Journal of Kufa for Chemical Science Vol(2).No(3). …………………….. Dec 2017

Kinetics Of Oxidation Of Threonine By N-Chlorosuccinimde Using Chloro Complex of Rh(III).

Noori . Y. Salman, Kismah . H. Alniami

Faculty of Dentistry, University of Kufa /Iraq

norvi.alanqshi@uokufa.edu.iq

الخلاصة:-

تم استخدام معقد كلوريد الروديوم الثلاثي كعامل مساعد متجانس في اكسدة الثرونين بواسطة n-كلوروسكسينميد **NClS** في وسط حامضي. اظهرت حركية التفاعل ان المرتبة من الدرجة الاولى في كل من **n** -كلوروسكسينميد **NClS** والروديوم الثلاثي ومن المرتبة الصفرية في الثرونين . كما تم اضافة ناتج التفاعل (سكسينميد) الى التفاعل ولم يلاحظ اي تاثير على سرعة تفاعل الاكسدة كما درس تاثير كل من القوة الايونية وثابت عزل الوسط وايون الكلوريد على سرعة تفاعل الاكسدة. اقترح في هده الدراسة ان H_2OBr^+ و $[Rh(H_2O)Cl_5]^{-2}$ هي المركبات الفعالة الناتجة من المركب **NClS** وكدلك كلوريد الروديوم الثلاثي في الوسط الحامضي. كما تم حساب ثوابت سرع التفاعل في اربع درجات حرارية مختلفة وحساب عوامل التنشيط الطاقية كما اثبت ان الناتج من تفاعل الاكسدة هو مركب الدهايدي.

Abstract

Rh(III) chloro complex as homogeneous catalyst has been used in the oxidation of threonine by N-chlorosccinimde (NClS) in acid medium. The reaction shows first order kinetics with respect to NClS and zero order in threonine concentrations, the reaction also shows first order kinetics with respect to Rh(III). The reaction product [succinimide] was added to the reactions and had no effect on the rate of oxidation of threonine by NClS using Rh(III). Changing ionic strength, dielectric constant and chloride ion of the medium has no effect on the rate of oxidation. H_2OBr^+ and $[Rh(H_2O)Cl_5]^{-2}$have been suggested to be the reactive species of NClS and Rh(III) chloride at this pH. The rates were determined at four different temperatures and the activation parameters were evaluated. Aldehyde have been identified to be the oxidation products of the reaction.

Introduction

The uses of N-chorosuccinimide (NClS) as an agent for allylic chlorination were reviewed in 1948 [1]. N-halo compounds also reacted with olefins to add chlorine to the double bond or as a source of hypohalous acids in aqueous solution[1]. This group of compounds such as N-bromosuccinimide[2-,3], N-chlorosuccinimide[4-5], Bromamine-T[6], N-chloronicotinamide[7], Chloroamine-T[8], N-bromophtalimide[9], and 1-chlorobenzotrialzole[10]have been used successfully as an effective agents for, oxidation,halogenation[11-12]and dehydrogenations[13-14]. Rhodium complexes are reported as versatile catalyst , which can be used for several oxidation reaction (15-17). The uses of Rh (III) chloro complex as homogeneous catalyst has been reported for the oxidation of reducing sugars by N-halocompounds[18-20] in acid medium. As a part of our kinetic investigations employing N-halosuccinimide reagents as oxidants[21]. We have investigated the kinetics oxidation of threonine by NClS at 308K^o and [H$^+$]=0.05M

Experimental Methods:

A recrystallized NClS compound[22-23] was used and the iodometric titration of active chlorine was used to determine the purity . Solution of NClS was freshly prepared, because decomposition occurs on standing or exposure to light · Preparation of Rh (III) chloride solution was by dissolving the sample in hydrochloric acid of known strength. A standard solution of mercuric acetate was acidified with acetic acid. All other standardized solution of potassium chloride, sodium perchlorate were prepared with doubly distilled water. Threonine (0.05 mol) and NClS (0.01 mol) made up to 50 ml in perchloric acid (0.25M) stored in the dark for 12 hr until completion of oxidation, the solution was then treated with excess of standard solution of 2,4-dinitrophenyl hydrazine in 2M hydrochloric acid. The precipitated 2,4-dinitrophenyl hydrazone was collected and filtration. TLC and melting point of mixture of DNF confirmed that the product was acetaldehyde. The stoichiometry was ascertained by treating (0.01 mole) threonine with (0.05 mole) NClS in presence of perchloric acid (0.25M) and estimation of consumed NClS showed that one mole of NClS was consumed to oxidize one mole of threonine, the following stoichiometric equation is suggested

Threonine + NClS ↔ RCHO + RNH_2+ Br^- + H^+

All UV kinetic measurements were performed using the absorbance reading at different time using the standard infinity method. The chosen bands were used for the kinetic runs were at wavelength 265nm (fig. 1).

