An Application of Catalytic Activity of Dysprosium rare metal complex of Quinoline Derivative

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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, Dysprosium complex.

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} 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. [1-7]

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.

In the present study, kinetic measurements and experimental procedures for all three second-order reactions were conducted according to established protocols [1-7]. 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

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

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

(ii) Reaction-2

$KBrO_3 + HCl \rightarrow KCl + HBrO_3$

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

(iii) Reaction-3

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

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

Table – 1 Reaction kinetics (without catalyst):

Reaction of : $K_2S_2O_8$ + KI + Methanol

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

Volume : 50ml 50ml 10ml (t_∞ =113.5 ml)

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 =0.0227M

Table – 2 Reaction kinetics table without catalyst

Reaction of : $KBrO_3$ + KI + HCl + Methanol

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

Volume : 25ml 25ml 10ml (t_∞ =25ml)

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**	**1.04×10^{-3}**
25	**9.0**	**0.9×10^{-3}**
30	**9.5**	**0.81×10^{-3}**

average k = 1.44×10^{-3}

a=b=initial concentrations of reactants=0.0227M

Table – 3 Reaction kinetics table without catalyst

Reaction of : H_2O_2 + KI + H_2SO_4 + Methanol
Concentration : (0.0091M) (0.0091M) --
Volume : 10ml 10ml 10ml ($t\infty$ =50ml)

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

average k = 6.78×10^{-5}

a=b=initial concentrations of reactants =0.0227M

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

Reactions (I)	**$K_2S_2O_8$ + KI + Dy-KYNA in 10 ml methanol** **(0.0227M) (0.0227M) (1 % MW)**	**$t\infty$ = 113.5 ml** **a=b= 0.0227M**
Reactions (II)	**$KBrO_3$ + HI + Dy-KYNA in 10 ml methanol** **(0.0091M) (0.0091M) (1 % MW)**	**$t\infty$ = 25 ml** **a=b= 0.0227M**
Reactions (III)	**H_2O_2 + HI + Dy-KYNA in 10 ml methanol** **(0.0091M) (0.0091M) (1 % MW)**	**$t\infty$ = 50 ml** **a=b= 0.0227M**

Table:- 5 Kinetic experiments with Dysprosium metal Complex

Reactions	k without Complexes	k with Dy –KYNA (1%)	% Increase reaction rate at T = 300K Dy -KYNA
$K_2S_2O_8 + KI$	**2.085 X 10^{-5}**	**3.75X 10^{-5}**	**79.85 %**
$KBrO_3 + HI$	**1.44 X 10^{-3}**	**2.25 X 10^{-2}**	**1462.50 %**
$H_2O_2 + HI$	**6.78 X 10^{-5}**	**2.15 X 10^{-4}**	**217.10 %**

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

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

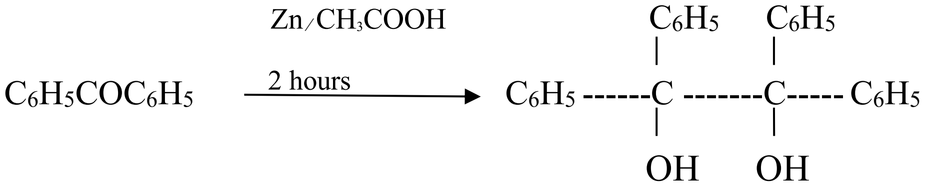
1 % MW of complex of Dy-KYNA = 0.104 % of mole of $KBrO_3$

1 % MW of complex of Dy-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 [8-12].



$$C_6H_5COC_6H_5 \xrightarrow{\substack{Zn/CH_3COOH \\ \text{2 hours}}} C_6H_5 \text{------} \underset{OH}{\overset{C_6H_5}{C}} \text{-------} \underset{OH}{\overset{C_6H_5}{C}} \text{-----} C_6H_5$$

Benzophenone **Benzpinacol**

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
Dy-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 63 % to 85% was possible for reaction (i) $K_2S_2O_8$ + KI and for reactions (ii) $KBrO_3$ + KI + Hl and (iii) H_2O_2 + HI, a profound increase from 100% to 250% 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 [13-17].

The reaction was conducted under identical experimental conditions both with and without the addition of catalysts. Among the synthesized complexes, Dy-KYNA (dysprosium 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[13-17].

