© INTERNATIONAL JOURNAL FOR RESEARCH PUBLICATION & SEMINAR
ISSN: 2278-6848 | Volume: 05 Issue: 05 | September - December 2014
Paper is available at www.jrps.in | Email : info@jrps.in

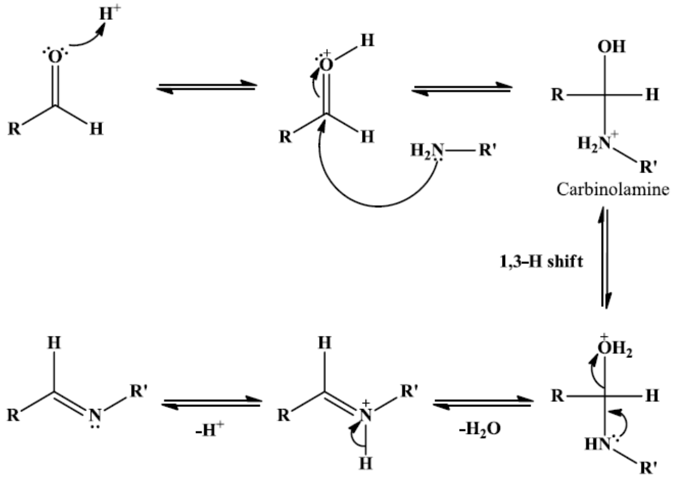
A review of Mechanism of Schiff bases formation Potential problem in Schiff base formation

[1]Hemant Kumar, [2]Dr. M. Z. Shahzada
[1]Research Scholar, Magadh University, Bodh Gaya
[2]Associate Professor, Department of Chemistry, K.L.S. College Nawada (M.U. Bodh Gaya)

Abstract : The general consensus of the mechanism of Schiff base formation, as shown in Figure, is nucleophilic addition to the carbonyl group. In the Schiff base formation, the nucleophile is the primary amine. In the first part of the mechanism, the lone pair of electrons in the amine nitrogen attacks the aldehyde or ketone to give an unstable addition compound called a carbinolamine.

Key Words : Schiff base, Schiff base formation

Introduction : A 1,3-hydrogen shift follows which facilitates losing water by either acid or base catalysis. Since the carbinolamine is an alcohol, it undergoes acid catalysed dehydration.



Mechanism of Schiff base formation.

The rate-determining step of Schiff base formation is the dehydration of carbinolamine, and that is the reason why the reaction is catalyzed by acids or Lewis acid. But the concentration of acid present for the catalysis cannot be too high as amines are basic compounds. If the amine is deprotonated and becomes non-nucleophilic, equilibrium is pulled to the left and the carbinolamine will go back to aldehyde or ketone and primary amine.

Base catalysis is also used for the dehydration of carbinolamines. The reaction of elimination is analogous to the E2 elimination of alkyl halides. Schiff base formation can be divided into two steps through an anionic intermediate, i.e. addition followed by elimination.

The geometry of the imine double bond generally adopts a *trans* orientation, which limits the steric interactions of the bulkier R group, with R being either aryl or alkyl substituents.

Potential problem in Schiff base formation - Hydrolysis

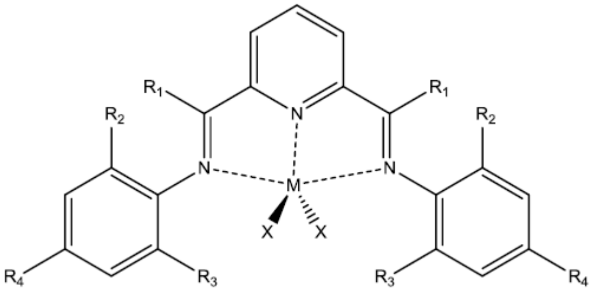
As mentioned previously during the mechanism of Schiff base formation, it is known that the formation of the imine can lead to a potential problem in which the imine double bond could be hydrolysed back to the starting materials. The successful completion is to separate the Schiff base compound or remove side product, H2O, or both. Although most Schiff base formation reactions are generally undertaken smoothly in normal co-ordinated dry solvent such as MeOH or EtOH, it still has the potential

problem in which the Schiff bases might be hydrolysed. The following three ways are focused on removing side product, water. (I), Schiff base formation involves drying agents such as anhydrous sodium sulphate or anhydrous magnesium sulphate in DCM or chloroform solvent; (II), in the 1990s an in situ method for water elimination was developed, using dehydrating solvents such as tetramethyl orthosilicate or trimethyl orthoformate; (III), For some reactants require forcing conditions such as heating to reflux in a high boiling solvent and may include the use of a Dean-Stark apparatus or molecular sieves.