Results and Discussion.

Kinetics pf oxidation of threonine in presence of Rh (III)chloride complex have been studied at 35^{o}c. The reactions were followed up to 70% reaction, pseudo-first order reactions were carried out by keeping an exess 10 times greater of the threonine over NClS. Several initial concentrations of reactants have been used. The pseudo first order rate constant, k_1 was computed from plots of log $[A_t\text{-}A_\infty]$ against time (fig.2). The pseudo first order rate constants are constant for varying the concentration of NClS and are given in table (1). No change occurred in the rate constant with increasing the concentration of threonine, so the reaction is zero order in threonine (table 2). Changing ionic strength and dielectric constant of the medium did not influence the oxidation rates. Different activation parameter have been calculated for the first order rate constants of the oxidation of threonine by NClS at different four temperatures (table 3, fig. 3). The reaction product [succinimide] was added to the reactions and had no effect on the rate of oxidation observed. In the reaction kinetics studies of Rhodium chloro complexes as hydrogenation catalysts, the anionic complexes have been reported[24] such as $[RhCl_6]^{-3}$, $[Rh(H_2O)Cl_5]^{-2}$ and $[Rh(H_2O)_2Cl_4]^-$ activate molecular hydrogen for reduction of ferric ion in aqueous acid solution. Harrod and Helpern[25] have carried out studies with $RhCl_3$ in 3-5M HCl solutions and suggested that $[RhCl_6]^{-3}$ was the predominant species in solution. In the oxidation of phenyl acetylene, the authors have assumed $[Rh(H_2O)_3Cl_3]$ as the main species of Rh(III)chloride in acidic medium. In this study the oxidation of threonine by NClS in acidic medium Rh(III)chloride has been used as homogeneous catalyst and prepared in 3M HCl, and in the kinetic run (10^{-9}M) of Rhodium (III) chloride was used, Hence the earlier literature reported explain that, the original solution of Rhodium(III) chloride prepared in 3M HCl will contain the lone species $[Rh(H_2O)\ Cl_5]^{-2}$and can be consider the reactive species of Rhodium (III) chloride in the oxidation of threonine by NClS in acidic medium. This suggestion can be supported by the observation of non- effect of $[Cl^-]$ on the rate of oxidation. The order of reaction was first with respect to [Rh (III)] and it 's evident from the observed values of first order rate constant which show increase when the concentration of [Rh (III)] is increased (table 4, fig. 4). No effect of the added succinmide on the rate of oxidation of threonine. This clearly rules out the possibility of Cl^+ being the reactive species of NClS in the present investigation, since considering N^+ClSH or H_2OBr^+ or both as the reactive species of NClS, should give a positive effect of $[H^+]$ on the rate of oxidation which is clearly observed by the positive effect of $[H^+]$ on the rate of oxidation (table 5, fig 5). Thus, H_2OCl^+ and N^+ClSH species remains as the reactive species of NClS for the oxidation of threonine in acidic medium.From this observation it is likely that in the absence of added mineral acid the oxidation species is HOCl. Literature survey of the reaction of primary alcohols by N-bromoacetamide[26], absence of a primary kinetic isotope effect for the alcohol-NBS reaction, give an explanation, that the C-H bond is not cleaved in the rate-determining step, hence the bond O-H rupture is involved in the rate determining step. the aldehyde will be formed in a fast step.

The UV-Vis spectra of NClS and Rh(III) chloride or threonine causes an increase in the absorbance, this confirm the existence of complex or complexes between various reactive species of the reactants have been investigated (Scheme 1).

$$\mathbf{RCHNH_2COOH + [Rh(H_2O)\,Cl_5]^{-2} \leftrightarrow \underset{X_1}{complex} + H_2O}$$

$$\mathbf{RNHCl + H_2O \rightarrow RNH_2 + HOCl}$$

$$\mathbf{HOCl + H_3O^+ \leftrightarrow H_2OCl^+ + H_2O}$$

$$\mathbf{H_2OCl^+ + (x_1) \rightarrow \underset{X_2}{complex} + [Rh(H_2O)Cl_5]^{-2}}\ \textbf{slow and R.D.S}$$

$$\mathbf{(x_2) \rightarrow RCHO + H^+ + Br^-}\ \textbf{fast}$$

$$\mathbf{R = k_1k_4k'\,[Rh(III)Cl_5]^{-2}\,[H_2OCl^+]\,[H^+]/k_5(k_1[H_2O] + k_4[H_2OCl^+])}$$

