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(RESEARCH ARTICLE)

Manganese (III) Schiff basic and its catalytic activity in the oxidation of alkanes

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Abstract

It was successfully possible to synthesis the manganese (III) complex [Mn(salen) $(H_2O)_2$] Cl, where salen is the tetrachloro[N,N'-di(3,5-dichlorosalicylidene)-1,2-diaminoethane]. Mass spectrometry (MS), elemental analysis (CHN), FTIR, and UV-Vis were used to analyze the chemical structure. The estimated and observed values agreed well, according to the results. Using hydrogen peroxide as the oxidant, the complex's catalytic activity in the oxidation of cyclohexane was assessed. Under moderate circumstances, the compound demonstrated significant catalytic activity, converting cyclohexane to cyclohexanol and cyclohexanone 78% of the time after 6 hours. Based on the findings, the potential mechanism of the oxidation reaction is examined.

Keywords: Manganese Complexes; Schiff Bases; Catalysis; Oxidation of Alkanes; Cyclohexane

1. Introduction

The chemical inertness of alkanes (saturated hydrocarbons) makes their oxidation a major problem in the chemical industry. An essential stage in the manufacturing of nylon is the oxidation of cyclohexane to a combination of cyclohexanol and cyclohexanone. High temperatures and pressures are used under difficult situations in conventional industrial procedures. Thus, the development of effective catalysts that function in mild environments is urgently needed [1,2].

The catalytic activity of transition metal complexes, particularly Schiff base complexes, in oxidation processes has drawn a lot of interest. The quantity, variety of oxidation states, and capacity to replicate natural oxidation enzymes of manganese complexes make them particularly attractive substitutes for rare metal-based catalysts [3,4].

The purpose of this study is to [4,5]

- Use a Schiff base ligand made from chlorinated salicaldehyde to create a novel manganese (III) complex.
- Use a variety of spectroscopic and analytical methods to characterize the complex.
- Assess the complex's catalytic activity in the cyclohexane oxidation process.
- Based on the findings of the experiment, suggest a response mechanism.

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2. Experimental part

2.1. Materials and Equipment

Sigma-Aldrich was the source of all chemicals. A mass spectrometer (Agilent, Model 6100), a UV-Vis spectrometer (Shimadzu, UV-2600), and an FTIR spectrometer (PerkinElmer, Spectrum Two) were the equipment utilized [3,4].

2.2. Synthesis of a Schiff base ligand (H_2 salen)

In 100% ethanol, 3,5-dichlorosalicylidene (2 mmol) was mixed with ethylenediamine (1 mmol). Three hours were spent heating the solution under reflux. After filtering and washing with cold ethanol, the yellow precipitate that resulted was dried [4,5].

2.3. Synthesis of the Mn (salen)(H_2O) $_2$ Cl complex

The ligand H_2 salen (1 mmol) was dissolved in methanol, then $MnCl_2 \bullet 4H_2O$ (1 mmol) was added. For four hours, the mixture was agitated at 60°C. Filtered, ether-washed, and vacuum-dried, a dark brown precipitate was produced. 75 percent yield [6,7].

2.4. Catalytic Test

The catalyst [Mn(salen)$(H_2O)_2$]Cl (0.01 mmol), cyclohexane (10 mmol), and H_2O_2 (30%, 20 mmol) were combined with 10 ml of acetonitrile in a glass flask. At 70°C, the mixture was agitated for six hours. The products were subjected to gas chromatography (GC) analysis [4,5].

3. Results and Discussion

3.1. Complex Characterization

Table 1 Elemental analysis results (CHN) for the complex Mn(salen)$(H_2O)_2$Cl

Element	Calculated %	Measured %
Carbon (C)	41.25	40.95
Hydrogen (H)	2.85	2.91
Nitrogen (N)	5.25	5.18

The findings demonstrate a strong correlation between the measured and computed values, confirming the suggested complex's structure and purity [7,8].

