

ออกซีเดชันอย่างเลือกจำเพาะของไฮโดรคาร์บอนเร่งปฏิกิริยาด้วย
สารประกอบเชิงซ้อนโลหะทรานซิชันที่ละลายได้



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จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์


คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2545

ISBN 974-17-1080-10

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

SELECTIVE OXIDATION OF HYDROCARBONS CATALYZED BY
SOLUBLE TRANSITION METAL-COMPLEXES



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สถาบันวิทยบริการ
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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science

Program of Petrochemistry and Polymer Science

Faculty of Science

Chulalongkorn University

Academic Year 2002

ISBN 974-17-1080-1

Thesis Title Selective Oxidation of Hydrocarbons Catalyzed by Soluble
Transition Metal-Complexes
By Mr. Nut Songsangcharoen
Field of Study Petrochemistry and Polymer Science
Thesis Advisor Assistant Professor Warinthorn Chavasiri, Ph.D.

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ณัฐ ส่องแสงเจริญ : ออกซิเดชันอย่างเลือกจำเพาะของไฮโดรคาร์บอนเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนโลหะทรานซิชันที่ละลายได้ (SELECTIVE OXIDATION OF HYDROCARBONS CATALYZED BY SOLUBLE TRANSITION METAL-COMPLEXES)

อ. ที่ปรึกษา: ผศ.ดร. วรินทร์ ชวศิริ, จำนวนหน้า 63 หน้า. ISBN 974-17-1080-1.

การศึกษากการเร่งปฏิกิริยาออกซิเดชันโดยสารประกอบเชิงซ้อนโลหะทรานซิชันที่ละลายได้ในกลุ่มของคาร์บอกซิเลตและแอซิติลแอซิทอเนต รวมทั้งศึกษาหาค่าปัจจัยต่างๆที่มีผลต่อปฏิกิริยาจากโลหะคาร์บอกซิเลต 9 ชนิด และโลหะแอซิติลแอซิทอเนต 5 ชนิดที่ได้นำมาศึกษา พบว่าโครเมียมสเตียเรต เป็นตัวเร่งปฏิกิริยาที่มีความเหมาะสมที่สุดสำหรับออกซิเดชันของไซโคลเฮกเซนโดยใช้เทอเชียรีบิวทิลไฮโดรเปอร์ออกไซด์เป็นสารออกซิไดซ์ ในแง่ของปริมาณผลิตภัณฑ์ที่ต้องการและความเลือกจำเพาะของอัตราส่วนคีโตนต่อแอลกอฮอล์ สารตั้งต้นชนิดอื่นๆ เช่น ไซโคลโดเดเคน ไซโคลเฮกซานอล 1,4-ไซโคลเฮกเซนไดออล ไซโคลเฮกซาโนน ไซโคลเฮกซีน แอลฟา-เมทิลสไตรีน เอทิล เบนซีน และ ไดเฟนิลซัลไฟด์ สามารถเปลี่ยนรูปไปเป็นผลิตภัณฑ์ที่ออกซิไดซ์ได้ในปริมาณปานกลางถึงสูง จากการศึกษาการเลือกจำเพาะในปฏิกิริยาออกซิเดชันของอดาแมนเทนทำให้เชื่อว่ากลไกการเกิดปฏิกิริยาในระบบที่พัฒนาขึ้นนี้เกิดผ่านอนุมูลอิสระ

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

หลักสูตร...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...	ลายมือชื่อนิสิต.....
สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...	ลายมือชื่ออาจารย์ที่ปรึกษา.....
ปีการศึกษา.....2545.....	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

4372254323 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
 KEY WORD: HYDROCARBONS / OXIDATION / CARBOXYLATE COMPLEXES
 NUT SONGSANGCHAROEN : SELECTIVE OXIDATION OF
 HYDROCARBONS CATALYZED BY SOLUBLE TRANSITION-
 METAL COMPLEXES
 THESIS ADVISOR : ASST.PROF. WARINTHRON CHAVASIRI, Ph.D.;
 63 pp. ISBN 947-17-1080-1.

The oxidation reactions catalyzed by soluble transition-metal complexes in a class of carboxylate and acetylacetonate were explored. Various factors influencing the reaction were evaluated. It was turned out that among nine metal carboxylates and five metal acetylacetonates studied, Cr(III)stearate was the most appropriate catalyst for cyclohexane oxidation using *tert*-butyl hydroperoxide as an oxidant in terms of good yield of desired products and the selectivity *one/ol* ratio. Other substrates such as cyclododecane, cyclohexanol, 1,4-cyclohexanediol, cyclohexanone, cyclohexene, α -methyl styrene, ethyl benzene and diphenyl sulfide could be transformed into their oxidized products in moderate to high yield. Supported by the regioselectivity study of adamantane oxidation the mechanistic pathway of this developed system was believed to take place *via* radical fashion.

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Program...Petrochemistry and Polymer Science...	Student's signature.....
Field of study...Petrochemistry and Polymer Science	Advisor's signature.....
Academic year2002....	Co-advisor's signature.....

ACKNOWLEDGEMENTS

The author would like to express his gratitude to his advisor, Assistant Professor Dr. Warinthorn Chavasiri for his very kind assistance, generous guidance and encouragement throughout the course of this research. In addition, the author also wishes to express deep appreciation to Associate Professor Dr. Supawan Tanayanon, Associate Professor Dr. Wimonrat Trakarnpruk, Assistant Professor Dr. Nuanphun Chantarasiri and Dr. Orawan Sanguanruang serving as the chairman and members of his thesis committee, respectively, for their valuable suggestions and comments.

Appreciation is also extended to the Department of Chemistry and Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University for granting financial support to fulfill this study and provision of experimental facilities. The special thanks for permitting to use some equipments, especially, Natural Products Research Laboratory are acknowledged.

Further acknowledgement is extended to his friends for their help and encouragement during his graduate studies. Finally, the author is very appreciated to his family and his good friends whose names are not mentioned here for their love, assistance and encouragement throughout his entire education. Without them, the author would have never been able to achieve this goal.

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LIST OF ABBREVIATIONS

atm	atmosphere
-ol	alcohol
b	broad
TBHP	<i>tert</i> -butylhydroperoxide
°C	degree Celsius
Eq	equation
Fig	figure
g	gram (s)
hr	hour (s)
H ₂ O ₂	hydrogen peroxide
IR	Infrared
-one	ketone
m.p.	melting point
mL	milliliter (s)
mmol	millimole
NAFK	Nafion 551 (the polymer potassium salt)
%	percentage
s	sharp
cm ⁻¹	unit of wavenumber
w	wide

CHAPTER I

INTRODUCTION

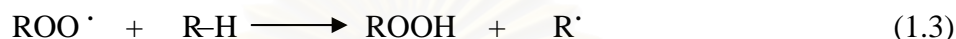
At present, petrochemical industries have been developed rapidly in Thailand. They are used primarily as fuels to generate energy and for space heating. Refined petroleum products provide gasoline, diesel fuel, heating oil, lubricating oil, waxes and asphalt.¹ A relatively small (4%) portion of oil is used as raw material to produce chemical products essential to our everyday life ranging from plastics to textiles to pharmaceuticals. Hydrocarbons are main products of petroleum, but many types of hydrocarbons generally are not expensive. Therefore, the concept of transforming hydrocarbons to their derivatives is essentially important. One of their derivatives are carbonyl compounds. To achieve this class of compounds, normally the oxidation reaction was considered to be as a principle tool. Saturated hydrocarbons are the largest component in petroleum products. Generally, the oxidation reaction of this class of compounds, however, required vigorous conditions such as high temperature or high pressure and employed cobalt or manganese complexes as catalyst.² The oxidation reaction in petrochemical industry was usually unselective, thence a mixture of products was invariably obtained. In this research, the oxidation of hydrocarbons was developed by using soluble metal complexes (metal carboxylate complexes and metal acetylacetonate complexes) as catalysts under mild conditions and none of extra solvent was used in the system.

1.1 Oxidation of alkanes³

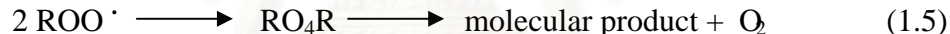
1.1.1 Autoxidation of alkanes

The slow oxidation of alkanes with ground-state (triplet) molecular oxygen in the liquid phase under mild conditions, called *autoxidation*, affords organic hydroperoxides as primary products through a free-radical chain reaction. The oxidation requires initiation by radical (\dot{I}) [Eq .1.1] . This may be formed by thermal decomposition of suitable organic compounds (azoalkanes, organic peroxides) added to the reaction mixture. Propagation, or addition of the alkyl radical to oxygen, is

usually a rapid, diffusion controlled reaction that leads to alkylperoxy radicals [Eq . 1.2] . A slow, in most cases rate-determining, hydrogen abstraction follows to yield alkyl hydroperoxides [Eq . 1.3] .



Eq uations (1.4) and (1.5) illustrate termination reactions. Depending on the structure of the alkyl group, disproportionation to alcohols and carbonyl compounds may take place.

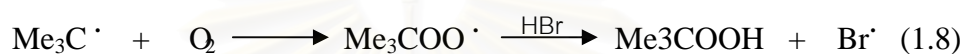


Autoxidation without added initiator may also occur. This process is generally characterized by an induction period and a much lower reaction rate since formation of alkyl radicals according to Eq . 1.6 is thermodynamically and kinetically unfavorable.

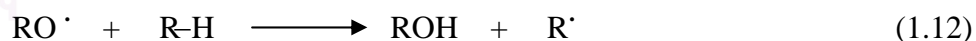
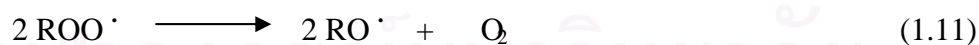
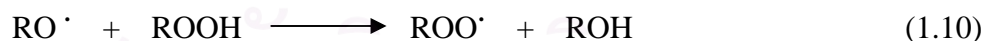
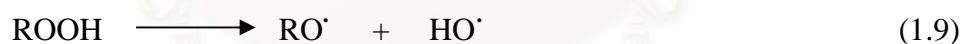


The reactivity of different C–H bonds in autoxidation changes in the order tertiary > secondary > primary. As a result, alkanes possessing tertiary hydrogen atoms may be selectively oxidized in the liquid phase to the corresponding *tert*-alkyl hydroperoxides. This selectivity difference may also be attributed to the significantly higher rate of termination of primary and secondary alkylperoxy radicals, resulting in a rather slow rate of autoxidation. The best example is the oxidation of isobutane to *tert*-BuOOH, which is a much studied process due to commercial importance of the

product. *tert*-BuOOH is used as an initiator in radical polymerizations and as an oxidizing agent in metal-catalyzed epoxidations. Autoxidation of isobutane is usually initiated by the addition of di-*tert*-butyl peroxide or by *tert*-BuOOH itself. The reaction is carried out in the liquid phase, in the temperature range 100-140°C. Selectivities higher than 90% can be achieved at low conversions. HBr was also found to be a powerful agent acting as both a coinitiator [Eq . 1.7] and a chain-transfer agent [Eq . 1.8] .

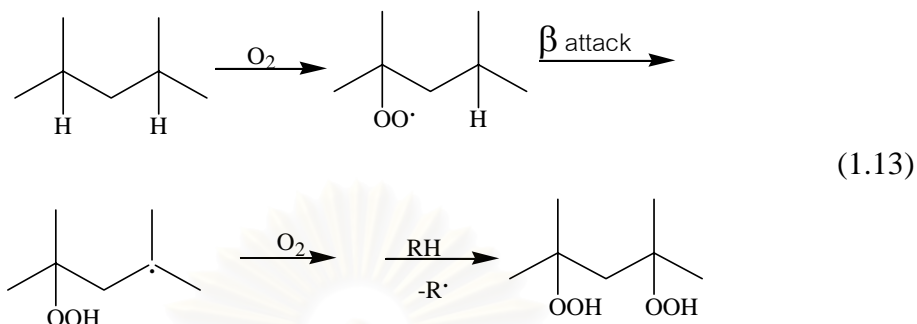


At elevated temperature alkyl hydroperoxides undergo thermal decomposition to alcohols [Eq s. 1.9-1.11] . This decomposition serves as a major source of free radicals in autoxidation. Because of side reactions, such as β -scission of alkylperoxy radicals, this process is difficult to control. Further transformation of the alkoxy radical with the substrate or with the solvent eventually also leads to an alcohol [Eq . 1.12] , or the radical decomposes with β -scission to give a ketone and an alkyl radical.

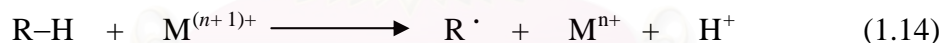


Selectivity of alcohol formation can be substantially increased by carrying out the autoxidation in the presence of a stoichiometric quantity of boric acid that reacts with the intermediate hydroperoxide to form alkyl borate. This observation gained practical importance in the commercial oxidation of alkanes.

Alkanes possessing two tertiary C-H bonds in β -scission or γ -position may form dihydroperoxides. The product is formed in an intramolecular peroxy radical attack that is highly efficient in the transformation of 2,4-dimethylpentane [Eq . 1.13] .



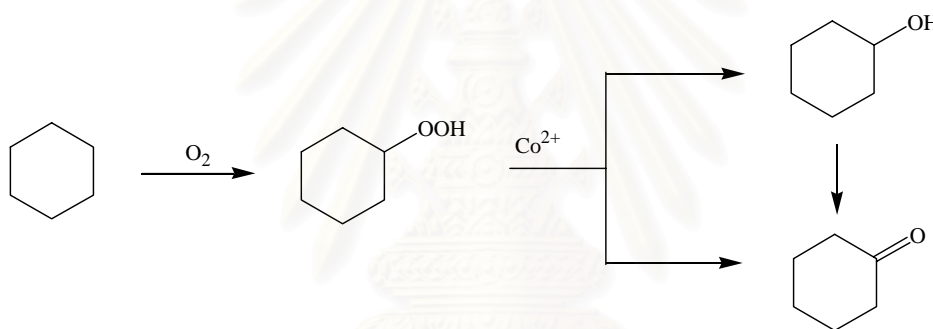
Autoxidation of alkanes may be carried out by metal catalysis. Although metal ions participate in all oxidation steps, their main role in autoxidation is not in their ability to generate free radicals directly by one-electron oxidation [Eq . 1.14] but rather their activity to catalyze the homolytic decomposition of the intermediate hydroperoxide according to [Eq s. 1.15 and 1.16]. As a result of this decomposition, metal ions generate chain-initiating radicals. The overall reaction is given in [Eq . 1.17] . At low metal ion concentration alkanes possessing tertiary C-H bond may be selectively converted to tertiary alcohol.



1.1.2 Oxidation of cyclohexane

The synthesis of cyclohexanol and cyclohexanone is the first step in the transformation of cyclohexane to adipic acid, an important compound in the manufacture of fibers and plastics. Cyclohexane is oxidized industrially by the air in the liquid phase to a mixture of cyclohexanol and cyclohexanone. Cobalt salts (naphthenate, oleate, stearate) produce mainly cyclohexanone at about 100°C and 10 atm. The conversion is limited to about 10% to avoid further oxidation by controlling the oxygen content in the reaction mixture. Combined yields of cyclohexanol and cyclohexanone are about 60-70%.