Scheme 1

Table 1. Effect of increasing the concentration NClS on the rate constant of oxidation of threonine , [Threonine]=0.03M, $[H^+]$= 0.05M, Rh(III) = $1.5x10^{-9}$M, Temp.= 308K°

10^3 [NClS] /$molL^{-1}$	1.0	3.0	5.0
$10k_1/s^{-1}$ (theronine)	0.223	0.255	0.211

Table 2. Effect of increasing the concentration [threonine] on the rate constant of oxidation of threonine by NClS, [NClS]= $3x10^{-3}$, [H^+]= 0.05M, Rh(III) = $1.5x10^{-9}$M, Temp.= 308K°

[theronine]/M	0.03	0.05	0.07	0.09
$10k_1/s^{-1}$	0.223	0.235	0.241	0.225

Table 3. Temperature dependence of reaction rate constant and activation parameters for oxidation of threonine by NClS

10k, s^{-1} at T, K						
303	**308**	**313**	**318**	**ΔH/kJ mol^{-1}**	**-ΔS/J mol^{-1}**	**ΔG/kJ mol^{-1}**
0.202	0.223	0.453	0.901	80.33	19.68	86.390

Table 4.Effect of [Rh(III)] on the rate constant of oxidation of threonine by NClS, [NClS]= $3x10^{-3}$, [H^+]= 0.05M, , Temp.= 308K°[threonine] = 0.03M

10^9[Rh(III)/ $molL^{-1}$	1.5	3.0	5.0	7.0
$10k_1/s^{-1}$	0.223	0.339	0.423	0.489

Table 5. Effect of increasing the concentration of H^+on the rate constant of oxidation of threonine by NClS, [NClS]= $3x10^{-3}$, [Rh(III)= $1.52x10^{-9}$M, Temp.= 308K°[threonine] = 0.03M

$[H^+]$/ $molL^{-1}$	0.03	0.05	0.07	0.10	0.15	0.2	0.3
$10k_1/s^{-1}$	0.223	0.233	0.244	0.251	0.321	0.399	0.412

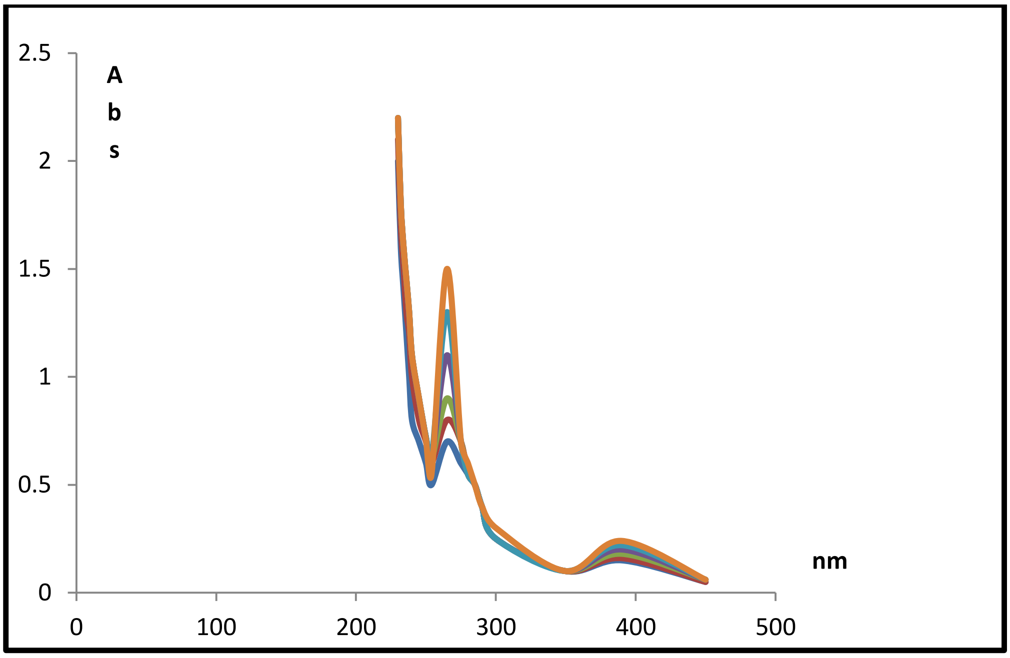

Fig. 1 UV absorpion spectra for the reaction between threonine and NClS, con. of threonine=0.03 M and NClS=0.003M

