



Research Article

ISSN : 0975-7384  
CODEN(USA) : JCPRC5

## Kinetics and mechanism of substitution in dichloro(2,2'-bipyridyl)Ni(II)

Fouzia Rafat

Department of Chemistry (Research & P. G. Section), Vinoba Bhave University, Hazaribagh, Jharkhand, India

### ABSTRACT

Dichloro(2,2'-bipyridyl)Ni(II) in nitrobenzene did not show an increase in molar conductance with time suggesting no solvent path in the present system. In the presence of nucleophilic reagent such as  $\text{CH}_3\text{COCl}$  the conductance increased sharply owing to the substitution of bipyridine by chloride ions. Plot of  $\log \left[ \frac{\Delta_\infty}{\Delta_\infty - \Delta_m} \right]$  against time was linear suggesting first order kinetics. The results show that the rate of substitution is independent of the concentration of the nucleophile and depends only on the first power of the concentration of the complex.

**Keywords:** Kinetics, molar conductance, nitrobenzene, bipyridine.

### INTRODUCTION

A great deal of work on nucleophilic substitution reaction in various types of transition metal complexes has already been reported in the literature.[1-5]

2,2'-bipyridine form stable complexes with a wide range of metal ions and are relatively easily functionalized. It has always attracted interest because free rotation about the linking bond allows the two nitrogens to separate. The complex containing bipyridine affords a nice chance to study the kinetics of substitution. Knowledge of the kinetic parameters and the reaction products for the reaction of metal complex with nucleophiles, e.g.  $\text{CH}_3\text{COCl}$  and  $\text{C}_6\text{H}_5\text{COCl}$ , is helpful to understand the mechanism of the reaction.

As an extension of previous work on the kinetics and mechanism of substitution reactions[6], in this communication the kinetics of substitution of dichloro(2,2'-bipyridyl)Ni(II) in nitrobenzene and the mechanism of successive replacement of bipyridine by chloride ion furnished by non-conducting nucleophile such as  $\text{CH}_3\text{COCl}$  are reported.

### EXPERIMENTAL SECTION

2,2'-Bipyridyl and hydrated metal chlorides (BDH) were used as received. The conductivity measurements were carried out with CM-82T Elico conductivity bridge in nitrobenzene. Dichloro(2,2'-bipyridyl)Ni(II) was synthesized as reported earlier.[7]

### RESULTS AND DISCUSSION

The kinetics of nucleophilic substitution reaction of  $[\text{Ni}(\text{bpy})\text{Cl}_2]$  in nitrobenzene by chloride ion has been followed conductometrically at room temperature.

The molar conductance of one millimolar solution of  $[\text{Ni}(\text{bpy})\text{Cl}_2]$  in nitrobenzene does not change with time. It means that no solvation of the complex occurs. However, when solution of the acetyl chloride or benzoyl chloride is added to it the conductance increases with time. The conductance was measured immediately after the addition of nucleophile and at five minute interval for a period of 2 h and after 24 h to get the value of  $\Delta_\infty$ . The rate of increase

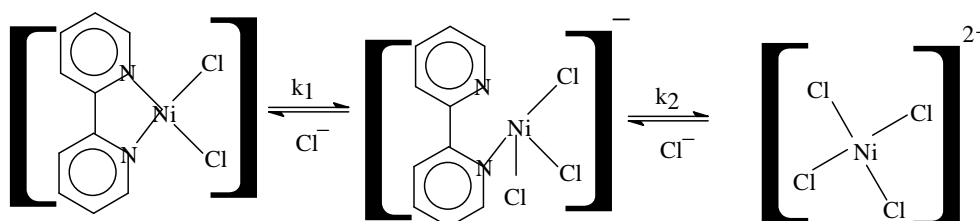
of conductance with the addition of acetyl chloride or benzoyl chloride indicates that the chloride ion is a stronger nucleophile than bpy or nitrobenzene.

On plotting of  $\log \left[ \frac{\Delta_{\infty}}{\Delta_{\infty} - \Delta m} \right]$  against time, a linear plot was obtained for different molar ratios of nucleophiles and the complex, which confirms that the reaction followed first order kinetics.

The order with respect to  $[\text{Ni}(\text{bpy})\text{Cl}_2]$  was evaluated by plotting the logarithm of the initial rate of reaction versus the logarithm of the molar concentration  $C$  of  $[\text{Ni}(\text{bpy})\text{Cl}_2]$  and was found to be one. Linear regression analysis using the least square method[8] of the calibration data was made to evaluate the slope, intercept and correlation coefficient. The correlation coefficient ( $r$ ) was found to be 0.998. The slope in the linear regression equation was also found to be 1 which confirms that the reaction is first order with respect to  $[\text{Ni}(\text{bpy})\text{Cl}_2]$ .

In the substitution reaction by chloride ions, two mutually intersecting lines were obtained. The specific rate constants  $k_1$  and  $k_2$  for the stepwise replacement of bipyridine by chloride ions were calculated from the slope of the first and second linear portions of the plots, respectively. The values are listed in Table. The rate constants were calculated by the equation

$$k = -\frac{2.303}{t} \log \left[ \frac{\Delta \alpha}{\Delta \alpha - \Delta m} \right]$$



Proposed mechanism of nucleophilic substitution of  $[\text{Ni}(\text{bpy})\text{Cl}_2]$  by chloride ion in nitrobenzene

