus 1/[THM] (Fig.4) shows an intercept which is in conformity with the complex formation. The formation of this complex was proved kinetically by Michaelis–Menten plot, i.e., a non-zero intercept. The probable structure of the complex is



The results can be verified by spectrophotometric measurements of the complex formation between the substrate and catalyst mixtures. A bathochromic shift, of complex ca .5 nm from 240 to 245 nm is observed. Analogous effects upon complex formation have been observed in other investigations [18].

The total effective concentration of CAT can be written as
 $[CAT]_t = [TsNH_2Cl^+] + [TsNHCl] + [X] + [Complex]$ (1)

On the basis of scheme 2, solving equations for [TsNH₂Cl⁺], [TsNHCl] and [X] and Substituting in equation 1 we get

$$[Complex] = \frac{K_1K_2K_3 [CAT]_t [THM] [Ru(III)]}{[H^+] + K_1 + K_1K_2 [Ru(III)] + K_1K_2K_3 [THM] [Ru(III)]}$$
 (2)

Since,

$$Rate = \frac{-d[CAT]}{dt} = k[Complex]$$
 (3)

Substituting equation (2) in equation (3), the following rate law can be obtained:

$$\text{Rate} = \frac{-d[\text{CAT}]}{dt} = \frac{kK_1K_2K_3[\text{CAT}]_t[\text{THM}][\text{Ru(III)}]}{[\text{H}^+] + K_1 + K_1K_2[\text{Ru(III)}] + K_1K_2K_3[\text{THM}][\text{Ru(III)}]} \quad (4)$$

Rate law 4 may be rearranged to Eq. 5, which leads to the following rate law:

$$\frac{\text{Rate}}{[\text{CAT}]_t} = K_{obs} = \frac{kK_1K_2K_3[\text{THM}][\text{Ru(III)}]}{[\text{H}^+] + K_1 + K_1K_2[\text{Ru(III)}] + K_1K_2K_3[\text{THM}][\text{Ru(III)}]} \quad (5)$$

Eq. (4) is the rate law on the basis of which observed kinetic orders with respect to the reactants of the reaction evaluated. On reversing Eq. (5), we get eq.(6)

$$\frac{1}{K_{obs}} = \frac{[\text{H}^+]}{kK_1K_2K_3[\text{THM}][\text{Ru(III)}]} + \frac{1}{kK_2K_3[\text{THM}][\text{Ru(III)}]} + \frac{1}{kK_3[\text{THM}]} + \frac{1}{k} \quad (6)$$

or

$$\frac{1}{K_{obs}} = \frac{1}{kK_3[\text{THM}]} \left\{ \frac{[\text{H}^+]}{K_1K_2[\text{Ru(III)}]} + \frac{1}{K_2[\text{Ru(III)}]} + 1 \right\} + \frac{1}{k} \quad (7)$$

The equation 7, indicates that the linear plots of $1/k_{obs}$ vs. $1/[\text{THM}]$, $[\text{H}^+]$ and $1/[\text{Ru(III)}]$ was obtained with a straight line and positive intercept on y-axis (Figs 4 and 5), this proves the validity of the rate law (4), and hence, the proposed reaction scheme has been derived. Similarly, k , K_1 , K_2 and K_3 was calculated and found as $5.32 \times 10^2 \text{ s}^{-1}$, $5.68 \times 10^3 \text{ mol l}^{-1}$, $4.12 \times 10^{-2} \text{ mol}^{-1} \text{ l}$, $3.11 \times 10^{-4} \text{ mol}^{-1}$, respectively. The values of catalytic constant kc was evaluated at different temperatures (298–318 K) and kc was found to be increased with the increase in temperature. Further, plots of $\log kc$ versus $1/T$ were linear ($r > 0.9823$) and the values of activation parameters for the catalysts were computed. All these values are shortened in Table 5. The proposed reaction mechanisms are supported by the experimental moderate values of activation energy. The other activation parameters were calculated and obtained a high positive asset value of the free energy of activation, and of the enthalpy of activation support the formation of highly solvated transition state. The value of ΔS^\ddagger within the range for radical reaction has been recognized in the nature of electron pairing and unpairing processes and to the loss of degrees of freedom to the reactants ahead in the formation of rigid transition state [49-50] The negative of ΔS^\ddagger value indicates that the complex is more ordered than the reactants [51].

