

## Iridium–Quinoline Coordination Complex in Catalysis

Dr. H.D. Chaudhari<sup>1</sup>, Dr. Haresh R. Patel<sup>2</sup>,

<sup>1</sup>Department of Chemistry, Hemchandracharya North Gujarat University, Patan, India

<sup>2</sup>Department of Chemistry, Navjivan School of Science(P.G.), Deesa, India

Email:- <sup>1</sup>haresh09032007@gmail.com , <sup>2</sup>hareshpatel6900@yahoo.com

### Abstract: -

The combination of certain rare metal ions with the biologically important ligand Quinoline derivative to form coordination compound represents a significant area of current research. In this study, the relatively less explored Quinoline derivative ligand was reacted with solutions of selected rare metal perchlorate to synthesize solid Quinoline derivative complex. These complex was characterized by various analytical techniques, including UV-Visible spectroscopy, IR spectroscopy, mass spectrometry, thermogravimetric analysis (TGA), and elemental analysis. Furthermore, the catalytic activity of these complex was investigated in both homogeneous and heterogeneous phases. The antimicrobial properties of the synthesized complex were also evaluated using standard methods, and efforts were made to correlate their structural features with the observed physicochemical and biological properties.

**Keywords:** -Quinoline derivative, Biologically, Characterization, antimicrobial activity, Iridium complex.

### Catalytic Activity:- Catalytic Study of Three Iodine-Forming Reactions Using Coordination Complexes

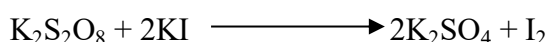
Three well-known redox reactions—(i)  $K_2S_2O_8 + KI$ , (ii)  $KBrO_3 + KI$ , and (iii)  $H_2O_2 + KI$ —were selected for catalytic investigation. These reactions are typically carried out in neutral or acidic media and proceed at moderate rates, with rate constants (K) in the range of  $10^{-2}$  to  $10^{-5} \text{ min}^{-1}$ . In each case, iodine is formed as the primary product, which is quantitatively titrated using standard aqueous sodium thiosulphate solution in the presence of starch as an indicator.

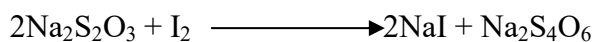
Due to the ease of monitoring reaction progress via simple kinetic methods, these systems offer an excellent platform for evaluating the catalytic efficacy[1-7] of synthesized coordination compounds.[1-7]

In the present study, kinetic measurements and experimental procedures for all three second-order reactions were conducted according to established protocols. All reactions were performed at ambient temperature. The synthesized complexes were dissolved in methanol, and blank experiments were conducted using the same volume of methanol to ensure identical solvent conditions. Catalytic quantities of each complex were then introduced into the respective reaction mixtures. The results of these kinetic studies are presented below.

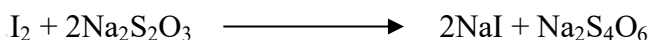
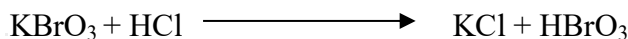
### Reactions:-

#### (i) Reaction-1

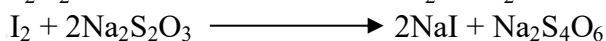
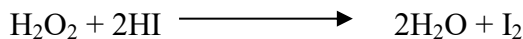




### (ii) Reaction-2



### (iii) Reaction-3



**Table – 1 Reaction kinetics (without catalyst):**

Reaction of :  $\text{K}_2\text{S}_2\text{O}_8$  + KI + Methanol

Concentration : (0.0227M) (0.0227M) --

Volume : 50ml 50ml 10ml ( $t_\infty = 113.5$  ml)

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

average  $k = 2.085 \times 10^{-5}$

a=b=initial concentrations of reactants =0.0227M

**Table – 2 Reaction kinetics table without catalyst**

Reaction of :  $\text{KBrO}_3$  + KI + HCl + Methanol

Concentration : (0.0096M) (0.0096M) --

Volume : 25ml 25ml 10ml ( $t_\infty = 25$ ml)

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

$$\text{average } k = 1.44 \times 10^{-3}$$

$$a=b=\text{initial concentrations of reactants}=0.0227\text{M}$$

**Table – 3 Reaction kinetics table without catalyst**

Reaction of :  $\text{H}_2\text{O}_2$  +  $\text{KI} + \text{H}_2\text{SO}_4$  + Methanol

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

Volume : 10ml 10ml 10ml ( $t_{\infty}=50\text{ml}$ )

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

$$\text{average } k = 6.78 \times 10^{-5}$$

$$a=b=\text{initial concentrations of reactants}=0.0227\text{M}$$

**Table:- 4 Common Reaction Kinetics- experimental Set ups with Catalyst**

Reactions (I)	$\text{K}_2\text{S}_2\text{O}_8$ + $\text{KI}$ + Ir-KYNA in 10 ml methanol (0.0227M) (0.0227M) (1 % MW)	$t_{\infty} = 113.5 \text{ ml}$ $a=b= 0.0227\text{M}$
Reactions (II)	$\text{KBrO}_3$ + $\text{HI}$ + Ir -KYNA in 10 ml methanol (0.0091M) (0.0091M) (1 % MW)	$t_{\infty} = 25 \text{ ml}$ $a=b= 0.0227\text{M}$
Reactions (III)	$\text{H}_2\text{O}_2$ + $\text{HI}$ + Ir -KYNA in 10 ml methanol (0.0091M) (0.0091M) (1 % MW)	$t_{\infty} = 50 \text{ ml}$ $a=b= 0.0227\text{M}$