The cobalt-catalyzed oxidation of cyclohexane takes place through cyclohexyl hydroperoxide with the cobalt catalyst acting primarily in the decomposition of the hydroperoxide to yield the products.



The oxidation catalyzed with boric acid (160-175°C, 8-10 atm) results in the formation of cyclohexyl esters. After hydrolysis a product mixture containing mainly cyclohexanol is formed. Since borate esters are less sensitive to further oxidation, better yields are usually achieved (85% at 12% conversion).

1.2 Homogeneous metal-catalyzed oxidations

In recent years much attention has been devoted to the metal-catalyzed oxidation of unactivated C-H bonds in the homogeneous phase. The aim of these studies is to elucidate the molecular mechanism of enzyme-catalyzed oxygen atom transfer reactions. Additionally, such studies may eventually allow the development of simple catalytic systems useful in functionalization of organic compounds, especially in the oxidation of hydrocarbons. These methods should display high

efficiency and specificity under mild conditions as characteristic of enzymatic oxidations.

Many of these studies focus on modeling the oxidation by cytochrome P-450. Heme-containing monooxygenases known as cytochrome P-450 mediate a number of biochemical processes by incorporating one oxygen atom into a substrate. Among others they catalyze selective hydroxylation of nonactivated hydrocarbons. The oxygen atom incorporated into the substrate may derive from O₂ in the presence of a reducing agent, or may result from single oxygen atom donors.

Cytochrome P-450, however, is such a powerful oxidant that it can bring about self-degradation of its own porphyrin ligands. Because of this disadvantage, metal complexes of synthetic porphyrin have been designed and used as chemical models of this enzyme. Of the different porphyrin complexes, Fe(II) and Mn(III) porphyrins exhibit the highest catalytic activity. The single oxygen atom donors most frequently used are iodosylbenzene (PhIO) and potassium hydrogen persulfate. Data for hydrogen peroxide, alkyl hydroperoxides, hypohalites, sodium chlorate⁴, tertiary amine *N*-oxides^{5,6}, and oxaziridine are also available.

The metalloporphyrin-PhIO system catalyzes the oxidation of alkanes mainly to alcohols under mild conditions. High selectivity for the hydroxylation at the tertiary carbon is observed. Yields of up to 40% based on the oxidant consumed are obtained. Acyclic alkanes usually exhibit very poor reactivity. A large isotope effect and retention of configuration in the oxidation of *cis*-decalin⁷ are additional important characteristics of the process.

Other homogeneous metal-catalyzed oxidations do not involve porphyrins. Investigation on the functionalization of nonactivated alkanes using nonporphyrinic catalysts led to the discovery of efficient catalytic systems known as “Gif” and “Gif-Orsay” systems. They operate under oxygen or air under mild conditions. The Gif system, discovered by Barton and coworkers at Gif-sur-Yvette, comprises hydrogen sulfide and iron powder in wet pyridine containing a proton source (CH₃COOH). Hydrogen sulfide serving to catalyze the dissolution of iron powder is not necessary in the reaction at 40°C. A crystalline complex, the Fe(II)Fe(III)O(OAc)₆(pyridine)_{3.5} cluster, was isolated and used to develop a catalytic system. In the Gif system metallic zinc serves as the reductant. In the electrochemical modification of the Gif-Orsay system a cathode replaces zinc as the electron source.

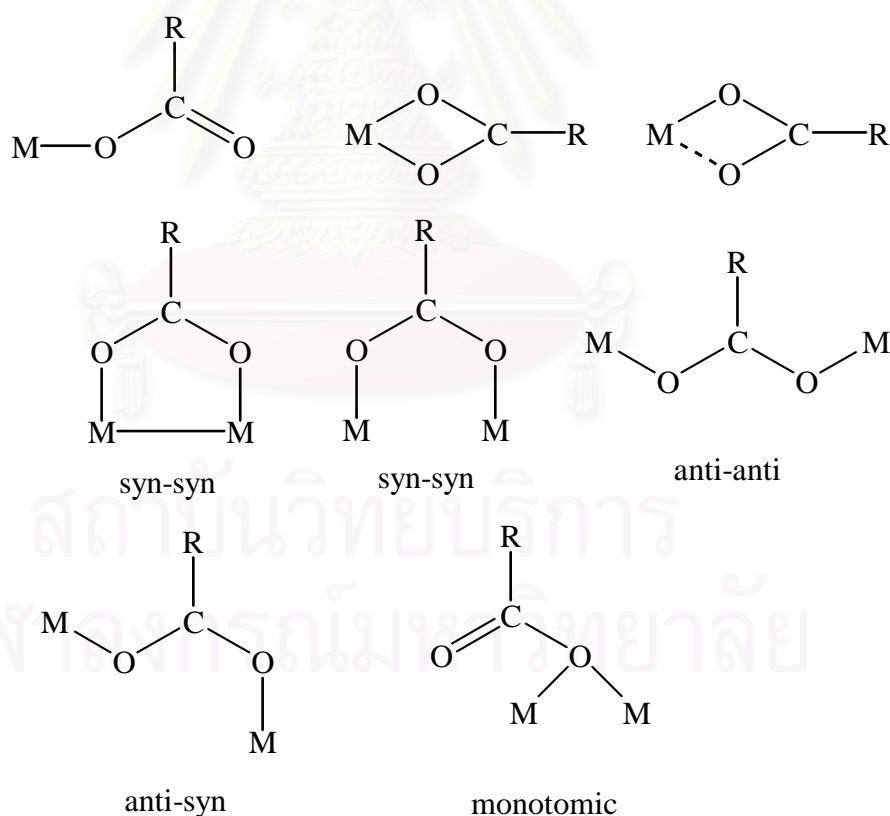
RuO_4 prepared *in situ* with NaIO_4 as the re-oxidant, as well as a ruthenium heteropolyanion with the usual oxidants (KHSO_5 , NaIO_4 , PhIO , *tert*- BuOOH), are also effective. Some of these catalytic systems are very efficient in direct ketonization of methylene groups. Methane monooxygenase, a nonheme monooxygenase, exhibits catalytic activity for oxygenation of simple alkanes and is believed to contain binuclear iron. This is the reason why these studies include several binuclear iron complexes with the aim of mimicking methane monooxygenase.^{11,12}

1.3 Some aspects of metal carboxylate catalyst

In this research, two types of ligands: carboxylates and acetylacetonates are selected to bind with transition metals.

1.3.1 Carboxylate ligands

The carboxylates are a very important class of ligands with the following bonding modes.



The most common forms are unidentate, symmetrical chelate, and symmetrical syn-syn bridging. Acetates and trifluoroacetates of weak Lewis acids are usually symmetric, those of very strong Lewis acids are often asymmetric. The other

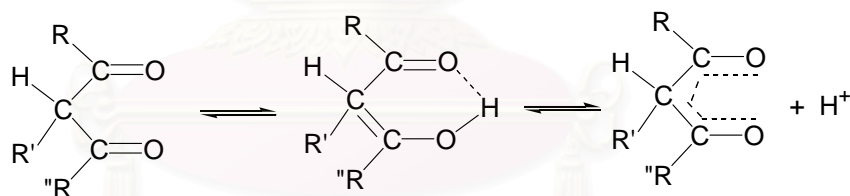
forms are not common, but anti-anti single bridging occurs in $[\text{Mnsalen}(\text{CO}_2\text{Me})_n]$ and anti-syn in $[(\text{PhCH}_2)_3\text{SnO}_2\text{CMe}]_n$. Trifluoroacetates are known only in unidentate and bridging forms.¹³

The main types of bonding can often be distinguished by IR and nmr spectra. The syn-syn bridging RCO_2^- ligand is extremely common and important in compounds with M-M quadruple bonds.

Straight-chain alkyl carboxylic acids derived from petroleum that also have a terminal cyclohexyl or cyclopentyl group are known as *naphthenic acids*. They form complexes, presumably polymeric, with many transition metals, and these compounds are freely soluble in petroleum. Copper naphthenates are used as fungicides, aluminum naphthenate was used as a gelling agent in "napalm," and cobalt naphthenates are used in paints.

1.3.2 Acetylacetonate ligand

Acetylacetonate is the most common ligand in β -ketoenolato class, in which $\text{R} = \text{R}' = \text{CH}_3$ and $\text{R}'' = \text{H}$. These β -ketoenolate ions form very stable chelate complexes with most metal ions.



Thus acetylacetonates of Zn, Ni, and Mn are trimeric, Fig. 1.1, while $\text{Co}(\text{acac})_2$ is tetrameric; all have bridging β -ketoenolate groups. The presence of bulky substituents on the β -ketones such as Me_3C sterically impedes oligomerization and monomers are formed. However, these are commonly solvated by H_2O , ROH, or pyridine to give five- or six-coordinate complexes, *trans*- $\text{M}(\text{diket})_2\text{L}_{1,2}$.¹³

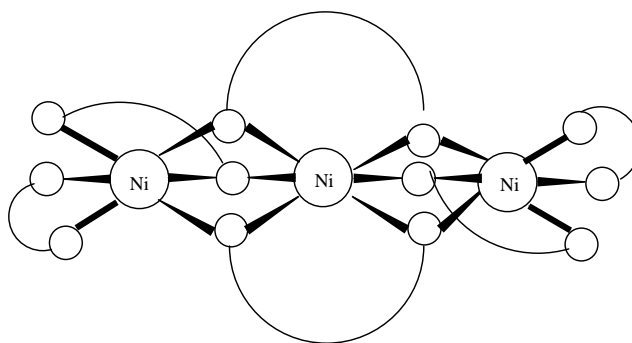


Fig. 1.1 The trimeric structure of nickel(II) acetylacetonate. The unlabeled circles represent O atoms and the curved lines connecting them in pairs represent the remaining portions of the acetylacetonate rings.

1.3.3 Chromium catalyst

The use of dichromates and chromic acid in organic oxidation is historically of much interest. The synthesis of alizarin from anthraquinone, made from anthracene by chromic acid oxidation, marked the first of a number of organic syntheses in which hexavalent chromium was originally the oxidant of choice. These processes have always been at a disadvantage because of the problem of regenerating or disposing of the quantities of trivalent chromium compounds formed. Therefore, as these organic products have reached large tonnages, catalytic and other oxidations have largely displaced the chromic acid route. A few such uses remain—the formation of ketosteroids and other pharmaceutical products; the oxidation of acenaphthene to naphthalic acid; the conversion of *o*-toluenesulfonamide to *o*-sulfonamidobenzoic acid in saccharin manufacture, benzoic acid from toluene, and quinone from aniline. Somewhat more extensive use is made of chromate oxidation in Germany, where chromates and various organic products are produced in the same plant. The chromic salts resulting are thus available for production of chromic oxide green or reconversion to dichromate.¹⁴

Some well known instances of chromium(III) complexes of organic acids are *Chromic acetylacetonate*, $\text{Cr}(\text{CH}_3\text{COCHCOCH}_3)_3$. Chromic acetylacetonate is obtained by adding ammonia to a solution of chromic salt and acetylacetone. The crystals behave like an organic compound in melting and boiling with slight decomposition. It is insoluble in water and soluble in chloroform and benzene. It is used in the preparation of organic chromium compounds, as a catalyst, and as combustion modifier for fuels and propellants.

Chromic naphthenate. The naphthenate, for which there is no definite formula, is obtained by dissolving hydrous chromic oxide in naphthenic acid. It has been suggested for use in combination with copper naphthenate as a textile preservative, and to prevent chalking of paints.

Chromic stearate, $\text{Cr}(\text{C}_{17}\text{H}_{35}\text{COO})_3$. This compound, a green pasty mass, is also obtained by dissolving the hydrous oxide in acid. It has been used in greases and in paint dryers.

1.4 Literature review on the oxidation of hydrocarbons

There are many systems which could provide high yield of the desired product with good selectivity, especially these catalyzed by transition metal complexes as catalyst in oxidation reaction.

Recent review on chemical literatures found that numerous oxidation systems have been developed. Those systems utilized transition metal complex as a catalyst, H_2O_2 or TBHP as oxidant in an organic solvent as a reaction medium. For instance, in 1988, Geletii and his colleagues reported the use of Cu(II) and Fe(II) perchlorates to catalyze cyclohexane oxidation. Hydrogen peroxide was used as an oxidant in pyridine solution. The main product was the ketone, the usual alcohol/ketone ratio being *ca.* 0.05-0.15.¹⁵

In 1998, Kanemoto and his co-workers reported the use of Cr(III)acetate NAFK to catalyze the oxidation of alcohol to ketone by using *tert*-BuOOH as an oxidant.¹⁶

In 1991, Sarneski and his colleagues presented that the new cluster $[\text{MnO}_4(\text{dipy})_4(\text{OH}_2)_2] (\text{ClO}_4)_4$ was particularly active for the oxidation of alkanes, alkenes, and alkylated arenes with alkyl hydroperoxides in CH_3CN . The oxidants used were *tert*-BuOOH or PhCMe₂OOH. These systems could work well even at low temperature (0°C). Though turnover/h of product is high, the selectivity (ketone/alcohol) is not good.¹⁷

In 1992, Barton and his colleagues reported the use of $\text{Cu}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as catalyst in *GoChAgg* system. *GoChAgg* system is the homogenous oxidation by Cu(II)- H_2O_2 in pyridine-acetic acid. Reactivity, selectivity and mechanistic study of system by using various cycloalkanes such as cyclohexane, cycloheptane, adamantane as substrate were thoroughly examined.¹⁸ The mechanism proposed was involved non-radical pathway.

In 1992, Muzart reported the use of various chromium catalysts catalyzed oxidation in organic synthesis. Two chromium catalysts: $\text{Cr}(\text{acac})_3$ and $\text{Cr}(\text{III})\text{stearate}$ were used to catalyze the oxidation reaction of many substrates such as alkanes, alcohol to give ketone and alcohol. The products are believed to derive from the decomposition of cyclohexyl hydroperoxide.¹⁹ Various oxidants were namely 1-methylcyclohexyl hydroperoxide, *tert*-butylhydroperoxide, oxygen, air and hydrogen peroxide.

In 1994, Barton and his colleagues developed a new process using no extra solvent in the oxidation system. Two types of catalysts: $\text{Fe}(\text{III})$ and $\text{Cu}(\text{II})$ complexes were used. *Tert*-BuOOH was employed as an oxidant. It was observed that cyclohexane was transformed into cyclohexanone and cyclohexanol in low yield during 24 hr. The reaction time must be increased to 96 and 264 hr for high yield of product. In addition, pyridine was found to be a good additive for the selectivity study of cyclohexane oxidation.²⁰

In 1996, Chavez and his co-workers reported the use of $\text{Co}(\text{III})$ alkyl peroxide to catalyze in oxidation reaction of cyclohexane to cyclohexanone and cyclohexanol by using excess *tert*-BuOOH as oxidant. The selectivity of the reaction was low but the time required for reaction was short.²¹

In 1998 and 2000, Chavez and his co-workers further reported the use of $\text{Co}(\text{III})$ alkyl peroxy complexes as catalysts for the oxidation of hydrocarbons. These systems could operate under mild conditions to produce the desired product: however the yield of product was not high. Various hydrocarbons were reported to be oxidized such as cyclooctane, cyclododecane, benzaldehyde, adamantane and *n*-heptane.^{22,23}

1.5 The goal of this research

The purpose of this research can be summarized as follows:

1. To synthesize metal carboxylate complexes and metal acetylacetonate complexes.
2. To study the optimum conditions for hydrocarbon oxidation by using metal carboxylate complexes.
3. To study the selectivity of this developed oxidation system.
4. To study reactivity of this developed oxidation system.

