## Cobalt(II) and Nickel(II) Complexes of N-benzylideneaniline Ligand as Catalyst for the Benzoylation of Phenol

### Catalytic studies on the metal complexes towards phenol benzoylation

The catalytic activities of synthesized Co(II) and Ni(II) complexes were studied for activity towards phenol benzoylation reaction. Both complexes showed good catalytic activity. The activities of the cobalt(II) complex was somehow higher than that of nickel(II) complex. In order to arrive at suitable reaction conditions for maximum transformation to phenyl benzoate, an optimum catalyst load was employed. Also, the effect of reaction temperature and time on the conversion efficiency was studied.

### Reaction kinetics of phenol benzoylation

**Effect of catalyst quantity:** The effect of amount of catalyst on the yield of phenyl benzoate was showed in Table 5. Three different concentrations of catalyst ($1 \times 10^{-5}$, $2 \times 10^{-5}$, and $2.5 \times 10^{-5}$ mol) were studied. The catalyst load which showed the highest activity during the test reaction was used for the fixed amount of phenol (0.01 mol, 0.94 g) and benzoyl chloride (0.01 mol, 1.41 g) later. An amount of $2.5 \times 10^{-5}$ mol gave comparable results in both cases with ca. 55.35% and 34.83% conversion to phenyl benzoate in 30 minutes of reaction time at 313 K for cobalt(II) and nickel(II) complexes respectively. Lower catalyst load results in poor conversion. The conversion increases linearly with catalyst concentration but eventually it decreases at elevated temperatures.

| %yield of phenyl benzoate | | |
|---|---|---|
| Catalyst load (mol) | $[Co(BA)_2(H_2O)_2]Cl_2.4H_2O$ | $[Ni(BA)_2(H_2O)_2]Cl_2.4H_2O$ |
| $1 \times 10^{-5}$ | 26.13 | 29.83 |
| $2 \times 10^{-5}$ | 40.84 | 31.83 |
| $2.5 \times 10^{-5}$ | 55.35 | 34.84 |

**Table 5:** The effect of catalyst quantity on conversion. Reaction temperature 313 K, reaction time 30 minutes.

**Effect of temperature:** Three different temperatures (300, 313 and 318 K) were studied to find the effect of reaction temperature on phenol benzoylation and the results are shown in Table 6, keeping other parameters same for the catalytic activity evaluation. Below 313 K, conversion to phenyl benzoate was drastically reduced. At the same time, above 313 K, the decomposition of product was found, which was not advantageous for phenol benzoylation.

| %yield of phenyl benzoate | | |
|---|---|---|
| Temperature (K) | $[Co(BA)_2(H_2O)_2]Cl_2.4H_2O$ | $[Ni(BA)_2(H_2O)_2]Cl_2.4H_2O$ |
| 300 | 40.84 | 31.83 |
| 313 | 91.99 | 36.13 |
| 318 | 44.55 | 34.03 |

**Table 6:** The effect of temperature on conversion. Reaction time 30 minutes, catalyst load $1 \times 10^{-5}$ mol.

**Effect of time:** The catalytic benzoylation of phenol, using benzoyl chloride was studied as a function of time. Too much of extended reaction time appears to result in poor product yield. Table 7 shows that the favorable reaction time was thirty minutes. There was no significant change in the conversion to phenyl benzoate beyond the specified time of reaction.

| %°°yield of phenyl benzoate | | |
|---|---|---|
| Reaction Time (minutes) | $[Co(BA)_2(H_2O)_2]Cl_2.4H_2O$ | $[Ni(BA)_2(H_2O)_2]Cl_2.4H_2O$ |
| 20 | 40.84 | 31.83 |
| 30 | 76.58 | 55.96 |
| 40 | 42.44 | 46.65 |

**Table 7:** The effect of reaction time in catalytic efficiency. Reaction temperature 313 K, catalyst load $1 \times 10^{-5}$ mol.

## Conclusion

The FT-IR spectral studies on the complexes revealed that, N-benzylideneaniline ligand was involved in coordination only through the azomethine nitrogen. This illustrates the monodentate behavior of the ligand. In addition, the vibrational bands provide evidence for coordination of water molecule to the central metal ions. The tentative structure of both complexes shown in Figure 2 suggests planer geometry. The electronic studies on both complexes demonstrate their transition in LMCT mode. In order to explore effective industrial applications, both cobalt(II) and Nickel(II) complexes were evaluated for their catalytic activities towards benzoylation of phenol. The conversion to phenyl benzoate was enhanced by increasing the catalyst load. The conversion data showed that, both complexes have only mild conversion efficiency as heterogeneous catalyst in the benzoylation of phenol.