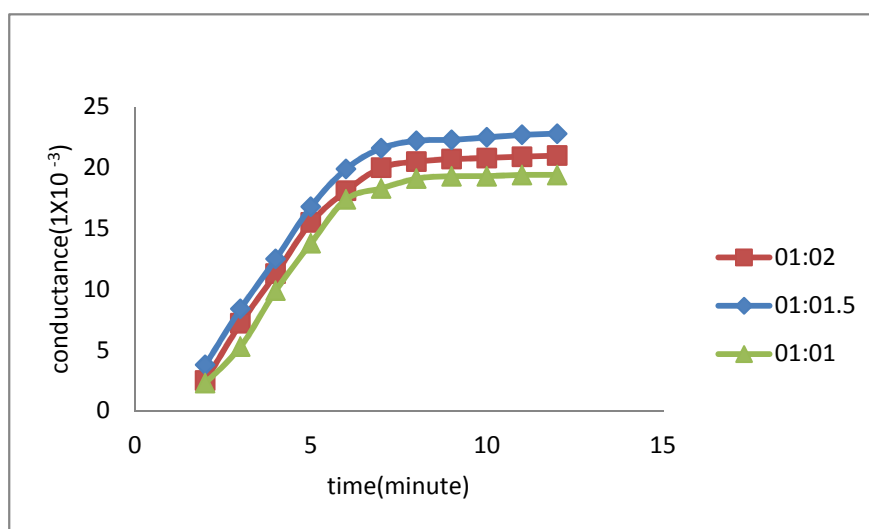


Figure1. Equivalent conductance versus time curves for  $[\text{Ni}(\text{bpy})\text{Cl}_2]$  in the presence of  $\text{CH}_3\text{COCl}$  in nitrobenzene

Table: 1

Molar ratio of compound to nucleophile ( $\text{CH}_3\text{COCl}$ )	(C) Conc. of compound dissolved in nitrobenzene	$k_1$ ( $\text{s}^{-1}$ )	$k_2$ ( $\text{s}^{-1}$ )
1:2	0.1	0.0180	0.041
1:1.5	0.1	0.0181	0.043
1:1	0.1	0.0183	0.044

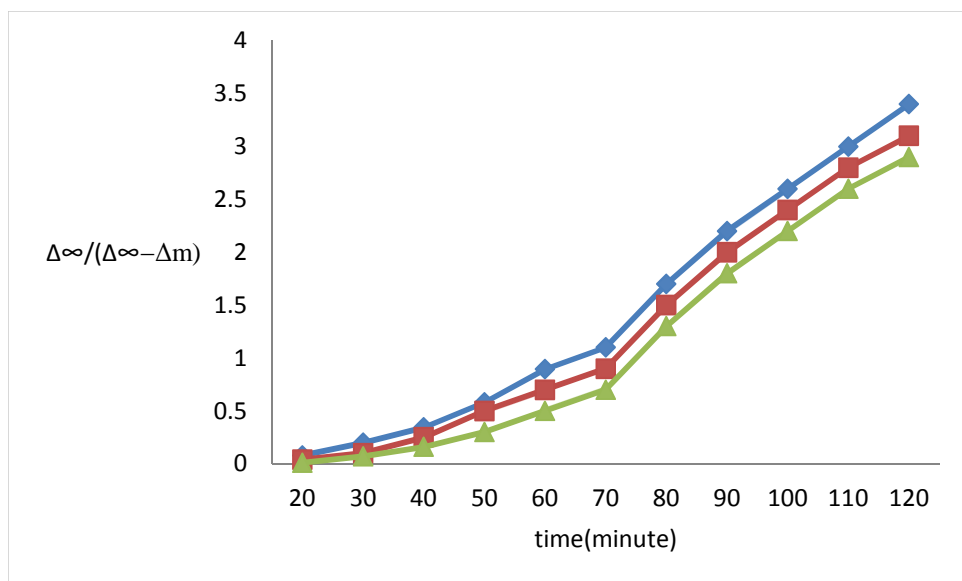


Figure 2. First order plots for substitution of chloride ions generated from  $\text{CH}_3\text{COCl}$  in  $[\text{Ni}(\text{bpy})\text{Cl}_2]$  at different molar ratios in nitrobenzene

### CONCLUSION

The studies presented in this paper have focussed on the kinetics of solvation and nucleophilic substitution reaction of  $[\text{Ni}(\text{bpy})\text{Cl}_2]$ . Dichloro(2,2'-bipyridyl)Ni(II) in nitrobenzene did not show an increase in molar conductance with time while in the presence of nucleophilic reagent such as  $\text{CH}_3\text{COCl}$  the conductance increased sharply. These findings lead us to believe that the rate of substitution is independent of the concentration of the nucleophile and depends only on the first power of the concentration of the complex.

### Acknowledgement

The author is thankful to Prof. K.S.Siddiqi, Department of Chemistry, A.M.U. Aligarh for a fruitful discussions on solvolysis.

### REFERENCES

- [1] RG Pearson; CR Boston; F Basolo. *J. Am. Chem. Soc.*, **1953**, 75, 3089-92.
- [2] RG Pearson; RE Meeker; F Basalo. *J. Am. Chem. Soc.*, **1956**, 78, 2673-79.
- [3] S Tachiyshiki. *Polyhedron*, **1983**, 2, 9.
- [4] SS Sandhu; A Singh. *J. Indian Chem. Soc.*, **1963**, 42, 744-47.
- [5] SS Sandhu; JC Bhatia. *J. Inorg. Nucl. Chem.*, **1969**, 31, 2445-49.
- [6] F Rafat; KS Siddiqi; MY siddiqi. *Pol. J. Chem.*, **2007**, 81, 313-326.
- [7] JS Killen; WR Browne; M Skupin; J Fuhrhop; G Vos. *New J. Chem.*, **2001**, 27, 1078- 83.
- [8] KJ Laidler. *Chemical Kinetics*, Tata McGraw-Hill Publishing Company Ltd., New Delhi, **1973**; 1-13.