CHAPTER II

EXPERIMENTAL

2.1 General Procedure

Spectrometers: FTIR spectra were recorded on a Fourier Transform Infrared Spectrophotometer model Nicolet z Impact 410, solid samples were incorporated to potassium bromide to form a pellet.

Chromatography: Thin layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel (Merck's, Kieselgel 60 PF₂₅₄). Column chromatography was performed on silica gel (Merck's, Kieselgel 60 G Art 7734(70-230 mesh)). Gas chromatography analysis was carried out on a Shimadzu Gas Chromatograph 9A instrument equipped with flame ionization detector with N₂ as a carrier gas. The columns used for chromatography were Carbowax 20M and DB-5MS.

Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected.

2.2 Chemicals

All solvents in this research were purified before use by standard methodology except for solvents which are reagent grades. The reagents for synthesizing the metal carboxylate complexes, metal acetylacetonate complexes and all organic substrates, *e.g.* cyclohexane, cyclohexene, cyclohexanol, ethyl benzene etc, were purchased from Fluka chemical company and were used without further purification.

2.3 Syntheses

2.3.1 Metal carboxylate complexes

General procedure for the syntheses of metal stearate complexes¹⁴

Stearic acid (6.26 g; 22 mmol) was dissolved in dilute sodium hydroxide solution (0.88 g NaOH in 20 mL distilled water) at 80°C. After solution was stirred until homogeneity, selected transition metal salts or compounds (7.3 mmol) dissolved in 10 mL distilled water was added in one portion causing the precipitation. The mixture was allowed to stir for another 30 min, then the precipitate was collected and dried *in vacuo*.

Co(II) stearate: pink solid (74 %), m.p. 86-90 °C. IR (KBr, cm⁻¹): 2856-2912(w), 1630-1701(b), 1545(s), 2856-2912(w), 1630-1701(b), 1545(s).

Cr(III) stearate: blue gray solid (82 %), m.p. 100-103 °C. IR (KBr, cm⁻¹): 2845-2910(w), 1710(s), 1541(s), 1461(s), 723(s).

Fe(III) stearate: orange solid (78 %), m.p. 94-96 °C. IR (KBr, cm⁻¹): 2846-2912(w), 1705(s), 1583(s), 1461(s), 723(s).

Ni(II) stearate: light green solid (87 %), m.p. 175-177 °C. IR (KBr, cm⁻¹): 2856-2903(w), 1564-1720(w), 1381(b), 721(s).

Mn(II) stearate: white solid (88 %), m.p. 108-111 °C. IR (KBr, cm⁻¹): 2856(b), 1569-1720(w), 1461(s), 718(s).

Cu(II) stearate: light blue solid (90 %), m.p. 138-145 °C. IR (KBr, cm⁻¹): 2903(s), 2846(s), 1592(s), 1404-1456(w), 721(s).

General procedure for the syntheses of Cr(III)carboxylate complexes

Carboxylic acid (22 mmol) was dissolved in dilute sodium hydroxide solution (0.88 g NaOH in 20 mL distilled water) at 80°C. After solution was stirred until homogeneity, Cr(III)chloride hexahydrate (1.95 g; 7.3 mmol) dissolved in 10 mL distilled water was added in one portion causing the precipitation. The mixture was allowed to stir for another 30 min, then the precipitate was collected and dried *in vacuo*.

Cr(III) palmitate: blue gray solid (81 %), m.p. 115-120 °C. IR (KBr, cm⁻¹): 2921(s), 2865(s), 1720(s), 1541(s), 1465(s), 721(s).

Cr(III) caproate: blue gray solid (47 %), m.p. 103-108 °C. IR (KBr, cm⁻¹): 2921-2959(w), 2378(s), 1545(b), 1447(s), 580-648(w).

Cr(III) behenate: blue gray solid (84 %), m.p. 125-130 °C. IR (KBr, cm⁻¹):

2846-2921(w), 1569-1724(w), 1465(s), 721(s).

2.3.2 Metal acetylacetonate complexes

*Tris-(2,4-pentanedionato)-Ferric(III) [Fe(acac)₃]*²⁴

Ferric chloride anhydrous (2.00 g; 10 mmol) was dissolved in distilled water 3 mL and the mixture was heated until homogeneity. After that concentrated ammonium hydroxide 4.5 mL was dropped slowly. The solution was stirred about 15-20 min on water bath (~ 80°C) and brown precipitation occurred. The brown solid was filtered off and washed with distilled water until no more chloride detected. Place the precipitate in Erlenmeyer flask, acetylacetone (6 mL; 10 mmol) was dropped slowly for 35 min on water bath (~ 80°C) and precipitation of red solid occurred. The products were filtered and recrystallized by 95% ethanol. The red solid was obtained (90%), m.p. 180-185 °C. IR (KBr, cm⁻¹): 1569(s), 1522(s), 1357(s), 1268(s), 1018(s), 929(s), 722(s), 662(s).

*Bis-(2,4-pentanedionato)-Cobalt(II) [Co(acac)₂]*²⁴

This complex was prepared by the same methodology as that described for Fe(acac)₃ but replacement of ferric chloride anhydrous (2.00 g; 10 mmol) with cobaltous(II) chloride hexahydrate (2.39 g; 10 mmol). The pink solid of Co(acac)₂ was obtained (8 %), m.p. 200-216 °C. IR (KBr, cm⁻¹): 1568(s), 1521(s), 1365(s), 1021(s), 932(s).

*Bis-(2,4-pentanedionato)-Chromium(III) [Cr(acac)₃]*²⁴

This complex was prepared by the same manner as that described for Fe(acac)₃ but replacement of ferric chloride anhydrous (2.00 g; 10 mmol) by chromium(III) chloride hexahydrate (2.66 g; 10 mmol). The blue gray solid of Cr(acac)₃ was obtained (75 %), m.p. 209-215 °C. IR (KBr, cm⁻¹): 1564-1640(w), 1381(s), 1282(s), 1028(s), 512(s).

2.4 The general procedure for the oxidation of hydrocarbons

A catalyst (metal carboxylate or metal acetylacetonate complex) (0.2 mmol) was added to hydrocarbon substrate (50 mmol) in round bottom flask. *tert*-Butylhydroperoxide (9.0 mmol) as an oxidant was added to the reaction mixture. 5 mL of isooctane was used as a solvent when the total volume of the reaction was smaller than 4 mL or a substrate was solid. The mixture was stirred for 24 hr at 70°C. After the reaction was finished, 1 mL of the reaction mixture was taken and extracted with diethyl ether. The combined extracts were washed with 25% H₂SO₄ and saturated

solution of NaHCO_3 , respectively. The organic layer was dried over anhydrous Na_2SO_4 and analyzed by GC with the addition of an exact amount of appropriate internal standard.

2.5 Study on the optimum conditions for the oxidation of cyclohexane and other hydrocarbons

Effect of metal stearate complexes

The cyclohexane oxidation reaction was conducted as described in general procedure by employing Co(II)stearate, Cr(III)stearate, Fe(III)stearate, Ni(II)stearate, Mn(II)stearate, Cu(II)stearate as catalyst.

Effects of type of carboxylate ligands

Following the general procedure for the oxidation reaction, Cr(III)acetate, Cr(III)caproate, Cr(III)palmitate, Cr(III)stearate, Cr(III)behenate and Cr(III)naphthanate were used as catalysts in the reaction. The total yield of product (alcohol and ketone) and selectivity of the reaction were determined.

Effect of type of oxidant

The oxidation reaction was carried out as described in general procedure using Cr(III)stearate as a catalyst. Different types of oxidant: *tert*-butylhydroperoxide, hydrogenperoxide and 2-ethylbutyraldehyde/ O_2 were varied.

Effect of temperature

The oxidation reaction was performed according to the general procedure mentioned earlier using Cr(III)stearate as a catalyst, but different reaction temperature was varied (30°C , 50°C , 70°C).

Effect of the amount of substrate

The oxidation reaction was carried out as described in the general procedure using Cr(III)stearate as a catalyst and different amount of selected substrate was varied (5, 10, 15, 20, 25 and 50 mmol).

Effects of the amount of catalyst

The oxidation reaction was conducted as described in general procedure using Cr(III)stearate as catalyst, but different amount of Cr(III)stearate was varied (0.01, 0.025, 0.05, 0.1 and 0.2 mmol).

2.6 Comparative kinetic study of the oxidation of cyclohexane catalyzed by Cr(III)stearate and Co(II)stearate

The general oxidation procedure of cyclohexane using Cr(III)stearate and Co(II)stearate as catalysts was carried out. At different reaction time proceeded (1, 3, 5, 8, 12 and 16 hr) an aliquot from the reaction mixture was taken, worked up and analyzed by GC.

2.7 The oxidation of cyclohexane catalyzed by metal acetylacetonate complexes

The oxidation reaction of cyclohexane was carried out in the same manner as previously described using metal acetylacetonate complexes as catalyst.

2.8 Chromium(III)stearate-catalyzed oxidation reaction of other hydrocarbons

The oxidation reaction was carried out as described in the general procedure by using Cr(III)stearate as a catalyst and different types of substrate were varied (cyclohexanol, cyclohexene, α -methyl styrene, ethyl benzene, diphenyl sulfide, etc.).

2.9 Comparative study of the oxidation between cyclododecane and cyclohexanol, cyclohexene, ethyl benzene and α -methyl styrene

Following the general procedure of oxidation reaction, equimolar amount (5 mmol) of cyclododecane and cyclohexanol, cyclohexene, ethyl benzene and α -methyl styrene were used as competitive substrates in the reaction.

2.10 The study of additive in oxidation reaction of cyclohexane catalyzed by Cr(III)stearate

The oxidation of cyclohexane was carried out as described in the general procedure. Lithium chloride, carbon tetrachloride and bromotrichloromethane were separately added to the oxidation reaction to observe the effect of additives.

2.11 Regioselectivity study on the oxidation reaction

Cr(III)stearate as employed as a catalyst in *tert*-butylcyclohexane, *n*-pentane and adamantane oxidation using reaction conditions described in the general procedure.

2.12 Comparative study on relative reactivity of cycloalkanes in oxidation reaction

Two competitive cyclohexanes with eq uimolar amount of cyclohexane and either cyclopentane, cycloheptane, cyclooctane or cyclododecane were oxidized respectively employing Cr(III)stearate as a catalyst.

2.13 The kinetic study of cyclohexane oxidation catalyzed by Cr(III)stearate in the presence of triphenylphosphine

Following the general procedure of the oxidation reaction, at different reaction time proceeded (1, 3, 5, 8, 12 and 16 hr), 1 mL of reaction mixture was added 5 mmol of triphenylphosphine before worked up, then work-up and analyzed by GC.

2.14 The study of cyclohexane oxidation catalyzed by co-catalyst of metal stearate complexes

The oxidation reaction was carried out as described in the general procedure but using co-catalyst of other metal stearates such as Ni(II)stearate, Mn(II)stearate, Co(II)stearate and Cu(II)stearate together with Cr(III)stearate as a main catalyst.

2.15 The effect of the amount of *tert*-butylhydroperoxide on the Co(II) stearate oxidation of cyclohexane

The oxidation reaction was carried out as described in the general procedure by using Co(II)stearate as catalyst. 9.0 mmol of TBHP was employed as an oxidant. The reaction was performed for 5 hr.

CHAPTER III

RESULTS AND DISCUSSION

During the last two decades, there have been numerous explored systems for the oxidation of hydrocarbons. This research was focused on the oxidation of hydrocarbons employing soluble transition-metal complexes as catalysts. The ligands of soluble transition-metal complexes in this work are carboxylates and acetylacetonates. In this study, cyclohexane was mainly used as a substrate for reaction conditions optimization. Other substrates such as cyclohexanol, cyclohexene, cyclohexanone, ethyl benzene, α -methyl styrene, diphenyl sulfide were selected to evaluate the oxidizing capability of catalysts. The soluble transition-metal complexes, Cr(III)carboxylates, was mostly examined as catalyst. The oxidant used was *tert*-butylhydroperoxide (TBHP). Under these examined conditions, no extra solvent was used.

3.1 Characterization of metal carboxylate complexes and metal acetylacetonate complexes

Nine metal carboxylate complexes and three metal acetylacetonate complexes were synthesized employing known procedures reported in chemical literatures.²⁴ Their identities were confirmed by comparison both physical properties and IR spectroscopic data with those reported.²⁶ The comparative results of physical properties and percentage yield of prepared metal carboxylate complexes and metal acetylacetonate complexes are presented in Table 3.1. IR spectroscopic data of these complexes are shown in Table 3.2.

Table 3.1 Physical appearance of metal carboxylate complexes and metal acetylacetonate complexes

Entry	Catalyst	Color	Melting point (°C)	% yield
1	Co(II) stearate	Pink	86-90	74
2	Cr(III) stearate	Blue gray	100-103	82
3	Fe(III) stearate	Orange	94-96	78
4	Ni(II) stearate	Light green	175-177	87
5	Mn(II) stearate	White	108-111	88
6	Cu(II) stearate	Light blue	138-145	90
7	Cr(III) palmitate	Blue gray	115-120	81
8	Cr(III) caproate	Blue gray	103-108	47
9	Cr(III) behenate	Blue gray	125-130	84
10	Fe(acac) ₃	Red	180-185	90
11	Co(acac) ₂	Pink	200-216	8
12	Cr(acac) ₃	Blue	209-215	75

Metal carboxylate complexes could be easily synthesized with high yield. The color of each metal carboxylate complex was varied depending on type of metal. Melting points of metal carboxylate complexes were about 100-150^oC.

Metal acetylacetonate complexes were also convenient to synthesize. The yield of metal acetylacetonate was also depended on type of metal. The color of each metal acetylacetonate complex was varied on type of metal. Melting points of metal acetylacetonate complexes were higher than metal carboxylate complexes.

Table 3.2 Infrared spectroscopic data of synthesized metal carboxylate and metal acetylacetonate complexes

Metal complexes	IR (cm ⁻¹)
Co(II) stearate	2856-2912(w), 1630-1701(b), 1545(s), 1461(s), 718(s)
Cr(III) stearate	2845-2910(w), 1710(s), 1541(s) 1461(s), 723(s)
Fe(III) stearate	2846-2912(w), 1705(s), 1583(s) 1461(s), 723(s)
Ni(II) stearate	2856-2903(w), 1564-1720(w), 1381(b), 721(s)
Mn(II) stearate	2856(b), 1569-1720(w), 1461(s), 718(s)
Cu(II) stearate	2903(s), 2846(s), 1592(s), 1404-1456(w), 721(s)
Cr(III) palmitate	2921(s), 2865(s), 1720(s) 1541(s), 1465(s), 721(s)
Cr(III) caproate	2921-2959(w), 2378(s), 1545(b) 1447(s), 580-648(w)
Cr(III) behenate	2846-2921(w), 1569-1724(w), 1465(s), 721(s)
Fe(acac) ₃	1569(s), 1522(s), 1357(s), 1268(s), 1018(s), 929(s), 722(s), 662(s)
Co(acac) ₂	1568(s), 1521(s), 1365(s) 1021(s), 932(s)
Cr(acac) ₃	1564-1640(w), 1381(s), 1282(s), 1028(s), 512(s)

From IR spectra, metal carboxylate complexes showed a significant absorption band of carbonyl C=O around 1600-1700 cm⁻¹. The C–O band of carboxylate group was observed around 1400-1450 cm⁻¹. IR spectra of metal acetylacetonate complexes displayed a characteristic carbonyl C=O absorption band around 1550-1650 cm⁻¹.

