

การออกซิไดส์สารไฮโดรคาร์บอนอิ่มตัวเร่งปฏิกิริยาด้วยสารเชิงซ้อน
1,3-ไดคาร์บอนิลออกโซวานเดียมเปรียบเทียบกับซิฟเบสออกโซวานเดียม

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**OXIDATION OF SATURATED HYDROCARBONS CATALYZED BY
1,3-DICARBONYL OXOVANADIUM COMPARED WITH SCHIFF'S
BASE OXOVANADIUM COMPLEXES**

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วรวัลย์ ชิววรรณรักษ์ : การออกซิไดส์สารไฮโดรคาร์บอนอิ่มตัวเร่งปฏิกิริยาด้วยสารเชิงซ้อน 1,3-ไดคาร์บอนิลออกโซวานาเดียมเปรียบเทียบกับซิทเบสออกโซวานาเดียม (OXIDATION OF SATURATED HYDROCARBONS CATALYZED BY 1,3-DICARBONYL OXOVANADIUM COMPARED WITH SCHIFF'S BASE OXOVANADIUM COMPLEXES)
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สารเชิงซ้อนซิทเบส และ 1,3-ไดคาร์บอนิลออกโซวานาเดียมสามารถใช้เป็นตัวเร่งปฏิกิริยา ในปฏิกิริยาออกซิเดชันของไซโคลแอลเคน ในระบบตัวทำละลายไพรีดีนและกรดแอซิดิก ณ อุณหภูมิห้อง ความดันบรรยากาศ ได้ผลิตภัณฑ์เป็นคีโตนอย่างเลือกจำเพาะ พบว่าสารเชิงซ้อนซิทเบสออกโซวานาเดียมให้ความเลือกจำเพาะในการเกิดคีโตนที่ดี มีอัตราเร็วในการเกิดปฏิกิริยาออกซิเดชัน และ catalytic turnover ดีกว่าสารเชิงซ้อน 1,3-ไดคาร์บอนิลออกโซวานาเดียม เมื่อพิจารณาปริมาณผลิตภัณฑ์รวม พบว่าสารเชิงซ้อน 1,3-ไดคาร์บอนิลให้ผลดีกว่าสารเชิงซ้อนซิทเบสออกโซวานาเดียม จากการศึกษา การเลือกจำเพาะทางเคมีพบว่า การเติมสารเติมแต่งมีผลต่ออัตราส่วนของคีโตนกับแอลกอฮอล์ นอกจากนี้ จากหลักฐานทางเคมีพบว่า สารตัวกลางหนึ่งคือ แอลคิลไฮโดรเปอร์ออกไซด์ และสารตัวกลางอีกชนิดหนึ่งเชื่อว่าไม่ใช่คาร์บอนพรีเรดิคัล

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หลักสูตร..ปีโตรเคมีและวิทยาศาสตร์พอลิเมอร์...	ลายมือชื่อนิสิต
สาขาวิชา..ปีโตรเคมีและวิทยาศาสตร์พอลิเมอร์...	ลายมือชื่ออาจารย์ที่ปรึกษา
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 HYDROCARBONS CATALYZED BY 1,3-DICARBONYL OXOVA-
 NADIUM COMPARED WITH SCHIFF'S BASE OXOVANADIUM
 COMPLEXES. THESIS ADVISOR: ASSIST. PROF. WARINTHORN
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Schiff's base and 1,3-dicarbonyl oxovanadium (IV) complexes could be employed as a catalyst in cycloalkane oxidation reaction in a pyridine-acetic acid media at room temperature and atmospheric pressure. Ketone was selectively obtained as a main product. It was observed that Schiff's base oxovanadium (IV) complexes gave better selectivity for ketone formation, the oxidation reaction rate and catalytic turnover than 1,3-dicarbonyl oxovanadium (IV) complexes. Considering the total amount of products, 1,3-dicarbonyl oxovanadium (IV) complexes provided better yield than Schiff's base oxovanadium (IV) complexes. Chemoselectivity study disclosed that additives in this system had an effect to ketone/alcohol ratio. In addition, from chemical evidence, possibly alkyl hydroperoxide as one of the intermediates. The other intermediate was believed not to be carbon free radical.

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LIST OF ABBREVIATIONS

Fig	figure
kcal	kilocalorie
°C	degree celsius
atm	atmosphere
mmol	millimole
NMR	nuclear magnetic resonance
IR	Infrared
g	gram (s)
mL	millilitre (s)
min	minute (s)
h	hour (s)
cm ⁻¹	unit of wavenumber
ppm	part per million
<i>J</i>	coupling constant
m	multiplet (NMR)
dd	doublet of doublet (NMR)
d	doublet (NMR)
s	singlet (NMR)
m.p.	melting point
dec	decomposed
lit	literature
%	percent

R _f	retardation factor
EtOAc	ethyl acetate
salen	Bis(salicylaldehyde)- <i>N,N'</i> -ethylenediimine
saltn	Bis(salicylaldehyde)- <i>N,N'</i> -trimethylenediimine
salophen	Bis(salicylaldehyde)- <i>N,N'</i> - <i>o</i> -phenylenediimine
haen	Bis(2-hydroxyacetophenone)- <i>N,N'</i> -ethylenediimine
oven	Bis(<i>o</i> -vanillin)- <i>N,N'</i> -ethylenediimine
hnen	Bis(2-hydroxy-1-naphthaldehyde)- <i>N,N'</i> -ethylenediimine
hnopen	Bis(2-hydroxy-1-naphthaldehyde)- <i>N,N'</i> - <i>o</i> -phenylene- diimine
sap	<i>N</i> -salicylalidene-2-aminophenol
sac	<i>N</i> -salicylalidene-anthranilic acid
mdb	4-methoxydibenzoylmethane
dmb	4,4'-dimethoxydibenzoylmethane
mtb	4-methoxy-4'- <i>tert</i> -butyldibenzoylmethane
TBHP	<i>tert</i> -butyl hydroperoxide

CHAPTER I INTRODUCTION

The world's natural gas and petroleum deposits represent by far the largest source of hydrocarbons that have also well-known as the largest group of organic chemicals in petroleum products.¹ The products from petroleum refining can be described as shown in Fig 1.1.

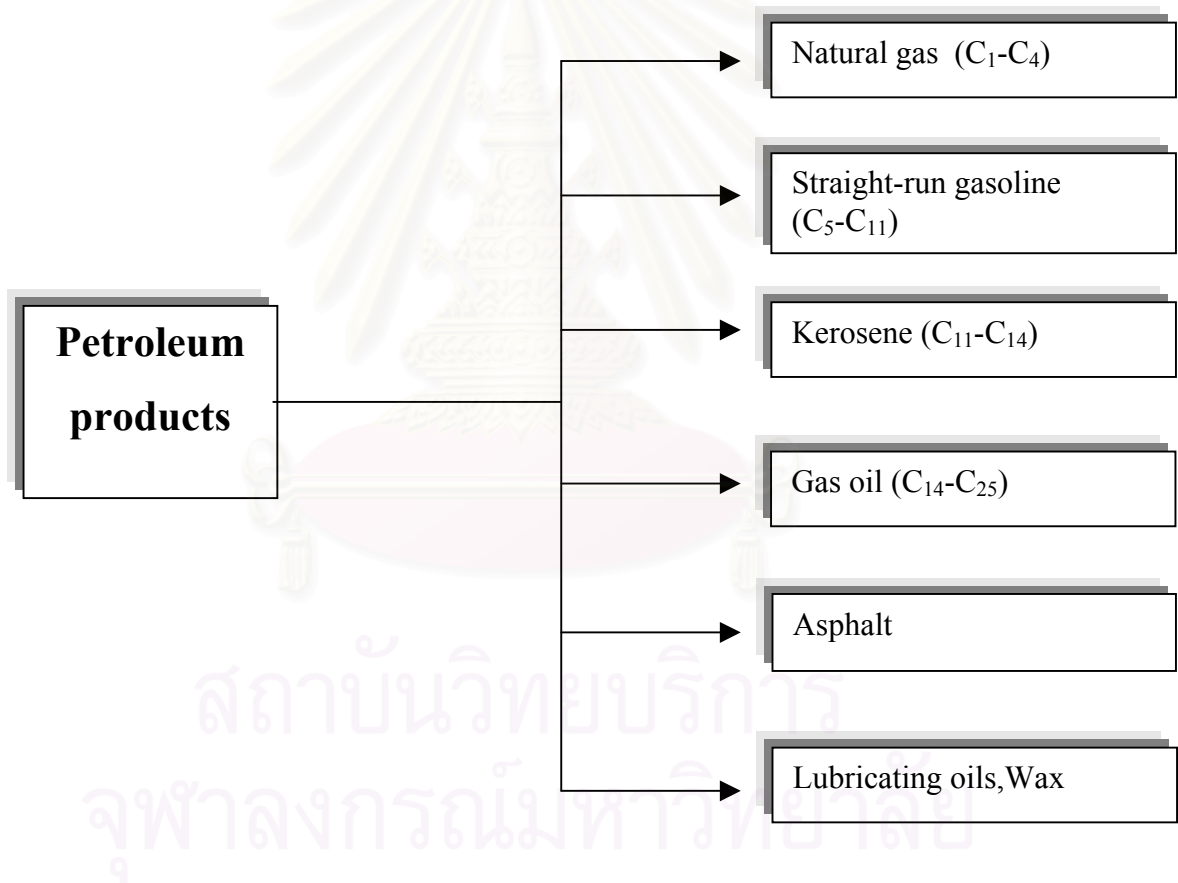
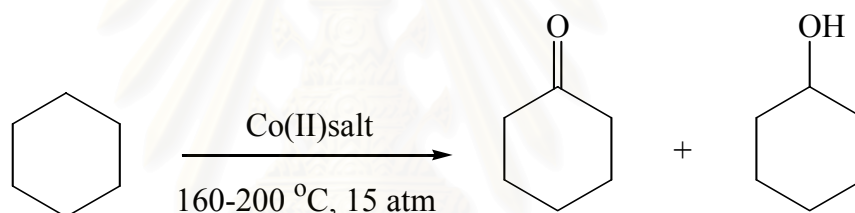
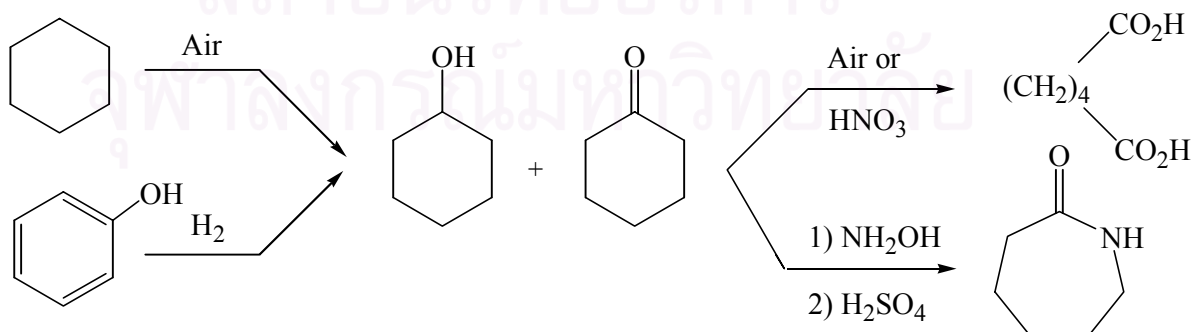


Fig 1.1 Products from petroleum refining

Although saturated hydrocarbons are the largest component in total hydrocarbons, they are mostly used solely as an energy supplier or as a fuel source and generally are not expensive. The attempts to utilize this class of compounds by direct functionalization of saturated hydrocarbons have been carried on for years. However, it has been realized that this is not a simple and easy task. This mainly stems from the inertness of C-H bonds in saturated hydrocarbons. Their bond dissociation energies (BDE) range from 85-91 kcal/mol for tertiary, to 90-95 kcal/mol for secondary and 97-104 kcal/mol for primary C-H bonds.² The breaking of these bonds thus usually requires high pressure, high temperature, basic or acidic conditions, or extremely strong and unselective reagents, etc. For example, cyclohexane is oxidized to cyclohexanone and cyclohexanol by using an oxidation soluble catalyst such as cobalt (II) salt (naphthenate or acetate) between 160 and 200 °C at 15 atm of air. Conversion is limited to about 4 %.³



The manufacturing of cyclohexanone and cyclohexanol is the first step for the preparation of an important intermediate in the production of nylon such as adipic acid and hexamethylene diamine for nylon 66 and caprolactam for nylon 6.⁴



The first industrial production of caprolactam dates from 1938 (BASF nylon-6). The starting material used was phenol. Other processes have been developed since then, using cyclohexanone and cyclohexanol as an intermediate. Although many units based on phenol are still in operation, new plants use cyclohexane as raw material, in 1987, 68 percent of worldwide caprolactam production capacity employed cyclohexane, 25 percent phenol and only 5 percent toluene⁵(Fig 1.2).

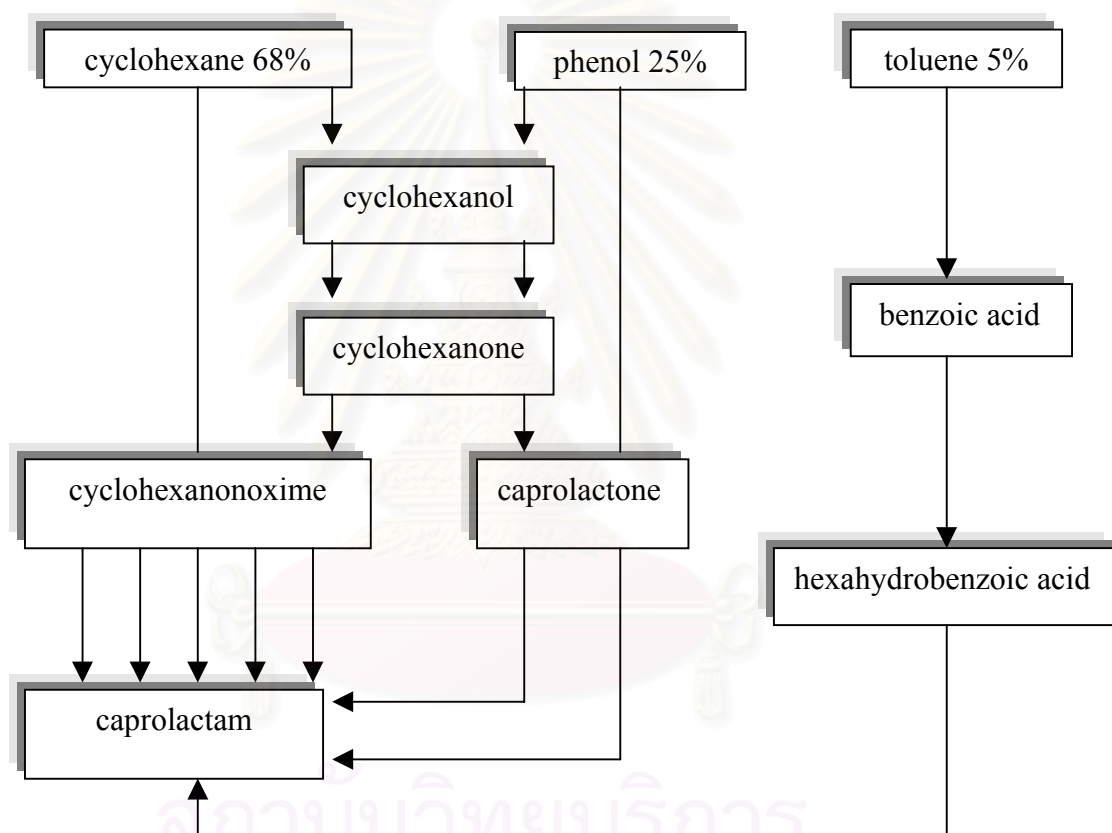
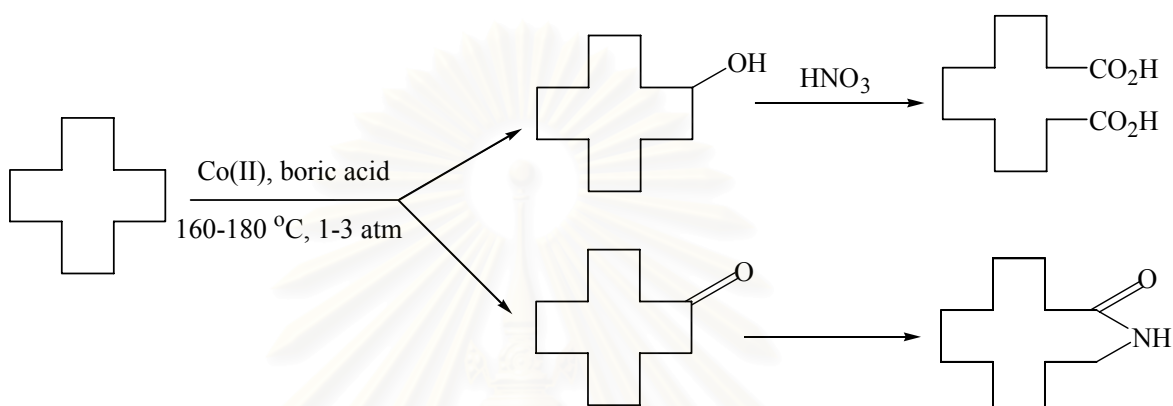


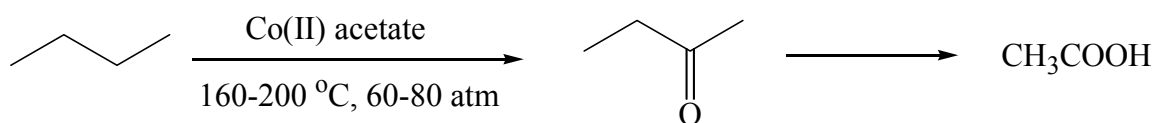
Fig 1.2 Different methods for producing caprolactam

Another major industrial application utilizing alkane is the synthesis of cyclododecanone and cyclododecanol from cyclododecane. These compounds are converted to dodecanedioic acid and lauryl lactam by chemistry shown below. These two products, with combined worldwide sale of 100 million pounds in 1990, are intermediates in the production of polyamides for several specialty applications.



