Epoxidation of olefins with sodium hypochloride catalysed by new Nickel(II)–Schiff base complexes

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Abstract

New Schiff-base complexes of Nickel(II), NiL^1 (where $H_2L^1 = N,N'$-bis(2-hydroxyphenyl)ethylenediimine) and NiL^2 (where $H_2L^2 = N$-((2-hydroxyphenyl)acetylaldimine)-N'-(2-hydroxyphenyl)acetamide) have been prepared in good yield by direct interaction of 2-aminophenol, glyoxal/methylacetatotate and $NiCl_2$ and characterised by physico-chemical analysis. Catalytic ability of NiL complex were examined and found that both the complexes can effectively catalyse the epoxidation of olefins viz. cyclohexene, 1-hexene, *cis*- and *trans*-stilbenes, indene with NaOCl. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The catalytic ability of Nickel(II)–Schiff base/macrocyclic complexes towards hydrocarbon oxidation have been well documented in the literature [1–4]. However, catalytic efficiency of these complexes remains inexplicable with regards to the general consideration of the systematic of the metal redox as a function of coordination environment and the nature of terminal oxidants. It appears that a specific ligand environment is required for Nickel(II) to participate in catalysis with a particular oxidant. We are presently engaged in developing non-porphyrinic transition metal complexes for hydrocarbon oxidation [4–7] with cheap and easy-to-handle oxidants. This paper reports synthesis and characterization of a new Schiff base complexes of Nickel(II) (NiL), where $H_2L = N,N'$-bis(2-hydroxyphenyl)ethylenediimine) and its ability to catalyze the epoxidation of various olefins in presence of sodium hypochloride (NaOCl).

2. Experimental

2.1. Materials

The NiL^1 complex (1) was prepared from 2-aminophenol by condensation with glyoxal in

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presence of $NiCl_2$. To a ethanolic solution (30 ml) of 2-aminophenol (0.1 mol, 10.9 g) was added glyoxal (0.05 mol, 2.27 ml). The reaction mixture was stirred for 10 min. On addition of $NiCl_2 \cdot 6H_2O$ (0.05 mol, 12 g) the colour of the resultant mixture changed to dark brown. The reaction mixture was stirred at room temperature in air for 6 h. A brown solid separated, which was filtered, washed thoroughly with methanol and water, and dried over fused $CaCl_2$ (Yield: 80%). Anal. $NiC_{14}H_{10}N_2O_2$ requires C, 56.62; H,3.37; N, 9.43; (Found C,57.1; H, 3.8; N, 9.7;), UV–vis in CH_3OH: 522 nm ($e_{max} = 280$), 293 nm ($e_{max} = 8700$) and 235 nm ($e_{max} = 14,340$), IR (KBr): 3360 cm^{-1} (broad), 1590 cm^{-1} (s), 1435^{-1} (s).

NiL^2 complex (**2**) was prepared by the same procedure as described for complex-1. Methylacetoacetate was used in place of glyoxal (Yield: 85%). Anal. $NiC_{16}H_{14}N_2O_3$ requires C, 56.3; H, 4.11; N, 8.21;(Found C,57.1; H, 3.9; N, 8.17;), UV–vis in CH_3OH: 542 nm ($e_{max} = 220$), 290 nm ($e_{max} = 7,500$) and 234 nm ($e_{max} = 13,445$), IR (KBr): 3360 cm^{-1} (broad), 1730 cm^{-1} (s), 1590 cm^{-1} (s), 1435^{-1} (s). All reagents were A.R. grade and were used without further purification. Double-distilled water was used throughout the experiments.

2.2. Instrumentation

Absorption was recorded on GBC Cintra 10 spectrophotometer. IR spectra were taken as KBr pallet using a Perkin Elmer spectrometer (Model 783). Electrochemical studies were carried out by using PAR Electrochemical equipment (Model 174A). Gas chromatographic analysis were performed with a Carlo Erba GC 8000 top series on a Tenax TA column connected with FID detector.

