International Research Journal of Natural and Applied Sciences
ISSN: (2349-4077)
Impact Factor- 5.46, Volume 4, Issue 7, July 2017
Website- www.aarf.asia, **Email** : editor@aarf.asia , editoraarf@gmail.com

KINETIC ACTIVITY AND CATALYTIC STUDY OF NOVEL COMPLEXES OF SELECTED TRANSITION AND D^{10} METAL IONS.

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ABSTRACT

Heterocyclic compounds and their derivatives represent an interesting class of compounds having a wide spectrum of biological activities such as antiinflammatory, anticancer, antitubercular, antiviral and antimicrobial properties. The present investigation involved the synthesized novel complexes's (Kynurenic acid-KYNA + Metal carbonates) chemical kinetic study with (i)$K_2S_2O_8$ + KI (ii) HBrO3 + HI and (iii) H_2O_2 + HI . The product of all these three reactions is iodine, and it was titrated with standard aqueous sodium thiosulphate by starch solution as indicator. The rates of all these reactions were measured by simple kinetic methods therefore one of the chief applications of coordination compounds, as catalysts was investigated. These complexes were used to investigate whether they own catalytic activity in homogeneous or heterogeneous phase. One organic reaction, formation of benzpinacol from benzophenone was studied. Catalytic effects of the complexes were studied and useful outcome was obtained.

Keywords: Kynurenic Acid(KYNA), Kinetic Study, Catalytic Activity.

INTRODICTION

Chemical kinetics is one of the component of chemistry and it deals with reaction rates and their reliance on various factors like reactant, concentration temperature, catalysis etc. Different reactions take place at different rates, like few of them as in the detonation of explosives go to close in fractions in a second, others continue for minutes, hours or days and still others, like those occurring in the earth's crust , may take tens hundreds or thousands of years.[1]

The reaction process investigates throughout the measurement of the rate with which a reaction happened and the dependence of this reaction rate on the concentration of the reacting species and on the temperature that is the central experimental approach. [2] The change of concentration per unit is identified as rate and its general unit is $mol.dm^{-3}s^{-1}$. Usually, the reaction rate rises with increase of concentration. [3] In a chemical reaction, the reactant's concentration reduces and that of a product augments as the reaction progresses. As per law of mass action the velocity of a chemical reaction rely on the concentration of the reactants. Since the concentration reduces with time, the reaction rate also decreases. So the reaction velocity commonly does not remain stable but varies with time. There are many of techniques for determination for the extent of reaction with respect of time. The reaction rate can be resolute with respect to any of the reactants or products. For accurate measurements, the temperature of the reaction must be kept constant, and it can be done by carrying out the reaction in a thermostat.

Experimental

Analytical grade chemicals were used throughout the whole experimental work. Spetroscopic grade solvents were taken for recording the spectra. The biologically active compound kynurenic acid (Sigma) was used as the ligand. All metal carbonates used were also A.R. grade. A calculated quantity of 70% $HClO_4$ was diluted with water to get 0.2M perchloric acid solution. The exact strength was resolute by pH metric titration against standard 0.2M NaOH solution. Solid metal carbonate was added in 75 ml 0.2 M perchloric acid till effervescences observed (slight excess addition was done). The solution was stirred for half an hour and filtered and thus the metal perchlorate in aqueous solution was achieved. The creation of complexes was done by mixing 50 mL (0.2M) metal perchlorate solution and 50 mL(0.2M) ligand in DMSO solution. The mole ratio of ligand and metal was (1:1). The reason for this ratio is lack of prior knowledge and then reaction mixture was refluxed for 3.0

hrs at 95 ^{0}C temperature. After 3.0 hrs the reaction mixture was cooled. There was no instant precipitation observed, then into this solution, ice water was supplemented and immediately precipitates were gained. The complexes thus obtained were washed with double distilled water and alcohol to remove unreacted metal and ligand. All the complexes were dried in an oven at 45° C to 55 ° C. These all complexes were then characterized by chemical and instrumental methods to elucidate their structures.[4] In this work, the set up of experiments and measurement of all the second order reactions has been done by standard procedures [5] at room temperatures. Solutions of all the seven complexes were prepared in DMSO and in the blank sets; the same volume of DMSO was added to equate the effect of solvent on the reaction. Catalytic quantities of complexes were added to the reaction systems.

Results and discutions

Part A : 3d Metal Ion Complexes (Kinetic Study)

Reaction:-1

In this testing, there were the same concentrations of the two reaction species of a second order reaction. In the calculation "a" and "b" taken are the primary concentration of potassium persulphate and potassium iodide in that order[6]. The second order reaction happening is

$$K_2S_2O_8 + 2KI \rightarrow 2K_2SO_4 + I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

Table – 1 Reaction kinetics (Without Catalyst):

Reaction of	: $K_2S_2O_8$	+ KI	+ DMSO	
Concentration	: (0.0227M)	(0.0227M)	--	
Volume	: 50ml	50ml	10ml	(t_∞ =125ml)

Temperature = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
5	3.2	4.20 X 10^{-5}
10	3.7	2.44 X 10^{-5}
15	4.1	1.80 X 10^{-5}
20	4.6	1.52 X 10^{-5}
25	5.0	1.33 X 10^{-5}
30	5.5	1.22 X 10^{-5}

Average k = 2.085 x 10^{-5}

a=b=initial concentrations of reactants = 0.022M

Reaction 2

In this step of the study, 1% catalytic amount of the Mn-KYNA[$Mn(C_{10}H_6NO_3)_3.H_2O$], was added in the same reaction ($K_2S_2O_8$ + KI), and all parameters were kept alike and remaining all the additions were accurately same as per Table1. After the addition of Mn-KYNA in the reaction mixture, the results of these catalytic experiments are noted in table -2.