Table 5. Values of the catalytic constant (k_c) at different temperatures and activation parameters for the oxidation of THM

Temperature (K)	$1/T \times 10^3$	$k_c \times 10^4 (s^{-1})$
293	3.413	4.34
298	3.356	7.51
303	3.300	7.56
308	3.246	7.86
Activation parameters		
E_a (kJ mol ⁻¹)	102.1	
ΔH^\ddagger (kJ mol ⁻¹)	98.2	
ΔS^\ddagger (J K ⁻¹ mol ⁻¹)	-112.5	
ΔG^\ddagger (kJ mol ⁻¹)	82.3	

The reduction product, PTS did not retard the reaction rate significantly, that means PTS is not involved in any step prior to the rate limiting step. A detailed mechanistic explanation is given in Scheme 3.

4. CONCLUSIONS

On the basis of experimental data, a detailed kinetic model of THM catalysis and oxidation is discussed in this research paper. Relevant information about the reaction mechanism, with highlights on the major reaction paths and intermediates, can be taken from this kinetic modeling work. This kinetic study points out that the free radicals and together with intermediates. The two main products, 4-amino-2-methyl-4,5-dihydropyrimidine-5-carbaldehyde and 2-(4-methyl-1,3-thiazol-5-yl)ethanol were separated, and identified by column chromatography, TLC and FT-IR. The oxidant, TsN₄Cl⁺ exists in acid medium as TsN₄Cl, which takes part in the chemical reaction. The rate constant of slow step and other equilibrium constants involved in the mechanism are evaluated and activation parameters with respect to slow step of reaction were computed. The overall mechanistic sequence described here, is consistent with the products formed.

ACKNOWLEDGEMENT

This work was funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under grant No. (130-066-D1434). The authors, therefore, acknowledge with thanks DSR technical and financial support.

References

1. A.F.Dannet and J.M. Calatayud, *Talanta*, 41(1994) 2147-2151.
2. F.A. Elessi, S.I. Alkhalil, A.Z. Abuzuhr and M.S. Abdelatif, *Talanta*, 44(1997)2051-2058.
3. K.Srividya and N. Balasubramanian, *Chem. Pharm. Bull.*, 45(1997)2100-2103