Table:- 5 Kinetic experiments with Iridium metal Complex

Reactions	k without Complexes	k with Ir –KYNA (1%)	% Increase reaction rate at T = 300K Ir - KYNA
$K_2S_2O_8 + KI$	$2.085 \times 10^{-5}$	$3.82 \times 10^{-5}$	83.21 %
$KBrO_3 + HI$	$1.44 \times 10^{-3}$	$2.19 \times 10^{-2}$	1420.83 %
$H_2O_2 + HI$	$6.78 \times 10^{-5}$	$2.05 \times 10^{-4}$	202.35 %

k = reaction rate constant for the second order reaction, 1% complex = 1 % molecular weight of the complex

1 % MW of complex of Ir-KYNA= 0.0435 % of mole of  $K_2S_2O_8$  ,

1 % MW of complex of Ir -KYNA = 0.104 % of mole of  $KBrO_3$

1 % MW of complex of Ir -KYNA = 0.11 % of mole of  $H_2O_2$

### Catalysis of Organic Reaction:- Synthesis of Benzpinacol from Benzophenone

A mixture containing benzophenone (7.5 g, 0.041 mol), zinc dust (4 g), glacial acetic acid (110 mL), and water (22 mL) was refluxed for 2 hours. After completion of the reaction, the mixture was filtered (if necessary) to remove unreacted zinc or insoluble impurities and then allowed to cool. The crude product, benzpinacol, precipitated upon cooling and was collected by filtration. The solid was recrystallized from glacial acetic acid to obtain purified benzpinacol. [8-12]

The final yield was 4.5 g (30%), and the melting point of the purified product was recorded as 188–189 °C, consistent with literature values [13-14].

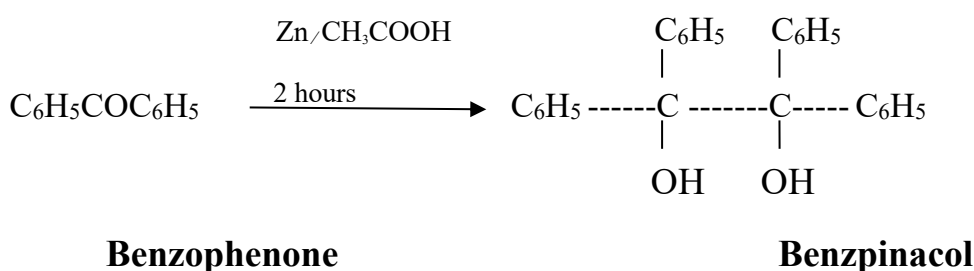


Table:- 11 % yield of without catalyst for different temperature

Sr. No	Temperature	% yield without catalyst (for 4 hours reaction)	% yield without catalyst (for 3 hours reaction)	% yield without catalyst (for 2 hours reaction)
1	368 K	64.44%	55.55%	30.00 %

Table :-12 percentage yield with catalyst metal complexes for 2 hours Temperature = 368 K

Complexes	For 1 % catalyst, yield obtained	For 5 % catalyst, yield obtained	For 10 % catalyst, yield obtained
Ir-KYNA	25%	30%	52%

1% MW of complex = 0.0243 % of mole of benzophenone

5% MW of complex = 0.121 % of mole of benzophenone

10% MW of complex = 0.243 % of mole of benzophenone

## Results and Discussion: -

It was apparent that rates of all the redox reactions selected were increased by the addition of catalytic amounts of individual complexes. An increase of 83% was possible for reaction (i)  $K_2S_2O_8 + KI$  and for reactions (ii)  $KBrO_3 + KI + HI$  and (iii)  $H_2O_2 + HI$ , a profound increase from 200% to 1420% was possible. Thus a significant increase in reaction rates could be achieved with help of two complexes and hence application of these complexes as catalyst is certainly of immense significance.

## Catalytic Role of Lanthanide Complexes in Reductive Coupling: Synthesis of Benzpinacol

The synthesis of benzpinacol from benzophenone represents a classic example of reductive coupling, wherein the carbonyl group is reduced by zinc dust, and two benzophenone units couple to form a new central carbon–carbon bond. This transformation, involving both reduction and C–C bond formation, presents a valuable model for investigating the catalytic potential of coordination compounds. Owing to this dual mechanistic nature, the reaction was selected to explore the application of lanthanide complexes as homogeneous catalysts [15-20].

The reaction was conducted under identical experimental conditions both with and without the addition of catalysts. Among the synthesized complexes, Ir-KYNA (Iridium complex of kynurenic acid) demonstrated effective homogeneous catalytic activity. The presence of catalytic amounts of the lanthanide complexes significantly reduced the reaction time and led to a notable increase in product yield, highlighting their potential as efficient catalysts for reductive coupling reactions [15-20].