In a process described by Chemische Werke Huls, as in the cyclohexane oxidation, cyclododecane which contains a trace of a cobalt (II) carboxylate is oxidized with air at 160-180 °C and 1-3 atmospheric pressure. The aqueous boric acid solution is concentrated and recycled to the oxidation reactor. Cyclododecanol and cyclododecanone (5:1) are formed in 80-82 % yield at 33 % conversion.⁶

Another example, butane from natural gas or from petroleum refining is relatively cheap and abundant. It became a major feedstock for acetic acid production by oxidation reaction. Butane is oxidized by air, in an acidic solution, catalyzed by cobalt (II) acetate. Reaction conditions are 160-200 °C and 60-80 atm air pressure. At 30% conversion acetic acid is obtained with 45 % selectivity. The by-products are propionic acid, butyric acid and 2-butanone. More recent procedures use milder conditions and can convert practically all by-products into acetic acid. Acetic acid is obtained in 75% yield at 85% conversion.⁷



Under these vigorous conditions, the chemical reaction is inevitably unselective and consequently many products are produced. Therefore, the direct oxidation of saturated hydrocarbons under mild conditions with high selectivity is an intellectually challenging and industrially important objective of current relevance.

Catalysis is the key to chemical transformations. Most industrial syntheses and nearly all biological reactions require catalysts. The catalysts can also influence the selectivity of chemical reactions. Similar to other organic transformations, the catalyst is of an important role in an oxidation reaction. The selective activation of particular varieties of C-H bonds and the reduction of the activation energy of the oxidation process can be controlled after the desired substitution has been achieved. Heterogeneous and homogeneous catalysts are both used in industry. In this research, homogeneous catalyst for the oxidation reaction is selected for investigation. Although the major disadvantage of homogeneous transition metal catalysts is the difficulty of separating a catalyst from products, it still possesses some intriguing properties. Homogeneous catalysts have a higher degree of dispersion in the reaction media than heterogeneous catalysts. In theory, in homogeneous catalysis each individual atom can be catalytically active, whereas heterogeneous catalysts only the surface atoms are active. Refer to their high degree of dispersion, homogeneous catalysts exhibit a high activity per unit mass of metal than heterogeneous catalysts. The high mobility of the molecules in the reaction mixture results in more collisions with substrate molecules. The reactants can approach the catalytically active center from any direction and a reaction at an active center does not block the neighboring centers. This allows the use of lower catalyst concentrations and milder reaction conditions. The most prominent feature of homogeneous transition metal catalysts are the high selectivities that can be achieved. Owing to the thermal stability of organometallic complexes in liquid phase, industrially realizable homogeneous catalysis is limited to temperature below 200 °C. In this temperature range homogeneous catalysts can readily be stabilized or modified by addition of ligands; considerable solvent effects

also occur. Table 1.1 summarizes the advantages and disadvantages of the two classes of catalysts.

Table 1.1 Comparison of homogeneous and heterogeneous catalysts

Features	Homogeneous	Heterogeneous
Active centers	All metal atoms	Only atoms on the surface
Concentration	Low	High
Selectivity	High	Lower
Reaction conditions	Mild (50-200°C)	Severe (often > 250 °C)
Separation	Complicated	Simple

Many new products designed specific biological activity must be made with a specified chirality. New science and technology to achieve enantioselective synthesis is and will continue to be one of most exciting areas in homogeneous catalysis. Rapid growth has continued in the use of homogeneous catalysis to make large volume chemical intermediates and polymers (Table 1.2).

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Table 1.2 Homogeneous and organometallic catalysis in the US chemical industry

Major reactions and products	Approximate production ^a (thousands of metric tons)	
	1980	1990
Olefin additions		
Adiponitrile	200	420 ^b
Olefin polymerizations and oligomerization		550 ^b
α-Olefins	105	1364 ^b
Propylene dimers	136	310 ^c
Polybutadiene (coordination catalysis)	239	8 ^b
Cyclododecatriene	10	5743 ^{b,c}
Polyethylene (HDPE and LLDPE)	2339	3781 ^c
Polypropylene	1658	256 ^c
Ethylene/propylene copolymers	144	
Carbonylations		
Oxo alcohols (hydroformylation)	1297	1818 ^b
Acetic acid (from methanol)	773	1164 ^b
Acetic anhydride (from methanol)	0	527 ^b
Olefin oxidation		
Acetaldehyde	409	273 ^b
Propylene oxide (Oxirane process)	362	815 ^b
Alkane and arene oxidation		
Terephthalic acid and esters	2752	3496 ^c
Adipic acid	668	746 ^c
Acetic acid	511	159 ^b
Benzoic, isophthalic acids	81	121 ^b
Condensation polymerization		
Polyester fiber	1813	1452
Halocarbons		
Dichloroethane	5049	6045 ^c
Chloroprene	151	116 ^b
Chlorofluoromethanes	309	296 ^c

^a From *Synthetic Organic Chemicals-19*, US International Trade Commission, unless shown otherwise.

^b From *Chemical Economics Handbook*, SRI International.

^c From *Chemical and Engineering News*, June 24, 1991.

Industrially the largest scale application of homogeneous catalysis is the oxidation of hydrocarbons by molecular oxygen. Oxidation process and their uses are listed in Table 1.3.

Table 1.3 Major industrial oxidations of hydrocarbons

Hydrocarbons	Oxidation products	Applications
Cyclohexane	Cyclohexanol and cyclohexanone	Converted to adipic acid and caprolactam (polyamide precursors)
Cyclododecane	$C_{12}H_{23}OH$ and $C_{12}H_{22}O$	Oxidized to dodecanedioic acid and lauryl lactam (polyamide precursors)
Butane	Acetic acid	Solvent, vinyl acetate polymers
Toluene	Benzoic acid Benzaldehyde	Caprolactam (polyamide precursors), phenol, and food preservative Agrochemicals, flavorings, and fragrances
<i>m</i> -Xylene <i>p</i> -Xylene	Isophthalic acid Terephthalic acid Terephthalate esters	Polymers and plasticizers Polyester fibers, films, and plastics, Plasticizers

1.1 Literature review on the oxidation of saturated hydrocarbons

It is well-known that there are many systems which could selectively oxidize saturated hydrocarbons; for example, Fenton's system and biological system such as Cytochrome P-450 enzyme.

Fenton's system or Fenton reaction has been reported that ferrous ion strongly promotes the oxidation of alkanes by hydrogen peroxide. The mechanism involved was thoroughly studied and was believed to concern with hydroxyl radical.⁸

Cytochromes P-450 are ubiquitous in nature for example, liver of mammal, insects, yeast and some bacteria.⁹ They have been reported to be able to transform saturated hydrocarbons such as cyclohexane to hydroxylated products and oxidative group transfer such as trichloroethylene under room temperature and atmospheric pressure or slightly above. Besides, these enzymes are found to catalyze in a variety of oxidation such as *N*-oxidation, sulfoxidation and epoxidation under mild conditions.¹⁰ Methane monooxygenase, propyl 4-hydroxylase, isopenicillin *N*-syntase and γ -butyrobetaine hydroxylase are other groups of biological systems that could oxidize saturated hydrocarbons to ketones and alcohols.¹¹

From these intriguing abilities of biological systems, several chemical models have been later developed. Working towards the main aim to carry on the reaction at ambient temperature and atmospheric pressure, it is a very promising idea because one can reduce the capital cost that is the main objective in petrochemical industries. For example, Barton and colleagues in 1983 described that the oxidation of adamantane to 2-adamantanone, 1-adamantanol and 2-adamantanol could be achieved with unusual efficiency using molecular oxygen and a system comprising hydrogen sulphide and iron powder in pyridine containing acetic acid and a little water under room temperature and 1 atm of oxygen.¹²

In 1990 Banfi and colleagues presented that cycloalkanes (cyclohexane, cyclooctane) and adamantane are converted into mixtures of ketones and alcohols at a rate of up to 125 turnovers/min in CH_2Cl_2 - H_2O solution at 0°C. The reaction is promoted by 30% H_2O_2 and catalysed by chemically robust manganese (III)-tetraaryl porphyrins.¹³ In the same year, About-Jaudet E. and colleagues observed that employing the GoAgg^{II} system (pyridine-acetic acid with a catalytic amount of FeCl_3 and hydrogen peroxide as

oxidant) the selective oxidation of cyclododecane to cyclododecanone could be accomplished. Besides, the addition of picolinic acid increases the rate of oxidation up to fifty folds. On the other hand, the addition of pyridine-2-phosphonic acid stops oxidation completely.¹⁴ Furthermore, Sheu and colleagues found that cyclohexane could be transformed with 72% efficiency to 95% cyclohexanone and 5% cyclohexanol. This system used pyridine/acetic acid as a solvent, bis(picolinato)iron(II) [Fe(PA)₂] as a catalyst and hydrogen peroxide as an oxidant for the selective ketonization of methylenic carbon ($>\text{CH}_2 \rightarrow \text{C}=\text{O}$).¹⁵

The biomimetic oxidation reactions of a variety of hydrocarbons with iron complexes, $\text{Fe}_2\text{O}(\text{OAc})_2(\text{bpy})_2\text{Cl}_2$, $\text{Fe}_4\text{O}_2(\text{OAc})_7(\text{bpy})_2(\text{ClO}_4)$, $\text{Fe}_2\text{O}(\text{OAc})(\text{tmima})_2(\text{ClO}_4)_3$ and $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ using $\text{H}_2\text{O}_2/\text{O}_2$ as an oxidant at ambient temperature under air were studied. $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ was found to be the most effective and selective in the oxidation reaction of cyclohexane. This was reported by Fish and colleagues in 1991.¹⁶

Barton and Chavasiri in 1994 presented the GoAgg^V oxidation system (pyridine-acetic acid with a catalytic amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, *tert*-butyl hydroperoxide as an oxidant with the addition of extra ligand such as picolinic acid). This system was capable to oxidize cycloalkanes such as cyclohexane and cyclododecane providing the oxidized products, with the ketone being the major products. The yield of the desired products and the ketone to alcohol ratio observed using this particular system were found to be greater than those in analogous systems using hydrogen peroxide as an oxidant.¹⁷

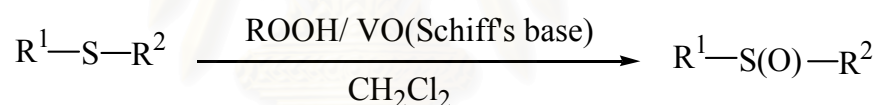
Employing pyridine/acetic acid/hydrogen peroxide system, Anantaprayoon and Intarakamthornchai observed in 1995 that cyclohexane could be selectively oxidized to ketone as a major product and alcohol as a minor one at room temperature and atmospheric pressure. It was found that the system composing of iron(III) and 1,3-dicarbonyl ligand bearing a donating group such as acetylacetone, benzoylacetone and dibenzoylmethane could also accelerate the rate of the oxidation of cyclohexane.¹⁸

Nuntasri and Loayfakajohn in 1996 showed that the iron Schiff's base complexes, especially $(\text{Fesalen})_2\text{O}$, exhibited the catalytic ability in pyridine/zinc-acetic acid system. Cyclohexane and cyclooctane could selectively be oxidized to mainly ketone at room temperature and atmospheric pressure. The efficiency of this oxidation system could be enhanced by the addition of ascorbic acid or by stepwise additions of zinc powder.¹⁹

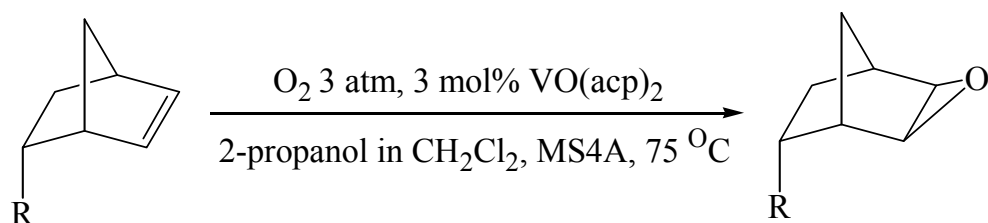
Besides in 1997, Barton and colleagues reported saturated hydrocarbons and hydrogen sulfide can be synergistically oxidised by oxygen to give efficiently ketones and the corresponding alcohols, employing catalysts based on Fe^{II}, picolinic acid and 4-*tert*-butylpyridine, acetonitrile as solvent at room temperature and nearly neutral pH.²⁰

1.2 Literature review on vanadium-catalyzed oxidation reactions

Vanadium is known as a biologically essential trace element²¹, and is found in some haloperoxidases²², a nitrogenase²³, blood cells of tunicates²⁴, etc. Furthermore, complexes with a vanadium-oxo moiety occupy an important place in inorganic chemistry. Indeed, this group is one of the most ubiquitous. Oxovanadiums, especially oxovanadium (IV) have been the subject of much experimental study and have been studied for application ranging from catalysis to oxidation reaction. Oxovanadium (IV) Schiff's base complexes have been used as a catalyst in the asymmetric oxidation of sulfides into the corresponding sulfoxides with organic hydroperoxides.²⁵



Poly(*p*-phenylene sulfide), an important engineering plastic was obtained from the oxovanadium catalyzed O₂-oxidative polymerization of diphenyl disulfide.²⁶ Mukaiyama and his colleagues in 1990 found that oxovanadium (IV) complexes with 1,3-dicarbonyl ligands, especially bis(2-acetylcyclopentanonato)oxovanadium (IV) : VO(acp)₂ could be employed as a catalyst in epoxidation reaction, norbornene analogues are monooxygenated into the corresponding epoxides in good yields.²⁷



(1a) R = H

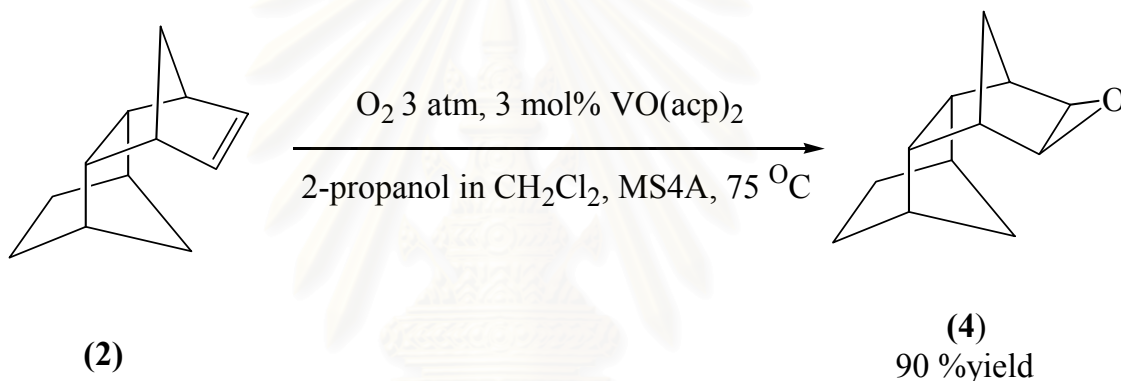
(1b) R = PhCO_2CH_2

(1c) R = $\text{PhCO}_2\text{CH}(\text{CH}_3)$

(3a) 78 %yield

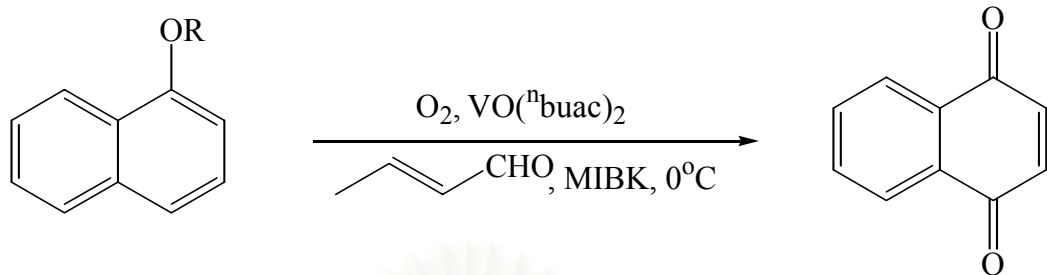
(3b) 68 %yield

(3c) 63 %yield



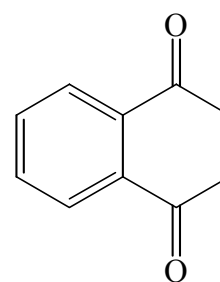
Furthermore, in 1994 they found that oxovanadium (IV) complexes were effectively employed as a catalyst for oxygenation of fused aromatic compounds such as naphthol and naphthalene derivatives yielding 1,4-naphthoquinones using molecular oxygen and crotonaldehyde as a reductant under an atmospheric pressure.²⁸

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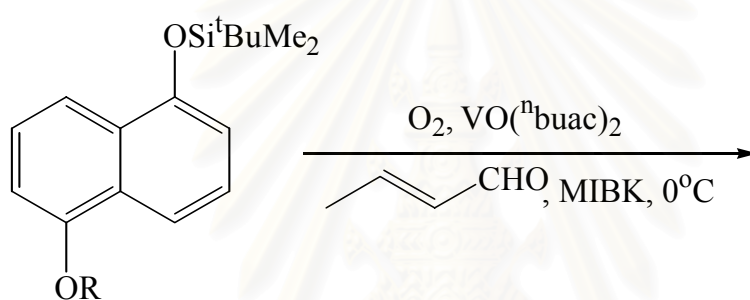
(5a) R = Si^tBuMe₂

