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Catalysis of alkene hydrogenation and oxidation by nickel-saloph complex; a novel bifunctional catalyst



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Abstract

Hydrogenation of cyclohexene to cyclohexane and cyclooctene to cyclooctane with H_2 in presence of $Ni(\text{saloph})$, **1**, ($\text{saloph} = \text{bis}(\text{salicylaldehyde})\text{-}o\text{-phenylenediamine}$) were carried out at moderately high pressure (60 atm) and temperature (50°C) in ethanol medium. At normal temperature and pressure, the same catalyst (complex **1**) catalyses the epoxidation of cyclohexene and cyclooctene with $KHSO_5$ in presence of CTAB (cetyl trimethyl ammonium bromide; a phase-transfer reagent) in CH_2Cl_2 . Cyclohexene oxide and cyclooctene oxide were found to be the major products of the epoxidation reactions.

Key words: alkene; bifunctional catalyst; hydrogenation; nickel; saloph

Introduction

Catalytic hydrogenations and oxidations of organic compounds in homogeneous solution is a demanding area of inventions. Over the past decade synthetic metalloporphyrinic complexes have come to occupy a unique place in the area of transition metal catalysed reactions [1], as they mimic certain biochemical enzymatic oxidation processes [2-5]. In our laboratory, we have been engaged in ruthenium catalysis and our past communications decisively revealed the catalytic ability of non-porphyrinic ruthenium(III) complexes in various oxidation [6-8], hydrogenation [9-10], carbonylation [11-13] reactions. However, one basic problem exists in ruthenium catalysis; the synthesis of ruthenium complexes, which is not always easy and in any case the starting material, $RuCl_3$, is costly. We undertook the present work for two principle reasons: firstly to search for a new low-cost catalyst which is easy to synthesise, and secondly to explore the possibility of nickel catalysis which has not received much attention [14-16]. We report herein the $[Ni(\text{saloph})]$ **1** catalysed hydrogenation of cyclohexene and cyclooctene with H_2 , at moderately

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high pressure and temperature and, epoxidations of the same substrates with KHSO_5 at normal temperature and pressure.

Experimental

The $[\text{Ni}(\text{saloph})]$ complex, **1**, was prepared by interacting $\text{Ni}(\text{OAc})_2$ with saloph [17] (salph = bis(salicylaldehyde)-*o*-phenylenediamine) in ethanol medium. To a stirred ethanolic solution of $\text{Ni}(\text{OAc})_2$ (1 mmol) the ligand saloph (1.1 mmol) was added in small portions and after completing the ligand addition, the whole reaction mixture was refluxed for 2 h. The red, solid product separated was filtered and washed repeatedly with cold ethanol and dried under vacuo.

Anal: Found (calc.): C 64.1 (64.4); H 4.1 (3.7); N 7.6 (7.5)%. UV-vis, $\lambda_{\text{max}}/\epsilon_{\text{max}}$ (nm/mol $^{-1}$ dm 3 cm) = 479 (11300), 379 (35260) IR, $\nu_{\text{C-N}}$ = 1610 cm $^{-1}$, $\nu_{\text{C-O}}$ = 1200 cm $^{-1}$. Figure 1 represents the structure of complex **1**. All other chemicals and solvents used were of analytical grade.

Elemental analysis were carried out using a Carlo Erba elemental analyser. Absorption spectra were recorded on a Shimadzu UV-vis spectrophotometer. IR spectra were recorded on a Beckman Acculab 10 spectrometer in the range 4000–600 cm $^{-1}$ and on a Perkin-Elmer 621 spectrometer in the range 600–200 cm $^{-1}$.

The catalytic hydrogenation reaction was studied in a stainless steel pressure reactor (PAR Instrument Co., USA). In a typical run, known amounts of substrate and catalyst were dissolved in 70 ml of ethanol and the system was pressurised with H_2 and adjusted to 60 atm when the experimental temperature was attained at 50°C. After 5 h of reaction, the liquid sample was withdrawn and subjected directly to GC analysis. Catalytic oxidation reactions were carried out normal temperature and pressure. In a typical experiment 0.1 mmol of catalyst, 0.12 mmol CTAB (cetyl trimethyl ammonium bromide; a phase-transfer catalyst), 1 mmol of KHSO_5 (commercially available as Oxone) and 10 mmol of substrate were stirred for 5 h (under N_2) in CH_2Cl_2 and aliquots of CH_2Cl_2 layer were subjected to GC analysis.

The reaction products were analyzed by gas chromatographic method

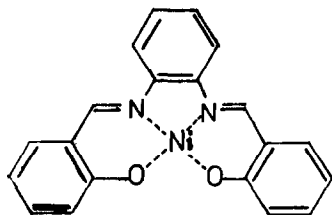


Fig. 1. Complex **1**.

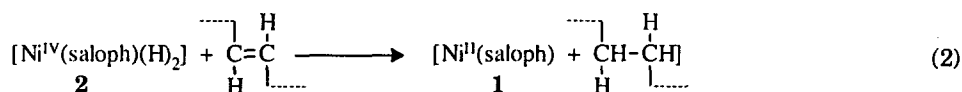
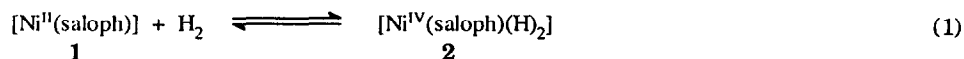
(Shimadzu GC-9A) as reported elsewhere [7,8]. GC parameters were quantified with the authentic samples of reaction products. The identities of all the major reaction products were further confirmed by ^{13}C NMR analysis carried out with a JEOL FX-100 FT-NMR spectrometer.