2.3. Catalytic epoxidation of olefins

In a typical 0.1 mmol of complex (**1/2**), 4.0 mmol alkene, and 0.1 mmol benzyltributylammoniumchloride (phase transfer catalyst, PTC)

were magnetically stirred with 20 ml of NaOCl (0.7 M) at room temperature. Aliquots of the CH_2Cl_2 layer was withdrawn at chosen interval of time and subjected to gas chromatographic (GC) analysis for product(s). GC parameters were quantified by the authentic product samples prior to the analysis.

3. Results and discussion

Based on spectral and physico-chemical analysis, the structures suggested for complex **1** and **2** is shown in Fig. 1. IR spectrum of Nickel complexes exhibited usual ligational bands (viz. 1590 cm^{-1} for C=N stretch) expected for coordinated Schiff base ligand, L. The absorption spectrum of complexes in CH_3OH showed bands characteristic of square-planar Nickel(II)–Schiff base type complexes [1]. The cyclic voltammetric studies revealed that Ni(II)-complexes (**1/2**) undergo reductive degradation in CH_3CN. A large anodic current observed on the reverse scan was indicative of the electrode pollution, which was further confirmed by electrode deposition. The redox potential for Ni^{3+}/Ni^{2+} couple determined from cyclic voltammetric studies was found to be 0.81 V (vs. Ag/AgCl) for **1** and 0.76 (vs. Ag/AgCl) for **2**. The potential of Ni^{3+}/Ni^{2+} redox couple reported for Ni(salen) complex (0.91 V vs. SCE) [8] is higher than that obtained for complexes **1** and **2**.

Catalytic oxidation of olefins was carried out in a biphasic medium (CH_2Cl_2/H_2O) in presence of a phase transfer catalyst (PTC) benzyltributylammonium chloride. The results of the epoxidation (see experimental for reaction conditions) are summarised in Table 1. A series of controlled experiments revealed the fact that each component is essential for an effective catalytic transformation and the basic system is relatively unaffected by changing the order of mixing. The results of the time dependence studies with regards to epoxide formation showed that the epoxidation process catalysed
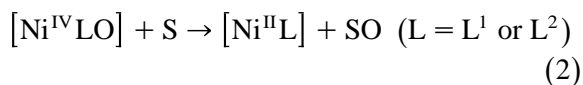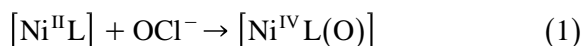
$$(H_2L^1)$$ $$(H_2L^2)$$
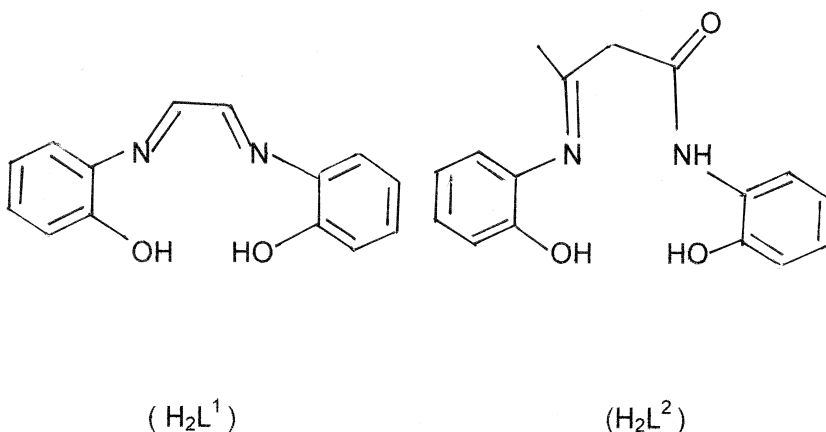
H_2L^1 = N ,N' - bis (2-hydroxyphenyl)ethylenediimine

H_2L^2 = N ,N' -((2-hydroxyphenyl)acetylaldimine)- N'-(2-hydroxyphenyl)acetamide

Fig. 1. Schematic representation of NiL^1 and NiL^2 complexes.