(5b) R = CH₃



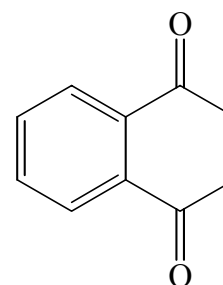
(8a) 86% yield

(8b) 68% yield



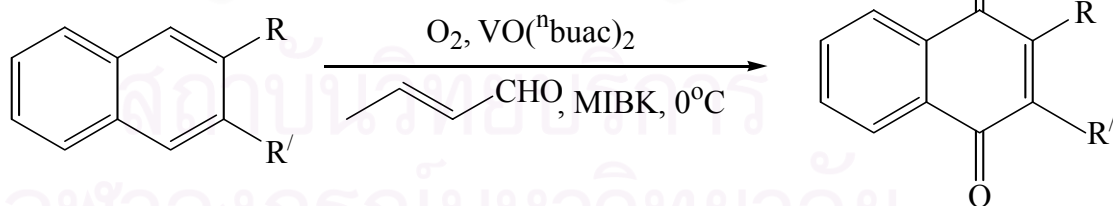
(6a) R = CH₃CO-

(6b) R = PhCO-



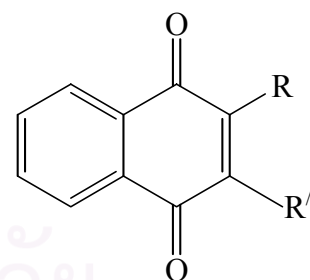
(9a) 79% yield

(9b) 62% yield



(7a) R = R' = CH₃

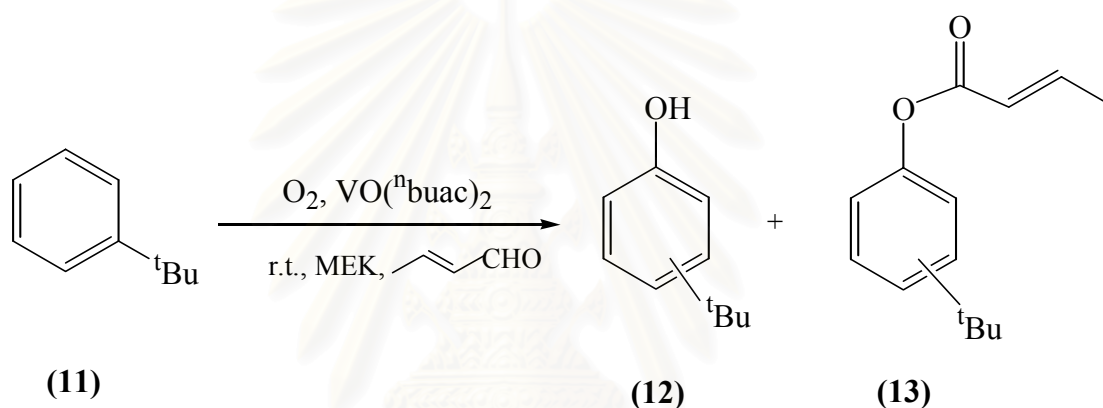
(7b) R = CH₃, R' = H



(10a) 67% yield

(10b) 55% yield

In the same year, they carried out the aerobic oxygenation of *tert*-butylbenzene (**11**) using various acetylacetonatometal complexes (such as Ni, Mn, Co, Cu, Pd and oxovanadium) as catalysts. The corresponding phenol derivatives, *tert*-butylphenol (**12**) and *tert*-butyl phenyl crotonate (**13**) were obtained in 17% total yield (15% and 2% yield, respectively) when bis(2,4-pentanedionato)oxovanadium (IV) : (VO(acac)₂) was employed as a catalyst. Other metal complexes did not give product. Among various 1,3-diketone-type ligands screened, oxovanadium (IV) complexes coordinated with 1,3-diketones bearing electron-donating substituents especially, 3-*n*-butyl-2,4-pentanedione (VO(ⁿbuac)₂) was the most effective catalyst to afford phenolic compounds.²⁹



1.3 Literature review on vanadium-catalyzed oxidation of saturated hydrocarbons

A few reports on vanadium catalyzed oxidation of saturated hydrocarbons justified has been found. In 1989, Moiseev and his colleagues reported the use of VO(acac)₂ as a catalyst for cyclohexane oxidation in the systems V(V)-H₂O₂-RCOOH, where R= CH₃, CF₃. The only products obtained from the oxidation of cyclohexane at 20-50°C in CH₃COOH were cyclohexanol and cyclohexanone. In CF₃COOH solution at -10-15°C, the main product was cyclohexyl trifluoroacetate. The rate of oxidation of cyclohexane in CF₃COOH solution is considerably higher than that in CH₃COOH.³⁰

In 1996, Munbunjong and colleagues reported cyclohexane that could be selectively oxidized at room temperature and atmospheric pressure to cyclohexanone as the main product employing Schiff's base oxovanadium (IV) complexes, especially, VO(IV) (salophen).³¹

1.4 The goal of this research

The purpose of this research can be summarized as follows :

1. To synthesize Schiff's base and 1,3-dicarbonyl ligands
2. To synthesize Schiff's base oxovanadium (IV) complexes and 1,3-dicarbonyl oxovanadium (IV) complexes
3. To study the optimum conditions for cycloalkanes oxidation by using Schiff's base oxovanadium (IV) and 1,3-dicarbonyl oxovanadium (IV) complexes
4. To compare the efficiency and selectivity for cycloalkane oxidation by using Schiff's base oxovanadium (IV) and 1,3-dicarbonyl oxovanadium (IV) complexes



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CHAPTER II

EXPERIMENTAL SECTION

2.1 Instruments

Melting points were determined on a Fisher-Johns melting point apparatus or Electrothermal digital melting point apparatus model IA9100 and are uncorrected. Column chromatography was carried out on silica gel (Merck Kieselgel 60, 70-230 mesh). Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck Kieselgel 60 PF₂₅₄). The FT-IR spectra were recorded on a Fourier Transform Infrared Spectrophotometer on Nicolet model Impact 410: solid samples were mixed with potassium bromide to form pellets and liquid samples were incorporated to sodium chloride cells. The ¹H- and ¹³C-NMR spectra were obtained in deuterated chloroform (CDCl₃) or deuterated dimethylsulfoxide (DMSO-d₆) with tetramethylsilane (TMS) as an internal reference on a Bruker model ACF 200 Spectrometer. Gas chromatography analysis was carried out on a Shimadzu Gas Chromatograph GC-9A and GC-14A instrument equipped with flame ionization detector (FID) with N₂ as a carrier gas. The column used for chromatography was a capillary column type of DB-wax (30 m × 0.250 mm) from J&W Scientific.

2.2 Chemicals

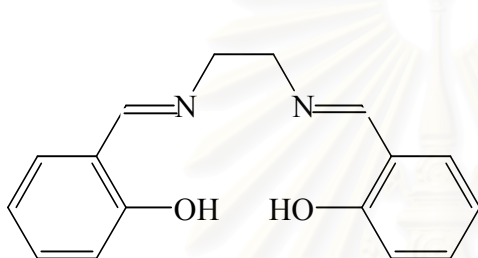
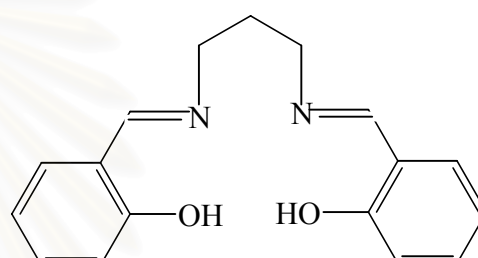
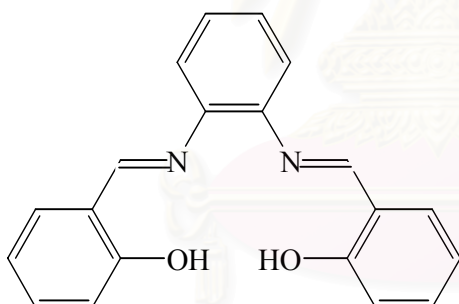
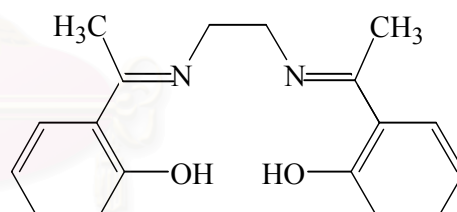
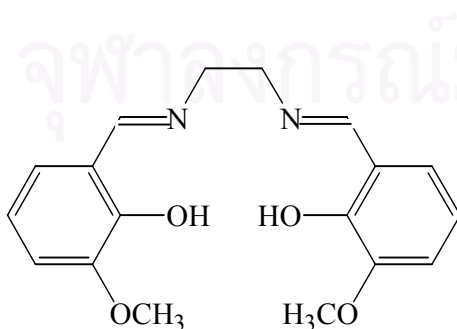
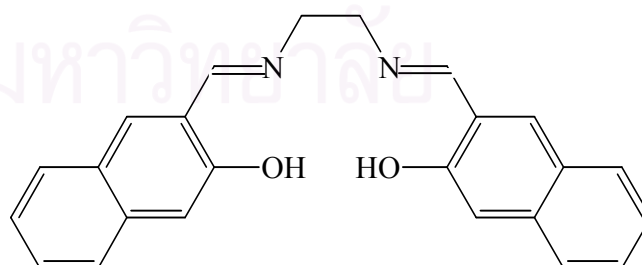
The reagents for synthesizing Schiff's base and 1,3-dicarbonyl ligands, Schiff's base oxovanadium (IV) and 1,3-dicarbonyl oxovanadium (IV) complexes were purchased from Fluka and Merck chemical companies. All solvents used in this research were purified prior to use by standard methodology except for those which were reagent grades.

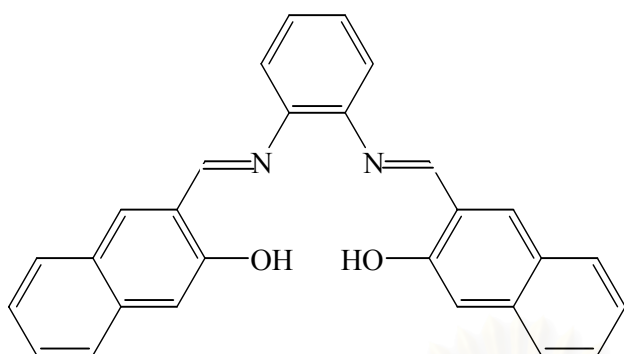
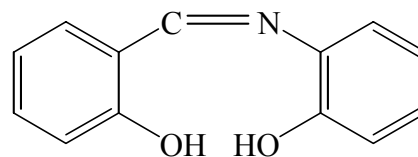
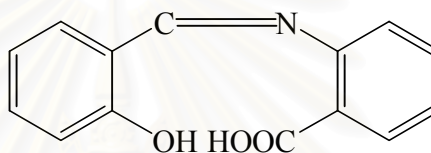
2.3 Syntheses

2.3.1 Syntheses of Schiff's base ligands

General procedure³²:

An interested aldehyde or ketone (1 or 2 mol-equiv) was slowly added to a solution of aromatic amine (1 mol-equiv) in methanol. The solution was stirred at room temperature until precipitate occurred. The precipitate was filtered off and recrystallized by an appropriate solvent. Nine synthesized Schiff's base ligands namely salen (**14**), saltn (**15**), salophen (**16**), haen (**17**), oven (**18**), hnen (**19**), hnopen (**20**), sap (**21**) and sac (**22**) are depicted as shown below.

salen (**14**)saltn (**15**)salophen (**16**)haen (**17**)oven (**18**)hnen (**19**)

hnopen (**20**)sap (**21**)sac (**22**)

*Bis(salicylaldehyde)-N,N'-ethylenediimine (salen)*³³ (**14**): Bright yellow plate crystal (97%), m.p. 125-126°C (95% ethanol), R_f 0.40 (dichloromethane). IR (KBr, cm^{-1}) 3500, 3050-3010, 2950-2870, 1640, 1600, 1450, 1280 and 1170; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 3.84 (4H, s), 6.83 (2H, dt, $J = 7.48, 1.22$ Hz), 6.93 (2H, d, $J = 8.24$ Hz), 7.18 (2H, dd, $J = 7.63, 1.83$ Hz), 7.26 (2H, dt, $J = 7.78, 1.53$ Hz), 8.29 (2H, s) and 13.20 (2H, s); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 59.5 (2C), 116.8 (2C), 118.5 (2 x 2C), 131.4 (2C), 132.2 (2C), 160.9 (2C) and 166.3 (2C).

*Bis(salicylaldehyde)-N,N'-trimethylenediimine (saltn)*³⁴ (**15**): Yellow plate crystal (93%), m.p. 51-52°C (*n*-hexane), R_f 0.71 (ethyl acetate). IR (KBr, cm^{-1}) 3500, 3080-3020, 2950-2860, 1640, 1600, 1450, 1290 and 1160; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 2.05-2.10 (2H, q, $J = 6.71$ Hz), 3.66-3.69 (4H, dt, $J = 6.72, 0.92$ Hz), 6.85 (8H, m), 8.33 (2H, s) and 13.42 (2H, s); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 31.6 (1C), 56.7 (2C), 116.8 (2 x 2C), 118.7 (2C), 131.2 (2C), 132.2 (2C), 118.5 (2C), 161.0 (2C) and 165.8 (2C).

*Bis(salicylaldehyde)-N,N'-o-phenylenediimine (salophen)*³⁵ (**16**): Orange needle crystal (82%), m.p. 191-192 °C (acetone), R_f 0.53 (dichloromethane). IR (KBr, cm^{-1}) 3500, 3050, 2950-2870, 1630, 1560-1485, 1275 and 1190; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 6.85 (2H, t, $J = 7.32$ Hz), 7.02 (2H, d, $J = 13.24$ Hz), 7.20 (4H, m), 7.31 (2H, m), 7.35 (2H, m) and 8.60 (2H, s); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 117.5 (2C), 118.9 (2C), 119.1 (2C), 119.6 (2C), 127.7 (2C), 132.3 (2C), 133.3 (2C), 142.4 (2C), 161.3 (2C) and 163.6 (2C).

*Bis(2-hydroxyacetophenone)-N,N'-ethylenediimine (haen)*³⁶ (**17**): Yellow needle crystal (83%), m.p. 199-200 °C (95% ethanol), R_f 0.60 (dichloromethane). IR (KBr, cm^{-1}) 3590-3270, 3070, 2950-2870, 1620, 1600, 1450, 1250, and 1180; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 2.37 (6H, s), 3.97 (4H, s), 6.78 (2H, dt, $J = 7.70, 1.28$ Hz), 6.91 (2H, dd, $J = 8.55, 1.28$ Hz), 7.27 (2H, dt, $J = 7.91, 1.28$ Hz) and 7.52 (2H, dd, $J = 7.91, 1.50$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 14.7 (2C), 50.2 (2C), 117.4 (2C), 118.5 (2C), 119.4 (2C), 128.1 (2C), 132.4 (2C), 163.1 (2C) and 172.7 (2C).

*Bis(o-vanillin)-N,N'-ethylenediimine (oven)*³⁷ (**18**): Yellow needle crystal (80%), m.p. 163-165 °C (ethanol) (lit.³⁷ m.p. 163-165 °C), R_f 0.50 (ethanol). IR (KBr, cm^{-1}) 3500, 3050, 2840-2990, 1630, 1465, 1255 and 1080; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 3.88 (6H, s), 3.94 (4H, s), 6.77 (2H, t, $J = 7.63$ Hz), 6.84 (2H, dd, $J = 7.94, 1.53$ Hz), 6.90 (2H, dd, $J = 7.94, 1.52$ Hz), 8.32 (2H, s), 13.55 (2H, s); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 56.0 (2C), 59.4 (2C), 114.1 (2C), 118.0 (2C), 118.4 (2C), 123.1 (2C), 148.3 (2C), 151.4 (2C) and 166.6 (2C).

*Bis(2-hydroxy-1-naphthaldehyde)-N,N'-ethylenediimine (hnen)*³⁸ (**19**): Lemon yellow solid (77%), m.p. 270-271 °C (acetone), R_f 0.64 (ethanol). IR (KBr, cm^{-1}) 3570-3300, 3050-3010, 2950-2900, 1640, 1600, 1450, 1250, and 1110.

Bis(2-hydroxy-1-naphthaldehyde)-N,N'-o-phenylenediimine (hnopen)^{38,39} (**20**): Yellow-orange solid (92%), m.p. 215-217 °C (ethanol), R_f 0.51 (ethanol). IR (KBr, cm^{-1}) 3550-3300, 3070, 2950-2870, 1640-1630, 1600, 1450, 1260 and 1180 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 7.05 (2H, d, $J = 9.12$ Hz), 7.32-7.57 (6H, m), 7.80 (2H, d, $J = 6.69$ Hz), 7.95 (4H, d, $J = 9.17$ Hz), 8.53 (2H, d, $J = 8.38$ Hz) and 9.68 (2H, s); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 109.2 (2 x 2C), 119.7 (2C), 120.6 (2C), 121.6 (2C), 123.6 (2C), 126.9 (2C), 127.4 (2C), 128.1 (2C), 129.0 (2C), 133.0 (2C), 136.8 (2C), 138.5 (2C) 157.3 (2C) and 168.6 (2C).