Table – 2 Reaction Kinetics Table With Mn –KYNA

Reaction of : $K_2S_2O_8$ + KI + Mn-KYNA

Concentration : (0.0227M) (0.0227M) DMSO solution

Volume : 50ml 50ml 10ml (t_∞ =125ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.3	9.71 X 10^{-5}
10	0.7	1.15 X 10^{-4}
15	1.0	1.11 X 10^{-4}
20	1.5	1.27 X 10^{-4}
25	1.8	1.24 X 10^{-4}
30	1.9	1.09 X 10^{-4}

Average k = 1.13 x 10^{-4}

a=b=initial concentrations of reactants =0.0227M

Reaction 3

In this step of the study, 1% catalytic quantity of the Co-KYNA [$Co(C_{10}H_6NO_3)_3$], was added in the same reaction ($K_2S_2O_8$ + KI), and all parameters were set matching and remaining all the additions were precisely the same as per Table-1. After the adding of Co-KYNA in the reaction mixture, the readings of these catalytic experiments are noted in table -3.

Table – 3 Reaction Kinetics Table With Co-KYNA solution

Reaction of : $K_2S_2O_8$ + KI + Co-KYNA

Concentration : (0.0227M) (0.0227M) DMSO solution

Volume : 50ml 50ml 10ml (t_∞ =125ml)

T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.6	1.96 X 10^{-4}
10	0.7	1.15 X 10^{-4}
15	0.7	7.68 X 10^{-5}
20	0.8	6.58 X 10^{-5}
25	0.8	5.28 X 10^{-5}
30	0.9	4.97 X 10^{-5}

Average k = 9.27 x 10^{-5}

a=b=initial concentrations of reactants =0.0227M

Reaction 4

In this stage of the study of the unchanged reaction ($K_2S_2O_8$ + KI) was conducted by adding of 1% catalytic amount of the Ni-KYNA [$Ni(C_{10}H_6NO_3)_3$] .H_2O. All the additions and circumstances were set precisely same as Table-1. After adding of the Ni-KYNA in the reaction mixture, the readings of these catalytic tests are reported in table -4.

Table – 4 Reaction Kinetics Table With Ni-KYNA

Reaction of : $K_2S_2O_8$ + KI + Ni-KYNA

Concentration : (0.0227M) (0.0227M) DMSO solution

Volume : 50ml 50ml 10ml (t_∞=125ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.8	2.64 X 10^{-4}
10	1.0	1.66 X 10^{-4}
15	1.2	1.34 X 10^{-4}
20	1.4	1.18 X 10^{-4}
25	1.6	1.09 X 10^{-4}
30	1.8	1.03 X 10^{-4}

Average k = 1.49 x 10^{-4}

a=b=initial concentrations of reactants = 0.0227M

Reaction 5

In this stage of the study, the identical reaction ($K_2S_2O_8$ + KI) was conducted by an addition of 1% catalytic amount of the Cu-KYNA [$Cu(C_{10}H_6NO_3)_2.(H_2O)_2$]. All the additions and factors were set accurately same as per Table-1. After the addition of Cu-KYNA, the readings of these catalytic tests are reported in table -5.

Table – 5 Reaction Kinetics Table With Cu-KYNA

Reaction of : $K_2S_2O_8$ + KI + Cu-KYNA

Concentration : (0.0227M) (0.0227M) DMSO solution

Volume : 50ml 50ml 10ml (t_∞ =125ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.7	2.30 X 10^{-4}
10	1.0	1.66 X 10^{-4}
15	1.0	1.11 X 10^{-4}
20	1.3	1.09 X 10^{-4}
25	1.4	9.49 X 10^{-5}
30	1.6	9.09 X 10^{-5}

Average k = 1.34 x 10^{-4}

a=b=initial concentrations of reactant = 0.0227M

Reaction: 6

The experimentation was done for one more second order reaction with two reacting species $HBrO_3$ and HI and their concentrations were the same. In the calculation "a" and "b" both are respectively the initial concentration of potassium bromate and potassium iodide respectively. The second order reaction going on is

$$KBrO_3 + HCl \longrightarrow KCl + HBrO_3$$

$$KI + HCl \longrightarrow KCl + HI$$

$$HBrO_3 + 6HI \longrightarrow HBr + 3H_2O + 3I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

For the handiness of calculations, the concentrations choosen are 0.0096M (for both). The calculated value of t_∞ became 25 ml in terms of 0.0096M hypo solution and the calculation is based upon the equivalence $N_1V_1=N_2V_2$ where N and V are molarities and volumes of potassium bromate and potassium iodide respectively.

There were two different reagent bottles with $HBrO_3$ and HI having 0.01 N HCl 25ml volume for the reaction with or without catalyst. In the reaction set, without catalyst, also 10ml of DMSO was supplement to HI having reagent bottle-2. Two solutions were mixed very well and the time was noted. After every five minutes lapse the progress of the reaction was verified by determining the concentration of liberated iodine by titration against sodium thiosulphate solution using starch as an indicator. From the reaction mixture, 25ml solution was taken at every five minute gap. Previous to this titration, ice was added to the flask to quench further development of the reaction. A solution of the catalyst in 10ml DMSO is supplemented to check the catalytic effect of the complexes prepared. The readings of kinetics and rate constant values ware noted in Table-6.