4. A. M. Romero, C. G. Benito and J. M. Calatayud, *Anal. Lett.*, 25(1992)1289-1308.
5. S. Garcia, C. T. Gomez Benito and C. J. Martinez, *Anal Chim Acta*, (1993)279-293.
6. F. M. R. Macias, *Appl. Microbiol.*, 5(1957)249-252.
7. R. H. J. Diebel, J. B. Evans and C. F. Niven, *J. Bacteriol.*, 74(1957) 818-821.
8. H. Chen, X. Cao, Q. Fang and J. Zhu, *Analyst*, 123(1998)1017-1021.
9. N. Jie, D. Yang, Q. Zhang, J. Yang and Z. Song, *Anal. Chim. Acta.*, 359 (1998) 87-92.
10. R. T. Perez, L. C. Martinez, V. Tomas and I. Ibarra, *Talanta*, 39 (1992)907-911.
11. N. Jie, J. Yang and Z. Zhan, *Anal Lett.*, 26(1993)2283-2289.
12. X. Q. Guo, J. G. Xu, Y. Z. Wu, Y. B. Zhao, X. Z. Huang and G. Z. Chen, *Anal. Chim. Acta.*, 276 (1993) 151-160.
13. C. M. Lozano, T. P. Ruiz, V. Tomas and C. Abellan, *Analyst*, 115 (1990) 217-220.
14. K. N. Mohana, N. Prasad and K. M. L. Rai, *Monatsh Chem.*, 139 (2008)1203-1210.
15. K. N. Mohana and K. R. Ramy, *J. Mol. Catal. A: Chem.*, 302 (2009) 80-85.
16. K. S. Byadagi, D. V. Naik, A. P. Savanur, S. T. Nandibewoor and S. A. Chimatadar, *Reac. Kinet. Mech. Cat.*, 99(2010)53-61.
17. N. Grekas and A. C. Calokerinos, *Talanta*, 37(1990)1043-1048
18. S. S. M. Hassan and E. Elnemma, *Talanta*, 36(1989)101.
19. A. Ciszewski and J. Wang, *Analyst*, 117(1992)985-988.
20. I. Y. Petukhova, M. A. Zarechenskii and A. N. Gaidukevich, *J Anal Chem* 51(1996)934.
21. M. A. Ryan and J. D. Ingle Jr, *Anal. Chem.*, 52(1980) 2177-2184.
22. K. S. Rangappa, K. M. Swamy, M. P. Raghavendra and N. M. M. Gowda, *Int. J. Chem. Kinet.*, 34(2002)49-55.
23. P. A. Prasantha. N. C. Sandhya. B. K. Kempegowda, D. G. Bhadregowda, K. Mantelingu, S. Ananda, K. Koppal, S. Rangappa and M. N. Kumara, *J. Mol. Catal. A: Chem.*, 353(2012)111-116.
24. Puttaswamy, A. Sukhdev and J. P. Shubha, *J. Mol. Catal. A: Chem.* 310 (2009) 24-33.
25. S. Jain and R. Nagwanshi, *Oxid Commun.*, 29(2006)41.
26. B. Pare, V. W. Bhagwat, C. Fogliani and P. Sing, *Int J Chem Sci* 5(2007)322.
27. A. K. Singh, R. Negi, Y. Katre and S. P. Singh, *J. Mol. Catal. A: Chem.*, 36(2009)302.
28. A. R. V. Murthy and B. S. Rao, *Pro. Indian Acad. Sci.*, 35(1952)69-72.
29. A. Shukla, S. Gupta and S. K. Upadhyay, *Int. J. Chem. Kinet.*, 23(1991)279-288.
30. Puttaswamy, T. M. nuradha, R. Ramachandrappa and N. M. M. Gowda, *Int. J. Chem. Kinet.*, 32(2000) 32, 221
31. A. A. P. Khan, A. M. Asiri, N. Azum, M. A. Rub, A. Khan and A. O. A. Youbi, *Ind. Eng. Chem. Res.*, 51(2012)4819-4824.
32. J. C. Morris, J. A. Salazar and M. A. Wineman, *J. Am. Chem. Soc.*, 70(1948) 2036.
33. T. M. Veeresh, C. V. Hiremath and S. T. Nandibewoor, *J. Phys. Org. Chem.*, 20(2007)55-64.
34. A. A. P. Khan, A. M. Asiri, A. Khan, N. Azum, M. A. Rub, M. M. Rahman, S. B. Khan, K. S. Siddiqi and K. A. Alamry, *J. Ind. Eng. Chem.*, 19(2013)595-600.
35. Puttaswamy, R. V. Jagadeesh, V. Nirmala and A. Radhakrishna, *J. Mol. Catal. A. Chem.*, 229 (2005) 211-220.
36. Puttaswamy, A. Sukhdev and J. P. Shubha, *J. Mol. Catal. A: Chem.*, 310 (2009) 24-33.
37. R. V. Puttaswamy, N. Jagadeesh, A. Vaz and Radhakrishna, *J. Mol. Catal. A: Chem.*, (2005)229.
38. E. Bishop and V. J. Jennings, *Talanta*, 32(1958)1082.
39. F. F. Hardy and J. P. Johnston, *J. Chem. Soc. Perkin. Trans 1*, 2(1973)742.
40. S. S. Narayanan and V. R. S. Rao, *Radiochim. Acta.*, 49 (1981)193.
41. E. A. Moelwyn-Hughes, *The Kinetics of Reaction in Solutions*. Oxford University Press London 297 (1947)
42. H. H. Cady and R. E. Connick, *J. Am. Chem. Soc.*, 80(1958) 2646-2652.
43. R. E. Connick and D. A. Fine, *J. Am. Chem. Soc.*, 82(1960) 4187-4191.

44. F.A. Cotton , G. Wilkinson, C.A. Murillo and M.Bochmann, *Advanced Inorganic Chemistry*, 4th ed, Wiley,New York(1999)
45. T. Davfokratova,*Analytical Chemistry of Ruthenium*.Academy of SciencesUSSR, 54(1963)
46. J.R. Backhours, F.D. Doyer and N. Shales, *Proc. Roy. Soc.*, (1950)146.
47. W.P.Griffit, *The Chemistry of Rare Platinum Metals*. Interscience New York 4 (1967)
48. A.A.P. Khan, A. Khan, A.M .Asiri and M.A. Rub, *J.Tai.Inst.Chem.Eng.*,1(2014)127–133.
49. C. Walling, *Free Radicals in Solution* (Academic Press, New York, 1957), p. 38
50. A.A.P. Khan, A.M. Asiri, A. Khan, N. Azum, M.A. Rub, M.M. Rahman and S.B. Khan, *Res. Chem.Intermed.*,39 (2013) 2379-2389.
51. A.A.P. Khan, A.M .Asiri, A. Khan, N.Azum, M.A.Rub, M.M. Rahman, S.B. Khan, K.S.Siddiqi and K.A. Alamry, *J. Ind. Eng. Chem.*, 19(2013)595–600.

© 2015 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).