The infrared spectra of two selected examples of prepared metal complexes namely Cr(III)stearate and Fe(acac)₃ are presented in Figs 3.1 and 3.2.

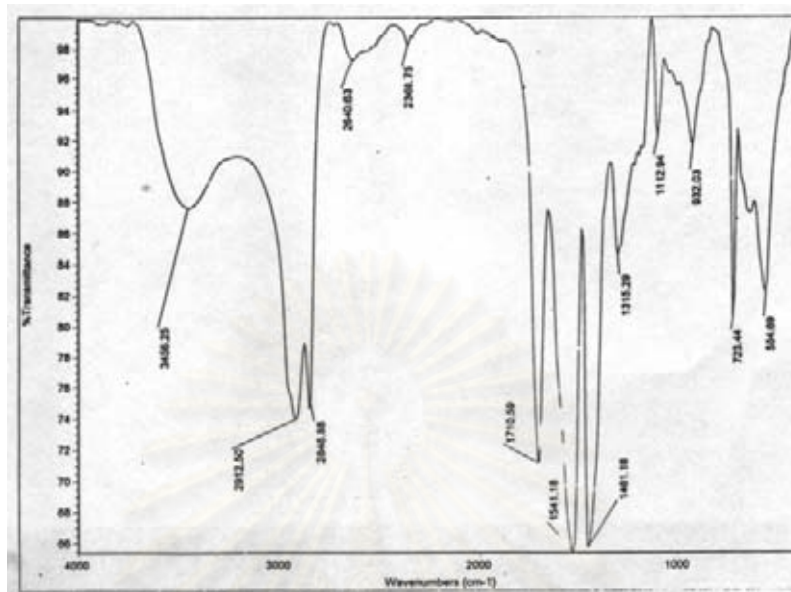


Fig 3.1 The IR spectrum of Cr(III)stearate

Likewise, Cr(III)stearate showed a significant absorption band of carbonyl at 1710 cm^{-1} . The C–O band of stearate group was observed around $1460\text{--}1540\text{ cm}^{-1}$. The C–H stretching band was detected around $2850\text{--}2900\text{ cm}^{-1}$.

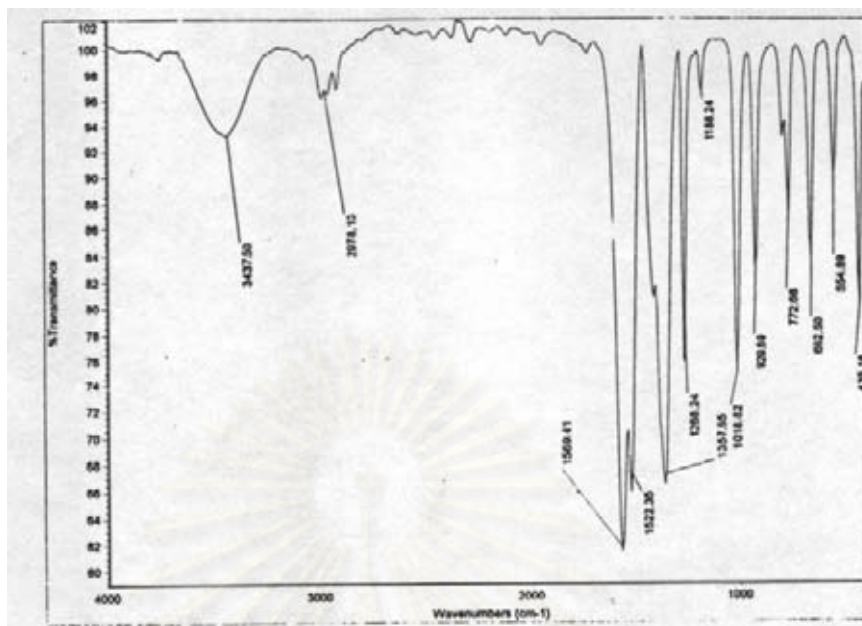


Fig 3.2 The IR spectrum of $\text{Fe}(\text{acac})_3$

The IR spectrum of $\text{Fe}(\text{acac})_3$ displayed a significant absorption band in the range of $1520\text{--}1570\text{ cm}^{-1}$ attributable to a carbonyl group ($\text{C}=\text{O}$) vibration. For free ligands, this band occurred at higher frequencies $\sim 15\text{--}20\text{ cm}^{-1}$ which was belonged to $\text{C}=\text{O}$.²⁶

3.2 Study on the optimum conditions for the oxidation of cyclohexane.

Various factors are required to evaluate prior to reach the optimal conditions for the hydrocarbon oxidation reaction. The parameters studied in this reaction are effects of metal stearate complexes, effects of carboxylate ligands, types of oxidant, effects of temperature, effects of the amount of substrate and catalyst.

3.2.1 Effects of metal stearate complexes

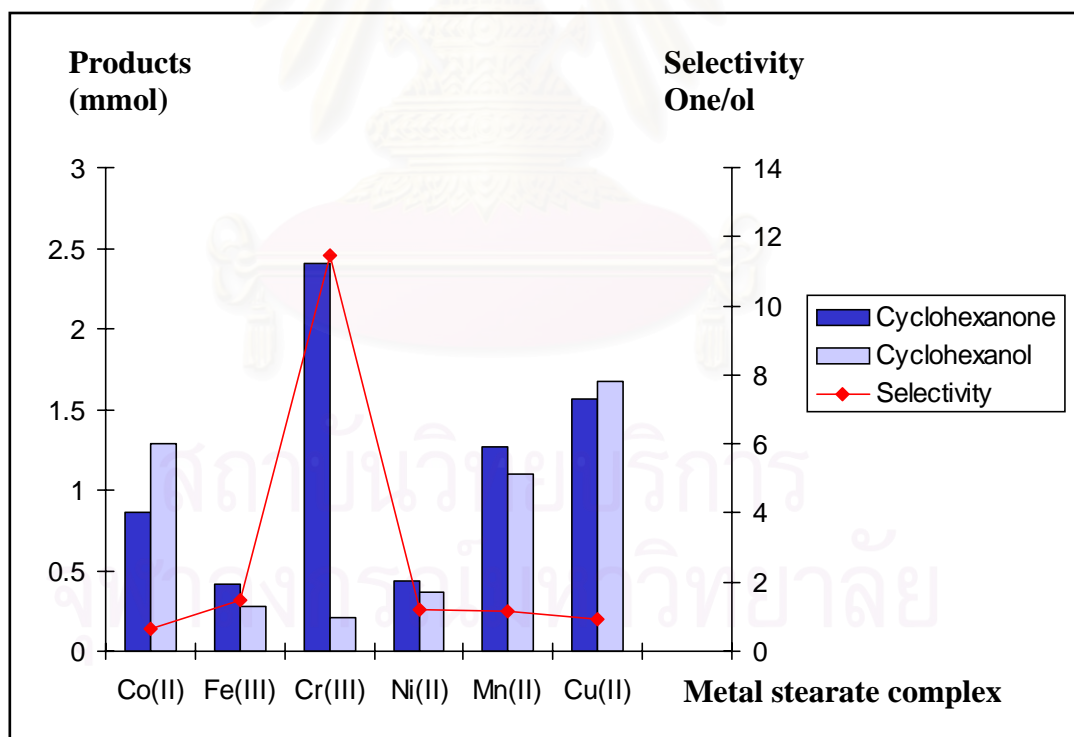
The aim of this study was to screen for appropriate metal stearate complexes that could catalyze the conversion of cyclohexane to cyclohexanone and cyclohexanol in high yield with good selectivity.²⁴ The results of the oxidation reaction catalyzed by various metal stearate complexes are presented in Table 3.3. The comparative results are also exhibited in Fig 3.1.

Table 3.3 The oxidation of cyclohexane catalyzed by various metal stearate complexes

Entry	Catalyst	Products (mmol)		Total (mmol)	Selectivity one/ol
		Cyclohexanone	Cyclohexanol		
1	Co(II) stearate	0.867	1.296	2.163	0.7
2	Cr(III) stearate	2.416	0.211	2.627	11.5
3	Fe(III) stearate	0.424	0.288	0.712	1.5
4	Ni(II) stearate	0.443	0.372	0.816	1.2
5	Mn(II) stearate	1.279	1.102	2.381	1.2
6	Cu(II) stearate	1.563	1.678	3.241	1.0

reaction conditions: cyclohexane (50 mmol), metal stearate complex (0.2 mmol),

TBHP (9.0 mmol), reaction time (24 hr) at 70°C

**Fig 3.3** The oxidation of cyclohexane catalyzed by various metal stearate complexes

From Table 3.3 and Fig 3.3, six transition metal stearate complexes in the first row of the periodic table were screened for potentially catalytic oxidation ability. It was found that the oxidation of cyclohexane proceeded with high efficient crucially depending on type of transition metal. The transition metal stearate complexes such as Cr(III)stearate, Co(II)stearate, Mn(II)stearate and Cu(II)stearate revealed good capability as catalyst for the oxidation reaction whereas those stearate complexes of Fe(III) and Ni(II) did not behave well as oxidation catalysts. It was noteworthy that Cr(III)stearate provided the highest yield of cyclohexanone and gave the best selectivity for the production of cyclohexanone over cyclohexanol (Entry 2). Interesting, Co(II)stearate and Cu(II)stearate gave the higher yield of cyclohexanol than that of cyclohexanone. Thus, in this research Cr(III)carboxylate complex will be utilized as a catalyst for oxidation of hydrocarbons.

3.2.2 Effects of type of carboxylate ligands

Carboxylate ligands with different carbon atoms in the chain: caproic acid (C₆), palmitic acid (C₁₆), stearic acid (C₁₈), behenic acid (C₂₂) and naphthenic acid were chosen to react with Cr(III) salt furnishing five Cr(III) carboxylate complexes. Each chromium complex as a catalyst was subjected to the oxidation reaction of cyclohexane to observe the effects of type of carboxylate ligands. The results are tabulated as shown in Table 3.4.

Table 3.4 The results of the oxidation of cyclohexane catalyzed by various Cr(III) carboxylate complexes

Entry	Cr(III) carboxylate complexes	Products(mmol)		Total (mmol)	Selectivity one/ol
		Cyclohexanone	Cyclohexanol		
1	Cr(III)caproate	3.458	0.244	3.702	14.2
2	Cr(III)palmitate	1.397	0.231	1.627	6.1
3	Cr(III)stearate	2.416	0.211	2.627	11.5
4	Cr(III)behenate	2.386	0.239	2.625	1.0
5	Cr(III)naphthenate	2.948	0.159	3.107	18.5

reaction conditions: cyclohexane (50 mmol), Cr(III)carboxylate (0.2 mmol),

TBHP (9.0 mmol), reaction time (24 hr) at 70°C

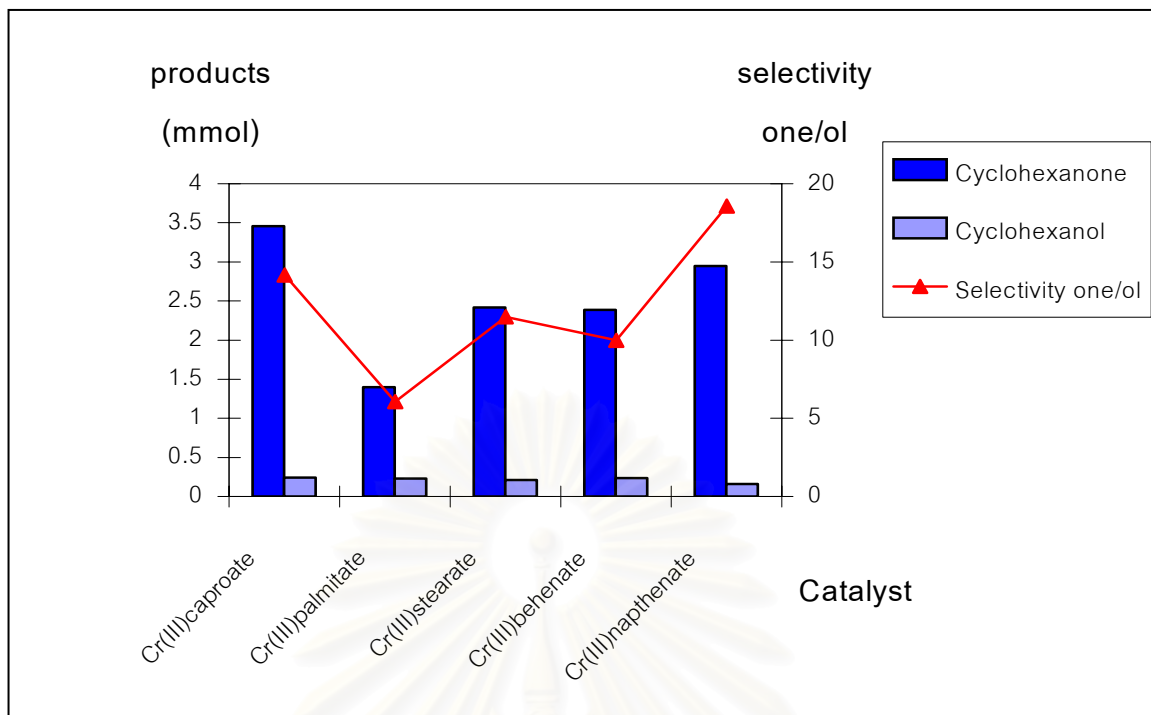


Fig 3.4 The effects of various carboxylate ligands of Cr(III) complexes in the cyclohexane oxidation reaction

From Table 3.4, it was disclosed that caproic acid was the best carboxylate ligand chosen to bind with Cr(III) salt. This complex could provide the highest yield of cyclohexanone with good selectivity. Nonetheless, the preparation of this complex is rather a hard task. When forming with metal, the complex was sticky and difficult to purify leading to poor yield of the desired complex compared with other Cr(III) carboxylate complexes. The influence of number of carbon atoms in the chain of ligand justified from the yield and selectivity of desired products. Palmitic acid (C_{16}) gave the lowest yield and selectivity. However, when the number of carbon atoms in chain of ligand was increased or decreased, the yield and selectivity of product were increased. The number of carbon atoms was also affected to the solubility in cyclohexane at room temperature. To illustrate this, the more carbon atoms in carboxylic acid chain, the better solubility in hydrocarbon solvent of complex was observed. Nonetheless, the reaction condition in this study was conducted at 70°C . Therefore, during the course of this research Cr(III)stearate was utilized as a catalyst. It should also be cited here that Cr(III)naphthenate also gave impressive results. This finding should be further investigated in the future work.

3.2.3 Effects of type of oxidants

The effect of type of oxidants was another parameter that needed to evaluate for optimizing reaction conditions. A proper composition of catalyst and oxidant may lead the reaction to the desired direction. The results of varying three types of common oxidants used with Cr(III)stearate catalyst are summarized as shown in Table 3.5.