Table – 6 Reaction Kinetics Table (Without Catalyst) :

Reaction of	:	$HBrO_3$	+ KI + HCl	+ DMSO	
Concentration	:	(0.0096M)	(0.0096M)	--	
Volume	:	25ml	25ml	10ml	(t_∞ =25ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
5	6.9	3.04 X 10^{-3}
10	7.4	1.68 X 10^{-3}
15	7.7	1.18 X 10^{-3}
20	8.6	1.04 X 10^{-3}
25	9.0	0.9 X 10^{-3}
30	9.5	0.81 X 10^{-3}

Average k = 1.44 X 10^{-3}

a=b=initial concentrations of reactants = 0.0096M

Reaction 7

In this step of the study, the same reaction ($HBrO_3$ + KI + HCl) was conducted by an addition of 1% catalytic amount of the Mn-KYNA [$Mn(C_{10}H_6NO_3)_3.H_2O$]. Remaining all the additions and circumstances were exactly equal as per table-6. After addition of the Mn-KYNA in the reaction mixture, the readings of these catalytic experiments are reported in table -7.

Table – 7 Reaction Kinetics Table With Mn –KYNA.

Reaction of : $HBrO_3$ + KI + HCl + Mn –KYNA

Concentration : (0.0096M) (0.0096M) DMSO solution

Volume : 25ml 25ml 10ml ($t\infty$ =25ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.4	1.30 X 10^{-4}
10	0.8	1.32 X 10^{-4}
15	1.0	1.11 X 10^{-4}
20	1.5	1.27 X 10^{-4}
25	1.8	1.24 X 10^{-4}
30	1.9	1.09 X 10^{-4}

Average k = 1.22 X 10^{-4}

a=b=initial concentrations of reactants = 0.0096M

Reaction 8

In this step of the study, the equal reaction ($HBrO_3$ + KI +HCl) was conducted by an addition of 1% catalytic quantity of the Co-KYNA [$Co(C_{10}H_6NO_3)_3$]. All the parameters were accurately equal as per Table-6. After addition of the Co-KYNA, the results of these catalytic experiments are reported in table -8.

Table – 8 Reaction Kinetics Table With Co-KYNA.

Reaction of : $HBrO_3$ + KI + HCl + Co-KYNA

Concentration : (0.0096M) (0.0096M) DMSO solution

Volume : 25ml 25ml 10ml ($t\infty$ =25ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.4	1.30 X 10^{-4}
10	0.6	9.83 X 10^{-5}
15	0.9	9.95 X 10^{-5}
20	0.9	7.46 X 10^{-5}
25	1.0	6.66 X 10^{-5}
30	1.0	5.55 X 10^{-5}

Average k = 8.741 X 10^{-5}

a=b=initial concentrations of reactants =0.0096M **Reaction 9**

In this step of the study, the same reaction ($HBrO_3$ + KI + HCl) was conducted by an addition of 1% catalytic quantity of the Ni-KYNA [$Ni(C_{10}H_6NO_3)_3$] .H_2O. Remaining all the additions were set accurately equal as per Table-6. After addition of the Ni-KYNA in the reaction mixture, the readings of these catalytic experiments are noted in table -9.

Table - 9 Reaction Kinetics Table With Ni-KYNA

Reaction of : $HBrO_3$ + KI + HCl + Ni-KYNA

Concentration : (0.0096M) (0.0096M) DMSO solution

Volume : 25ml 25ml 10ml ($t\infty$ =25ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.5	1.6 X 10^{-4}
10	0.6	9.8 X 10^{-5}
15	0.8	8.7 X 10^{-5}
20	0.9	7.4 X 10^{-5}
25	0.9	5.9 X 10^{-5}
30	1.0	5.5 X 10^{-5}

Average k = 8.93 X 10^{-5}

a=b=initial concentrations of reactants = 0.0096 M

Reaction 10

In this step of the study, the similar reaction ($HBrO_3$ + KI + HCl) was conducted by an addition of 1% catalytic quantity of the Cu-KYNA [$Cu(C_{10}H_6NO_3)_2.\ (H_2O)_2$]. Remaining all the additions were set accurately equal as per Table-6. After addition of the Cu-KYNA in the reaction mixture, the readings of these catalytic experiments are noted in table -10.

Table – 10 Reaction Kinetics Table With Cu-KYNA

Reaction of : $HBrO_3$ + KI + HCl + Cu-KYNA

Concentration : (0.0096M) (0.0096M) DMSO solution

Volume : 25ml 25ml 10ml ($t\infty$ =25ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k= 1/at * X/(a-x) (lit.mol^{-1} min^{-1}
05	0.8	2.64 X 10^{-4}
10	1.0	1.66 X 10^{-4}
15	1.1	1.22 X 10^{-4}
20	1.3	1.09 X 10^{-4}
25	1.4	9.49 X 10^{-5}
30	1.6	9.09 X 10^{-5}

Average k = 1.41 X 10^{-4}

a=b=initial concentrations of reactants = 0.0096M

Reaction – 11

$$H_2O_2 + 2HI \longrightarrow 2H_2O + I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

In this test, the concentrations of the two reacting substances were equal and the equation of the second order has to be used, as the reaction is a second order reaction. For the calculation of this reaction, "a" and "b" are used as preliminary concentrations of hydrogen peroxide and HI in that order. For both the reactants, selected concentrations are 0.009N and 0.01 N,10 ml H_2SO_4 was added to the bottle having HI and the considered value of the t_∞ became 45.5 ml in terms of 0.002N hypo solution. The calculation is based upon the equivalence $N_1V_1 = N_2V_2$ where N and V are molarities and volumes of hydrogen peroxide and sodium thiosulphate (denoted by 1 and 2 in that order) respectively.