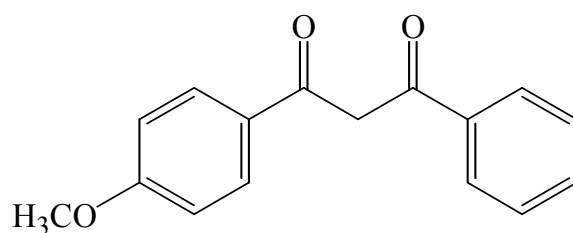
*N-salicylalidene-2-aminophenol (sap)*⁴⁰ (**21**): Bright red needle crystal (90%), m.p. 186-188 °C (acetone), R_f 0.44 (ethanol). IR (KBr, cm⁻¹) 3500, 3050, 1640, 1600-1460, 1280 and 1150 cm⁻¹; ¹H-NMR (CDCl₃) δ (ppm): 5.79 (1H, s), 6.95-7.09 (4H, m), 7.15 (1H, dd, *J* = 7.79, 1.53 Hz), 7.22 (1H, dt, *J* = 7.94, 1.53 Hz), 7.40-7.45 (2H, m), 8.69 (1H, s) and 12.25 (1H, s); ¹³C-NMR (CDCl₃) δ (ppm): 115.9 (1C), 117.3 (1C), 118.3 (1C), 119.3 (1C), 119.6 (1C), 121.0 (1C), 128.8 (1C), 132.7 (1C), 133.7 (1C), 135.8 (1C), 149.9 (1C), 160.6 (1C) and 164.0 (1C).

*N-salicylalidene-anthranilic acid (sac)*⁴⁰ (**22**): Orange solid (67%), m.p. 182-184 °C (ethanol), R_f 0.70 (ethanol). IR (KBr, cm⁻¹) 3500, 3100-3050, 1620, 1600, 1450, 1580-1460 and 1120 cm⁻¹; ¹H-NMR (CDCl₃) δ (ppm): 1.50 (1H, s), 6.66 (1H, dd, *J* = 8.54, 0.91 Hz), 6.67 (1H, dd, *J* = 8.53, 1.22 Hz), 6.99 (1H, d, *J* = 8.85 Hz), 7.03 (1H, dd, *J* = 7.33, 0.92 Hz), 7.30 (1H, dt, *J* = 7.78, 1.52 Hz), 7.52 (1H, dt, *J* = 7.64, 1.83 Hz), 7.56 (1H, dd, *J* = 7.78, 1.53 Hz), 7.90 (1H, dd, *J* = 8.29, 1.83 Hz), 9.90 (1H, s) and 11.0 (1H, s); ¹³C-NMR (CDCl₃) δ (ppm): 114.5 (1C), 116.3 (1C), 117.2 (1C), 119.0 (2C), 119.4 (1C), 131.1 (1C), 133.6 (1C), 136.4 (1C), 130.4 (1C), 151.5 (1C), 160.7 (1C), 169.6 (1C) and 191.8 (1C).

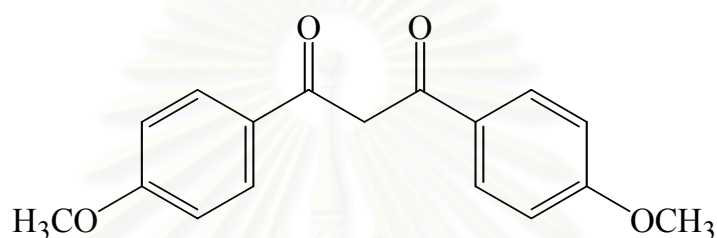
2.3.2 Syntheses of 1,3-dicarbonyl ligands

General synthesis of dibenzoyl methane⁴¹:

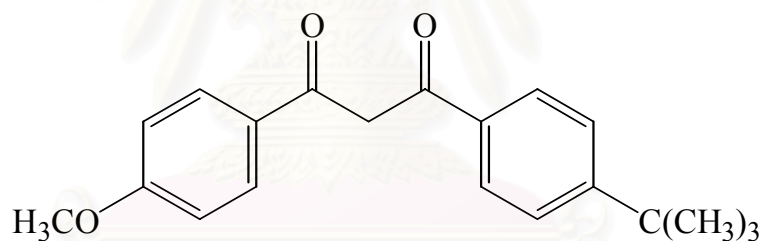
Substituted acetophenone (1 mol-equiv) in dry benzene 50 mL and ethyl benzoate or ethyl benzoate derivatives⁴² (1 mol-equiv) in dry benzene 50 mL were added dropwise to a suspension of 60% NaH (washed with cyclohexane). The mixture was refluxed and monitored the progress of the reaction by thin layer chromatography using 30% EtOAc/hexane as a eluant solvent. The reaction mixture was cooled down to room temperature and quenched with 10% HCl solution. The mixture was extracted with EtOAc, washed with brine and dried over MgSO₄. After removal of the solvent, the residue was recrystallized from an appropriate solvent or purified by silica gel column chromatography using 10% EtOAc/hexane. Three 1,3-dicarbonyl ligands namely, mdb (**23**), dmb (**24**) and mtb (**25**) are depicted as shown below.



mdb (23)



dmb (24)



mtb (25)

*4-methoxydibenzoylmethane (mdb)*⁴³ (23): Yellowish plate crystal (40%), m.p. 129 °C (benzene) (lit.¹³ m.p.126-127 °C), R_f 0.51 (EtOAc : hexane; 3 : 7). IR (KBr, cm^{-1}) 2970, 2830, 1610, 1520, 1470, 1260, 1230 and 1190; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 3.87 (3H, s), 6.79 (1H, s), 6.97 (2H, d, $J = 8.88$ Hz), 7.42-7.51 (3H, m), 7.93-7.99 (4H, m), 9.68 (2H,s); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 56.9 (1C), 94.0 (1C), 115.6 (2C), 127.1 (2C), 127.7 (2C), 128.6 (2C), 130.7 (1C), 133.8 (1C), 135.5 (1C), 163.4 (1C), 184.0 (1C) and 186.2 (1C).

*4,4'-dimethoxydibenzoylmethane (dmb)*⁴³ (**24**): Yellowish solid (42%), m.p. 113-114 °C (ether/hexane) (lit.¹³m.p.114-116 °C), R_f 0.35 (EtOAc : hexane; 3 : 7). IR (KBr, cm^{-1}) 2980, 2840, 1690, 1610, 1520, 1430, 1270, 1230 and 1180; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 3.85 (6H, s), 6.73 (1H, s), 6.91 (4H, d, $J = 8.81$ Hz), 8.04 (4H, d, $J = 8.93$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 55.5 (2C), 91.5 (1C), 113.4 (4C), 129.1 (4C), 131.3 (2C), 163.0 (2C) and 184.6 (1C).

*4-methoxy-4'-tert-butylidibenzoylmethane (mtb)*⁴⁴ (**25**): Yellowish plate crystal (38%), m.p. 215-217 °C (column chromatography), R_f 0.48 (EtOAc : hexane; 3 : 7). IR (KBr, cm^{-1}) 2970, 2830, 1610, 1520, 1470, 1260, 1230 and 1190; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 1.34 (9H, s), 3.85 (3H, s), 6.77 (2H, s), 6.95 (2H, dd, $J = 2.11$, 7.81 Hz), 7.50 (2H, dd, $J = 8.93$ Hz), 7.90 (2H, dd, $J = 8.81$ Hz), 7.95 (2H, d, $J = 8.93$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 3.85 (6H, s), 6.73 (1H, s), 6.91 (4H, d, $J = 8.81$ Hz), 8.04 (4H, d, $J = 8.93$ Hz) ; $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 31.5 (3C), 35.1 (1C), 55.5 (1C), 92.1 (1C), 114.0 (2C), 125.7 (2C), 128.3 (2C), 129.2 (2C), 131.3 (1C), 132.8 (1C), 155.9 (1C), 163.1 (1C), 184.2 (1C) and 185.8 (1C).

2.3.3 Syntheses of Schiff's base oxovanadium (IV) complexes

General procedure⁴⁵ :

To an aqueous ethanolic solution of Schiff's base ligand (1 mol-equiv) and $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (1 mol-equiv), a solution of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ was added. A crystalline solid formed immediately. The mixture was further refluxed for approximately 3 h and then cooled overnight. The solid was washed with H_2O , EtOH and Et_2O and dried *in vacuo*.

Bis(salicylaldehyde)-N,N'-ethylenediimine-Vanadium(IV)^{45,46} (**26**): Dark green solid (52%), m.p. 168 °C, R_f 0.42 (30% dichloromethane in ethanol). IR (KBr, cm^{-1}): 3500, 3020, 2920, 1630 and 994.

Bis(salicylaldehyde)-N,N'-trimethylenediimine-Vanadium(IV)^{34,47} (**27**): Orange solid (76%), dec. about 244 °C, R_f 0.79 (30% dichloromethane in ethanol). IR (KBr, cm^{-1}): 3500, 3050, 2920, 1630, 970 and 860.

*Bis(salicylaldehyde)-N,N'-o-phenylenediimine-Vanadium(IV)*⁴⁵ (**28**): Greenish solid (84%), dec. about 170 °C, R_f 0.79 (30% dichloromethane in ethanol). IR (KBr, cm^{-1}): 3500, 3010, 2890, 1620 and 988.

*Bis(2-hydroxyacetophenone)-N,N'-ethylenediimine-Vanadium(IV)*⁴⁷ (**29**): Black solid (78%), dec. about 290 °C, R_f 0.80 (30% dichloromethane in ethanol). IR (KBr, cm⁻¹): 3500, 3020, 2900, 1605 and 972.

Bis(o-vanillin)-N,N'-ethylenediimine-Vanadium(IV) (**30**): Brown solid (88%), dec. about 239 °C, R_f 0.14 (acetone). IR (KBr, cm⁻¹): 3500, 3020, 2960, 1605 and 994.

Bis(2-hydroxy-1-naphthaldehyde)-N,N'-ethylenediimine-Vanadium(IV)(**31**): Green solid (98%), dec. about 289 °C, R_f 0.73 (acetone). IR (KBr, cm⁻¹): 3500, 3010, 2910, 1620 and 988.

Bis(2-hydroxy-1-naphthaldehyde)-N,N'-o-phenylenediimine-Vanadium(IV) (**32**): Yellow-brown solid (90%), dec. about 255 °C, R_f 0.83 (30% dichloromethane in ethanol). IR (KBr, cm⁻¹): 3500, 3030, 2940, 1610 and 983.

N-salicylalidene-2-aminophenol-Vanadium(IV) (**33**): Dark-brown solid (95%), dec. about 261 °C, R_f 0.52 (acetone). IR (KBr, cm⁻¹): 3500, 3010, 2930, 1615 and 994.

N-salicylalidene-anthranilic acid-Vanadium(IV) (**34**): Black solid (20%), dec. about 298 °C, R_f 0.50 (ethanol). IR (KBr, cm⁻¹): 3500, 3030, 2940, 1605 and 984.

2.3.4 Syntheses of 1,3-dicarbonyl oxovanium (IV) complexes

General procedure²⁸ :

To the stirred mixture of 1,3-dicarbonyl ligands (2 mol-equiv) in methanol, VOSO₄·5H₂O (1 mol-equiv) in water was added under nitrogen atmosphere. After stirring for 10 min, aqueous sodium acetate (2 mol-equiv) was added over 10 min and stirring was continued for 1 h. Precipitated solid was filtered and washed with methanol and water, after drying *in vacuo*.

Bis(Acetylacetonato)-Vanadium(IV)^{14,28} (**35**): Grayish blue crystal (40%), dec. 256 °C, R_f 0.35 (dichloromethane). IR (KBr, cm⁻¹): 2980, 1600, 1372 and 998.

Bis(Benzoylacetonato)-Vanadium(IV) (**36**): Dark green solid (83%), dec. 219 °C, R_f 0.53 (dichloromethane). IR (KBr, cm⁻¹): 2990, 1600, 1520, 1495 and 995.

Bis(Dibenzoylmethanato)-Vanadium(IV) (**37**): Green solid (95%), dec. 250 °C, R_f 0.74 (dichloromethane). IR (KBr, cm⁻¹): 2980, 1600, 1530, 1480 and 995.

Bis(4-Methoxydibenzoylmethanato)-Vanadium(IV) (**38**): Green solid (71%), dec. 235 °C, R_f 0.48 (EtOAc : hexane; 3 : 7). IR (KBr, cm⁻¹): 2810, 1605, 1530, 1485 and 994.

Bis(4,4'-Dimethoxydibenzoylmethanato)-Vanadium(IV) (39): Green solid (99 %), dec. 238 °C, R_f 0.45 (dichloromethane). IR (KBr, cm^{-1}): 2840, 1600, 1520, 1470 and 988.

Bis(4-Methoxy-4'-tert-butylidibenzoylmethanato)-Vanadium(IV) (40): Green solid (77%), m.p. 89 °C, R_f 0.58 (EtOAc : hexane; 3 : 7). IR (KBr, cm^{-1}): 2960, 1600, 1540, 1495 and 995.

2.4 Oxidation of cycloalkanes catalyzed by oxovanadium (IV) complexes

Various factors affecting the oxidation reaction of cycloalkanes involved the amount of catalysts, substrates, carboxylic acids and solvents were thoroughly examined. Moreover, Schiff's Base or 1,3-dicarbonyl oxovanadium (IV) complexes was used as a catalyst to compare their efficiency in this alkane oxidation.

2.4.1 General procedure for the oxidation of cycloalkanes⁴⁸

Catalyst (0.25 mmol), cycloalkane (5 or 20 mmol), zinc grit (20 mmol) and acetic acid (2.3 mL) and pyridine (28 mL) were placed in an Erlenmeyer flask. The mixture was stirred continuously for 16 h at room temperature and atmospheric pressure. After the reaction was proceeded for a designed period of time, 1 mL of the reaction mixture was acidified with cold 25% H_2SO_4 and extracted with diethyl ether. The combined extracts were washed with saturated solution of NaHCO_3 . The organic layer was dried over anhydrous Na_2SO_4 and analyzed by GC with the addition of an exact amount of an appropriate internal standard.

2.5 Optimum conditions study for cycloalkane oxidation

2.5.1 Effect of the amount of catalysts

The oxidation reaction of cyclohexane was carried out according to the general procedure, but the amount of (28) was varied to 0.10, 0.25, 0.50, 0.75 and 1.00 mmol.

2.5.2 Effect of the amount of substrate

The oxidation reaction was carried out in the same fashion as general procedure, but the amount of cyclohexane was changed to 5, 10, 20, 30 and 50 mmol.

2.5.3 Effect of solvents

The oxidation reaction of cyclohexane was carried out according to the general procedure, but the varied solvents (pyridine, 2-picoline, 3-picoline, 4-picoline,

acetone, dimethylsulfoxide, cyclohexane, *tert*-butanol and acetonitrile) and a solvent mixture (pyridine and varied solvents; 1: 1 v/v) were experimented. The amount of pyridine (mL) and acetonitrile (mL) was varied with a ratio of 28.0: 0, 14.0: 14.0, 7.0: 21.0, 3.0: 25.0 and 0: 28.0.

2.5.4 Effect of zinc

The oxidation reaction of cyclohexane was carried out as that described in the general procedure, but Zn powder was used instead of Zn grit.

2.5.5 Effect of carboxylic acids

The oxidation reaction of cyclohexane was carried out according to the general procedure, but the varied carboxylic acids (formic acid, butyric acid, pivalic acid, chloroacetic acid, dichloroacetic acid, 2-chloropropionic acid and 2-picolinic acid) were employed to replace acetic acid. The effect of the amount of acetic acid was further studied by deviating to 0, 1.0, 2.3, 3.0 and 5.0 mL.

2.6 Effect of Schiff's base oxovanadium (IV) complexes on reactivity of cyclododecane oxidation

Schiff's base oxovanadium (IV) complexes, **(26)-(34)** were employed as a catalyst in cyclododecane oxidation reaction using reaction conditions described in the general procedure.

2.7 Effect of 1,3-dicarbonyl oxovanadium (IV) complexes on reactivity of cyclododecane oxidation

Using the same general procedure, cyclododecane was oxidized using 1,3-dicarbonyl oxovanadium (IV) complexes, **(35)-(40)** as catalyst.

2.8 Comparative study of Schiff's base and 1,3-dicarbonyl oxovanadium (IV) complexes

According to the general oxidation procedure, equimolar amount (0.25 mmol) of Schiff's base oxovanadium (IV) complexes **(26)-(34)** and 1,3-dicarbonyl oxovanadium (IV) complexes, **(35)-(40)** were used as a catalyst and cyclododecane (5 mmol) was used as a substrate in the reaction.

2.9 Comparative kinetic study on the reaction rate of cyclohexane oxidation

The general oxidation procedure of cyclohexane utilizing $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and oxovanadium complexes (26), (28), (34), (35), (38) and (40) as catalysts was carried out. At different reaction time proceeded (30, 60, 120, 240, 360 and 480 min), an aliquot from the reaction mixture was taken, worked up and analyzed by GC.

2.10 Chemoselectivity study

Following the general oxidation procedure, absolute ethanol, isopropanol, ethylene glycol, hydroquinone and derivatives, triethylamine, aniline, *N,N'*-dimethylaniline, *N,N'*-dimethylacetamide, 2-mercaptoethanol, benzenethiol, diphenylsulfide, anisole, methyl benzoate, ethylene glycol, anisole, bibenzyl, triethylamine, 2-mercaptoethanol, ascorbic acid and triphenylphosphine were separately added as a co-substrate to the oxidation reaction of cyclododecane.

2.11 Comparative study on relative reactivity of cycloalkane in oxidation reactions

Two competitive cycloalkanes; cyclohexane and either cyclopentane, cycloheptane, cyclooctane or cyclododecane, respectively, were oxidized employing the general oxidation procedure.