Table 3.5 The effects of the type of oxidant on the oxidation reaction

Entry	Oxidant	Products (mmol)		Total (mmol)	Selectivity one/ol
		Cyclohexanone	Cyclohexanol		
1	<i>tert</i> -butylhydroperoxide	2.416	0.211	2.627	11.5
2	30% hydrogen peroxide	0.054	0.056	0.110	1.0
3	2-ethylbutyraldehyde, O ₂	0.177	0.062	0.239	2.9

Reaction conditions: cyclohexane (50 mmol), Cr(III)stearate (0.2 mmol), oxidant (9.0 mmol), reaction time (24 hr) at 70°C

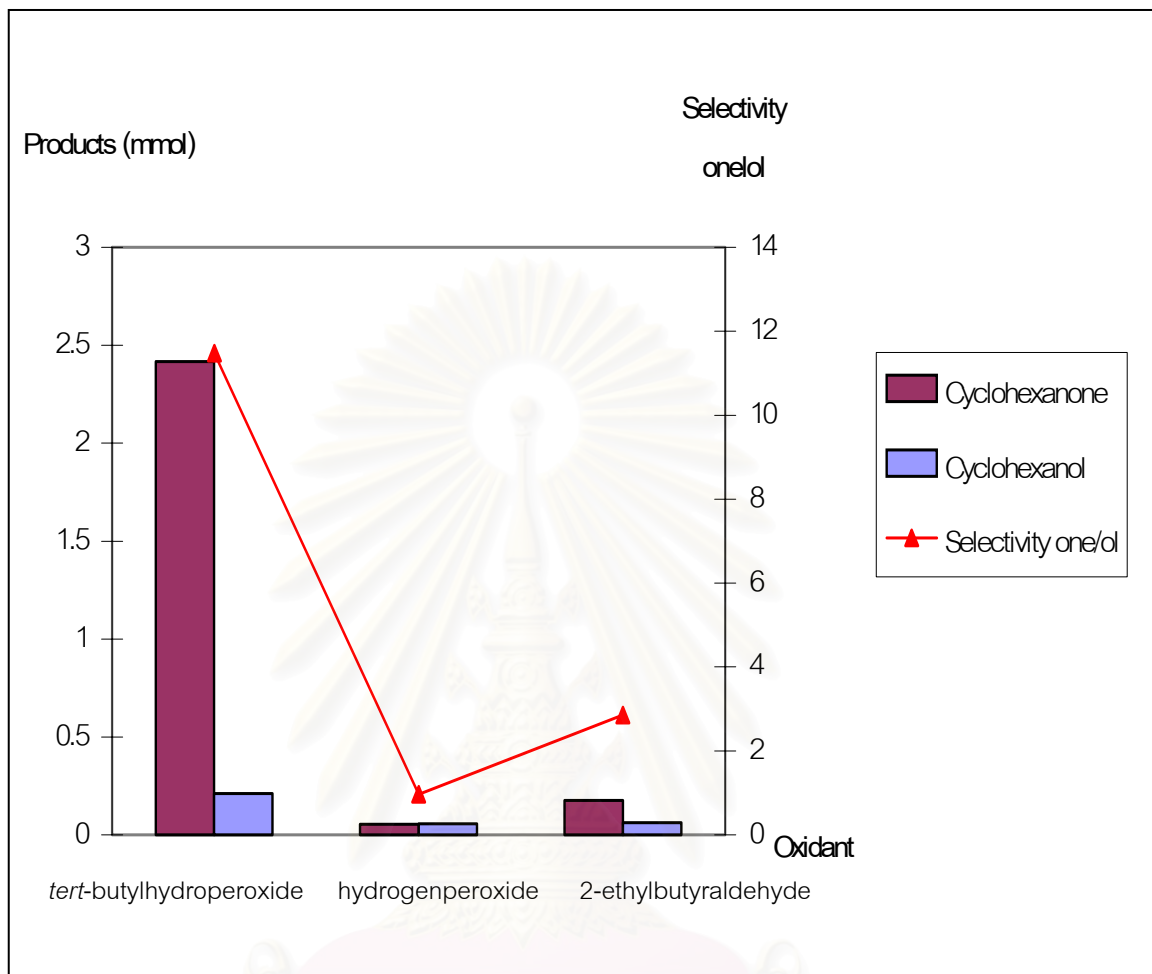


Fig 3.5 The effect of type of oxidant in cyclohexane oxidation reaction

All three types of oxidants have generally been employed in the oxidation reactions. The results under this particular conditions revealed that TBHP was the most appropriate oxidant for cyclohexane oxidation reaction. In contrast, hydrogen peroxide and 2-ethylbutyraldehyde, O_2 exhibited less capability as oxidant. Therefore, TBHP was further investigated as oxidant for the oxidation reaction.

3.2.4 Effects of temperature

Temperature is another important parameter for condition optimization. The temperature examined reaction was room temperature (30°C), 50°C and 70°C. The results are collected in Table 3.6 and Fig. 3.4.

Table 3.6 The effect of the reaction temperature in cyclohexane oxidation reaction

Entry	Reaction temperature	Products(mmol)		Total (mmol)	Selectivity one/ol
		Cyclohexanone	Cyclohexanol		
1	Room temperature (30°C)	0.187	trace	0.187	-
2	50°C	1.783	0.099	1.882	18.0
3	70°C	2.416	0.211	2.627	11.5

reaction conditions: cyclohexane (50 mmol), Cr(III)stearate (0.2 mmol), TBHP (9.0 mmol),
reaction time (24 hr)

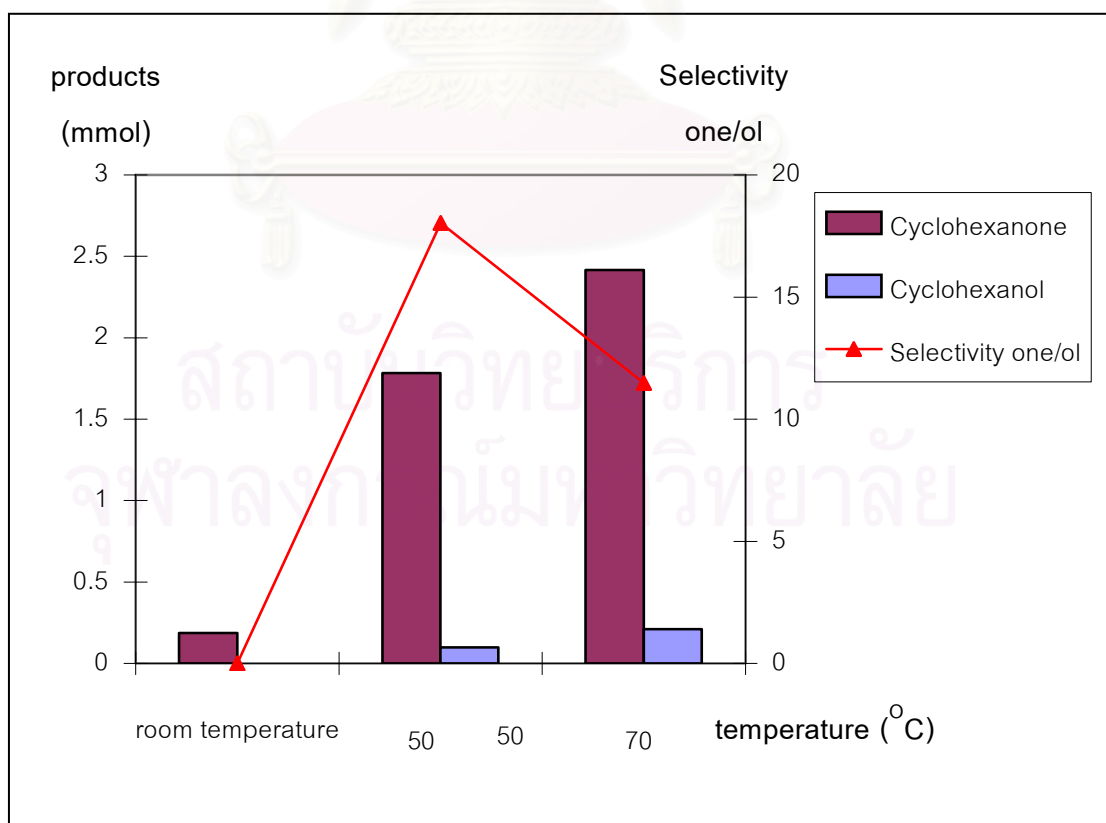


Fig 3.6 The effect of temperature on the cyclohexane oxidation reaction

From Table 3.6 and Fig 3.6, it was observed that at 70°C, the highest yield of cyclohexanone and cyclohexanol was accomplished. The results were in good agreement with those reported in literature that TBHP when used at 70°C gave good yield of product.²⁰⁻²² At the temperature lower than 70°C, TBHP did not work well. This was probably because TBHP was not homolytically dissociated to form a radical to initiate oxidation reaction.

3.2.5 Effects of the amount of substrate

The amount of substrate in the reaction was varied from 5-50 mmol in order to find the most appropriate amount of substrate that provided the highest yield of the desired product. The results are presented in Table 3.7.



Table 3.7 The effect of the amount of cyclohexane on the oxidation reaction

Entry	Substrate (mmol)	Products(mmol)		Total (mmol)	Selectivity one/ol	%yield based on substrate	%yield based on TBHP
		cyclohexanone	cyclohexanol				
1	5	0.345	trace	0.345	-	6.90	3.83
2	10	1.341	0.109	1.45090	12.3	14.50	16.11
3	15	1.975	0.178	2.153	11.1	14.35	23.89
4	20	2.371	0.203	2.573	11.7	12.87	28.55
5	25	2.236	0.203	2.439	11.0	9.75	27.10
6	50*	2.416	0.211	2.627	11.5	5.25	29.67

reaction conditions: Cr(III)stearate (0.2 mmol), isooctane (3 mL), TBHP (9.0 mmol), reaction time (24 hr) at 70°C

*no extra solvent was used

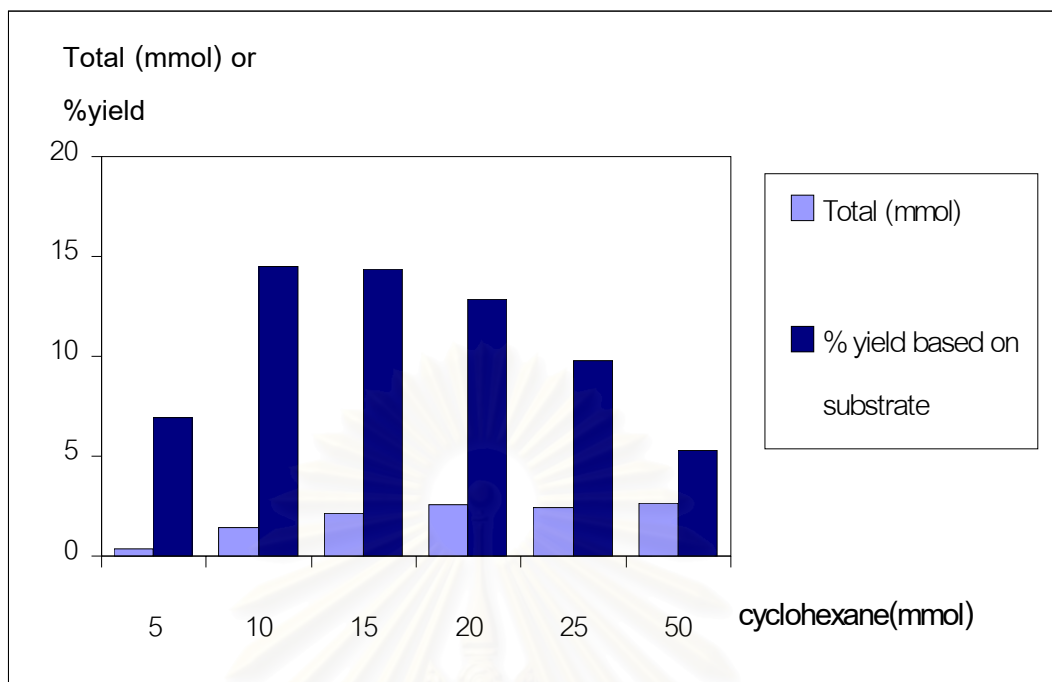


Fig 3.7 The effect of the amount of cyclohexane on the oxidation reaction

When decreasing the amount of cyclohexane in the reaction from 50 to 25, 20, 15 and 10 mmol, it was noticed that %yield of product was increased. Isooctane was used as an extra solvent in some reactions when total volume of the reaction was smaller than 4 mL. The best percentage yield of products based upon TBHP was found to be approximately 30 %.

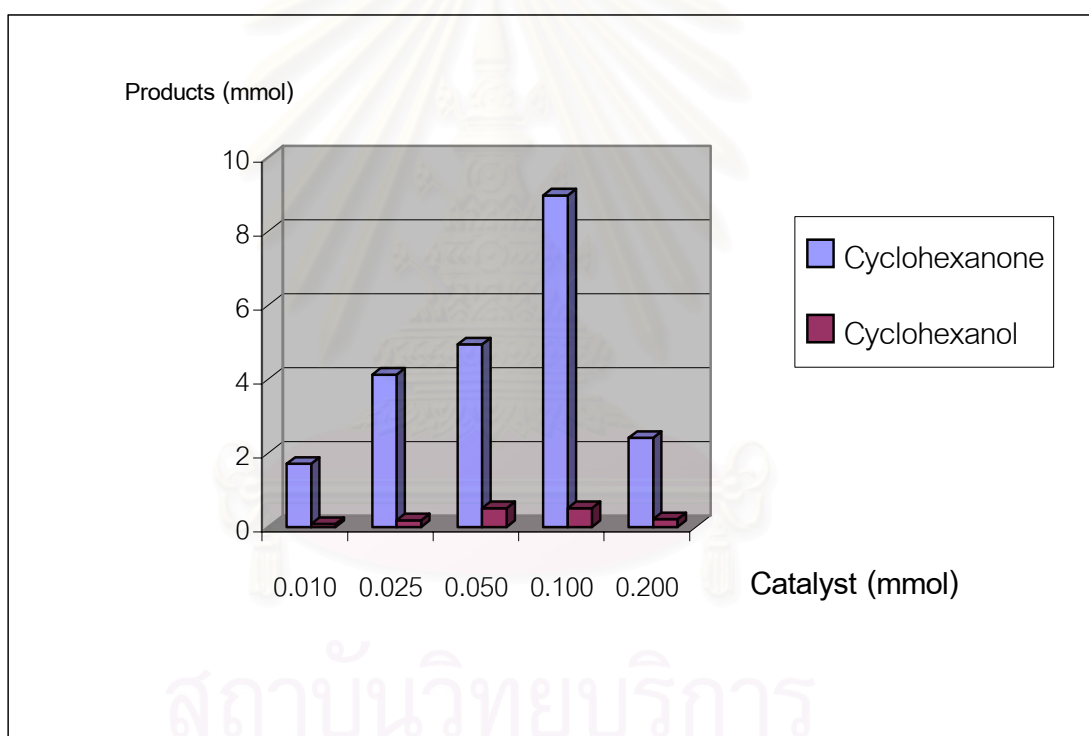
3.2.6 Effects of the amount of catalyst

Variable amounts of catalysts: 0.010, 0.025, 0.050, 0.100 and 0.200 mmol were tested to search for the appropriate amount of catalyst in this oxidation reaction. The results are presented in Table 3.8.