The H_2O_2 solution was standardized by standard $KMnO_4$ solution and then after the necessary dilution was made. 1% MW of the complex was used as the cataly Two reagent bottles with the solution of hydrogen peroxide and potassium iodide were taken and the volume and concentration of the two solutions were set equal. Solutions of these two reagent bottles were mixed well after fixed time required to get equal temperature. After every ten minutes the growth of the reaction was verified by measuring the concentration of liberated iodine by titration against 0.002N sodium thiosulphate solution. The experiments were done with and without catalyst.

Table – 11 Reaction Kinetics Table (Without Catalyst)

Reaction of : H_2O_2 + KI + H_2SO_4 + DMSO

Concentration : (0.0091M) (0.0091M) --

Volume : 10ml 10ml 10ml (t_∞ =50ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
5	1.2	9.8 X 10^{-5}
10	1.7	7.03 X 10^{-5}
15	2.3	6.42 X 10^{-5}
20	2.9	6.15 X 10^{-5}
25	3.4	5.83 X 10^{-5}
30	3.8	5.48 X 10^{-5}

Average k = 6.78 X 10^{-5}

a=b=initial concentrations of reactants = 0.0091M

Reaction – 12

In this step of the study, the similar reaction (H_2O_2 + KI + H_2SO_4) was conducted by an addition of 1% catalytic amount of the Mn-KYNA[$Mn(C_{10}H_6NO_3)_3.H_2O$].

All the additions were set exactly equal as per Table-11. The readings of these catalytic experiments are noted in table -12.

Table – 12 Reaction Kinetics Table With Mn-KYNA

Reaction of : H_2O_2 + KI + H_2SO_4 + Mn-KYNA

Concentration : (0.0091M) (0.0091M) DMSO solution

Volume : 10ml 10ml 10ml ($t\infty$ =50ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k= 1/at * X/(a-x) (lit.mol^{-1} min^{-1}
05	0.5	1.63 X 10^{-4}
10	0.9	1.49 X 10^{-4}
15	1.0	1.11 X 10^{-4}
20	1.5	1.27 X 10^{-4}
25	1.8q	1.24 X 10^{-4}
30	1.9	1.09 X 10^{-4}

Average k = 1.30 X 10^{-4}

a=b=initial concentrations of reactants = 0.0091M

Reaction- 13

In this step of the study, the same reaction (H_2O_2 + KI + H_2SO_4) was conducted by an addition of 1% catalytic quantity of Co-KYNA [$Co(C_{10}H_6NO_3)_3$]. Lasting all the additions and parameters were set accurately equal as per Table-11. Readings of these catalytic experiments are noted in table -13.

Table –13 Reaction Kinetics Table With Co-KYNA

Reaction of : H_2O_2 + KI + H_2SO_4 + Co-KYNA

Concentration : (0.0091M) (0.0091M) DMSO solution

Volume : 10ml 10ml 10ml ($t\infty$ =50ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0,7	2.30 X 10^{-4}
10	0.8	1.32 X 10^{-4}
15	0.9	9.95 X 10^{-5}
20	1.0	8.33 X 10^{-5}
25	1.1	7.39 X 10^{-5}

30	1.1	6.12×10^{-5}

Average k = 1.13×10^{-4}

a=b=initial concentrations of reactants = 0.0091M

Reaction- 14

In this table, the same reaction (H_2O_2 + KI + H_2SO_4) was conducted by an addition of 1% catalytic quantity of the Ni-KYNA $[Ni(C_{10}H_6NO_3)_3] .H_2O$. Then all the additions and parameters were kept faithfully same as per Table-11. Readings of these catalytic tests are noted in table -14.

Table – 14 Reaction Kinetics Table With Ni-KYNA

Reaction of : H_2O_2 + KI + H_2SO_4 + Ni-KYNA

Concentration : (0.0091M) (0.0091M) DMSO solution

Volume : 10ml 10ml 10ml ($t\infty$ =50ml) T= 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.6	1.96×10^{-4}
10	0.6	9.83×10^{-5}
15	0.7	7.66×10^{-5}
20	0.8	6.61×10^{-5}
25	0.9	5.97×10^{-5}
30	1.0	5.54×10^{-5}

Average k = 9.166×10^{-5}

a=b=initial concentrations of reactants = 0.0091M

Reaction- 15

In this study, the same reaction (H_2O_2 + KI + H_2SO_4) had been carried out by an addition of 1% catalytic quantity of the Cu- KYNA $[Cu(C_{10}H_6NO_3)_2.(H_2O)_2]$. Then all the additions and parameters were kept precisely same as per Table-11. Readings of these catalytic experiments are noted in table -15

Table – 15 Reaction Kinetics Table With Cu-KYNA

Reaction of : H_2O_2 + KI + H_2SO_4 + Cu-KYNA

Concentration : (0.0091M) (0.0091M) DMSO solution

Volume : 10ml 10ml 10ml ($t\infty$ =50ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) ($lit.mol^{-1}$ min^{-1}
05	0.9	2.98×10^{-4}
10	1.2	2.01×10^{-4}
15	1.1	1.22×10^{-4}
20	1.3	1.09×10^{-4}
25	1.4	9.49×10^{-5}
30	1.6	9.09×10^{-5}

Average k = 1.5233×10^{-4}

a=b=initial concentrations of reactants = 0.0091M

Table – 16 Overall results of catalytic activity for complexes of 3d metal ions. (Mn-KYNA, Co-KYNA, Ni-KYNA, Cu-KYNA)