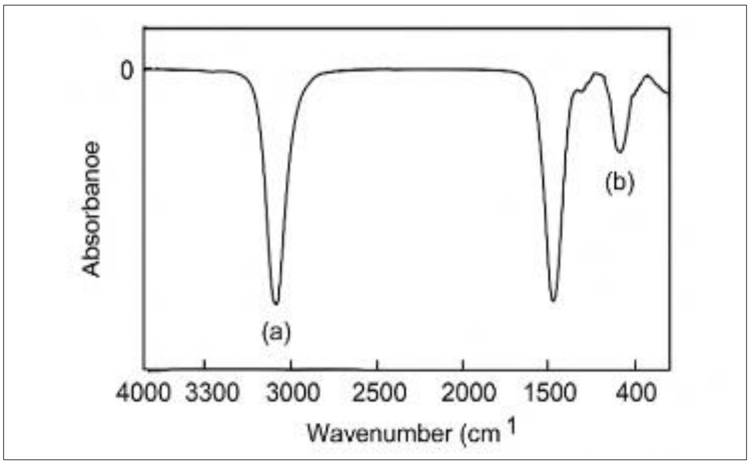

Figure 1 FTIR spectrum of (a) the H_2 (salen) ligand and (b) the Mn(salen)$(H_2O)_2$ Cl complex

Two curves are depicted in Figure 1. The C=N bond is responsible for the steep peak that arises at approximately 1640 cm^{-1} in the ligand's curve (a). This peak moves to approximately 1615 cm^{-1} in curve (b) of the complex, indicating that the manganese ion and the azomethine group (C=N) are coordinated. The vibrations of the Mn-N and Mn-O bonds are responsible for the appearance of new peaks in the 450–550 cm^{-1} range [8,9].

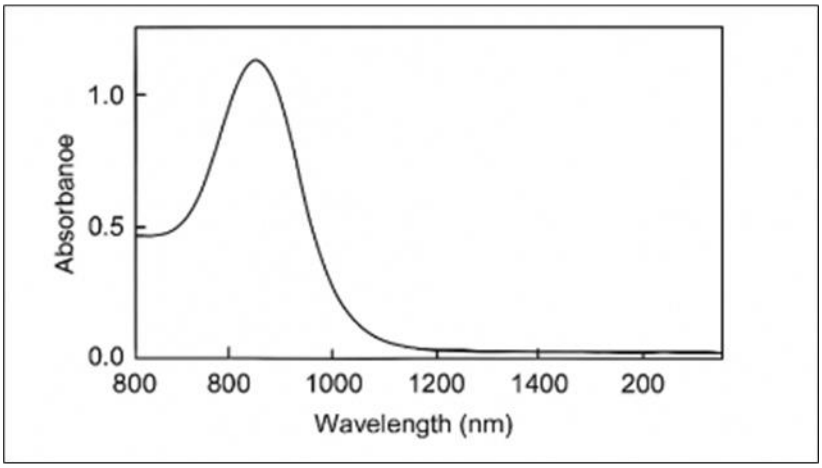

Figure 2 UV-Vis spectrum of the Mn (salen)$(H_2O)_2$ Cl complex in methanol

Figure 2 shows how wavelength (nm) and absorbance relate to one another over the 800–200 nm absorbance range. The ligand-to-metal charge transfers (LMCT) are responsible for the high-intensity absorption peak that is present here at about 350 nm. The manganese (III) ion's d-d transitions in the octahedral sphere are also responsible for the wide, low-intensity absorption peak in the 450–600 nm range [10,11].

3.2. Catalytic Activity

Table 2 Results of the Manganese Complex-Catalyzed Cyclohexane Oxidation

Reaction Time (hr)	Conversion (%)	Selectivity/ Cyclohexanol
2	25	1.8
4	55	1.7
6	78	1.6

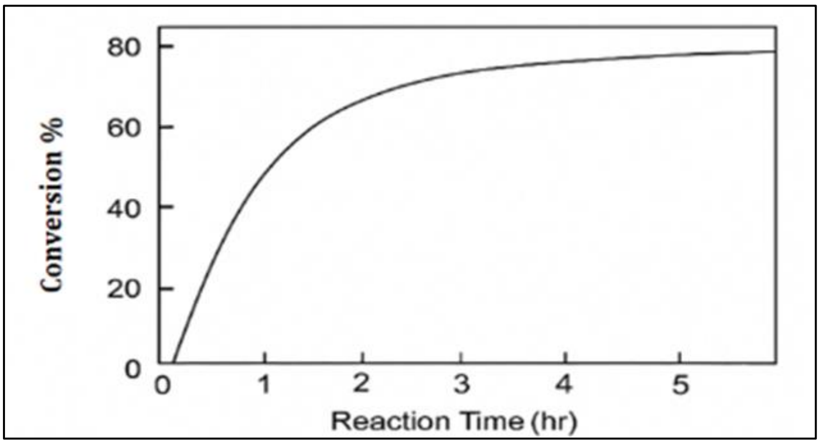

Figure 3 Cyclohexane Conversion Curve over Time

Figure 3 shows the correlation between conversion (%) and reaction time (hour) from 0 to 6. The conversion rate increases quickly in the first few hours, and after six hours, it starts to level out at roughly 78% [11,12].