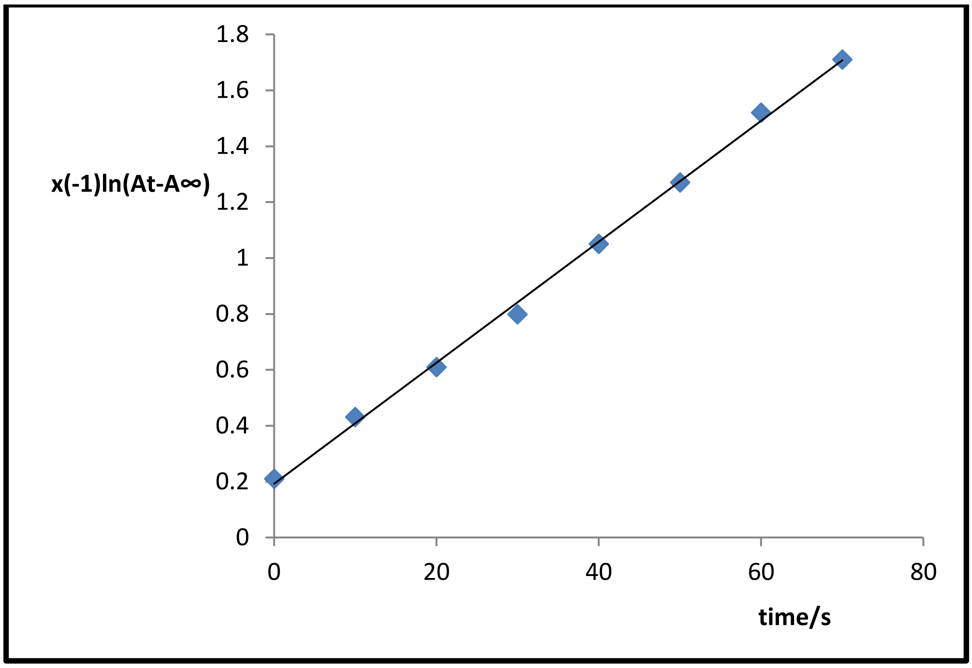

Fig. 2 shows the kineic data for the oxidation of threonine by NClS ,at308K, concentrations of threonine =0.03M, H+ =0.05M, Rh=1.5x10-9 M and

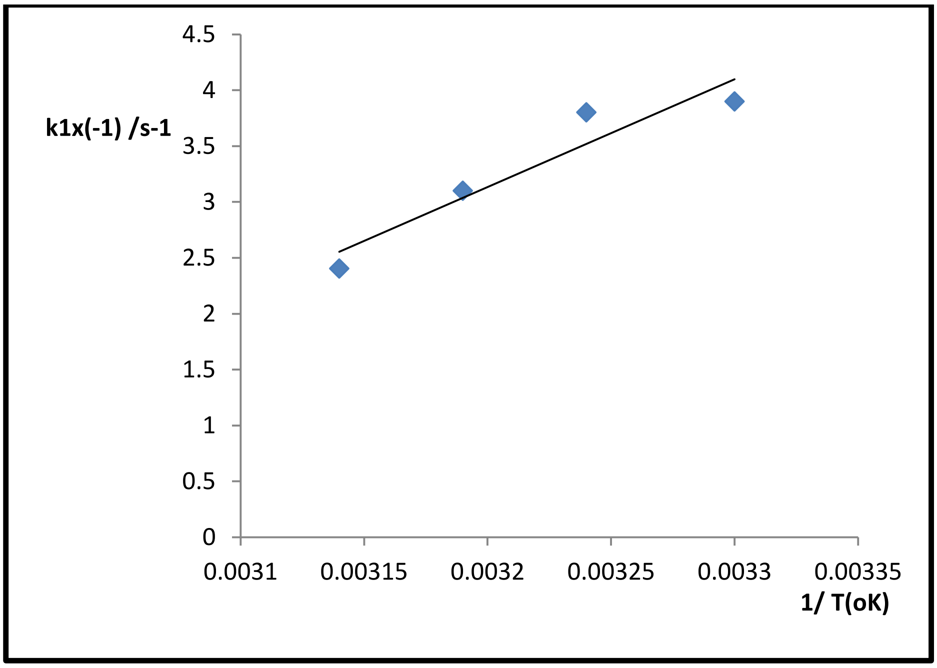

Fig. 3 shows the efffect of increasing temperature on the rate of oxidaion of theronine by NClS at 308Ko