Catalytic activities of Schiff base transition metal complexes4 Many salen Schiff bases complexes of metal ions show high catalytic activity.

Polymerization reactions

Britovsek and co-workers20 claimed a new active family of olefin polymerization catalysts. These homogeneous catalysts are based on 2,6-bis(imino)pyridyl Schiff base ligands complexed to iron(II) or cobalt(II) ions. With the data they observed that both Fe(II) and Co(II) had high activities, however the activities of the iron are exceptionally higher. When the substituents R1, R2, R3 and R4 are equal to methyl, the Fe(II) complex achieved the highest result in ethylene polymerisation. It was notable that the activities had a dramatic decrease when the *ortho*-substituent R3 was changed to hydrogen. The reason for this could be explained by steric protection of the active site in controlling activities and molecular weight.



M = Fe, Co X = Cl

Figure : The structure of homogeneous catalysts based on Schiff base complexes.

In order to optimise this homogeneous catalyst, heterogenization is required by avoiding fouling the reactor, overheating of the particle and melting of the polymer. Most often, inorganic support materials such as silica has been used to heterogenize soluble polymerization catalysts. Kim and co-workers reported silica-supported Fe(II) and Introduction
Co(II) catalysts based on bis(imino)-pyridyl group with silicon ethoxide functionality.

A comparison of the catalytic activities between homo- and hetero-geneous catalysts established that the silica-supported heterogeneous iron and cobalt catalysts showed high activities in ethylene polymerization (supported iron catalysts observed activity of 4.87 × 107 (g of PE/(mol of Fe-cat. h bar)) at 50 °C, while the cobalt supported catalysts showed 1.60 × 107 (g of PE/(mol of Co-cat. h bar)) at same temperature). Though due to the reduced activated site or limited diffusion of monomer into the interior pores of the supported catalysts, both homogeneous catalysts observed 100-folder higher activity than the heterogeneous, the resulted molecular weight of the polyethylene produced by silica-supported catalysts were higher than that of polyethylene by analogue homogeneous catalysts (up to 2.02 × 105).

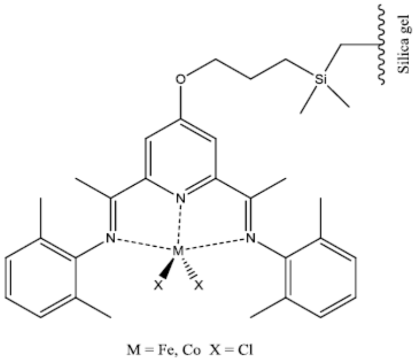


Figure Silica-supported 2,6-bis(imino)pyridyl Fe(III) and Co(II) complexes.[24,20,25]

References :

1. P. Gurumoorthy, J. Ravichandran, N. Karthikeyan, P. Palani and A.K. Rahiman, *Bull. Korean Chem. Soc.*, 2012, **33**, 2279.
2. Z.H. Chohan, M. Arif, M.A. Akhtar and C.T. Supuran, *Bioinorg. Chem. Appl.*, 2006.
3. Z.H. Chohan, A. Scozzafova and C.T.J. Supuran, *J. Enzyme Inhib. Med. Chem.*, 2003, **18**, 259
4. K. Matsufuji, H. Shiraishi, Y. Miyasato, T. Shiga, M. Ohba, T. Yokoyama and H. Okawa, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 851.
5. B.-H. Ye, X.-Y. Li, I.D. Williams and X.-M. Chen, *Inorg. Chem.*, 2002, **41**.
6. R. Rl, T. Wb and L. Sj, *New J. Chem.*, 1991, **15**, 417