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References: -

1. de Carvalho, A. R., del Nogal Sánchez, M., Wattoom, J., & Brereton, R. G. (2006). Comparison of PLS and kinetic models for a second-order reaction as monitored using ultraviolet visible and mid-infrared spectroscopy. *Talanta*, *68*(4), 1190-1200.
2. Rudzinski, W., & Plazinski, W. (2006). Kinetics of solute adsorption at solid/solution interfaces: a theoretical development of the empirical pseudo-first and pseudo-second order kinetic rate equations, based on applying the statistical rate theory of interfacial transport. *The Journal of Physical Chemistry B*, *110*(33), 16514-16525.
3. Minella, M., Giannakis, S., Mazzavillani, A., Maurino, V., Minero, C., & Vione, D. (2017). Phototransformation of Acesulfame K in surface waters: Comparison of two techniques for the measurement of the second-order rate constants of indirect photodegradation, and modelling of photoreaction kinetics. *Chemosphere*, *186*, 185-192.
4. Rodríguez, E., Majado, M. E., Meriluoto, J., & Acero, J. L. (2007). Oxidation of microcystins by permanganate: reaction kinetics and implications for water treatment. *Water Research*, *41*(1), 102-110.
5. Bektaş, N., & Kara, S. (2004). Removal of lead from aqueous solutions by natural clinoptilolite: equilibrium and kinetic studies. *Separation and Purification Technology*, *39*(3), 189-200.
6. Mondal, S. K., Saha, A. K., & Sinha, A. (2018). Removal of ciprofloxacin using modified advanced oxidation processes: kinetics, pathways and process optimization. *Journal of cleaner production*, *171*, 1203-1214.
7. Arenas, L. R., Gentile, S. R., Zimmermann, S., & Stoll, S. (2021). Nanoplastics adsorption and removal efficiency by granular activated carbon used in drinking water treatment process. *Science of the Total Environment*, *791*, 148175.
8. Pitts Jr, J. N., Letsinger, R. L., Taylor, R. P., Patterson, J. M., Recktenwald, G., & Martin, R. B. (1959). Photochemical reactions of benzophenone in alcohols1. *Journal of the American Chemical Society*, *81*(5), 1068-1077.
9. Albiter Escobar, E., Valenzuela Zapata, M. Á., Alfaro Hernández, S., Flores Valle, S. O., Ríos Berny, O., González Ángeles, V. J., & Córdova Reyes, I. (2010). Photocatalytic reduction of benzophenone on TiO2:

Effect of preparation method and reaction conditions. *Journal of the Mexican Chemical Society*, *54*(3), 133-138.

10. Mhalsekar, M., Kole, P., & Borker, V. (2024). Synthesis, characterization and application of MWCNT/TiO2 composite for photocatalytic reduction of benzophenone to benzopinacol. *Journal of Environmental Chemical Engineering*, *12*(6), 114681.
11. Siopa, F., & Afonso, C. A. (2016). 11.2. Synthesis of Benzopinacolone via Benzophenone Photoreduction Followed by Pinacol Rearrangement.
12. Meira, A. J. O., Queiroz, T. B. D., & Omori, A. T. (2024). One-Pot Synthesis of Benzopinacolone Derivatives from Acetophenones. *Journal of the Brazilian Chemical Society*, *36*(1), e-20240153.
13. Shibasaki, M., & Yoshikawa, N. (2002). Lanthanide complexes in multifunctional asymmetric catalysis. *Chemical reviews*, *102*(6), 2187-2210.
14. Aspinall, H. C. (2002). Chiral lanthanide complexes: coordination chemistry and applications. *Chemical reviews*, *102*(6), 1807-1850.
15. Bochkarev, M. N. (2002). Synthesis, Arrangement, and Reactivity of Arene− Lanthanide Compounds. *Chemical reviews*, *102*(6), 2089-2118.
16. Chaudhari, H. D., Patel, H. R., & Vora, J. J. Catalytic and Biochemical Study of Novel Complexes of Some Lanthanides. *International Journal of Research and Scientific Innovation”(IJRSI)*, *10*(2).
17. Streuff, J. (2013). The electron-way: metal-catalyzed reductive umpolung reactions of saturated and α, β-unsaturated carbonyl derivatives. *Synthesis*, *45*(03), 281-307.