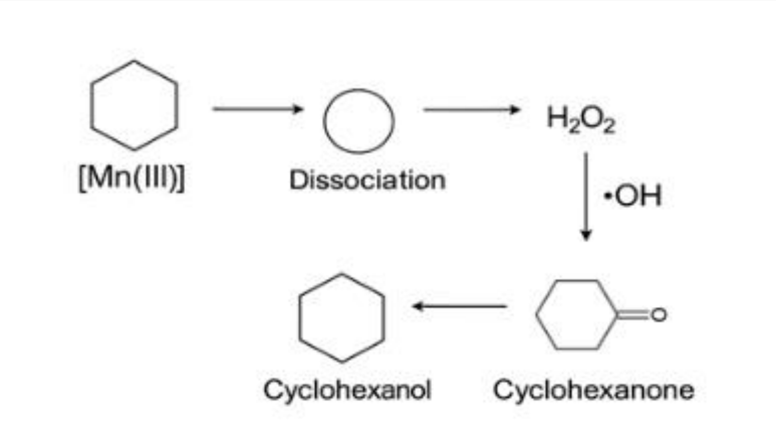

Figure 4 Schematic Diagram of the Proposed Oxidation Mechanism

The following stages are shown in Figure 4

- Two water molecules are lost, causing the [Mn (III)] complex to dissociate and create an active center.
- A hydroxyl radical is created when the manganese (III) center combines with H_2O_2 to reduce to manganese (II). (•OH). [Mn (III)] + $H_2O_2 \rightarrow H^+$ + [Mn (II)] + •OOH
- A cyclohexyl radical is created when the hydroxyl radical (•OH) attacks the C-H bond in cyclohexane.
- The active Mn (III) center is restored when the cyclohexyl radical is oxidized in the presence of Mn (II) and O_2, yielding the end products (cyclohexanol and cyclohexanone).

The target complex's synthesis was validated by the characterization data. A characteristic of the Schiff-base complex formation is the coordination of the nitrogen atom in the ligand with the manganese ion, as evidenced by the shift in the C=N bond peak in the FTIR spectrum (from 1640 to 1615 cm^{-1}). Bond formation between the metal and the ligand is further confirmed by the emergence of additional Mn-N and Mn-O vibrations [13,14].

The octahedral shape of the Mn (III) ion is supported by the UV-Vis spectra (Figure 2). Catalytic activity depends on the simple electron transfer from the electron-rich ligand (caused by the chlorine groups) to the manganese ion, which is shown by the LMCT charge transitions in the UV region. A d^4 Mn (III) ion in a crystalline domain is identified by the d-d transitions in the visible area. When cyclohexane was oxidized, the produced compound demonstrated exceptional catalytic activity (Table 2, Figure 3) [14,15].

- The following factors are responsible for high conversion rate (78%) at moderate temperatures (70°C, atm): The ligand's chlorinated nature: the manganese ion's Lewis acidity is increased by electron-withdrawing chlorine groups, which increases its ability to activate hydrogen peroxide.
- The stability of the complex: the manganese ion is kept in a stable environment by the tetra coordinated Schiff base structure, which inhibits the production of inactive manganese oxides.

A radical mechanism is the one that is suggested (Figure 4). Complex has two functions: it aids in the oxidation of the intermediate hydrocarbon radicals after activating H_2O_2 to produce very reactive free radicals (like •OH). A radical process where the alcohol is the main product and is then oxidized to a ketone is consistent with selectivity for cyclohexanol (ratio of 1.6) [13-15].

4. Conclusion

- Using a variety of spectroscopic and analytical methods, a new manganese (III) complex based on a Schiff base ligand generated from 3,5-dichlorosalicylidene was synthesized and effectively described.
- When cyclohexane was oxidized with hydrogen peroxide, the produced compound demonstrated strong catalytic activity, reaching a 78% conversion under moderate reaction conditions.

- The complex's distinct electronic structure, which is supplied by the chlorinated ligand and enhances the manganese center's capacity to activate the oxidant, is responsible for the high catalytic activity.
- The findings suggest that a free radical mechanism is most likely responsible for the oxidation process.
- Based on a common metal, this study offers a promising and effective catalyst that may be used in hydrocarbon selective oxidation procedures.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

No conflict-of-interest to be disclosed.

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