*Decrease in the reaction rate

Reactions	K without complex	k with Mn-KYNA (1%)	k with Co-KYNA (1%)	k with Ni-KYNA (1%)	k with Cu-KYNA (1%)	% Increase in reaction rate at T = 300 K Mn-KYNA	% Increase in reaction rate at T = 300 K Co-KYNA	% Increase in reaction rate at T = 300 K Ni-KYNA	% Increase in reaction rate at T = 300 K Cu-KYNA
$K_2S_2O_8$ +KI	2.085×10^{-5}	1.13×10^{-4}	9.27×10^{-5}	1.49×10^{-4}	1.34×10^{-4}	441	344	614	542
HBrO3 + HI	1.44×10^{-3}	1.22×10^{-4}	8.74×10^{-5}	8.93×10^{-5}	1.41×10^{-4}	-91.52*	-93.93*	-93.79*	-90.20*
H_2O_2 + HI	6.78×10^{-5}	1.30×10^{-4}	1.13×10^{-4}	9.166×10^{-5}	1.523×10^{-4}	91.74	66.66	35.19	124

k = reaction rate constant for the second order reaction,

% Rate Increase Formula

$$\text{Percentage Increase} = \frac{\text{Reaction rate with catalyst -- Reaction rate without catalyst}}{\text{Reaction rate without catalyst}} \times 100$$

Results

Normally coordination compounds are known to be good catalysts for majority of reactions. Based upon the above, the four complexes Mn-KYNA, Co-KYNA, Ni-KYNA and Cu-KYNA were subjected to the well known redox reactions. Out of the three selected reactions, it was observed that the $HBrO_3$ +HI reaction could not be catalyzed by any of the four complexes. But, $K_2S_2O_8$ + KI and H_2O_2+HI reactions were indeed catalyzed positively by these four complexes. The highest increase observed was 614 %. The Cu-KYNA and Ni-KYNA complexes, in particular, were successful in increasing the reaction rates to a great extent and they need to be explored further.

Part B : $3d^{10}$ Metal Ion Complexes

Kinetic Experiments With Complexes Of Some $3d^{10}$ Metal Ions.

(Homogeneous catalysis) (Zn-KYNA, Cd-KYNA and Hg-KYNA)

Reaction 16

The test was carried out by two reacting species $K_2S_2O_8$ and KI with their equivalent concentrations. This reaction is carried out as per reaction-1 noted as Table-1 shows the kinetic data of the reaction among $K_2S_2O_8$ and KI not including addition of any catalyst. 1% Molecular weight of $3d^{10}$ metal complex was used as catalyst.

Reaction 17

This reaction, potassium persulphate and potassium iodide was conducted with 1% catalytic amount of the Zn-KYNA, $[Zn(C_{10}H_6NO_3)_2.2H_2O]$ and all other parameters were kept equal. Then all the additions were set accurately same as per Table-1. The results of these catalytic experiments are noted in table -17

Table – 17 Reaction Kinetics Table With Zn-KYNA

Reaction of	:	$K_2S_2O_8$	+ KI	+ Zn-KYNA	
Concentration	:	(0.0227M)	(0.0227M)	DMSO solution	
Volume	:	50ml	50ml	10ml	(t_∞ =125ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
5	4.0	1.52 X 10^{-3}
10	4.3	8.25 X 10^{-4}
15	4.4	5.66 X 10^{-4}
20	4.7	4.62 X 10^{-4}
25	5.1	4.09 X 10^{-4}
30	5.2	3.48 X 10^{-4}

Average k = 6.88 X 10^{-4}

a=b=initial concentrations of reactants = 0.0227 M

Reaction 18

This experiment, potassium persulphate and potassium iodide was conducted with 1% catalytic quantity of the Cd-KYNA, $[Cd(C_{10}H_6NO_3)_3.H_2O]$ $.4H_2O$ and all other parameters were kept similar. Remaining all the additions were set accurately equal as per Table-1. The readings of these catalytic experiments are noted in table -18.

Table – 18 Reaction Kinetics Table With Cd-KYNA

Reaction of : $K_2S_2O_8$ + KI + Cd-KYNA

Concentration : (0.0227M) (0.0227M) DMSO solution

Volume : 50ml 50ml 10ml (t_∞ =125ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.7	2.30 X 10^{-4}
10	1.2	2.01 X 10^{-4}
15	1.4	1.57 X 10^{-4}
20	1.9	1.64 X 10^{-4}
25	2.1	1.46 X 10^{-4}
30	2.1	1.21 X 10^{-4}

Average k = 1.69 X 10^{-4}

a=b=initial concentrations of reactants =0.0227 M

Reaction 19

This experiment, potassium persulphate and potassium iodide was carried out by 1% catalytic quantity of the Hg-KYNA [$Hg(C_{10}H_6NO_3)_3$] and all other factors were set identical. Then all the additions were accurately similar as Table-1. The readings of these catalytic experiments are noted in table -19.

Table – 19 Reaction Kinetics Table With Hg-KYNA

Reaction of : $K_2S_2O_8$ + KI + Hg - K Y N A

Concentration : (0.0227M) (0.0227M) DMSO solution

Volume : 50ml 50ml 10ml (t_∞ =125ml)

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.7	2.30 X 10^{-4}
10	1.5	2.55 X 10^{-4}
15	1.1	1.22 X 10^{-4}
20	1.0	8.33 X 10^{-5}
25	1.7	4.80 X 10^{-5}
30	1.0	5.54 X 10^{-5}

Average k = 1.32 X 10^{-4}

a=b=initial concentrations of reactants = 0.0227 M

Reaction: 20

The experiment was conducted with two reacting species $HBrO_3$ and KI (in presence of HCl) and their concentrations were set equivalent. A solution without catalyst in 10ml DMSO is added to verify the catalytic effect. The results of kinetics and rate constant values are reported as below. The reaction kinetics table without catalyst is on the table no-6.

Reaction 21

In this step of the study, the same reaction ($HBrO_3$ + KI in presence of HCl) was conducted with an addition of 1% catalytic amount of the Zn-KYNA, [$Zn(C_{10}H_6NO_3)_2.2H_2O$]. Then all the additions were set precisely equivalent as per table-6, the results of these catalytic experiments are noted in table -20 shown below.