Table 3.8 The effect of the amount of catalyst on the cyclohexane oxidation

Entry	Catalyst (mmol)	Products (mmol)		Total (mmol)	Turnover
		Cyclohexanone	Cyclohexanol		
1	0.010	1.710	0.086	1.796	179
2	0.025	4.120	0.185	4.305	172
3	0.050	4.948	0.517	5.465	109
4	0.100	8.970	0.510	9.480	90
5	0.200	2.416	0.211	2.627	13

reaction conditions: cyclohexane (50 mmol), TBHP (9.0 mmol), reaction time (24 hr)
at 70°C

**Fig 3.8** The effect of the amount of Cr(III)stearate on the oxidation reaction

From Table 3.8, when Cr(III)stearate 0.1 mmol was used, the reaction gave the highest yield of product. In addition, when the amount of catalyst was increased or decreased from 0.1 mmol, the yield was decreased. The use of Cr(III)stearate 0.2 mmol was also found to be too much for the reaction. Catalyst may be disordered and obstructed to catalyze the reaction.

Therefore, the optimum conditions in this study were 0.1 mmol of Cr(III)stearate as a catalyst, 20 mmol of cyclohexane as a substrate, 9.0 mmol of *tert*-butylhydroperoxide as an oxidant and reaction time 24 hr.

3.3 Comparative kinetic study of the oxidation of cyclohexane catalyzed by Cr(III)stearate and Co(II)stearate

Two metal complexes: Cr(III)stearate and Co(II)stearate were used for kinetic study of the oxidation of cyclohexane to examine the appropriate time of the reaction. In general, the rate of the reaction was dependent on type of catalyst. This could be visualized by the determination of the quantity of product and time used for reaction to complete.¹⁸ The kinetic analysis results of cyclohexane oxidation catalyzed by Cr(III)stearate and Co(II)stearate are presented in Fig. 3.9.

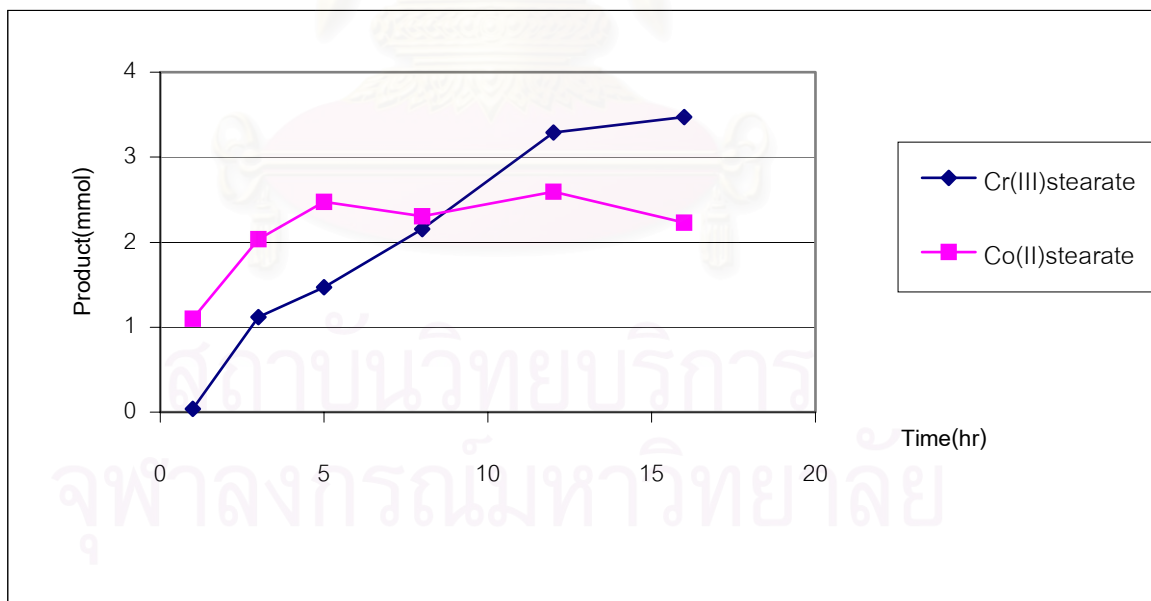


Fig 3.9 Kinetic study on cyclohexane catalyzed by Cr(III)stearate and Co(II)stearate

From Fig. 3.9, it was found that the rate of the oxidation reaction employing Co(II)stearate was faster than that of Cr(III)stearate. Half-lives of the reaction were approximately 8 and 5 hr for Cr(III)stearate and Co(II)stearate, respectively. Considering in terms of total yield of the desired products, it was clearly observed that Cr(III)stearate could provide more significant amount of cyclohexanone than the other catalyst studied. From industrial point of view,³ however, Co(II)stearate was perhaps more appreciable than Cr(III)stearate. This was because Co(II)stearate could initiate the oxidation to proceed more rapidly and the rate of the reaction was faster. Nonetheless, from laboratory viewpoint, Cr(III)stearate gave more impressive results on both selectivity and yield of the desired products than Co(II)stearate.

3.4 The oxidation of cyclohexane catalyzed by metal acetylacetonate complexes

Besides, metal carboxylate complexes used as catalyst in the oxidation reaction, metal acetylacetonate complexes were another metal-soluble group of catalyst explored in this study.¹⁹ Under the same reaction conditions, five metal acetylacetonates were screened for their catalytic activity towards cyclohexane oxidation. The results are presented as shown in Table 3.9.

Table 3.9 The oxidation of cyclohexane catalyzed by various metal acetylacetonate complexes

Entry	Catalyst	Products (mmol)		Total (mmol)	Selectivity one/ol
		Cyclohexanone	cyclohexanol		
1	Fe(acac) ₃	0.362	0.317	0.679	1.5
2	Ni(acac) ₂	0.507	0.379	0.886	1.3
3	V(acac) ₃	0.484	0.467	0.951	1.0
4	Co(acac) ₂	1.845	1.651	3.496	1.1
5	Cr(acac) ₃	2.489	0.429	2.918	5.8

reaction conditions: cyclohexane (50 mmol), metal acetylacetonate complex

(0.2 mmol), TBHP (9.0 mmol), reaction time (24 hr) at 70^oC

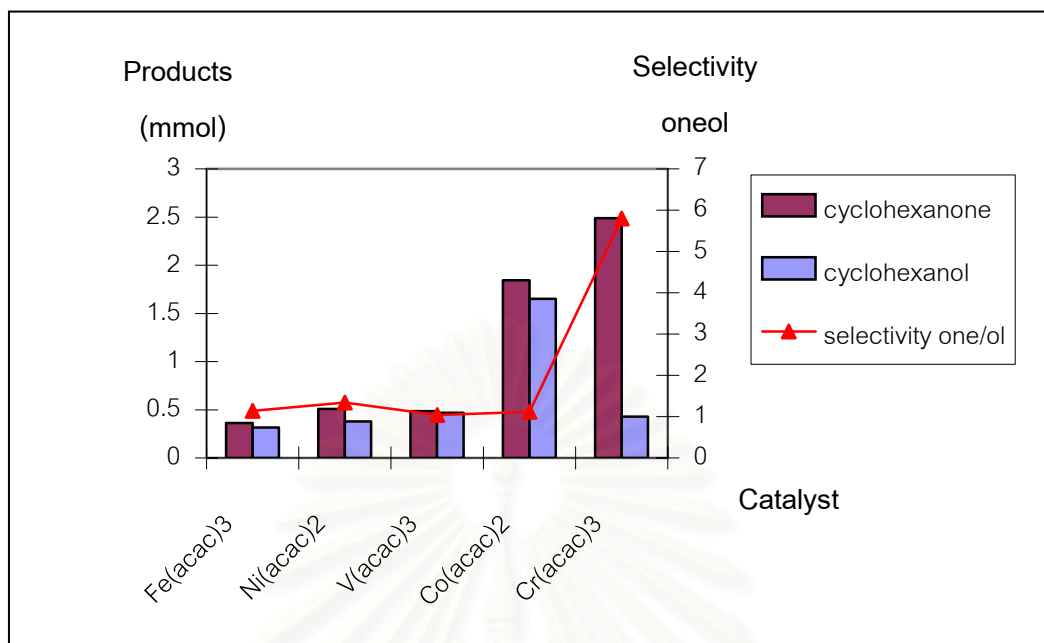


Fig 3.10 The oxidation of cyclohexane catalyzed by various metal acetylacetonate complexes

The oxidation of cyclohexane catalyzed by various metal acetylacetonate complexes gave the results similar to those obtained from using metal carboxylate complexes as catalyst. Cr(III) complex was found to be the most appropriate complex for this regard. Particularly the selectivity attained from Cr(III) complex was superior to those derived from other metal complexes. Co(II) acetylacetonate was another intriguing catalyst since it gave the highest yield of product.

Taking into an account, it was clearly seen that both soluble metal complexes could provide almost the same amount of the desired product, cyclohexanone. Nevertheless, the selectivity achieved from employing Cr(III)stearate was found not to be questionable that this complex was selected for further study compared with its acetylacetonate analogues. The comparative results utilizing these two classes of metal soluble complexes are summarized in Table 3.10.

Table 3.10 Comparative results of the cyclohexane oxidation catalyzed by Co(II)stearate, Cr(III)stearate, Co(acac)₂ and Cr(acac)₃

Entry	Catalyst	Products (mmol)		Total (mmol)	Selectivity one/ol
		cyclohexanone	cyclohexanol		
1	Co(II)stearate	0.867	1.296	2.163	0.7
2	Cr(III)stearate	2.416	0.211	2.627	11.5
4	Co(acac) ₂	1.845	1.651	3.496	1.1
5	Cr(acac) ₃	2.489	0.429	2.918	5.8

reaction conditions: cyclohexane (50 mmol), metal complex (0.2 mmol), TBHP (9.0 mmol), reaction time (24 hr) at 70^oC

It could be observed manifestly that Cr(III) catalysts provided better selectivity one/ol ratio than Co(II) catalysts. In terms of total yield, Co(II) catalysts were in turn disclosed to be more prevailed than Cr(III) catalysts.

3.5 Chromium(III)stearate-catalyzed oxidation reaction of other organic substrates

Other organic substrates were selected as models for evaluating the capability of this oxidation system. Those substrates include cyclohexane, cyclododecane (alkane), cyclohexanol, 1,4-cyclohexanediol (alcohol), cyclohexanone (ketone), cyclohexene, α -methyl styrene (alkene), ethyl benzene (substrate with benzylic position) and diphenyl sulfide (sulfide). The results are accumulated in Table 3.11.

Table 3.11 Chromium(III)stearate-catalyzed oxidation reaction of organic substrates


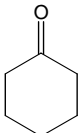
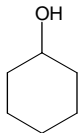
Entry	Substrate (mmol)	Isooctane (mL)	Reaction Time (hr)	Product (mmol) (% yield)	
1	 50	0	24	 2.41 (5)	 0.21 (~0.4)
	15	5	24	1.97 (13)	0.18 (~1.0)

Table 3.11 (cont.)

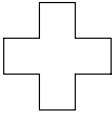
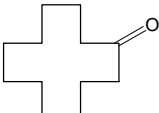
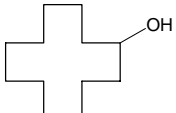
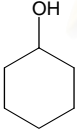
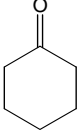
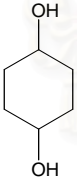
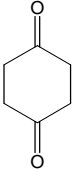
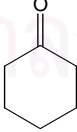
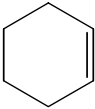
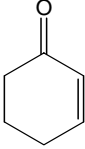
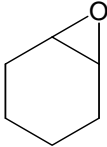
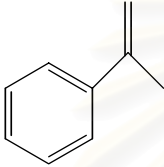
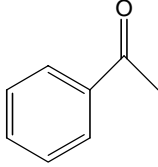
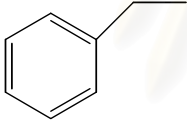
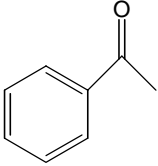
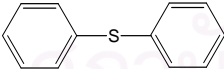
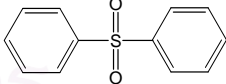
Entry	Substrate (mmol)	Isooctane (mL)	Reaction Time (hr)	Product (mmol) (% yield)
2				 
	5	5	24	0.56 (11) 0.01 (~0.2)
	5	5	24	0.63 (13) 0.01 (~0.2)
	5	5	48	1.23 (25) 0.02 (~0.4)
3				
	5	5	24	4.72 (94)
4				
	10	5	48	5.74 (57)
5				
	50	0	24	-

Table 3.11 (cont.)

Entry	Substrate (mmol)	Isooctane (mL)	Reaction Time (hr)	Product (mmol) (% yield)
6	 50	0	24	 4.43 (9)  trace
7	 50	0	24	 4.92 (10)
8	 50	0	24	 9.74 (20)
		5	24	4.78 (96)
9	 5	5	48	 3.65 (73)

reaction conditions : Cr(III)stearate 0.2 mmol, TBHP 9.0 mmol, 70°C

* TBHP 18 mmol was used

From Table 3.11, the Cr(III)-catalyzed oxidation of various organic substrates with different functionality was thoroughly investigated. The reaction conditions of each substrate was sometime adjusted. In addition, in some reactions the volume of the mixture was too small, isooctane was added as an extra hydrocarbon solvent.

Cyclohexane and cyclododecane (entries 1-2) were two cycloalkanes chosen for this study. In this system both compounds could be oxidized to the corresponding ketone and alcohol in high yield with good selectivity. The yield of product was also depended on the amount of TBHP used, and reaction time. In case of cyclododecane when using 18 mmol of TBHP, reaction time 24 hr, the amount of cyclododecanone was increased from 11% to 25% with good mass balance (102%). From previous report, in 1992 Barton and his co-workers used iron(II) and iron(III) catalyzed the oxidations of cyclohexane and cyclododecane by using H_2O_2 and TBHP as oxidants. Cyclohexane and cyclododecane could be oxidized to ketone and alcohol in lower yield than that obtained from this research. In case of cyclohexane yield of total products was 5%.^{27,28}

For alcohol, cyclohexanol and 1,4-cyclohexanediol (entries 3-4) were selected as substrate. Cyclohexanol could be oxidized to cyclohexanone in high yield (94 %) whereas 1,4-cyclohexanediol was oxidized to 1,4-cyclohexanedione in only 57% yield. The more appreciable yield could be obtained if the reaction conditions for this substrate was further optimized. Nevertheless, these results showed that this system could be utilized to oxidize alcohol to ketone efficiently. The oxidation of alcohol with other Cr catalysts were reported in literature. Cr(V) and Cr(VI) were used as catalysts to oxidize many types of alcohols such as cyclohexanol, 1,4-butanediol, benzyl alcohol, etc. It was found that Cr(V) and Cr(VI) could be oxidized alcohol to ketone efficiently. Cyclohexanol was produced to cyclohexanone 94% yield.²⁹⁻³¹

Cyclohexanone (entry 5) was selected as a substrate for two reasons. The first one was as a representative compound of ketone group. The other was to observe whether the major product obtained from cyclohexane oxidation would further oxidize under this studied conditions. From Table 3.11, it was found that cyclohexane could not be oxidized further to other product.