## Acknowledgement

The authors express their sincere gratitude to Hemchandracharya North Gujarat University, Patan, India, for providing the necessary chemicals, high-grade glassware, and excellent laboratory facilities essential for this research. We also extend our thanks to the Central Instrumental Maintenance Facilities (CIMF) Laboratory, Hemchandracharya North Gujarat University, Patan, for granting access to advanced spectral analysis instrumentation.

## References

1. Gao, C., Wang, J., Xu, H., & Xiong, Y. (2017). Coordination chemistry in the design of heterogeneous photocatalysts. *Chemical Society Reviews*, 46(10), 2799-2823.
2. Qin, R., Liu, K., Wu, Q., & Zheng, N. (2020). Surface coordination chemistry of atomically dispersed metal catalysts. *Chemical Reviews*, 120(21), 11810-11899.
3. Kainat, S. F., Hawsawi, M. B., Mughal, E. U., Naeem, N., Almohyawi, A. M., Altass, H. M., ... & Ahmed, S. A. (2024). Recent developments in the synthesis and applications of terpyridine-based metal complexes: a systematic review. *RSC advances*, 14(30), 21464-21537.
4. Wang, K. Y., Zhang, J., Hsu, Y. C., Lin, H., Han, Z., Pang, J., ... & Zhou, H. C. (2023). Bioinspired framework catalysts: From enzyme immobilization to biomimetic catalysis. *Chemical Reviews*, 123(9), 5347-5420.
5. Wang, K. Y., Zhang, J., Hsu, Y. C., Lin, H., Han, Z., Pang, J., ... & Zhou, H. C. (2023). Bioinspired framework catalysts: From enzyme immobilization to biomimetic catalysis. *Chemical Reviews*, 123(9), 5347-5420.
6. Sharma, R. K., Yadav, P., Yadav, M., Gupta, R., Rana, P., Srivastava, A., ... & Gawande, M. B. (2020). Recent development of covalent organic frameworks (COFs): synthesis and catalytic (organic-electro-photo) applications. *Materials Horizons*, 7(2), 411-454.
7. Saha, R., Mondal, B., & Mukherjee, P. S. (2022). Molecular cavity for catalysis and formation of metal nanoparticles for use in catalysis. *Chemical Reviews*, 122(14), 12244-12307.
8. McLean Jr, J. A. (1959). *Some Metal-and Silicon-Containing Polymers*. University of Illinois at Urbana-Champaign.
9. Taylor, I. Z. (2006). *Development of a Synthetic Route to Polycyclic Benzopyrans*. The University of Manchester (United Kingdom).
10. Iyer, S., & Liebeskind, L. S. (1987). Regiospecific synthesis of 2-methoxy-3-methyl-1, 4-benzoquinones from maleoylcobalt complexes and alkynes via Lewis acid catalysis. A highly convergent route to isoquinoline quinones. *Journal of the American Chemical Society*, 109(9), 2759-2770.
11. Aljuhani, A. A. (2014). *Covalently Linked Dyads and Triads of Phthalocyanines and Porphyrins* (Doctoral dissertation, University of East Anglia).

12. Leung, P. T. (1972). *Synthetic and Conformational Studies of Some 9-Methylene-9, 10-Dihydroanthracenes*. University of Illinois at Urbana-Champaign.
13. Amer, M. (2016). *Improved Synthesis of Neocryptolepine-type Indoloquinolines: Applications for New Fluorescent Labelled Derivatives and Anticancer Activity Evaluations* (Master's thesis, The University of Manchester (United Kingdom)).
14. Iyer, S. (1986). *PART I: REGIOCHEMISTRY OF BENZOQUINONE FORMATION FROM MALEOYLCOBALT COMPLEXES AND RELATED SYNTHETIC APPLICATIONS; PART II: A VERY GENERAL, REGIOSPECIFIC SYNTHESIS OF HIGHLY SUBSTITUTED QUINONES (ISOQUINOLINE QUINONE, COBALT ACYL MIGRATION)*. Emory University.
15. Moore, A. F. (2016). *Substituted benzophenone synthesis for biological and catalytic applications* (Doctoral dissertation, Macquarie University).
16. Spanomanolis, C. (1978). *Studies directed towards the step-growth photopolymerization of carbonyl compounds* (Doctoral dissertation, Durham University).
17. Orr, R. S. (1964). *Reduction of aromatic ketones and pinacolones*. University of Delaware.
18. Allen, R. A. (2023). *Natural Product Inspired Complementary Approaches to Counter Antimicrobial Resistance: Synthetic and Biological Investigations of Antibacterial Small Molecules* (Doctoral dissertation, Emory University).
19. Surendhran, R. (2024). *Catalyst Development and Reaction Engineering for Chemical Upgrading of Emerging Feedstocks*. University of Delaware.
20. Rausch, M. D., McEwen, W. E., & Kleinberg, J. (1954). Anodic Reductions. I. Conversion of benzophenone to benzopinacol by unipositive magnesium. *Journal of the American Chemical Society*, 76(14), 3622-3625.