Table – 20 Reaction Kinetics Table With Zn-KYNA

Reaction of : $HBrO_3$ + KI + HCl + Zn-KYNA

Concentration : (0.0096M) (0.0096M) DMSO solution

Volume : 25ml 25ml 10ml ($t\infty$ =25ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
5	4.2	1.60 X 10^{-3}
10	4.5	8.76 X 10^{-4}
15	4.7	6.14 X 10^{-4}
20	4.9	4.86 X 10^{-4}
25	5.1	4.09 X 10^{-4}
30	5.3	3.57 X 10^{-4}

Average k = 7.25 X 10^{-4}

a=b=initial concentrations of reactants =0.0096 M

Reaction 22

In this study, the same reaction ($HBrO_3$ + KI in presence of HCl) was conducted with an addition of 1% catalytic amount of the Cd-KYNA, $[Cd(C_{10}H_6NO_3)_3.H_2O]$ $.4H_2O$. Further all the additions were set precisely similar as per table-6. The results of these catalytic experiments are noted in table -21.

Table – 21 Reaction Kinetics Table With Cd-KYNA

Reaction of : $HBrO_3$ + KI + HCl + Cd-KYNA

Concentration : (0.0096M) (0.0096M) DMSO solution

Volume : 25ml 25ml 10ml ($t\infty$ =25ml) T = 300K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.9	2.98 X 10^{-4}
10	1.3	2.19 X 10^{-4}
15	1.5	1.69 X 10^{-4}
20	1.9	1.90 X 10^{-2}
25	2.2	1.54 X 10^{-4}
30	2.3	1.34 X 10^{-4}

Average k = 1.94 X 10^{-4}

a=b=initial concentrations of reactants = 0.0096M

Reaction 23

In this study, the same reaction ($HBrO_3$ + KI in presence of HCl) was conducted with an addition of 1% catalytic quantity of the Hg-KYNA [$Hg(C_{10}H_6NO_3)_3$]. Further all the additions were set accurately same as per table-6. The results of these catalytic studies are reported in table -22.

Table – 22 Reaction Kinetics Table With Hg-KYNA

Reaction of : $HBrO_3$ + KI + HCl + Hg-KYNA

Concentration : (0.0096M) (0.0096M) DMSO solution

Volume : 25ml 25ml 10ml ($t\infty$ =25ml), T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.8	2.64 X 10^{-4}
10	1.6	2.72 X 10^{-4}
15	1.1	1.22 X 10^{-4}
20	1.0	8.33 X 10^{-5}
25	0.7	4.80 X 10^{-5}
30	1.0	5.54 X 10^{-5}

Average k = 1.408 X 10^{-4}

a=b=initial concentrations of reactants = 0.0096M

Reaction 24

The experiment, hydrogen peroxide with potassium iodide in presence of H_2SO_4 was done as per reaction -11. The reaction kinetics table, not including catalyst, is presented in table-11.

Reaction- 25

In this experiment, the reaction (H_2O_2 + KI in presence of H_2SO_4) was conducted with an addition of 1% catalytic amount of the Zn-KYNA, [$Zn(C_{10}H_6NO_3)_2.2H_2O$] and further all the additions were set exactly equal like Table-11. The results of these catalytic studies are reported in table -23.

Table – 23 Reaction Kinetics Table With Zn-KYNA

Reaction of : H_2O_2 + KI + H_2SO_4 + Zn-KYNA

Concentration : (0.0091M) (0.0091M) DMSO solution

Volume : 10ml 10ml 10ml ($t\infty$ =50ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
5	4.0	1.52 X 10^{-3}
10	4.3	8.28 X 10^{-4}
15	4.4	5.66 X 10^{-4}
20	4.7	4.62 X 10^{-4}
25	5.1	4.09 X 10^{-4}
30	5.2	3.48 X 10^{-4}

Average k = 6.88 X 10^{-4}

a=b=initial concentrations of reactant= 0.0091M

Reaction 26

In this experiment, the same reaction (H_2O_2 + KI in presence of H_2SO_4) conducted with an addition of 1% catalytic amount of the Cd-KYNA, $[Cd(C_{10}H_6NO_3)_3.H_2O]$.$4H_2O$. Further all the additions were set exactly identical as per Table-11. The results of these catalytic studies are reported in table -24.

Table – 24 Reaction Kinetics Table With Cd-KYNA

Reaction of : H_2O_2 + KI + H_2SO_4 + Cd-KYNA

Concentration : (0.0091M) (0.0091M) DMSO solution

Volume : 10ml 10ml 10ml ($t\infty$ =50ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.9	2.98 X 10^{-4}
10	1.1	1.84 X 10^{-4}
15	1.7	1.94 X 10^{-4}
20	1.7	1.45 X 10^{-4}
25	2.3	1.62 X 10^{-4}
30	2.5	1.47 X 10^{-4}

Average k = 1.88 X 10^{-4}

a=b=initial concentrations of reactants= 0.0091M

Reaction- 27

In this experiment, the similar reaction (H_2O_2 + KI in presence of H_2SO_4) was conducted with adding 1% catalytic amount of the Hg-KYNA [$Hg(C_{10}H_6NO_3)_3$] and further all the factors were precisely same as per Table-11. The results of these catalytic study are reported in table -25.