2.12 Oxidation reaction of cyclohexene

According to the same manner as previously described, cyclohexene was used as a substrate instead of cyclohexane.

2.13 Competitive studies on the oxidation of cycloalkane and cycloalkene

Following the general oxidation procedure, both cyclohexane and cyclohexene were used as substrates in competitive oxidation reactions.

2.14 Competitive studies on the oxidation of cycloalkane and alcohol

The oxidation reaction was carried out in the same fashion as general procedure, but cyclohexane and cyclooctanol or cyclooctane and cyclohexanol were used as substrate.

2.15 Comparative study of Schiff's base and 1,3-dicarbonyl oxovanadium (IV) complexes using *tert*-butyl hydroperoxide as an oxidant

The oxidation reaction of cyclooctane was carried out as described in the general procedure. *tert*-Butyl hydroperoxide (TBHP) as an oxidising agent was added in both Schiff's base oxovanadium (IV) complex, **(28)** and 1,3-dicarbonyl oxovanadium (IV) complex, **(40)** systems. This reaction aliquot was taken, worked up at 24, 48 and 72 h and analyzed by GC.



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CHAPTER III

RESULTS AND DISCUSSION

This research was mainly focused on one of industrially important processes, the oxidation of cycloalkanes, especially cyclohexane, cyclooctane and cyclododecane to their corresponding ketones and alcohols. This study is composed of utilizing either a Schiff's base or a 1,3-dicarbonyl oxovanadium (IV) complex as a catalyst, an oxidant in a reaction medium. Cyclohexane is used as a substrate for reaction conditions optimization. A mixture of pyridine and acetic acid was mostly used as a solvent.

3.1 Syntheses and characterization of ligands and their complexes

3.1.1 Schiff's base ligands and Schiff's base oxovanadium (IV) complexes

Nine Schiff's base ligands (**14**)-(22) were synthesized using condensation reaction by combining aldehyde or ketone with appropriate primary diamines according to the literature procedure.⁴⁹ Their identities were checked by IR and NMR techniques prior to use for synthesizing Schiff's base oxovanadium (IV) complexes (**26**)-(34). IR spectra of these complexes showed a characteristic absorption band in the range of 1630-1650 cm^{-1} attributable to azomethine group (C=N) vibration. For free ligands, this band occurs at higher frequencies ~ 10 -15 cm^{-1} space which was belonged to C=N.⁵⁰ Moreover, IR spectra of synthesized complexes showed V=O stretching vibration frequencies around 964 to 995 cm^{-1} .⁵¹

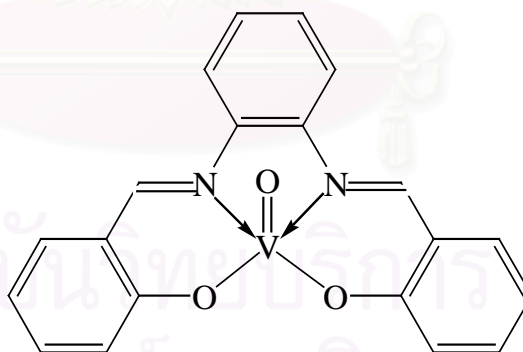
3.1.2 1,3-Dicarbonyl ligands and 1,3-dicarbonyl oxovanadium (IV) complexes

Three dibenzoylmethane (1,3-dicarbonyl) ligands (**23**)-(25) were prepared according to the method reported by Swamer *et al.*⁴¹ 1,3-Dicarbonyl compounds were prepared by using substituted acetophenones and ethyl benzoate or ethyl benzoate derivatives. Their purities were analyzed by IR and NMR techniques prior to use for synthesizing 1,3-dicarbonyl oxovanadium (IV) complexes (**35**)-(40). IR spectra of complexes showed V=O stretching frequencies around 995 to 1005 cm^{-1} .⁵²

3.2 Study on the optimum conditions for the oxidation of cycloalkanes

3.2.1 Effect of the amount of catalysts

The amount of catalyst was one of the crucial parameters that needed to be evaluated. Bis(salicylaldehyde)*N,N'*-*o*-phenylenediimine-vanadium (IV) (**28**) was selected as a catalyst and cyclohexane (**41**) was used as a substrate. It was clearly seen that in the absence of (**28**), the oxidation did not occur. The final yield was depended on the amount of catalyst used. The sample was taken at 2 and 16 h interval. The first taken time was performed to observe how fast the oxidation could take place, while the last one was done to determine the total amount of the desired products gained and the selectivity of the reaction. It was found that using catalyst (**28**) 0.25 mmol (entry 2) gave the highest reaction yield and highest selectivity of ketone to alcohol ratio compared with other entries. When the amount of (**28**) used was less or more than 0.25 mmol, the reaction rate decreased. It was also found that the excess or lack of (**28**) provided poor results. Therefore, the amount of a suitable catalyst has an important role to the amount of products occurred in this oxidation reaction. The reason was probably because the excess of catalyst used may cause side oxidation reactions occur competitively with cyclohexane oxidation. For instance, the decomposition of intermediate responsible for alkane oxidation occurred rapidly or the oxidation of solvent took place parallelly.⁵³ The results are presented in Table 3.1 and Fig 3.1.



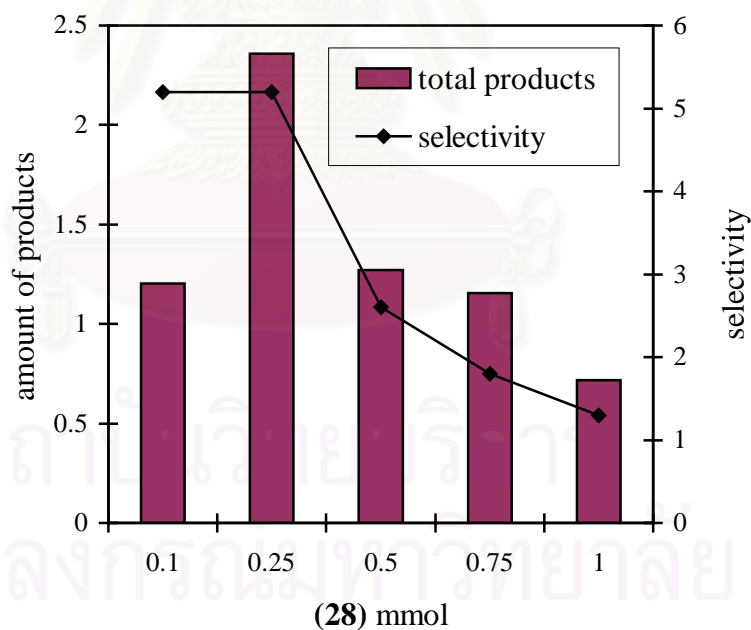
Bis(salicylaldehyde)*N,N'*-*o*-phenylenediimine-vanadium (IV) (**28**)

Table 3.1 Effect of the amount of catalyst **(28)** on cyclohexane oxidation^a

Entry	(28) (mmol)	Products (mmol)					(42)/(43)
		2 h		16 h			
		(42)	(43)	(42)	(43)	(42)+(43)	
1	0.10	0.857	0.155	1.008	0.195	1.203	5.2
2	0.25	0.963	trace	1.981	0.378	2.359	5.2
3	0.50	0.643	0.266	0.916	0.355	1.271	2.6
4	0.75	0.369	0.227	0.738	0.418	1.156	1.8
5	1.00	trace	trace	0.400	0.317	0.717	1.3

a. Reaction conditions: cyclohexane (20 mmol), **(28)** (varied), pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(42) cyclohexanone **(43)** cyclohexanol

**Fig 3.1** Effect of the amount of catalyst **(28)** on cyclohexane oxidation at 16 h

3.2.2 Effect of the amount of substrates

The effects of amount of substrate (cyclohexane) were examined. The results are summarized in Table 3.2 and Fig 3.2. It was clearly seen that the amount of the desired products (cyclohexanone and cyclohexanol) increased when the amount of the substrate used increased. Among various amounts of cyclohexane studied, using cyclohexane 20 mmol gave the highest selectivity of ketone to alcohol ratio compared with other amount tested. Moreover, it was found that using cyclohexane 30 or 50 mmol did not give significantly different amount of products. Thus, the amount of cyclohexane 20 mmol was kept constant for further optimization condition study.

Table 3.2 Effect of the amount of cyclohexane in oxidation reaction^a

(41) (mmol)	Products (mmol) at 16 h			(42)/(43)
	(42)	(43)	(42)+(43)	
5	0.593	trace	0.593	-
10	0.715	trace	0.715	-
20	1.986	0.381	2.367	5.2
30	2.037	0.431	2.468	4.7
50	2.196	0.601	2.797	3.7

a. Reaction conditions: cyclohexane (varied), (28) (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(41) cyclohexane (42) cyclohexanone (43) cyclohexanol

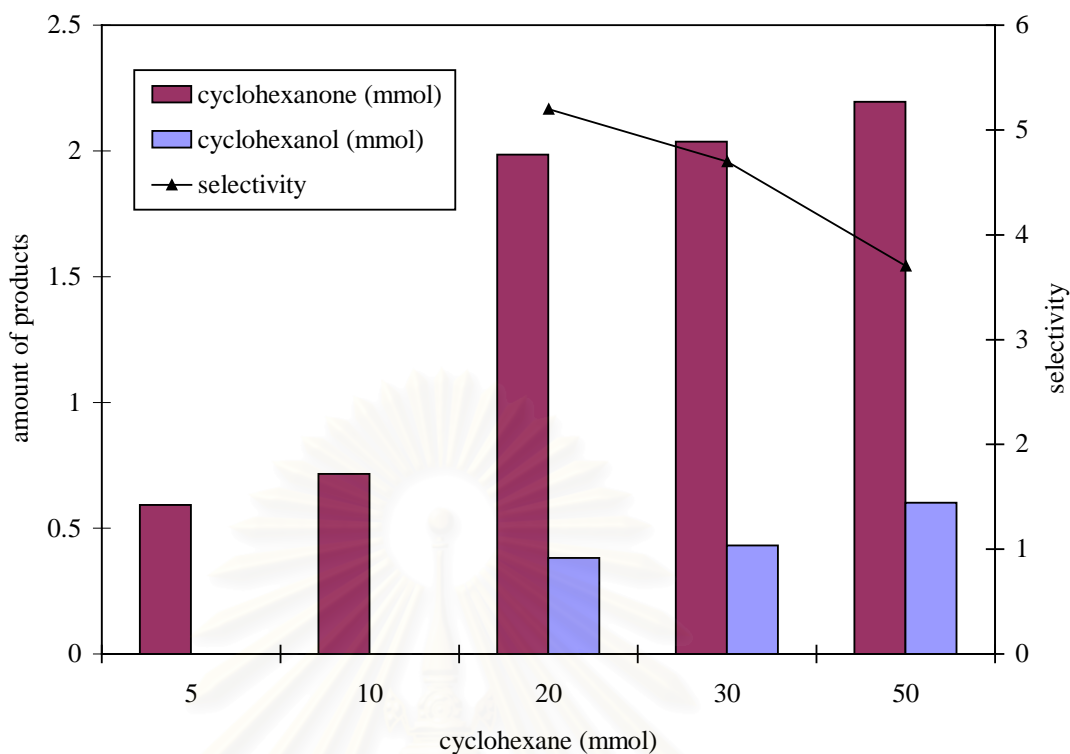


Fig 3.2 Effect of the amount of cyclohexane in the oxidation reactions

3.2.3 Effect of solvents

In this study, the solvent that could provide the homogenous reaction was required. From the experiments described above, pyridine was the first solvent chosen as a reaction medium because it could dissolve both oxovanadium (IV) complex catalyst and organic substrate. Other solvents were also selected to examine whether they can replace pyridine in this oxidation reaction. The effects of solvent are shown in Table 3.3 and Fig 3.3.

Table 3.3 Effect of solvents on the oxidation reaction^a

Entry	Solvent	Products (mmol) at 16 h			(42)/(43)
		(42)	(43)	(42)+(43)	
1	Pyridine	1.981	0.378	2.359	5.2
2	2-Picoline	0.213	trace	0.213	-
3	3-Picoline	0.607	0.165	0.772	3.7
4	4-Picoline	0.633	0.194	0.827	3.3
5	Acetone	0	trace	trace	-
6	Dimethylsulfoxide	trace	trace	trace	-
7	Cyclohexane	0	0	0	-
8	<i>tert</i> -Butanol	0	0	0	-
9	Acetonitrile	0	0	0	-

a. Reaction conditions: cyclohexane (20 mmol), (**28**) (0.25 mmol), solvent (28 mL) acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(42) cyclohexanone (43) cyclohexanol

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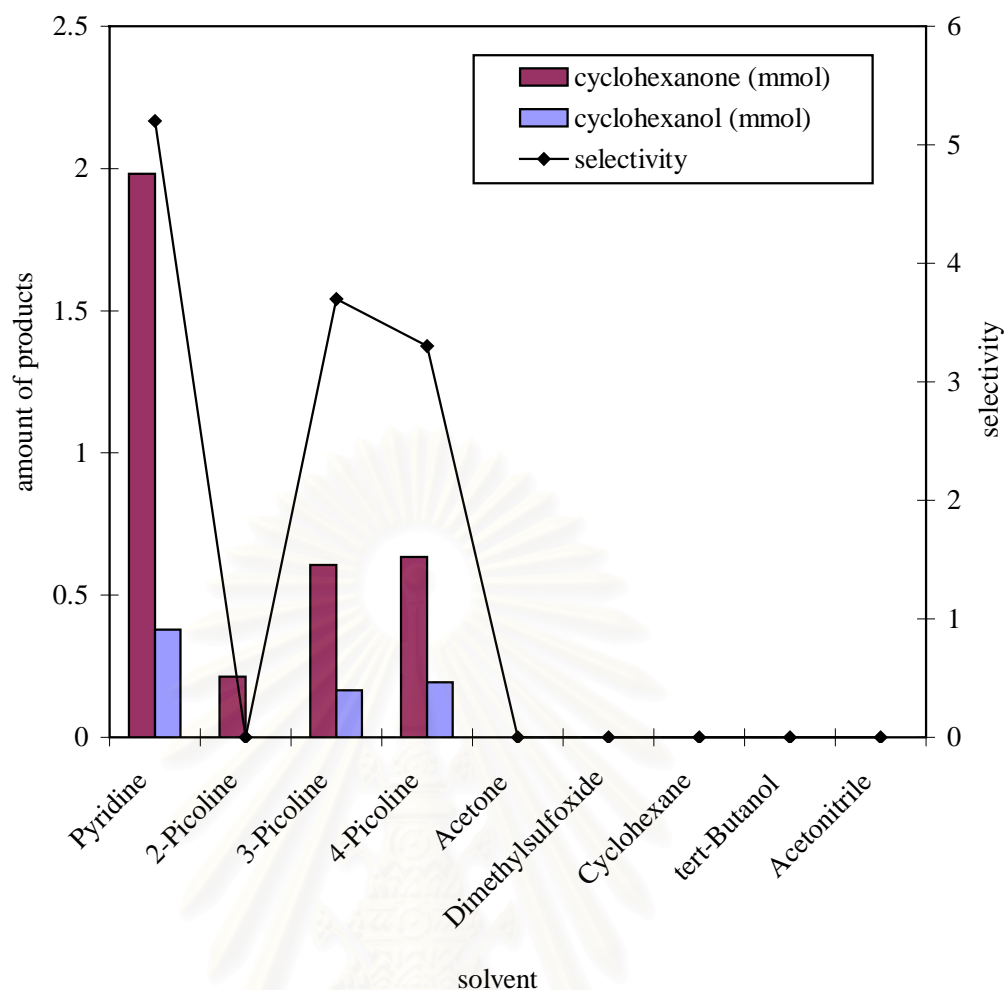


Fig 3.3 Effect of solvents on the oxidation reaction

2-, 3- and 4-Picolines, acetone, dimethylsulfoxide, cyclohexane, *tert*-butanol and acetonitrile were examined whether they could replace pyridine in this oxidation reaction. It was found that the amount of desired products (cyclohexanone and cyclohexanol) was significantly less when the reaction media was altered from pyridine to 2-,3- and 4-picolines. When employing acetone or dimethylsulfoxide as a solvent, the oxidation reaction was also found to produce a small amount of the desired products. In the case of using cyclohexane, *tert*-butanol and acetonitrile the oxidation reaction of cyclohexane seemed not to take place. Unwanted side reactions may rapidly occur instead. The possible reaction was perhaps involved the decomposition of species containing real

oxidizing power.⁵⁴ This study clearly showed the necessity of pyridine as a solvent under these studied conditions.

Since the high cost of pyridine and its toxicity, the attempts to reduce the amount of pyridine were investigated. The variation of the amount of co-solvent 14 mL and pyridine 14 mL is tabulated in Table 3.4 and Fig 3.4.