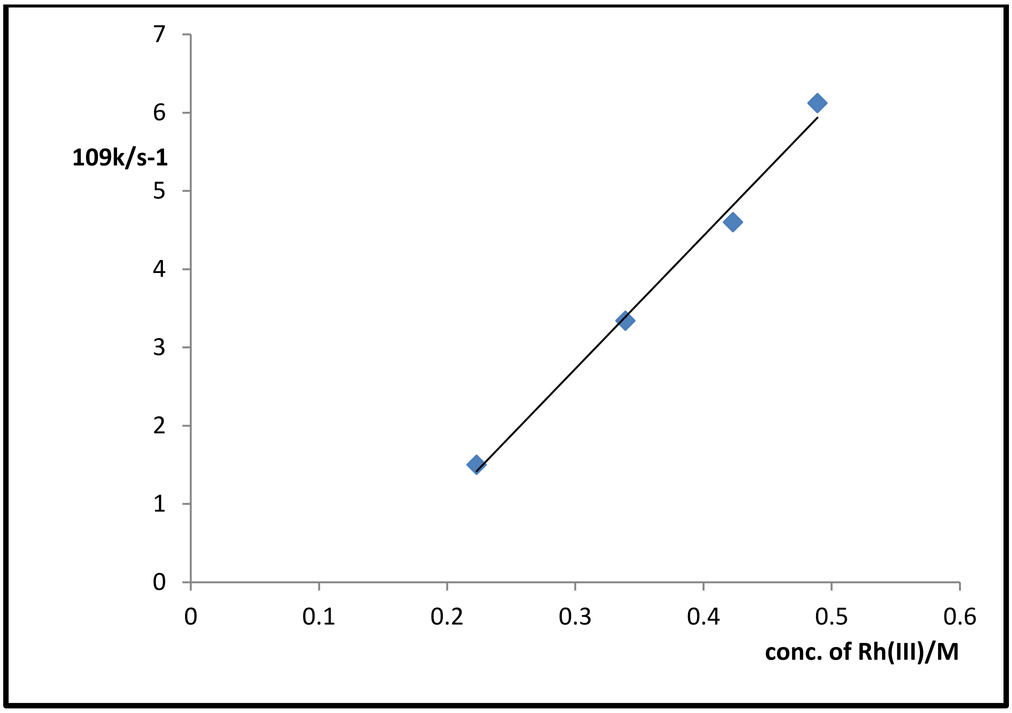

Fig. 4 shows the effect of increasing the conc. of Rh(III) on the rate of reacion between theronine and NClS, [theronine]=0.03M, [NClS]=0.003M at 308Ko