Table – 25 Reaction Kinetics Table With Hg-KYNA

Reaction of : H_2O_2 + KI + H_2SO_4 + Hg-KYNA

Concentration: (0.0091M) (0.0091M) DMSO solution

Volume : 10ml 10ml 10ml ($t\infty$ =50ml) T = 300 K

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1}
05	0.9	2.96 X 10^{-4}
10	1.7	2.88 X 10^{-4}
15	1.1	1.22 X 10^{-4}
20	1.0	8.33 X 10^{-5}
25	0.7	4.80 X 10^{-5}
30	1.0	5.54 X 10^{-5}

Average k = 1.485 X 10^{-4}

a=b=initial concentrations of reactants =0.0091M

Table :- 26 overall results of catalytic activity for complexes of $3d^{10}$ ions. (Zn-KYNA, Cd-KYNA, Hg-KYNA)

% Rate Increase Formula

$$\text{Percentage Increase} = \frac{\text{Reaction rate with catalyst -- Reaction rate without catalyst}}{\text{Reaction rate without catalyst}} \times 100$$

Reactions	k without complex	k with Zn-KYNA (1%)	k with Cd-KYNA (1%)	k with Hg-KYNA (1%)	% Increase in reaction rate at T = 300 K Zn-KYNA	% Increase in reaction rate at T = 300 K Cd-KYNA	% Increase in reaction rate at T = 300 K Hg-KYNA
$K_2S_2O_8$ +KI	2.085×10^{-3}	6.88×10^{-4}	1.32×10^{-4}	1.32×10^{-4}	3199.7	533.1	533.09
$HBrO_3$ + HI	1.44×10^{-3}	7.25×10^{-4}	1.408×10^{-4}	1.40×10^{-4}	1474	575.2	1462
H_2O_2 + HI	6.78×10^{-5}	6.88×10^{-4}	1.485×10^{-4}	1.48×10^{-4}	914.7	612.2	118.2

k = reaction rate constant for the second order reaction

Results and Discussion

Zn-KYNA, Cd-KYNA and Hg- KYNA complexes were employed as catalysts for the $K_2S_2O_8$+KI, $HBrO_3$+HI and H_2O_2+HI reactions. It was observed that all the complexes proved to be very good catalysts. In particular, Zn-KYNA was found to be an excellent catalyst for increasing the rates of all the selected reactions to a great extent. $K_2S_2O_8$+KI reaction was catalyzed to increase the rate as high as 3200%. over all catalytic activity of d^{10} complexes were very high compared to 3d metal complexes.

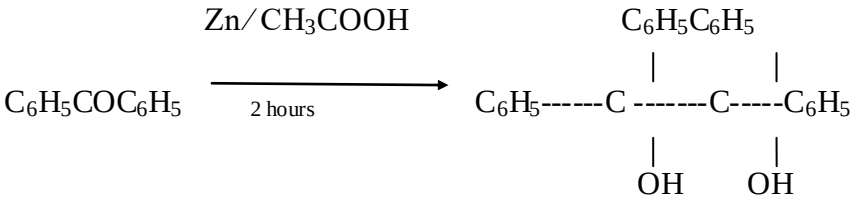
CATALYTIC STUDY

Catalysis of Organic Reaction

The catalyst is a variety of molecule that accelerates a chemical reaction. In homogeneous catalysis, the reactant(s) coordinate to the catalyst (or viceversa), are transformed to product, which are then released from the catalyst [7].

In this study, mixture of benzophenone (7.5 gm , 0.041 mole) zinc dust (4 gm) glacial acetic acid (110 ml) and water (22 ml) is refluxed for 2 hours. The solution is filtered (if needed) and then cooled. The separated benzpinacol is filtrated and it was crystallized from glacial acetic acid. The yield normally acquired would be around 4.5 gm (30%).

The product melting point is 188- 189 ^{0}C.



Benzophenone Benzpinacol

The preparation of benzopinacol from benzophenone is an example of reductive coupling. The carbonyl group is concentrated with zinc dust. Concurrently two units couple to form a new carbon-carbon bond in the middle of the product molecule. As this reaction is an example of two processes, (reduction and new C-C bond formation) so it was favoured for possible application of 3d and d^{10} transition metal as homogeneous catalyst[8].The exactly weighed quantity of catalyst was added to the reaction mixture unswervingly in solid form.

Table: -27 Percentage yield without catalyst for different reaction times

Sr. No	Temperature	% yield without catalyst (for 3 hours reaction)	% yield without catalyst (for 2 hours reaction)
1	366 K	32.46 %	29.66 %

CATALYSIS WITH 3d METAL COMPLEXES

MN-KYNA

The same reaction (as shown on page 31) was conducted with Mn-KYNA. Benzophenone (7.5 gm, 0.041 mole), zinc dust (4 gm), glacial acetic acid (110 ml) and water (22 ml) are refluxed for 2 hours. 1% Mn-KYNA complex was supplemented as solid in this reaction mixture. When Mn-KYNA was added, in the beginning the mixture became creamy white shade. All the factors and conditions were set equal as per the standard -reaction. The yield was 30.53% (4.53 gm) with Mn-KYNA. (Table -28)

Co-KYNA

The same reaction (as shown on page 31) was conducted with Co-KYNA. Benzophenone (7.5 gm, 0.041 mole), zinc dust (4 gm), glacial acetic acid (110 ml) and water (22 ml) are refluxed for 2 hours. 1% Co-KYNA was supplemented as solid in this reaction mixture. When Co-KYNA was added, in the beginning the mixture became creamy white shade. All the factors and conditions were equal as per the standard -reaction. The yield was 31.55% (4.68 gm) with Co-KYNA.(Table -28)