## References

1. Nazihah W, Ibrahim W, Shamsuddin M (2012) Symmetrical Palladium (II) N, N, O, O-Schiff Base Complex: Efficient Catalyst for Heck and Suzuki Reactions. Cryst Struct Theory Appl 1: 25-29.
2. Yang D, Gao L, Zhao W (2008) Synthesis Characterization and Catalytic Activity of Dialdehyde Starch-Schiff Base Co(II) Complex in the Oxidation of Cyclohexane. J Catal Lett 126: 84-88.
3. Murahashi SI, Noji S, Komiya N (2004) Catalytic Enantioselective Oxidation of Alkanes and Alkenes Using (Salen) Manganese Complexes Bearing a Chiral Binaphthyl Strapping Unit. Adv Synth Catal 346: 195-198.
4. Cenini S, Gallo E, Caselli A, Ragaini F, Fantauzzi S, et al. (2006) Coordination Chemistry of Organic Azides and Amination Reactions Catalyzed by Transition Metal Complexes. Coord Chem Rev 250: 1234-1253.
5. Ando R, Mori S, Hayashi M, Yagyu T, Maeda M (2004) Structural Characterization of Pentadentate Salen-type Schiff-Base Complexes of Oxovanadium (IV) and their Use in Sulfide Oxidation. Inorg Chim Acta 357: 1177-1184.
6. Chatterjee D, Mukherjee S, Mitra A (2000) Epoxidation of Olefins with Sodium Hypochloride Catalysed by New Nickel(II)–Schiff Base Complexes. J Mole Cat 154: 5-8.
7. Che CM, Huang JS (2003) Metal Complexes of Chiral Binaphthyl Schiff-Base Ligands and Their Application in Stereoselective Organic Transformations. Coord Chem Rev 242: 97-113.

8. Cerchiaro G, Micke GA, Tavares MF, da Costa Ferreira AM (2004) Kinetic Studies of Carbohydrate Oxidation Catalyzed by Novel Isatin–Schiff Base Copper(II) Complexes. J Mole Cat A 221: 29-39.
9. Schafer G, Bode JW (2011) Friedel-Crafts Benzylation of Activated and Deactivated Arenes. Chem Int Ed 50: 10913-10916.
10. Amit RY, Vijaya VD, Gaurav BP, Anand SA (2014) Synthesis, Characterization, Biological and Electrical Conductivity Studies of some Schiff Base Metal Complexes. Bull Chem Soc Ethiop 28: 255-264.
11. Akrawi BA, Ali AM (2008) The Electrical Conductivity of Some Transition Metal Complexes with 2,2'-Bipyridyl in Different Solvents at 298.16 K. Nat J Chem 31: 491-500.
12. Figgis BN, Lewis J (1964) The Magnetic Properties of Transition Metal Complexes. Prog Inorg Chem 6: 37-239.
13. Archana S (2013) Synthesis and characterization of schiff base salicylaldehyde and thiohydrazones and its metal complexes. Adv Appl Sci Res 4: 152-154.
14. Huheey JE, Keiter EA, Keiter RL (2000) Inorganic Chemistry. 4th edn. Pearson Education, Singapore, Delhi, India, p: 456.
15. Chaudhuri P, Verani CN, Bill E, Bothe E, Weyhermüller T (2001) Electronic Structure of Bis(o-iminobenzosemiquinonato) metal Complexes (Cu, Ni, Pd). The Art of Establishing Physical Oxidation States in Transition-Metal Complexes Containing Radical Ligands. J Am Chem Soc 123: 2213-2223.
16. Azam F, Singh S, Khokhra SL, Prakash O (2007) Synthesis of Schiff bases of naphtha(1,2-d) thiazol-2-amine and metal complexes of 2-(2'-hydroxy) benzylideneaminonaphthothiazole as potential antimicrobial agents. J Zhejiang Univ Sci B 8: 446-452.
17. Ali H, Amee A, Ahmed A, Emad Y (2015) Synthesis and characterization of some transition metal (II) complexes with 1,2,4-triazole schiff base. J Chem Pharm Res 7: 531-535.
18. Bhalu A, Vilapara K, Maru M, Shah M (2014) Synthesis and Characterization of Cu(II), Ni(II) and Co(II) Coordination Compounds with Nitrogen and Oxygen Containing Schiff Base. Orient J Chem 30: 303-307.
19. Kalaskar MM, Wadekar MP (2013) Synthesis and Characterization of Fe(III)- azomethine Complex. Der Pharma Chemica 5: 199-204.
20. Sönmez M, Levent A, Ekerci M (2004) Synthesis, Characterization, and Thermal Investigation of Some Metal Complexes Containing Polydentate ONO-Donor Heterocyclic Schiff Base Ligand. Rus J Coord Chem 30: 655-659.
21. Swati B, Mithlesh A (2015) Synthesis, Characterization, Spectral and Antimicrobial Studies of Macrocyclic Complexes of Mg (II), Ca (II), Sr (II) and Ba (II). Int J Sci Res 4: 963-967.
22. Khalil S, Borham N (2000) Indirect Atomic Absorption Spectrometric Determination of Pindolol, Propranolol and Levamisole Hydrochlorides Based on Formation of Ion-associates with Ammonium Reineckate and Sodium Cobaltinitrite. J Pharm Biomed Anal 22: 235-240.
23. Yimer AM, Baraki T, Upadhyay RK, Akhtar M (2014) Spectro-Magnetic and Antimicrobial Studies on some 3d Metal Complexes with Ethylenedianil of Ortho-Hydroxyphenylglyoxal. Am J Appl Chem 2: 15-18.