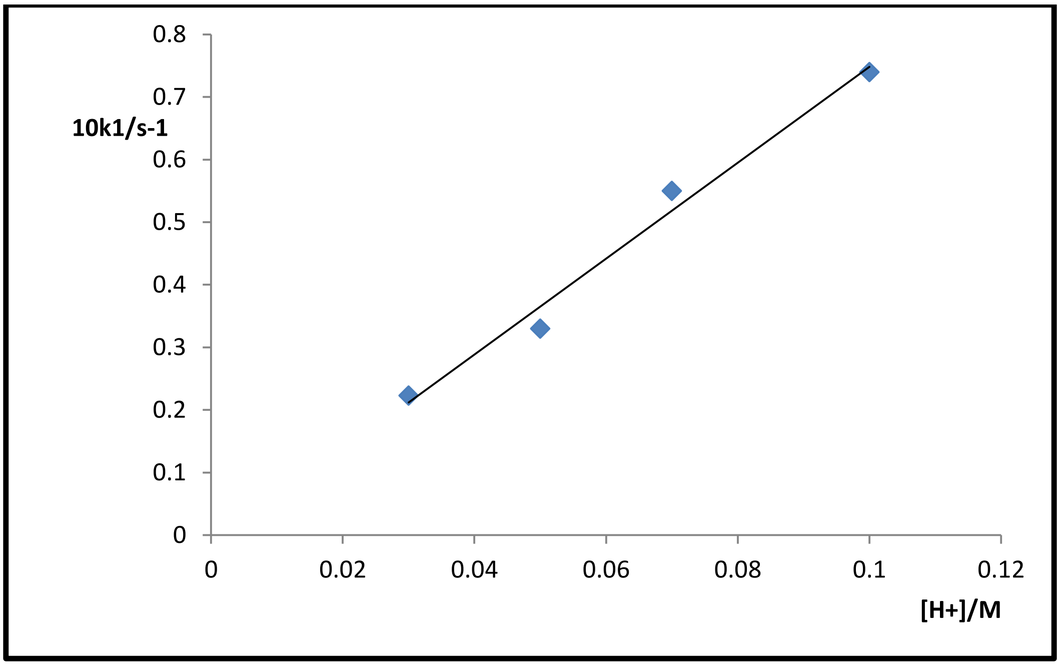

Fig. 5 shows the effect of increasing the concentration of H+ on rate of oxidation of threonine by NClS at 308Ko , [NClS] =0.003 M & [threonine]

References:

1-C.D. Jerassi, , (1948*)*. ***Chem. Rev***., 43, 271.

2- Thiagarajan V. and N. Venkatasubramanium, (1970). ***Indian J. Chem****,* 8, 809.

3- G. Gopalakrishanan and B. R. Pai, , (1979). ***Indian J. Chem,*** 18, 92.

4- N. S. Srinivassan and N. Venkatasurbramanian, (1974). ***Tetrahedron,*** 30, 419.

5- S. C. Negi and K. K. Benergji, (1982). ***Indian J. Chem, Sec.B***. 21, 846.

6- A. K. Bharat sigh and B. L. Saxena, (1982). ***Tetrahedron Letts*.,** 40, 5203. 7- N. Mathiyalagan, R. Sridharan and V. Priya, (2005) ***Indian J. Chem,*** **Soc**., 82, 795.

8- H. M. K. Naidu and D. S. Mahadevappa, (1988). ***Indian J. Chem***. 27, 880.

9- BharadJagdish and Ubla Milind, (2009). ***Indian J. Chem,*** **Soc**. 86, 481.

10- R. Hiremath and M.S. Mayanna, (2005). ***J. Chem*** . Sci. 177, 333.

11-S.Sivakamasundari and R.Gansen, (1980). ***Int. J. Chem. Kinest*.**, XII, 837.

.12-B. Singh , J. Sharma, L. Pandey and S. M. Pandey, (1990). ***Tetrahedron,*** 38, 169.

13-V. Venkatasubramanian and V. Thiagarajan, (1969) ***Canad.,J. Chem***., 47, 694.

14-H. S. Kipton, C. E. Badwel and J. Agric, (1973). ***Fd Chem***. 21, 235.

13- R. Filler, (1963). ***Chem. Rev***., 63, 21 .

14- S. Kothari and K.K. Banerji, (1985*)*. ***Can. J. Chem*.** 63**,** 2726.

15- S. Srivastava, S. Singh and A. Jaiswall, (2007). ***Bull, Cata. Soc. India***, 6**,** 121.

16- P. K. Tondon and M. Dhusia, (2009). ***Transition Met. Chem***. 34, 121.

17- P. S. Radhakrishnamurti and S. A. Misra, (1982). ***Int. J. Chem. Kinet***., 14, 631.

18- A. K. Singh, R. Singh, J. Srivastava, S. Rahmani and S. Srivastava, (2007). ***J. Organo metallic Chem*.,** 692, 4270**.**

19- A. K. Singh, R. K. Singh, J. Srivastava, S. Rahmani and S. Srivastava, (2010). ***Transition Met. Chem***. 35, 349

20- A. K. Singh, R. K. Singh, J. Srivastava, S. Rahmani, S. Yadav and S. Srivastava

(2011). ***J. Iranian Chem*. Soc**., 8, 622.

21-N. Y. Salman and K. H. alniami, (1999). ***Ibn al-haitham J. for pure & app*. Sci** 10,(2)

22- A. J. Berka , J. Vulterin and J. Zyka, (1963). ***Newer Redox Titrants*, New York**, 37.

23-A. R. Murthy and B. S. Rao, (1952). ***Proc. Indian acad*. Sci**, 35, 69.

24- B. R. James and G. L. Rempel, (1966). ***Can. J. Chem***., 44**,** 233.

25- J. F. Harrod and J. Halpern, (1959).***Can. J. Chem***., 37**,** 1933.

26- J. R. Balyeat, (1979). ***Gov. Rep. Announce.* Index** (U.S), 79, 106.