Table 3.4 Effect of co-solvent on cyclohexane oxidation^a

Entry	Pyridine: Co-solvent (14 mL: 14 mL)	Products (mmol) at 16 h			(42)/(43)
		(42)	(43)	(42)+(43)	
1	Pyridine	1.981	0.378	2.359	5.2
2	2-Picoline	0.897	0.317	1.214	2.8
3	3-Picoline	0.969	0.284	1.253	3.4
4	4-Picoline	1.116	0.291	1.407	3.8
5	Acetone	1.636	0.513	2.149	3.2
6	Dimethylsulfoxide	trace	trace	-	-
7	Cyclohexane	0.953	0.582	1.535	1.6
8	<i>Tert</i> -Butanol	0.797	0.167	0.964	4.8
9	Acetonitrile	2.024	0.482	2.506	4.2

a. Reaction conditions: cyclohexane (20 mmol), (28) (0.25 mmol), solvent (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(42) cyclohexanone (43) cyclohexanol

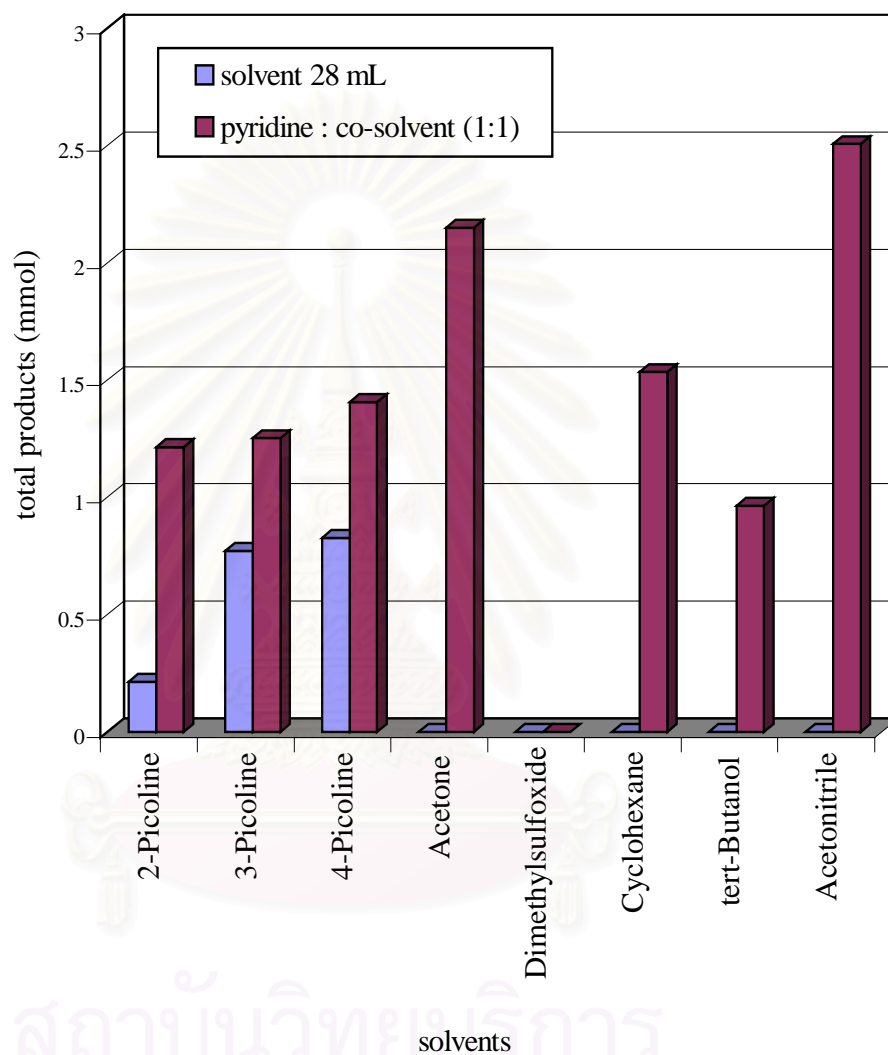


Fig 3.4 Effect of co-solvents

It was found that when pyridine 14 mL was used as a counterpart solvent with other co-solvents, the amount of cyclohexanone and cyclohexanol was increased compared with the reaction using only co-solvent media without pyridine. In addition, the use of pyridine 14 mL and acetonitrile 14 mL gave the highest yield. The further study on the variation of the amount of acetonitrile and pyridine is presented in Table 3.5.

Table 3.5 Variation of the amount of pyridine and acetonitrile in the oxidation reaction^a

Entry	Pyridine:Acetonitrile (mL : mL)	Products (mmol) at 16 h			(42)/(43)
		(42)	(43)	(42)+(43)	
1	28.0 : 0	1.981	0.378	2.359	5.2
2	14.0 : 14.0	2.024	0.482	2.506	4.2
3	7.0 : 21.0	1.706	0.513	2.219	3.3
4	3.0 : 25.0	0.849	0.554	1.403	1.5
5	0 : 28.0	0	0	0	-

a. Reaction conditions: cyclohexane (20 mmol), (28) (0.25 mmol), solvent (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(42) cyclohexanone (43) cyclohexanol

From this table, it was observed that using the reaction medium containing the ratio of pyridine to acetonitrile 1:1 (entry 2) the reaction yielded the highest amount of product compared with other ratios tested. Taking to the consideration from selectivity, using pyridine 28 mL still gave the highest selectivity of ketone to alcohol production.

3.2.4 Effects of zinc

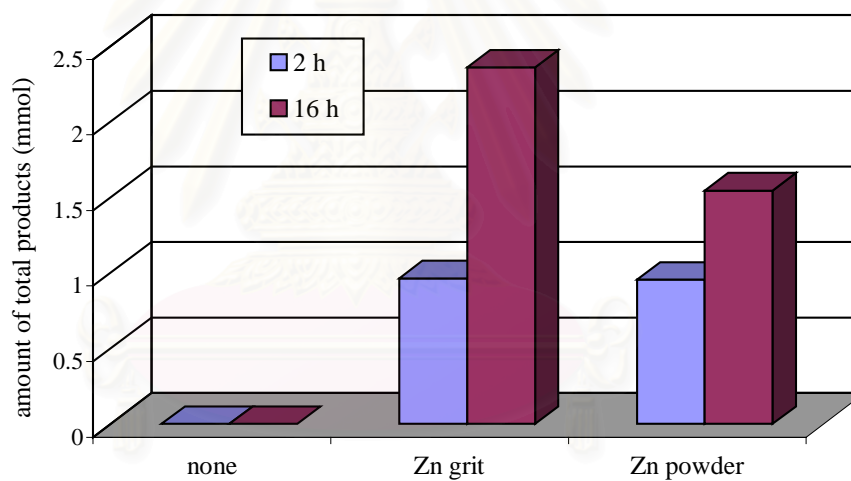
The system comprising of zinc and oxygen will commonly be known to produce superoxide which was believed to be the real oxidant in this reaction.⁵⁵ The type of zinc used was therefore another influent factor to be considered in this oxidation system. The results are presented in Table 3.6 and Fig 3.5. It was observed that the products did not occurred in the absence of zinc grit. By using zinc powder, the amount of cyclohexane at 2 h did not show any difference compared with using zinc grit. Nevertheless, the amount of final yield at 16 h was less than the other one. Therefore, zinc grit was an important component in this system. It should be noted that although, zinc powder had surface active area more than zinc grit, this oxidation reaction using oxovanadium as a catalyst seemed not to be affected.

Table 3.6 Effect of zinc in the oxidation reaction^a

Zinc	Products (mmol)					(42)/(43)
	2 h		16 h			
	(42)	(43)	(42)	(43)	(42)+(43)	
None	0	0	0	0	0	-
Grit	0.963	trace	1.981	0.378	2.359	5.2
Powder	0.955	trace	1.545	trace	1.545	-

a. Reaction conditions: cyclohexane (20 mmol), (28) (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), zinc (varied) (1.31 g) at RT

(42) cyclohexanone (43) cyclohexanol

**Fig 3.5** Effect of zinc in the oxidation reaction

3.2.5 Effect of carboxylic acid

Carboxylic acid was another crucial parameter in this oxidation reaction. Preliminary studies revealed that acetic acid profoundly affected on cyclohexane oxidation reactions. Cyclohexanone and cyclohexanol did not occur in the absence of acetic acid. The variation of amount of acetic acid was studied. The most appropriate amount of acetic acid was found to be 2.3 mL (the highest yield observed). The extra or less of acetic acid gave comparable or poor results. Consequently, the amount of proper acid has also a notable part to the amount of product occurred in this oxidation reaction. Owing to the dissolved time period of zinc grit by acid, its effect gave the different amount of products. The results are presented in Table 3.7 and Fig 3.6.

Table 3.7 Effect of the amount of acetic acid on cyclohexane oxidation reaction^a

Acetic acid (mL)	Products (mmol) at 16 h		
	(42)	(43)	(42)+(43)
0	0	0	0
1.0	0.429	0.184	0.613
2.3	1.981	0.378	2.359
3.0	1.850	0.358	2.208
5.0	1.737	0.255	1.992

a. Reaction conditions: cyclohexane (20 mmol), (**28**) (0.25 mmol), pyridine (28 mL), acetic acid (varied), zinc grit (1.31 g) at RT
(**42**) cyclohexanone (**43**) cyclohexanol

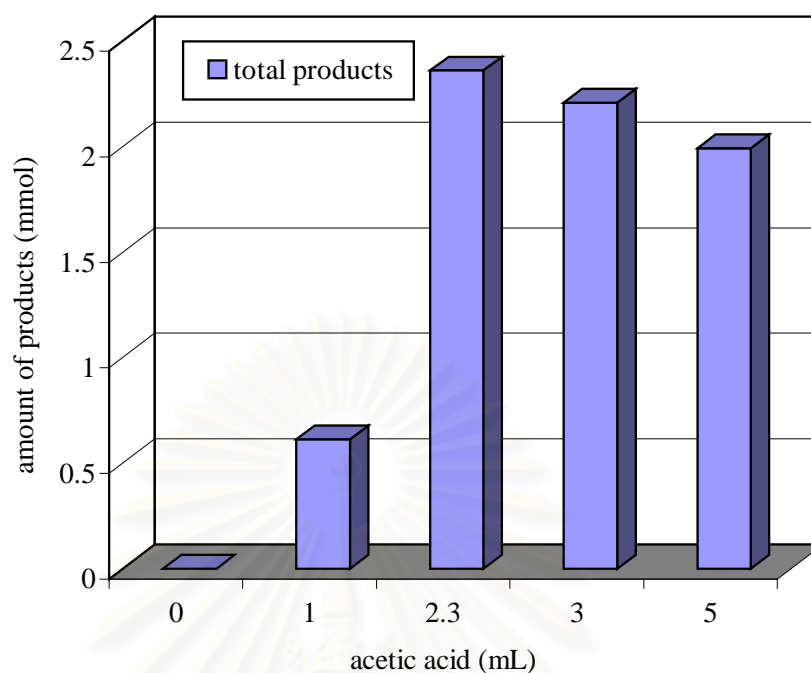


Fig 3.6 Effect of the amount of acetic acid on cyclohexane oxidation reaction

Considering from the amount of products obtained, the search for other appropriate carboxylic acids were tried whether they can take the place of acetic acid in this oxidation reaction. It was presented that acetic acid was still a suitable carboxylic acid in this system among various carboxylic acids studied judged from the highest yield and selectivity (both cyclohexanone and cyclohexanol) at 16 h. The effects of carboxylic acids are shown in Table 3.8 and Fig 3.7.

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Table 3.8 Effect of various carboxylic acids on the oxidation reaction^a

Carboxylic acid	Products (mmol)					
	2 h		16 h			
	(42)	(43)	(42)	(43)	(42)+(43)	(42)/(43)
None	0	0	0	0	-	-
Formic acid	trace	0	1.042	trace	1.042	-
Acetic acid	0.963	trace	1.981	0.378	2.359	5.2
Butyric acid	trace	trace	0.761	trace	0.761	-
Pivalic acid	trace	trace	1.195	trace	1.195	-
Chloroacetic acid	0.981	0.259	1.043	0.271	1.314	3.8
Dichloroacetic acid	trace	trace	0.125	trace	0.125	-
2-Chloropropionic acid	trace	trace	0.914	trace	0.914	-
2-Picolinic acid	trace	trace	1.272	trace	1.272	-

a. Reaction conditions: cyclohexane (20 mmol), **(28)** (0.25 mmol), pyridine (28 mL), carboxylic acid (40 mmol), zinc grit (1.31 g) at RT

(42) cyclohexanone **(43)** cyclohexanol

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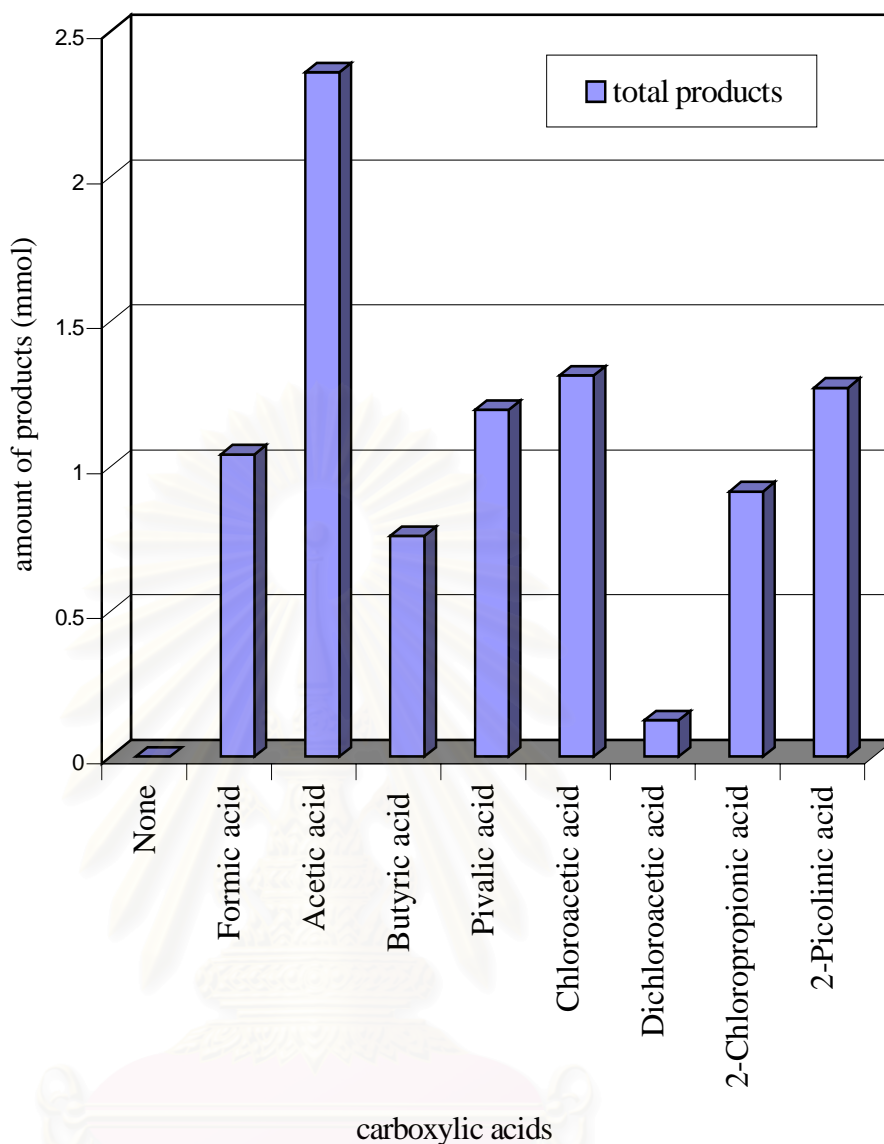
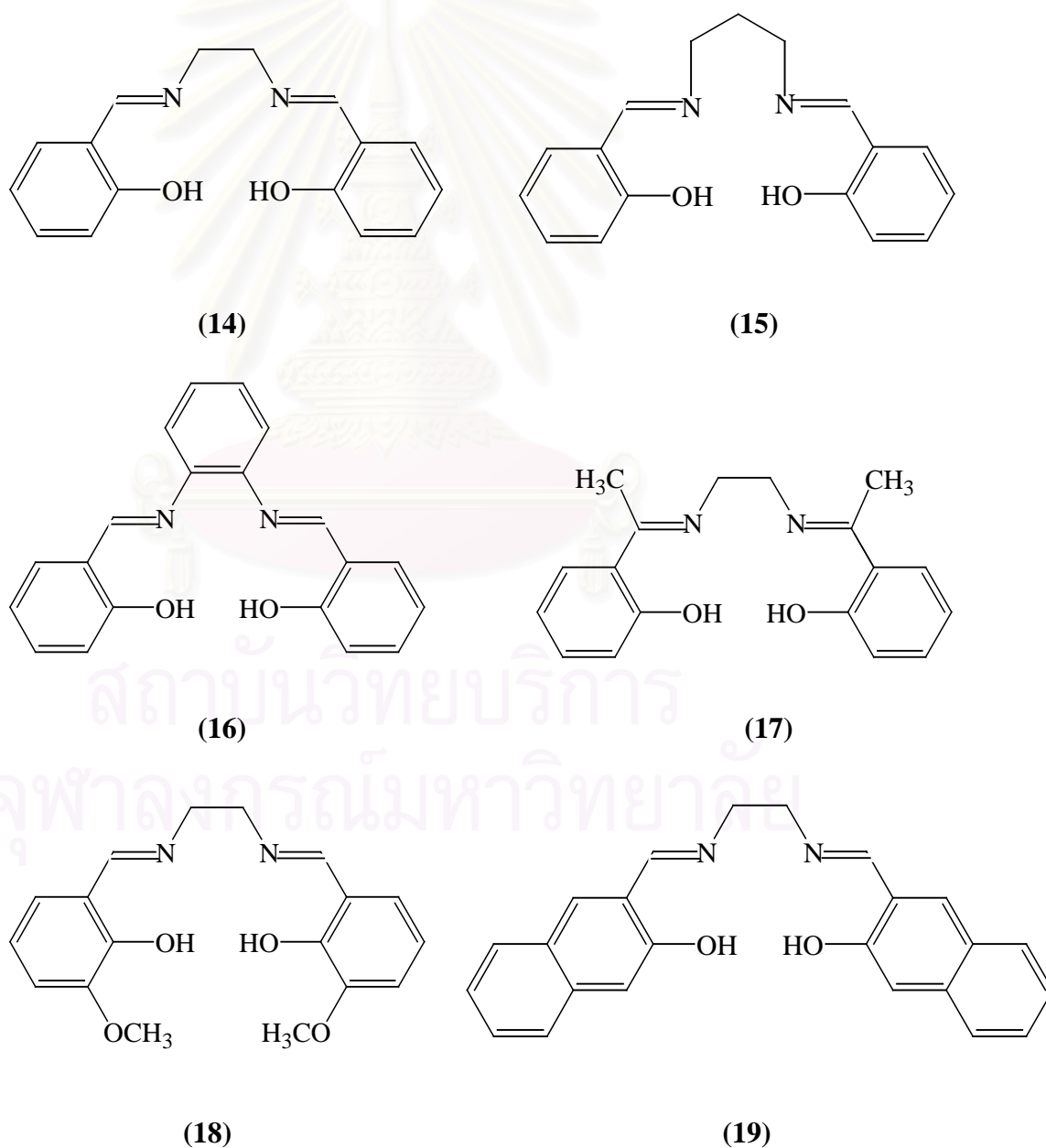