Cyclohexene (entry 6) an example of alkene was chosen to examine. Under this condition cyclohexenone was produced mainly with trace of cyclohexene

oxide. The results obtained from this study revealed that Cr(III)stearate-TBHP was another promising oxidation system for allylic oxidation, not epoxidation. However, in the case of a compound bearing a terminal methylene, the C=C cleavage was detected as a prevailed pathway. This was supported by an example substrate as α -methyl styrene (entry 7). The main product detected was acetophenone. From previous report, Sarneski and his co-workers carried on the oxidation of alkenes fruitfully by the use of Mn catalyst and TBHP as an oxidant to furnish high selectivity (ketone/alcohol).¹⁷ In 1993, Barton and his colleagues presented that Cu(II)(OAc)₂•H₂O could catalyze cyclooctene and cyclododecene to allylic alcohol as the major reaction product.³²

A benzylic substrate such as ethyl benzene was also examined. It was observed that ethyl benzene could be oxidized to acetophenone in high yield. Especially, when using 5 mmol of ethyl benzene, almost quantitative yield of acetophenone was achieved. In 1986, Muzart used Cr(VI) complex to catalyze the benzylic oxidations with TBHP. The %conversion and selectivity obtained were not high.³³ In 1987, Chidambaram and Chandrasekaran addressed the use of pyridinium dichromate as a catalyst and TBHP as an oxidant for benzylic oxidations. Percentage of conversion and yield were higher than 80% in some cases.³⁴

The oxidation of diphenyl sulfide (entry 9), a representative of sulfide compound, under this condition produced diphenyl sulfone in 73 % yield. With the optimization of reaction conditions, the better yield was hopefully gained.

Aforementioned information clearly exhibited that with this developed oxidation system various organic compounds could be selectively transformed into their oxidized products with high efficiency.

3.6 The effect of additive in the oxidation reaction of cyclohexane catalyzed by Cr(III)stearate

The addition of an additive to the reaction system would provide some clues for the mechanistic pathway of the studied system. Two additives, namely carbon tetrachloride and bromotrichloromethane were chosen.

3.6.1 Effect of carbon tetrachloride

Carbon tetrachloride was the first additive that would prove the idea for the existence of an intermediate. The results are shown in Table 3.12.

Table 3.12 Effects of CCl₄ on the oxidation of cyclohexane

Entry	CCl ₄ (mmol)	Products (mmol)			Ratio one+ol/-Cl
		Cyclohexanone	Cyclohexanol	Cyclohexyl chloride	
1	0	2.416	0.211	-	11.5
2	1	2.487	1.397	0.480	1.8
3	3	2.446	0.868	0.431	2.8
4	5	1.795	0.829	0.433	2.2
5	10	1.178	0.553	1.290	2.1

reaction conditions: cyclohexane (50 mmol), Cr(III)stearate (0.2 mmol), TBHP (9.0 mmol), reaction time (24 hr) at 70°C

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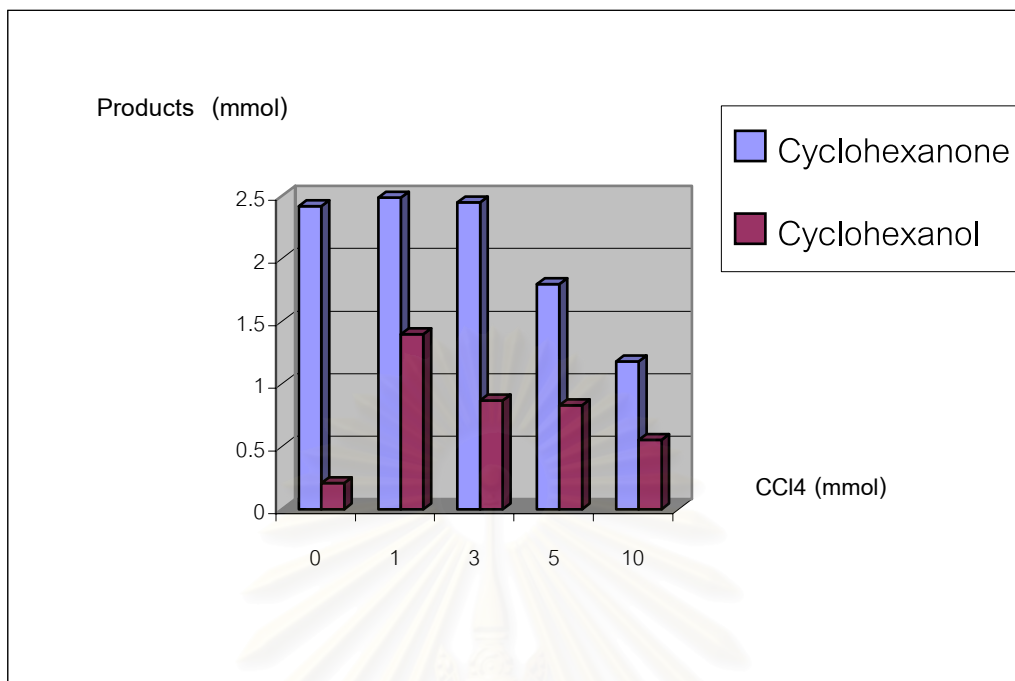


Fig 3.11 Effects of CCl₄ on the oxidation of cyclohexane

From Table 3.12, when carbon tetrachloride 1 mmol was added to the reaction, cyclohexanol was increased. Trend of oxidized products: cyclohexanone and cyclohexanol were decreased when the amount of carbon tetrachloride in the reaction was increased. The amount of cyclohexylchloride was clearly observed in the reaction when carbon tetrachloride 10 mmol was added. This could be postulated that carbon tetrachloride may trap the intermediate of the reaction and transformed into cyclohexylchloride with the suppression of the formation of oxidized products. This derived information suggested that mechanism of the reaction be taken place *via* the radical pathway.

3.6.2 Effect of bromotrichloromethane

Bromotrichloromethane a well-known radical trapping reagent was another trapping agent in this study. The results are shown in Table 3.13.

Table 3.13 Effects of BrCCl₃ on the oxidation of cyclohexane

Entry	BrCCl ₃ (mmol)	Products (mmol)			Ratio one+ol/-Br
		Cyclohexanone	Cyclohexanol	Bromocyclohexane	
1	0	2.416	0.211	-	-
2	5	0.185	0.155	2.760	0.123
3	10	0	0.380	7.044	0.053

reaction conditions: cyclohexane (50 mmol), Cr(III)stearate (0.2 mmol),
TBHP (9.0 mmol), reaction time (24 hr) at 70°C

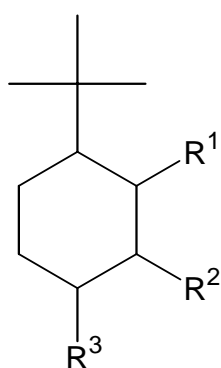
For ensure results of trapping agent to propose the mechanism of the reaction system, bromotrichloromethane was selected as another trapping agent. From Table 3.13, it was found that when 5 mmol of bromotrichloromethane was added to the reaction, the amount of cyclohexanone and cyclohexanol were suppressed and did not give cyclohexanone when bromotrichloromethane 10 mmol was added. High yield of bromocyclohexane was instead detected. Therefore, the outcome from the addition of bromotrichloromethane supported the results obtained from the experiment in the presence of carbon tetrachloride (Table 3.12). To illustrate this, both carbon tetrachloride and bromotrichloromethane acted as a radical trap. Therefore, the possible the mechanism for this reaction should occur *via* a free radical pathway.

3.7 Regioselectivity study

The regioselectivity study would provide the important characteristics of the reaction. For further study on the regioselectivity of this oxidation system, the oxidation of *tert*-butylcyclohexane, *n*-pentane and adamantane was investigated using Cr(III)stearate as a catalyst. The results are presented in Tables 3.14 - 3.16.

3.7.1 The oxidation of *tert*-butylcyclohexane

The oxidation of *tert*-butylcyclohexane catalyzed by Cr(III)stearate was carried out under standard conditions. The results are shown in Table 3.14.



tert-butylcyclohexane $R^1 = H, R^2 = H, R^3 = H$

2-*tert*-butylcyclohexanone $R^1 = O, R^2 = H, R^3 = H$

3-*tert*-butylcyclohexanone $R^1 = H, R^2 = O, R^3 = H$

4-*tert*-butylcyclohexanone $R^1 = H, R^2 = H, R^3 = O$

2-*tert*-butylcyclohexanol $R^1 = OH, R^2 = H, R^3 = H$

3-*tert*-butylcyclohexanol $R^1 = H, R^2 = OH, R^3 = H$

4-*tert*-butylcyclohexanol $R^1 = H, R^2 = H, R^3 = OH$

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Table 3.14 The oxidation of *tert*-butylcyclohexane catalyzed by Cr(III)stearate

Products	Systems	
	A ^a (mmol)	B ^b (mmol)
2- <i>tert</i> -butylcyclohexanone	0.178	0.028
3- <i>tert</i> -butylcyclohexanone	1.089	0.901
4- <i>tert</i> -butylcyclohexanone	0.427	0.386
2- <i>tert</i> -butylcyclohexanol	trace	trace
3- <i>tert</i> -butylcyclohexanol	trace	trace
4- <i>tert</i> -butylcyclohexanol	trace	trace

- a. Reaction conditions : *tert*-butylcyclohexane (50 mmol), Cr(III)stearate (0.2 mmol), TBHP (9.0 mmol), 70^oC, 24 hr
- b. Reaction conditions : *tert*-butylcyclohexane (30 mmol), iron(III) porphyrin (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g), RT, 24 hr

From Table 3.14, both systems A and B provided similar results that the positions 3- and 4- in *tert*-butylcyclohexane were preferentially oxidized. The little oxidation occurred at the 2-position. The reason of this may be due to the steric effect of *tert*-butyl group in cyclohexane to cause the 2-position difficult to be attacked by active species. Compared with the oxidation system using iron porphyrin as a catalyst which was previously studied,³⁵ it was found that when considering at 2-position, system A gave 2-*tert*-butylcyclohexanone higher than system B. Moreover, the ratio of 2-one : 3-one : 4-one in system A (1 : 6 : 2) exhibited lower selectivity than system B (1 : 32 : 14). This observation displayed that *tert*-butyl substituent on cyclohexane had a profound effect on the oxidation reaction and induced the oxidation to take place at 3-position.

3.7.2 The oxidation of *n*-pentane

N-pentane, straight chain hydrocarbon, was another substrate selected to observe for regioselectivity study. The results of the oxidation of *n*-pentane are presented in Table 3.15.

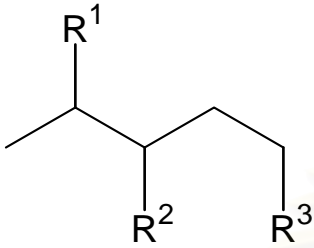
	<i>n</i> -pentane	$R^1 = H, R^2 = H, R^3 = H$
	2-pentanone	$R^1 = O, R^2 = H, R^3 = H$
	3-pentanone	$R^1 = H, R^2 = O, R^3 = H$
	1-pentanol	$R^1 = OH, R^2 = H, R^3 = H$
	2-pentanol	$R^1 = H, R^2 = OH, R^3 = H$
	3-pentanol	$R^1 = H, R^2 = H, R^3 = OH$

Table 3.15 The oxidation of *n*-pentane catalyzed by Cr(III)stearate

Products	Systems	
	A ^a (mmol)	B ^b (mmol)
2-pentanone	2.140	trace
3-pentanone	trace	0.990
1-pentanol	0	0.235
2-pentanol	trace	0
3-pentanol	0	0.051

- Reaction conditions : *n*-pentane (50 mmol), Cr(III)stearate (0.2 mmol), TBHP (9.0 mmol), 70^oC, 24 hr
- Reaction conditions : *n*-pentane (30 mmol), iron(III) porphyrin (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g), RT, 24 hr

From Table 3.15, different results derived from two reaction systems were observed. It was found that in system A 2-pentanone was a major product whereas 3-pentanone was detected as a main component in system B. The formation of 2-pentanone by system A was not surprising since the attack of reactive species to the 2^o position of *n*-pentane could conceivably prefer statistically.

Nonetheless with system B the main product was 3-pentanone which was totally different from system A. This unique production made this system interesting to further exploration.

The selectivity of systems A and B were different because the catalytic system and oxidant were diversified. The oxidation reaction of system A using Cr(III)stearate as a catalyst and TBHP as an oxidant was believed to take place *via* a radical pathway. While the oxidation reaction of system B utilizing iron(II)porphyrin complex as a catalyst and zinc grit/air was proved to be non-radical pathway.³⁴ Considering from the different reaction systems used, another influence factor such as solvent may perhaps affect the selectivity of each reaction condition.

3.7.3 The oxidation of adamantane

Another selected important saturated hydrocarbon to be examined is adamantane.³⁶ Adamantane has been widely used as a chemical probe for verifying the regioselectivity of the oxidation reaction. The results of the oxidation of adamantane is presented as shown in Table 3.16.

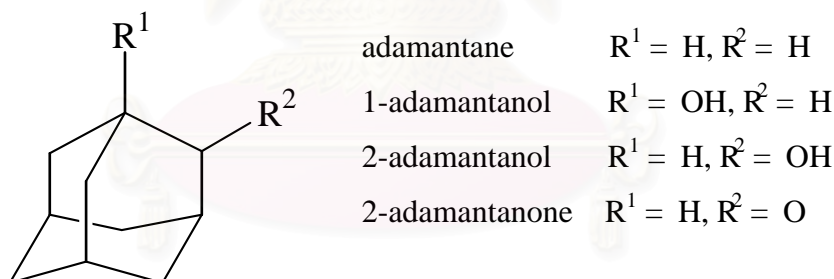


Table 3.16 The oxidation of adamantane catalyzed by Cr(III)stearate

Substrate	Products (mmol) (% yield)			Secondary/ tertiary
	1 - adamantanol	2 - adamantanol	2 - adamantanone	
Adamantane (5mmol)	1.895 (37.9)	0.034 (0.68)	0.709 (14.8)	0.39

reaction conditions : adamantane (5 mmol), Cr(III)stearate (0.2 mmol), TBHP (9.0 mmol), 70°C, 24 hr

From Table 3.16, adamantane was oxidized mainly to 1-adamantanol (37.9%), 2-adamantanone (14.8%) and 2-adamantanol (0.68%). This affords a C²/C³ ratio of 0.39. From the literature of the oxidation of adamantane, Barton and

co-workers oxidized adamantane employing GoChAgg system [Cu(II) catalyst, hydrogen peroxide, in pyridine-acetic acid] , GoAgg^{II} [Fe(III) catalyst, hydrogen peroxide, in pyridine-acetic acid] at 1 atm. C^2/C^3 ratio was 0.74 and 0.96, respectively. Both systems were believed to take place *via* non-radical pathway. However, Chavez and his colleagues studied the selectivity of adamantane oxidation using Co(Py₃P)(OO^tBu) and Co(PyPz₂P)(OO^tBu) systems and found that C^2/C^3 ratio was 0.24 and 0.25, respectively. These systems were concluded to occur *via* radical pathway. Therefore, the oxidation of adamantane using Cr(III)stearate as catalyst and TBHP as oxidant was believed to take place *via* radical mechanism.