Results and discussion

Hydrogenation of cyclohexene and cyclooctene

After equilibrating the system containing complex **1**, substrate and H_2 (see details in experimental section) at 50°C and adjusting the pressure at 60 atm (with H_2), a drop of pressure from 60 atm to 40 atm (after 5 h) was observed which accompanied the hydrogenation of cyclohexene to cyclohexane and cyclooctene to cyclooctane as revealed by GC analysis. The percentage yields of the reaction products under specified conditions are summarised in Table 1. A negligible amount of cyclohexane and cyclooctane was obtained when the hydrogenation reactions were carried out in absence of complex **1** at the above described temperature and pressure.

On the basis of the above observations we conclude that complex **1** catalyses the hydrogenation of cyclohexene and cyclooctene at moderately high temperature and pressure, a working mechanism is proposed in eqns. 1 and 2 for the above described hydrogenation reactions.



In the suggested mechanism H_2 reacts with complex **1** to give a high-valent transient intermediate **2** in an oxidative addition step (eqn. 1) which transfers hydrogen atoms in a subsequent step to give hydrogenated substrate and complex **1** back as ultimate reaction products. Formation of high-valent nickel species was reported earlier [18] in certain enzymatic (hydrogenase) reactions. In our case catalytically active dihydrido- Ni^{IV} complex (**2**) seems to be highly reactive, as we did not observe any spectral evidence (UV-vis and solution IR) in favour of complex **2** formation at normal temperature and pressure. We believe that complex **2** only forms at high H_2 pressure, and once it forms it rapidly transfers hydrogen atoms to the substrate in one rapid step or decomposes back (in absence of substrate) to complex **1** and H_2 . It is interesting to note that cyclohexene is more reactive than cyclooctene. This may be due to a decrease in nucleophilicity of the substrate, cyclooctene, by the increase in ring size.

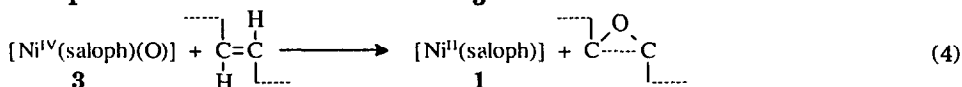
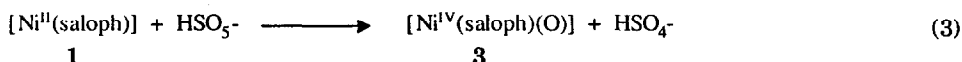
TABLE 1

Ni^{II}(saloph) catalysed hydrogenation and oxidation of cyclohexene and cyclooctene^a

Hydrogenation ^b			Oxidation ^c		
Substrate	Product	Yield (%) ^d	Substrate	Product	Yield (%) ^d
cyclohexene	cyclohexane	63	cyclohexene	cyclohexene oxide cyclohexene-2-ol	12 trace
cyclooctene	cyclooctane	37	cyclooctene	cyclooctene oxide cyclooctene-2-ol	8 trace

^aSee Experimental for reaction conditions.^bReaction was carried out for 5 h at 50°C and 60 atm.^cReaction was carried out for 5 h at normal temperature and pressure.^dYield based on substrate taken.*Oxidation of cyclohexene and cyclooctene*

Catalytic oxidation of cyclohexene and cyclooctene was carried out in a biphasic medium (CH₂Cl₂/H₂O) in presence of a phase-transfer catalyst cetyl trimethyl ammonium bromide (CTAB). In a typical experiment, an aqueous solution of KHSO₅ (pH of the solution was adjusted to 8 by using phosphate buffer) was added to a solution of complex **1**, CTAB and the substrate in CH₂Cl₂ and stirred vigorously for 5 h, and then aliquots of the CH₂Cl₂ layer were withdrawn and subjected to GC analysis which revealed the formation of substrate epoxides in the reaction mixture along with trace amounts of diols (Table 1). The basic system was relatively unaffected by changing the order of mixing the components, and from successive blank experiments it was concluded that each component is essential for a successful reaction. On the basis of the above experimental observations and considering the earlier mechanism [14-16] for olefin epoxidation catalysed by nickel(II) complexes we propose the following working mechanism (eqns. 3 and 4) for the epoxidation of cyclohexene and cyclooctene with KHSO₅ catalysed by complex **1**:



In the proposed mechanism KHSO₅ reacts with complex **1** to give a high-valent nickel(IV)-oxo species (**3**), which is capable of oxygen atom transfer to the reacting substrate to yield corresponding epoxide and complex **1** back as reaction products. The appearance of a greyish-brown suspension in the reaction mixture upon addition of KHSO₅ to a solution of complex **1** probably implies the formation of a high-valent Ni^{IV}-oxo species (**3**), which could not be isolated. However, addition of a strong two-electron reductant *viz.* ascorbic

acid immediately restores the orange-red colour of complex **1**, which supports our assumption in favour of the formation of Ni^{IV}-oxo species (**3**) during the course of reaction.

In conclusion, the above studies clearly show that complex **1** catalyses both hydrogenation and oxidation of unsaturated hydrocarbons, and the catalytic activity of complex **1** towards hydrogenation is more than that in oxidation reactions. Further, on the basis of recent reports [19–21], we believe that encapsulation of complex **1** in zeolite will increase its catalytic activity (in both hydrogenation and oxidation of unsaturated hydrocarbons) in terms of selectivity as well as yields. Active research pertinent to this matter is in progress.

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