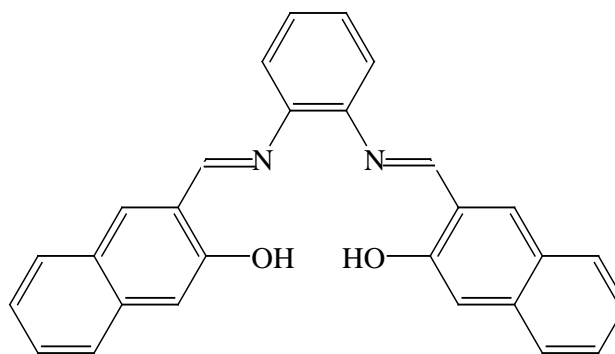
Fig 3.7 Effect of carboxylic acid on the oxidation reaction

3.3 Effect of Schiff's base structure on reactivity of cyclododecane oxidation

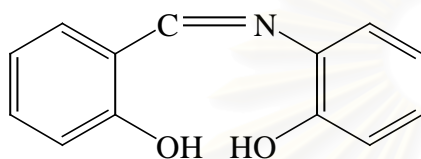
This section focused on the effects of Schiff's base ligands on the oxidation reaction. Cyclododecane (**44**) was chosen for this study because it could give a good mass balance with respect to the hydrocarbon and its oxidation products, cyclododecanone (**45**) and cyclododecanol (**46**). The oxidation of cyclododecane was examined to observe both the rate of the reaction (observed at 2 h) and the amount of the desired products obtained

(observed at 16 h). Nine Schiff's base ligands, namely, bis(salicylaldehyde)*N,N'*-ethylenediimine (**14**), bis(salicylaldehyde)*N,N'*-trimethylenediimine (**15**), bis(salicylaldehyde)*N,N'*-*o*-phenylenediimine (**16**), bis(2-hydroxyacetophenone)*N,N'*-ethylenediimine (**17**), bis(*o*-vanillin)*N,N'*-ethylenediimine (**18**), bis(2-hydroxy-1-naphthaldehyde)*N,N'*-ethylenediimine (**19**), bis(2-hydroxy-1-naphthaldehyde)*N,N'*-*o*-phenylenediimine (**20**), *N*-salicylalidene-2-aminophenol (**21**), *N*-salicylalidene-anthranilic acid (**22**) were complexed with oxovanadium (IV) to gain Schiff's base oxovanadium (IV) complexes (**26**)-(34), respectively. The effects of various Schiff's base oxovanadium (IV) complexes on cyclododecane oxidation are presented in Table 3.9 and Fig 3.8.

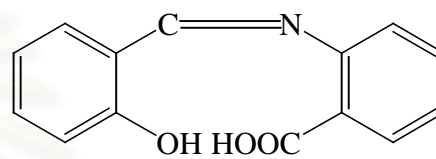




(20)



(21)



(22)

Table 3.9 Effect of various Schiff's base oxovanadium (IV) complexes on cyclododecane oxidations^a

Schiff's base oxovanadium (IV) complexes	% yield at 16 h			% Mass balance
	(44)	(45)	(46)	
(26)	89.69	10.70	trace	100.39
(27)	89.06	11.34	trace	100.40
(28)	88.07	11.10	trace	99.17
(29)	90.65	9.95	trace	100.60
(30)	89.66	8.37	trace	98.03
(31)	92.84	8.59	trace	101.43
(32)	86.85	11.61	trace	98.46
(33)	90.80	9.82	trace	100.62
(34)	86.68	12.41	trace	99.09

a. Reaction conditions: cyclododecane (5 mmol), Schiff's base oxovanadium (IV) complex (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(44) cyclododecane (45) cyclododecanone (46) cyclododecanol

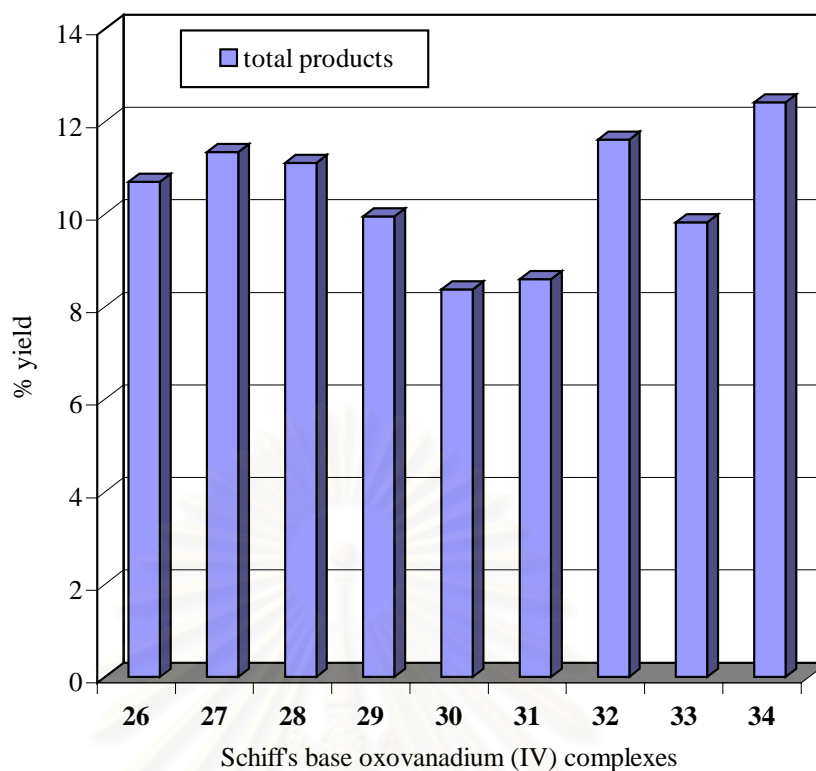


Fig 3.8 Effect of different Schiff's base oxovanadium (IV) complexes on cyclododecane oxidation

From Table 3.9 and Fig 3.8, it could be observed that all nine Schiff's base oxovanadium (IV) complexes could be employed as a catalyst in this oxidation system. Cyclododecanone was a major product while cyclododecanol was found to be produced in a small amount. Considering the structures of all Schiff's base ligands, each structure of Schiff's base ligand gave different yields. Among them, ligands that provided good results were ligands (26), (27), (28), (32) and (34).

3.4 Effect of 1,3-dicarbonyl compounds on reactivity of cyclododecane oxidations

Like Schiff's base ligands, 1,3-dicarbonyl compounds were another group of ligands used to complex with oxovanadium (IV) and used as a catalysts in cyclododecane oxidation reactions. In this study, six 1,3-dicarbonyl ligands, namely, acetylacetone (**acac**), benzoyl acetone (**bza**), dibenzoyl methane (**dbm**), 4-methoxydibenzoyl methane (**mdb**) (23), 4,4'-dimethoxydibenzoyl methane (**dmb**) (24) and 4-methoxy-4'-*tert*-butyl-dibenzoyl methane (**mtb**) (25) were examined. Six 1,3-dicarbonyl compounds were complexed with oxovanadium (IV) to yield 1,3-dicarbonyl oxovanadium (IV) complexes (35)-(40),

respectively. The effects of various 1,3-dicarbonyl oxovanadium (IV) complexes on cyclododecane oxidations are presented in Table 3.10 and Fig 3.9.

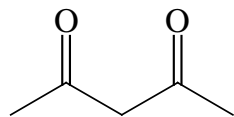
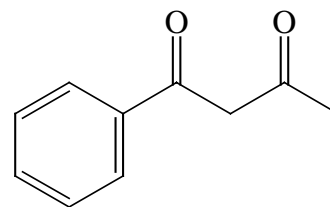
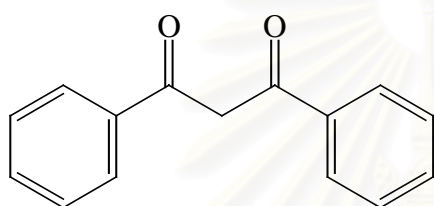
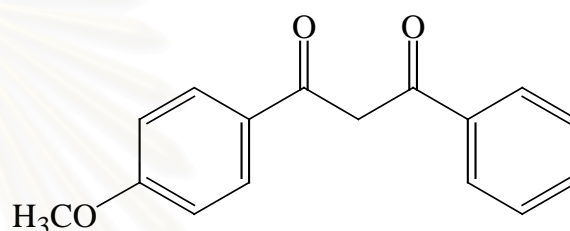
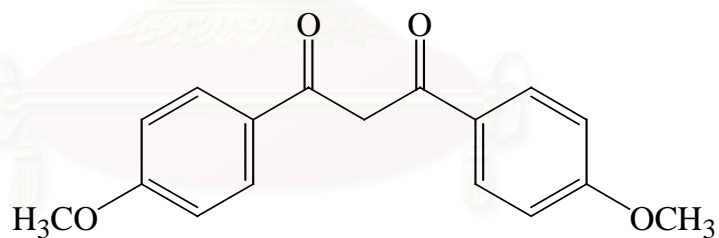
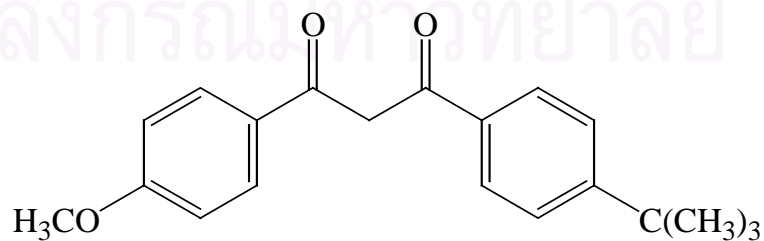
**(acac)****(bza)****(dbm)****mdb (23)****dmb (24)****mtb (25)**

Table 3.10 Effect of different 1,3-dicarbonyl oxovanadium (IV) complexes on cyclododecane oxidations^a

1,3-Dicarbonyl oxovanadium (IV) complexes	% yield at 16 h			% Mass balance
	(44)	(45)	(46)	
(35)	83.51	12.36	3.51	99.38
(36)	84.54	12.83	2.60	99.97
(37)	82.57	13.23	3.22	99.02
(38)	82.97	13.55	3.06	99.58
(39)	82.54	15.49	3.81	101.84
(40)	84.40	13.63	3.87	101.90

a. Reaction conditions: cyclododecane (5 mmol), 1,3-dicarbonyl oxovanadium (IV) complex (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL) zinc grit (1.31 g) at RT

(44) cyclododecane (45) cyclododecanone (46) cyclododecanol

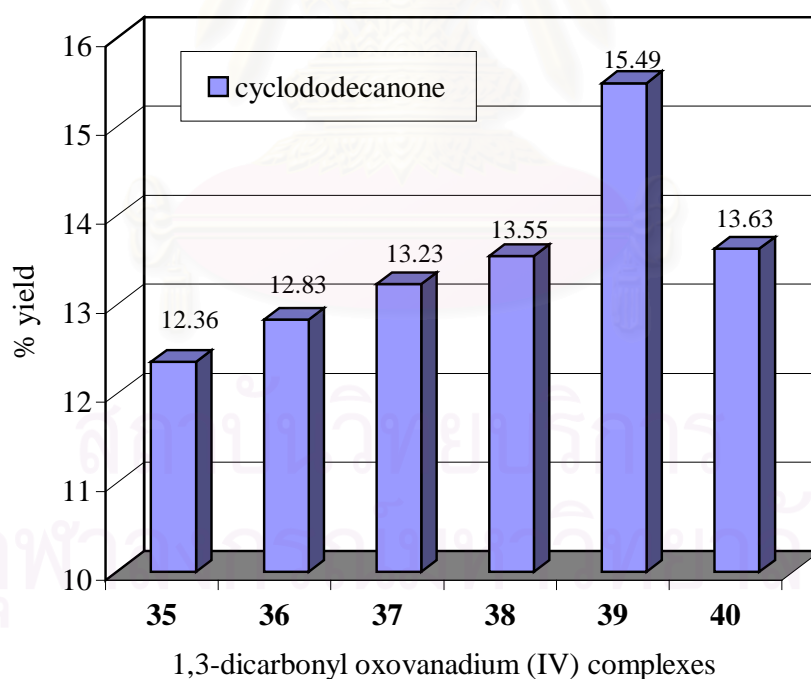


Fig 3.9 Effect of different 1,3-dicarbonyl oxovanadium (IV) complexes on cyclododecane oxidations

From the above data, it was found that complex **(39)** which contained ligand **dmb (24)** gave superior oxidation product yield. It was clearly observed that the electron donating groups that were able to donate electron to metals make possible to form the appropriate metal complex and activate alkane oxidation much faster. As indicated in Table 3.10 and Fig 3.9, it showed that the amount of cyclododecanone at 16 h increased when 1,3-dicarbonyl ligand bearing a more efficient electron donating group.

3.5 Comparative study on the reactivity of Schiff's base and 1,3-dicarbonyl oxovanadium (IV) complexes

In order to search for an appropriate oxovanadium (IV) complex that could catalyze the oxidation reaction converting cyclododecane to cyclododecanone and cyclododecanol selectively, various Schiff's base and 1,3-dicarbonyl oxovanadium (IV) complexes were examined. The results are presented in Table 3.11. Among nine Schiff's base oxovanadium (IV) complexes **(26)-(34)** and six 1,3-dicarbonyl oxovanadium (IV) complexes **(35)-(40)** chosen as catalyst in this oxidation reaction, it was observed that complexes **(26)-(40)** exhibited promising ability as catalyst for oxidation of saturated hydrocarbons. It could clearly be seen that cycloalkane could be oxidized in the presence of catalysts. Cyclododecanone was formed with significant amount observed at 2 h using every oxovanadium (IV) complex, except for **(16)**. Considering about reaction selectivity, it could be noticed that Schiff's base oxovanadium (IV) complexes provided better selectivity. The amount of cyclododecanone occurred smoothly while the amount of cyclododecanol occurred only in trace amount both at 2 and 16 h. On the other hand, from a view point of a total percentage yield, 1,3-dicarbonyl oxovanadium (IV) complexes were found to assist to produce more total products than Schiff's base oxovanadium (IV) complexes (see Fig 3.10).

Table 3.11 The results of cyclododecane oxidation catalyzed by various oxovanadium (IV) complexes^a

Oxovanadium (IV) complexes	Products (% yield)						
	2 h		16 h				
	(45)	(46)	(45)	(46)	(45)+(46)	(45)/(46)	% Mass balance
(26)	6.01	trace	10.70	trace	10.70	-	100.39
(27)	5.69	trace	11.34	trace	11.34	-	100.40
(28)	8.27	trace	11.10	trace	11.10	-	99.17
(29)	trace	0	9.95	trace	9.95	-	100.60
(30)	4.45	trace	8.37	trace	8.37	-	98.03
(31)	4.85	trace	8.59	trace	8.59	-	101.43
(32)	8.24	trace	11.61	trace	11.61	-	98.46
(33)	7.46	trace	9.82	trace	9.82	-	100.62
(34)	8.25	trace	12.41	trace	12.41	-	99.09
(35)	5.58	2.57	12.36	3.51	15.87	3.5	99.38
(36)	8.06	2.23	12.83	2.60	15.43	4.9	99.97
(37)	10.61	trace	13.23	3.22	16.45	4.1	99.02
(38)	10.28	2.35	13.55	3.06	16.61	4.4	99.58
(39)	10.83	trace	15.49	3.81	19.30	4.1	101.84
(40)	10.65	3.01	13.63	3.87	17.50	3.5	101.90

a. Reaction conditions: cyclododecane (5 mmol), oxovanadium (IV) complex (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31g) at RT

(45) cyclododecanone (46) cyclododecanol

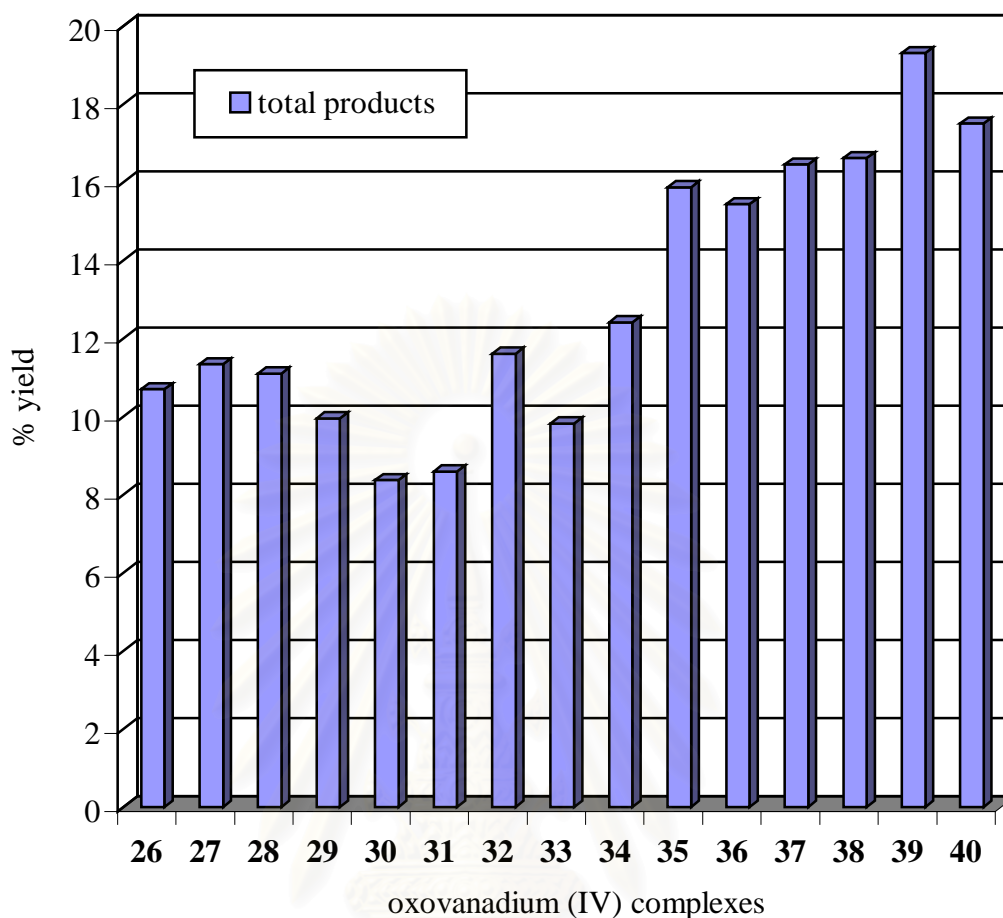


Fig 3.10 Comparative study on the oxidation of cyclododecane catalyzed by various oxovanadium (IV) complexes

3.6 Kinetic study on the reaction rate of cyclohexane oxidation

Various recent catalytic models that mimic enzymatic systems had an attempt to develop the reactions to be of a capability to proceed at room temperature and atmospheric pressure. Nevertheless, the rates of these reactions are generally slow and need to spend more time to complete the reaction. Therefore, the catalytic systems that consume less time to complete the reaction should be illicitly needed. The rate of cyclohexane oxidation catalyzed by $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{VO}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$, Schiff's base oxovanadium (IV) complexes (**26**), (**28**), (**34**) and 1,3-dicarbonyl oxovanadium (IV) complexes (**35**), (**38**), (**40**) were studied. The kinetic analysis results are presented in Fig 3.11.