Ni-KYNA

The similar reaction (as shown on page 31) was conducted with Ni-KYNA. Benzophenone (7.5 gm, 0.041 mole), zinc dust (4 gm), glacial acetic acid (110 ml) and water (22 ml) are refluxed for 2 hours. 1% Ni-KYNA was supplemented as solid in this reaction mixture. When Ni-KYNA was added, in the beginning the mixture became creamy white shade. All the factors and conditions were set equal as per the standard -reaction. The yield was 26.29 % (3.90 gm) with Ni-KYNA.(Table -28)

Cu-KYNA

The similar reaction (as shown on page 31) was conducted with Cu-KYNA. Benzophenone (7.5 gm, 0.041 mole), zinc dust (4 gm), glacial acetic acid (110 ml) and water (22 ml) are refluxed for 2 hours. 1% Cu-KYNA was supplemented as solid in this reaction mixture. When Cu-KYNA was added, primarily the mixture became creamy white shade. All the factors and conditions were set equal as per the standard -reaction. The yield was 27.43% (4.07 gm) with Cu-KYNA.(table -28)

Table :-28 Percentage Yield With Catalyst Metal Complexes

(For 2 Hours Reaction Time) Temperature = 368 K (Yield Without Catalyst Is 29.66%)

	Product Weight Without metal Complex (3 hours)	Product Weight without Metal complex 2 hours	Product weight using Mn-KYNA as catalyst 2 hours	Product weight using Co-KYNA as catalyst 2 hours	Product weight using Ni-KYNA as catalyst 2 hours	Product weight using Cu-KYNA as catalyst 2 hours
Weight in gram	4.87	4.45	4.53	4. 68	3.90	4.07
% yield	32.46	29.66	30.53	31.55	26.29	27.43

Results and Discussion

The reaction was conducted with similar conditions for with catalyst and without catalyst. Mn-KYNA, Co-KYNA, Ni-KYNA and Cu-KYNA operated as homogeneous catalysts in this reaction. It was detected that addition of all the complexes in catalytic amounts notably reduced the time requirement and changed reaction rate and percentage of product in the same interval. Order of efficiency as catalyst obtained was Co-KYNA > Mn-KYNA > Cu-KYNA > Ni-KYNA. At very low catalyst additions, the percentage product a little decreased (for Cu-KYNA and Ni-KYNA).

CATALYSIS WITH d^{10} METAL COMPLEXES

Zn-KYNA

The same reaction (as shown on page 31) was conducted with Zn-KYNA. Benzophenone (7.5 gm, 0.041 mole), zinc dust (4 gm), glacial acetic acid (110 ml) and

water (22 ml) are refluxed for 2 hours. 1% Zn-KYNA was supplemented as solid in this reaction mixture. When Zn-KYNA was added, primarily the mixture became creamy white shade. All the factors and conditions were set equal as per the standard -reaction. The yield was 30.20% (4.48 gm) with Zn-KYNA.(Table -29)

Cd-KYNA

The same reaction (as shown on page 31) was conducted with Cd-KYNA. Benzophenone (7.5 gm, 0.041 mole), zinc dust (4 gm), glacial acetic acid (110 ml) and water (22 ml) are refluxed for 2 hours. 1% Cd-KYNA was supplemented as solid in this reaction mixture. When Cd-KYNA was added, primarily the mixture became creamy white shade. All the factors and conditions were set equal as per the standard -reaction. The yield was 30.67% (4.55 gm) with Cd-KYNA.(Table -29)

Hg -KYNA

The same reaction (as shown on page 31) was conducted with Hg-KYNA. Benzophenone (7.5 gm, 0.041 mole), zinc dust (4 gm), glacial acetic acid (110 ml) and water (22 ml) are refluxed for 2 hours. 1% Hg-KYNA was supplemented as solid in this reaction mixture. When Hg-KYNA was added, primarily the mixture became creamy white shade. All the factors and conditions were set equal as per the standard -reaction. The yield was 26.69% (3.96 gm) with Hg-KYNA.(Table -29)

Table:- 29 Percentage Yield With Catalyst Metal Complexes
(For 2 Hours Reaction Time)Temperature = 368 K (Yield Without Catalyst Is 29.66%)

	Product Weight without Metal complex (3 hours)	Product Weight without Metal complex 2 hours	Product weight using Zn-KYNA as catalyst 2 hours	Product weight using Cd-KYNA as catalyst 2 hours	Product weight using Hg-KYNA as catalyst 2 hours
Weight in gram	4.87	4.45	4.48	4. 55	3.96
% yield	32.46	29.66	30.20	30.67	26.69

Results and Discussion

The reaction was conducted with the same conditions with and without catalyst. Zn-KYNA, Cd-KYNA and Hg-KYNA worked as homogeneous catalysts in this reaction. It

was spoted that addition of all the complexes in catalytic quantities significantly reduced the time requirement and changed the reaction rates within same time interval. Order of efficiency as catalyst found was Cd-KYNA >Zn-KYNA. At low catalyst additions, the percentage yield slightly decreased for Hg-KYNA.

CONCLUSION

Complexes of selected 3d and d^{10} metal ions with ligand (kynurenic acid), were very much effective to proliferate the rates of selected reduction, oxidation and reductive coupling reactions to a considerably high extent. These complexes are quite hopeful in their apparent applications to industrial chemical synthesis and this would be proper extensions of the current research work. Through help of further mechanistic studies, two further accomplishments are possible (1) deciding the mechanism of catalytic actions (2) applications to industrial (in bulk) reactions. In particular, Zn-KYNA was found to be everywhere effective as a very useful catalyst for all the selected reactions.

ACKNOWLEDGEMENTS

Authers are very thankful to GUJCOST for the financial support in the form of a minor research project (GUJCOST/MRP/14-15/1460). Authors are also thankful to the principal and staff members of M.G. Science institute, Ahmedabad. Our sincere thanks to Dr. Devang Pandya for his valuable discussions.

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