by Ni-complexes undergoes an induction period (typically of 15–25 min) while no detectable epoxide is formed. Formation of Nickel perox-

Table 1
NiL catalysed oxidation of olefins[a]

Catalyst complex	Substrate	Product[b]	Yields (%)[c]
NiL^1	Cyclohexene	Cyclohexene epoxide	16
	1-Hexene	1-Hexene epoxide	29
	cis-Stilbene	*trans*-Stilbene oxide	13
		Benzaldehyde	10
		Benzoic acid	trace
	trans-Stilbene	*trans*-Stilbene oxide	35
		Benzaldehyde	7
		Benzoic acid	trace
	Indene	Indene oxide	25
NiL^2	Cyclohexene	Cyclohexene epoxide	14
	1-Hexene	1-Hexene epoxide	21
	cis-Stilbene	*trans*-Stilbene oxide	11
		Benzaldehyde	9
		Benzoic acid	trace
	trans-Stilbene	*trans*-Stilbene oxide	31
		Benzaldehyde	7
		Benzoic acid	trace
	Indene	Indene oxide	21

[a] See Section 2 for reaction conditions.
[b] After 6 h of reaction.
[c] Based on substrate taken.

ide was also evidenced in the present case by the appearance of a fine black suspension in the reaction mixture as observed in case of Ni(salen) catalysed epoxidation of olefins with OCl^- [3]. On the basis of the above experimental observations and considering the formation of a high-valent Nickel(IV)-oxo is the reactive intermediate as proposed by earlier workers [1–3] we propose the following working mechanism (Eqs. (1) and (2)) for the epoxidation of enlisted alkenes.

$$\left[Ni^{II}L \right] + OCl^- \rightarrow \left[Ni^{IV}L(O) \right] \qquad (1)$$

$$\left[Ni^{IV}LO \right] + S \rightarrow \left[Ni^{II}L \right] + SO \ (L = L^1 \text{ or } L^2) \qquad (2)$$

In the proposed mechanism Nickel(IV)-oxo intermediate (formed in the reaction of $Ni^{II}L$ with OCl^-) transfer its oxo-atom to the reacting olefin (S) to produce corresponding epoxide (SO). The epoxide formation probably takes place through an open chain radical pathway as the catalytic system lacks stereospecificity and substantial amount of benzaldehyde as side product is formed in the epoxidaton of oxidation of stilbenes.

NiL-catalyzed epoxidation of olefins was found to be ineffective when CH_3CN was used as solvent. This may be due to the fact that the formation of Nickel(IV)-oxo species (catalytically active intermediate) is kinetically not favoured as it perhaps involves the coordination of OCl^- through the substitution of axially coordinated CH_3CN (which is a stronger nucleophile than OCl^-).

4. Conclusion

The results of the present studies convincingly demonstrate the catalytic ability of Nickel(II)-complexes (**1/2**) towards epoxidation of olefins with NaOCl. Comparison of the present results with that of reported for Ni(salen) catalysed olefin epoxidation [3] add further toward evolving the generalization that the Schiff-base type ligands (with N,O donor sites) are suitable for Nickel catalysed epoxidation of olefins with NaOCl. The black precipitate appeared upon addition of NaOCl (due to formation of Nickel-peroxide) which could not effect olefin epoxidation, but turned colorless when ascorbic acid, stronger electron donor was added. Absence of the black precipitate and no catalytic activity in the presence of a stronger coordinating solvent (CH_3CN) is further suggestive of the fact that transient coordination of terminal oxidant is the key-step for the formation of the high-valent LNi(IV)-oxo intermediate which effects oxo-transfer to olefins. The formation of Nickel-peroxide as observed in the present case and also reported earlier [3] is associated with the loss of Nickel from catalyst complexes in presence of hypochloride at high pH ($\sim$ 12). Active research related to the development of better Nickel (II) oxo-transfer catalysts with other cheap oxidants is in progress.

Acknowledgements

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