3.8 Comparative study on relative reactivity on cycloalkanes in oxidation reaction.

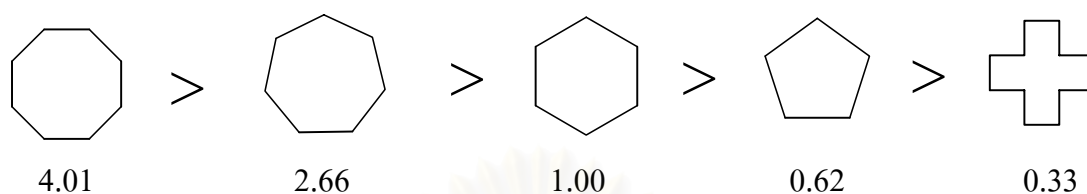
It is widely well-known that there are two possible mechanisms proposed for the oxidation of saturated hydrocarbons catalyzed by metal catalysts. First the reaction took place *via* a free radical pathway. The other was believed that not to involve the radical pathway. Many approaches have been studied to confirm the reaction mechanism. Among them, competitive study on relative reactivity on cyclohexane could be used as a tool. The comparison of relative reactivity order per hydrogen towards a series of cyclic saturated hydrocarbons under the standard Cr(III)stearate catalyzed reactions was systematically studied. The results are summarized in Table 3.17.

Table 3.17 Comparison of reactivity order per hydrogen for a series of cyclic saturated hydrocarbons

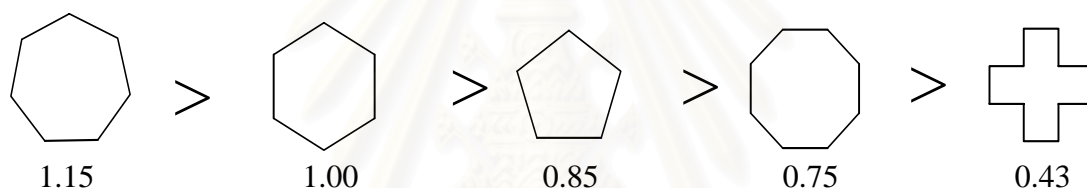
Entry	R ¹ H	R ² H	R ¹ H or R ² H (mmol)	Product(mmol)		Relative Reactivity R ² (H)/R ¹ (H)
				R ¹ =O	R ² =O	
1	cyclohexane	cyclopentane	15	1.606	0.822	0.6
2	cyclohexane	cycloheptane	15	0.748	2.309	2.7
3	cyclohexane	cyclooctane	15	0.291	1.540	4.0
4	cyclohexane	cyclododecane	15	1.316	0.867	0.3

reaction condition: substrates (15 mmol each), Cr(III)stearate (0.2 mmol), TBHP (9.0 mmol), reaction time (24 hr), at 70°C

From Table 3.17, it was found that the relative reactivity for a series of cyclic saturated hydrocarbons catalyzed by Cr(III)stearate was :



The order of relative reactivity was different from the relative reactivity of non-radical in the literature.¹⁸ The relative reactivity in the oxidation of cycloalkanes catalyzed by iron catalyst in GoAgg^{II} type system :



The relative reactivity of oxidation of cycloalkanes by Cr(III)stearate was found to be different from GoAgg^{II} system.¹⁸ This implied that the mechanism of the oxidation of cycloalkanes catalyzed by Cr(III)stearate in this study may be take place *via* the radical pathway.

3.9 Comparative study of the oxidation between cyclododecane and cyclohexanol, cyclohexene, ethyl benzene and α -methyl styrene

Cyclododecane was chosen to be a base substrate to study the relative reactivity towards the oxidation of hydrocarbons by cyclohexanol, cyclohexene, ethyl benzene and α -methyl styrene. The results of relative reactivity of hydrocarbons are exhibited in Table 3.18.

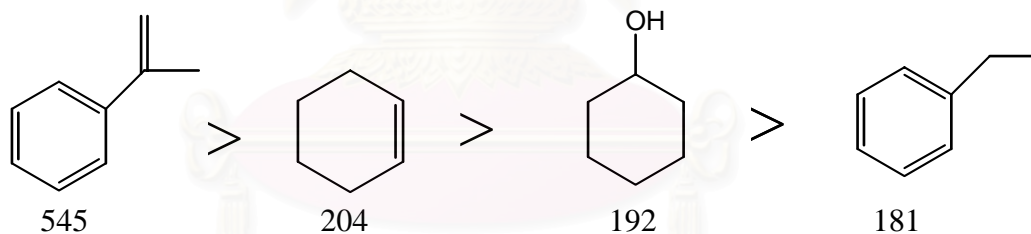
Table 3.18 The competition study catalyzed by Cr(III)stearate

Entry	Substrate	Products (mmol)		
		Cyclododecanone	Ketone	Reactivity Cyclododecanone/Ketone
1	Cyclododecane + Cyclohexanol	0.213	3.413	192
2	Cyclododecane + Cyclohexene	0.038	1.290	204
3	Cyclododecane + Ethyl benzene	0.400	6.031	181
4	Cyclododecane + α -methyl styrene	0.143	6.501	545

Reaction conditions: substrates (5 mmol each), Cr(III)stearate (0.2 mmol), isoctane (3 mL), TBHP (9.0 mmol), reaction time (24 hr), at 70°C

*Ketone is cyclohexanone, cyclohexenone or acetophenone for entries 1, 2 and 3-4 respectively.

From Table 3.18, it was found that the reactivity of saturated hydrocarbon (cyclododecane) and other substrates could be arranged as the following order :



From the series of relative reactivity of hydrocarbon oxidation showed that α -methyl styrene was the highest reactive substrate. From this data it was possible that the reaction of each substrate underwent different type of reaction. The reaction of α -methyl styrene was carbon-carbon bond cleaved reaction while other substrates the oxidation reaction took place.

3.10 The kinetic study of the effect of triphenylphosphine on the Cr(III)stearate oxidation of cyclohexane

Triphenylphosphine was used to prove the mechanism of cyclohexane oxidation catalyzed by Cr(III)stearate since it was a good reducing agent which perhaps will react with a viable intermediate present. The results are shown in Table 3.19.

Table 3.19 The kinetic study of the effect of triphenylphosphine on the Cr(III)stearate oxidation of cyclohexane

Entry	Reaction time (hr)	Products(mmol)		Work up with PPh ₃	
		Cyclohexanone	Cyclohexanol	Cyclohexanone	Cyclohexanol
1	1	0.000	0.039	1.433	0.409
2	3	1.001	0.119	2.510	0.876
3	5	1.318	0.155	2.622	1.045
4	8	1.946	0.209	2.767	1.098

reaction condition : cyclohexane 50 mmol, Cr(III)stearate (0.2 mmol),
TBHP (9.0 mmol) at 70°C

* 5 mmol of triphenylphosphine was added in 1 mL of aliquot, then worked up and analyzed by GC.

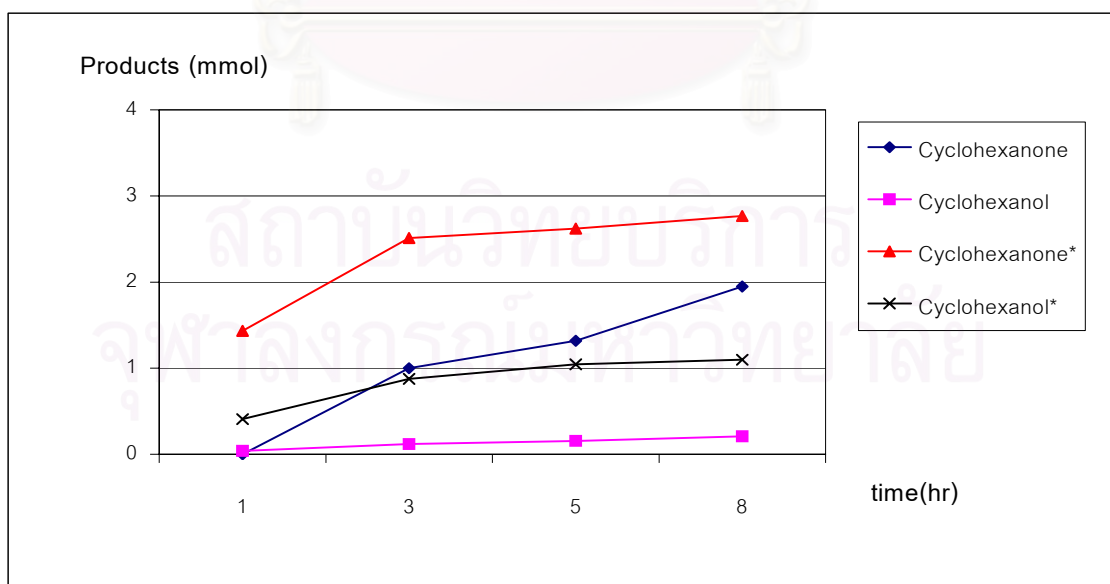


Fig. 3.12 The kinetic study of the effect of triphenylphosphine on the Cr(III)stearate oxidation of cyclohexane

From Table 3.19 and Fig 3.12, when triphenylphosphine 5 mmol was added in an aliquot taken, cyclohexanone and cyclohexanol were noticeably increased. It could be seen that the addition of triphenylphosphine as a reducing agent was reduced an intermediate in the process, possibly cyclohexyl hydroperoxide, to cyclohexanone and cyclohexanol.

3.11 The proposed mechanistic pathway for Cr(III)stearate catalyzed oxidation of cyclohexane

Besides the regioselectivity study, the comparative study on the relative reactivity of saturated hydrocarbon from above results also indicated that the mechanism of this oxidation reaction was proceeded *via* free radical pathway. It was proposed that superoxide from TBHP was transferred to Cr(III) and the reaction was carried on by high-valent Cr(V) oxo species. After that, high-valent Cr(V) oxo species might abstract hydrogen from cyclohexane and hence produced cyclohexyl radical. Cr(V) was transformed to Cr(IV)-OH which then reacted with cyclohexyl radical giving cyclohexanol. In addition, oxygen may react with the produced carbon radical to form cyclohexyl hydroperoxide which then collapsed to cyclohexanone. TBHP may homolytically cleavage and produced *t*-butyl peroxy radical (*t*-BuOO•) that may abstract hydrogen from cyclohexane and hence produced cyclohexyl radical. The proposed mechanism of the Cr(III) catalyzed functionalization of cyclohexane using TBHP as an oxidant is shown in Scheme 3.1.^{19, 22, 37}

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3.12 The study of cyclohexane oxidation catalyzed by co-catalyst of metal stearate complexes

Cr(III)stearate was used as a main catalyst in the presence of other metal stearate (Co(II)stearate, Mn(II)stearate, Ni(II)stearate and Cu(II)stearate) in the ratio of 3:1 to catalyze the oxidation of cyclohexane. The results are presented in Table 3.20.

Table 3.20 The oxidation of cyclohexane catalyzed by Cr(III)stearate and co-metal stearate catalysts

Entry	Catalyst	Products (mmol)		Total (mmol)	Selectivity One/ol
		Cyclohexanone	Cyclohexanol		
1	Cr	2.416	0.211	2.627	11.5
2	Cr : Co	0.773	1.551	2.324	0.5
3	Cr : Mn	3.154	0.812	3.966	3.9
4	Cr : Ni	1.914	1.115	3.029	1.7
5	Cr : Cu	3.120	0.849	3.969	3.7

reaction conditions : cyclohexane 50 mmol, catalysts 0.2 mmol (Cr(III)stearate : other metal stearate = 3 : 1), TBHP (9.0 mmol), 24 hr at 70°C

Table 3.20 presents a series of the utilization of co-catalyst in Cr(III)stearate catalyzed oxidation of cyclohexane. It was observed that the best selectivity one/ol ratio was gained when Cr(III)stearate alone was used as a catalyst. Nevertheless, %yield of total products was dramatically increased in the presence of co-catalysts such as Cr-Mn, Cr-Cu systems. Interestingly, cyclohexanol was produced as a major product in Cr-Co system. These interesting observations are still called for further thoroughly investigation.

3.13 The effect of the amount of *tert*-butylhydroperoxide on the Co(II)stearate oxidation of cyclohexane

From the kinetic study of cyclohexane oxidation using Co(II)stearate as a catalyst (Table 3.21), it was found that after 5 hr the quantity of cyclohexanone and cyclohexanol were not increased. The idea to add another portion of

tert-butylhydroperoxide to the reaction system was raised since cyclohexane used was 50 mmol, but *tert*-butylhydroperoxide in the reaction was only 9.0 mmol. Another portion of TBHP was added to the oxidation system after the reaction was run for 5 hr. The results are presented in Table 3.21.

Table 3.21 The effect of the amount of *tert*-butylhydroperoxide catalyzed by Co(II)stearate

Entry	TBHP	Products(mmol)		Total (mmol)	Selectivity one/ol	Efficiency of TBHP
		Cyclohexanone	Cyclohexanol			
1	9	0.867	1.296	2.163	0.7	24.0
2	18	2.720	2.705	5.425	1.0	30.1

reaction condition : cyclohexane 50 mmol, Co(II)stearate (0.2 mmol), reaction time 24 hr at 70°C, TBHP 9.0 mmol was added after 5 hr of reaction time.

Co(II)stearate was disclosed to be a good catalyst for cyclohexane oxidation. The reaction, however, ceased within 5 hr interval. The efficiency of the system based on TBHP was 24.0. The addition of another portion of TBHP (9.0 mmol) successfully provided more than 150% of total yield of desired product. The selectivity gained and the efficiency based on TBHP was found to be prevailed.

CHAPTER IV

CONCLUSION

The goal of this research is to search for suitable methodology for functionalization of organic compounds and to develop catalytic system for soluble transition metal-complexes catalyzed oxidation reaction. From this research, it was found that the oxidation of organic compounds catalyzed by Cr(III)stearate with TBHP among fourteen metal carboxylate and metal acetylacetonate complexes studied could be carried out at 70°C and atmospheric pressure with high yield and good selectivity for the production of ketone. The optimum conditions were cyclohexane 20 mmol as a substrate, Cr(III)stearate 0.1 mmol as a catalyst and TBHP 9.0 mmol as an oxidant. The oxidation of cyclohexane under this condition uniquely produced mainly cyclohexanone with a small amount of cyclohexanol. The kinetic study showed that the half-life of cyclohexane oxidation catalyzed by Cr(III)stearate was approximately 8 hr and the reaction was finished within 24 hr.

The utilization of this developed oxidation systems for oxidation of organic substrates revealed that the reaction produced mainly ketone with a small amount of alcohol. Cr(III)stearate could oxidize catalyzed various organic substrates (cyclohexane, cyclododecane, cyclohexanol, 1,4-cyclohexanediol, cyclohexene, ethyl benzene, α -methyl styrene and diphenyl sulfide) to their corresponding oxidized products. The use of carbon tetrachloride and bromotrichloromethane suggested the presence of an intermediate in this oxidation system. The study for the possible mechanism of this system was performed and concluded based upon the information of regioselectivity study, relative reactivity of cycloalkanes and the addition of trapping agents, the route of mechanism of cyclohexane oxidation was believed to take place *via* a free radical pathway.

Co-catalysts of metal stearate complexes with a main Cr(III)stearate was examined, it was observed that lower selectivity was obtained compared with the use of only Cr(III)stearate as catalyst, but the total yield of product was superior.

Suggestion for the future work

The modification of this catalytic system to the larger scale experiments that could be applied in a pilot scale of petrochemical industry may be the one of important things to carry out. The oxidation of other organic compounds should be scrutinized in details for each class of compounds in order to evaluate as a synthetic tool for organic transformation. Co-catalysts should also be studied in details since the preliminary results provided promising finding.



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