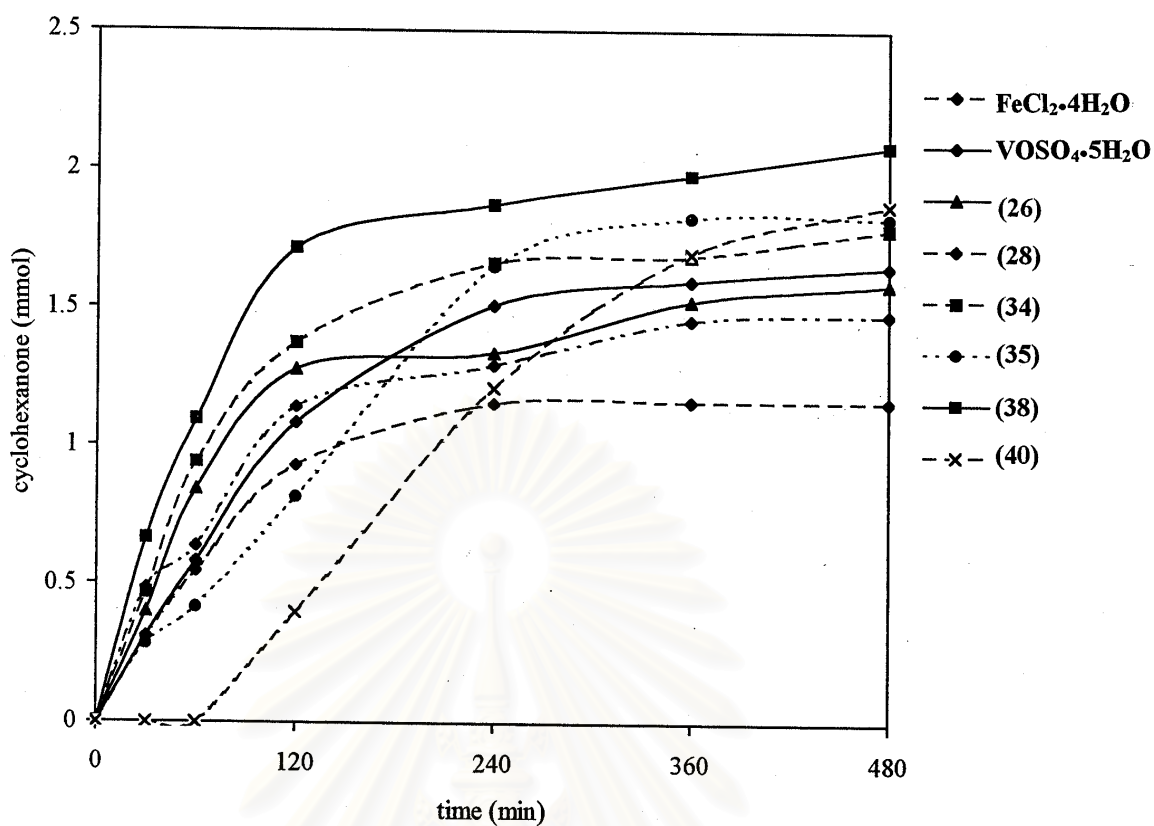


Fig 3.11 Kinetic study on cyclohexane oxidation catalyzed by various catalysts

Half-life of the reaction is a significant factor to reflect the kinetic oxidation rate of the system. The reaction with less half-life would proceed faster and therefore would be more applicable. Half-life of various catalysts used in cyclohexane oxidation reaction were determined and the results are shown in Table 3.12.

Table 3.12 Half-life of various catalysts studied in cyclohexane oxidation reaction

Catalyst	Half-life (min)
FeCl ₂ •4H ₂ O	65
VOSO ₄ •5H ₂ O	89
(26)	57
(28)	59
(34)	57
(35)	134
(38)	56
(40)	200

Comparing with salts that used in previous oxidation reaction reported,⁵⁶ FeCl₂•4H₂O and VOSO₄•5H₂O, oxidation catalysts in this study could be divided into two groups. The first one was the complexes assisted the reaction proceed faster than FeCl₂•4H₂O and VOSO₄•5H₂O, *i.e.*, oxovanadium (IV) complexes **(26)**, **(28)**, **(34)** and **(38)**. The second group of catalysts provided half-life more than FeCl₂•4H₂O and VOSO₄•5H₂O: oxovanadium (IV) complexes **(35)** and **(40)**. In addition, it was found that almost cyclohexane oxidation reaction catalyzed by synthesized oxovanadium (IV) complexes occurred approximately twice faster than using iron and vanadium salts, except for **(35)** and **(40)**. Moreover, it was also found that cyclohexane oxidation reaction using Schiff's base oxovanadium (IV) complexes **(26)**, **(28)** and **(34)**, the oxidation reaction rate was faster than using 1,3-dicarbonyl oxovanadium (IV) complexes **(35)** and **(40)**, expect for **(38)**. This series of experiments also displayed the importance of ligand around metal ions. The appropriate ligands may assist the reaction to take place with satisfied rates and in some case may elevate the selectivity of reactions as required.

3.7 Comparative study on catalytic turnover between Schiff's base and 1,3-dicarbonyl oxovanadium (IV) complexes

In this section, Schiff's base oxovanadium (IV) complex (**28**) and 1,3-dicarbonyl oxovanadium (IV) complex (**39**) were selected as a representative catalyst for each group in cyclohexane oxidation reaction in order to find the efficiency of each type of catalyst. Catalytic turnover is one of criteria to determine the efficiency of the reaction. The catalytic turnover value is exhibited in Table 3.13.

Table 3.13 Catalytic turnover of catalysts (**28**) and (**39**) in cyclohexane oxidation reaction^a

(mmol)	(28)		(39)	
	(42)+(43) (mmol)	Catalytic turnover	(42)+(43) (mmol)	Catalytic turnover
0	0	-	0	-
0.001	0.295	295	trace	-
0.010	0.702	70	trace	-
0.050	0.866	17	1.015	20
0.100	1.203	12	1.627	16
0.250	2.359	9	2.111	9
0.500	1.271	3	1.805	4
0.750	1.156	2	1.659	2
1.000	0.717	1	1.529	2

a. Reaction conditions: cyclohexane (20 mmol), oxovanadium (IV) complex (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(42) cyclohexanone (43) cyclohexanol

Considering all concentrations of each catalyst employed, it was observed that (**39**) gave higher amount of products and catalytic turnover value than (**28**) except for the concentrations of 0.001 and 0.010 mmol. Furthermore, it is noteworthy to address that at 0.25 mmol both (**28**) and (**39**) gave the highest amount of products compared with other concentrations tested.

3.8 Chemoselectivity study

Another important feature that needs to be carefully evaluated is the chemoselectivity. The addition of an additive to the system would provide some clues for the chemoselectivity of the studied system. The results are summarized in Table 3.14 and Fig 3.12.

Table 3.14 Chemoselectivity study^a

Entry	Additives	% yield at 16 h			% Mass balance
		(45)	(46)	(45)+(46)	
1	None	11.10	trace	11.10	99.17
2	Absolute ethanol	11.65	4.20	15.85	100.29
3	Isopropanol	10.83	3.22	14.05	99.28
4	Ethylene glycol	9.68	2.37	12.05	98.42
5	Hydroquinone	6.29	7.64	13.93	100.79
6	2-Methylhydroquinone	5.28	9.24	14.52	100.73
7	2,3-Dimethylhydroquinone	5.14	11.21	16.35	100.64
8	<i>tert</i> -Butylhydroquinone	6.37	10.75	17.12	102.74
9	2,5-di- <i>tert</i> -Butylhydroquinone	5.36	13.05	18.41	100.83
10	Triethylamine	8.37	6.50	14.87	100.75
11	Aniline	3.61	7.34	10.95	102.17
12	<i>N,N'</i> -Dimethylaniline	3.31	0	3.31	99.96
13	<i>N,N'</i> -Dimethylacetamide	11.56	3.31	14.87	100.65
14	2-Mercaptoethanol	3.14	4.15	7.29	98.40
15	Benzenethiol	3.34	4.03	7.37	102.76
16	Diphenylsulfide	10.10	3.01	13.11	101.19
17	Anisole	11.99	3.35	15.34	99.02
18	Methyl benzoate	14.15	3.17	17.32	102.50
19	Ascorbic acid	13.14	9.16	22.30	97.16
20	Triphenylphosphine	7.83	13.98	21.81	100.46

a. Reaction conditions: cyclododecane (5 mmol), **(28)** (0.25 mmol), additive (5 mmol) pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT
(45) cyclododecanone **(46)** cyclododecanol

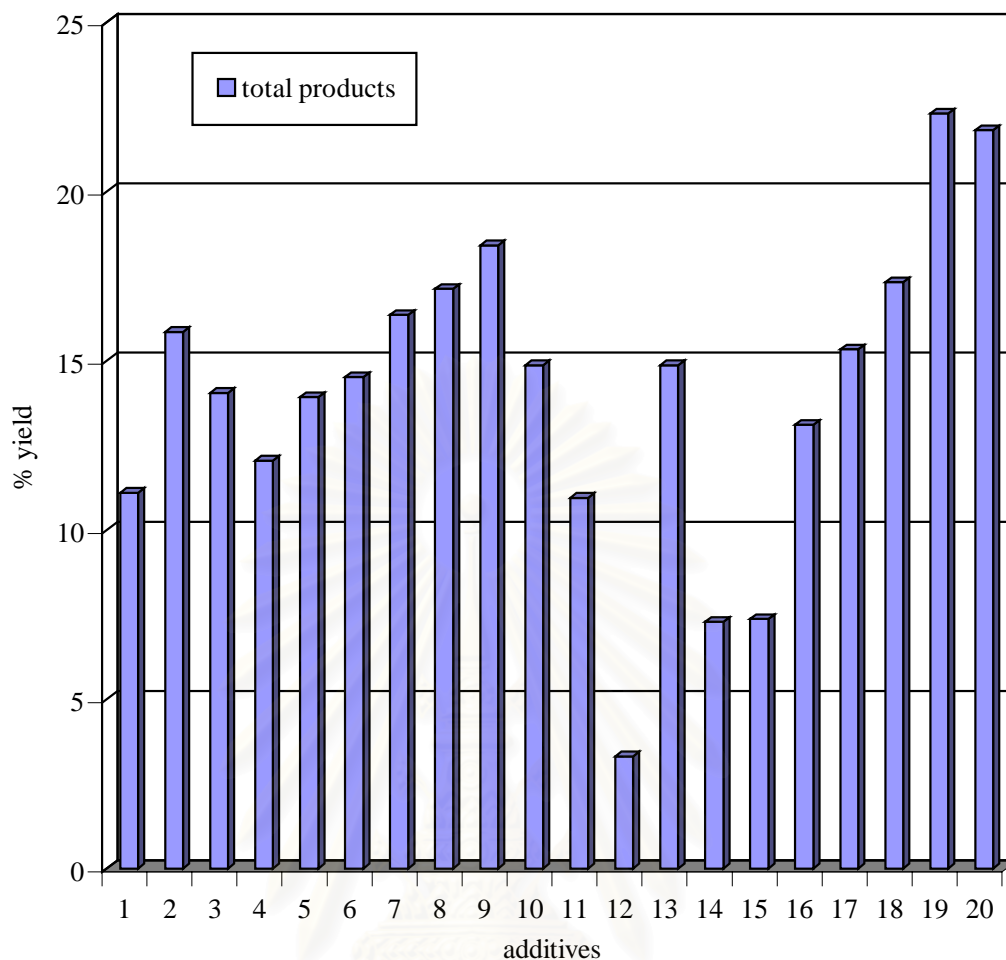


Fig 3.12 Chemoselectivity study

Absolute ethanol, isopropanol, ethylene glycol, hydroquinone, 2-methylhydroquinone, 2,3-dimethylhydroquinone, *tert*-butylhydroquinone, 2,5-di-*tert*-butylhydroquinone, triethylamine, aniline, *N,N'*-dimethylaniline, *N,N'*-dimethylacetamide, 2-mercaptoethanol, benzenethiol, diphenylsulfide, anisole, methyl benzoate, ascorbic acid and triphenylphosphine (entries 2-20) were used as an additive in the oxidation reaction of cyclododecane. It could be seen that cyclododecane oxidation process was little suppressed by the effect of these additives. Especially, in the case of absolute ethanol, isopropanol and ethylene glycol which were known as easily oxidizable compounds, the activation process of saturated hydrocarbon still occurred to produce the corresponding cyclododecanone. Cyclododecanol was also occurred as a minor product expect for entry 12 comparing with an ordinary oxidation system that normally proceeded (entry 1). This observation implied that the high valent intermediate generated should selectively

oxidized C-H bonds of saturated hydrocarbon. In addition an excess amount of absolute ethanol and isopropanol 5, 10, 15 and 50 mmol, respectively was experimented. It was observed that even in the presence of excess of ethanol or isopropanol, cycloalkane oxidation reaction still took place. Therefore, the proposed high valent oxovanadium intermediate was formed and selectively oxidized saturated hydrocarbon to ketone and alcohol. The results are presented in Table 3.15.

Table 3.15 Effect of ethanol and isopropanol in cyclododecane oxidation^a

Additive	(mmol)	% yield at 16 h			% Mass Balance
		(45)	(46)	(45)+(46)	
None	0	11.10	trace	11.10	99.17
Absolute EtOH	5	11.65	4.20	15.85	100.29
	10	14.45	4.97	19.12	101.34
	15	8.05	2.69	10.74	100.21
	50	5.56	trace	5.56	101.72
Isopropanol	5	10.83	3.22	14.05	99.28
	10	9.54	3.17	12.71	98.64
	15	9.78	3.61	13.39	98.83
	50	6.91	3.49	10.40	99.98

a. Reaction conditions: cyclododecane (5 mmol), (28) (0.25 mmol), additive (varied) pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(45) cyclododecanone (46) cyclododecanol

The addition of various substituted hydroquinones such as hydroquinone, 2-methylhydroquinone, 2,3-dimethylhydroquinone, *tert*-butylhydroquinone, 2,5-di-*tert*-butylhydroquinone in cyclododecane oxidation reaction provided another interesting outcome. Hydroquinones are another class of organic compounds that were well-known to be easily transformed to quinones by various metal-catalyzed oxidation systems.⁵⁷ Thus, it was clearly supported that the high valent oxovanadium intermediate should be responsible for the oxidation of alkanes over the additives. This assumption was justified from the activation process of cyclododecane which was still occurred to produce the

corresponding ketone and alcohol. Nonetheless, the amount of alcohol and total products was significantly increased especially in the presence of hydroquinones bearing electron donating groups. Accordingly, 2,5-di-*tert*-butylhydroquinone gave more total products than *tert*-butylhydroquinone, 2,3-dimethylhydroquinone, 2-methylhydroquinone and hydroquinone, respectively. The increasing amount of alcohol observed from this series of experiment was strongly implied the presence of the second intermediate of the system. To illustrate this, the second intermediate ought to be a species that could be reduced to the corresponding alcohol in the presence of a reducing agent such as hydroquinone compounds. This plausible species would believe to be a hydroperoxide compound which was used to verify its occurrence in Gif-type oxidation system.⁵⁸ The results are observed in Table 3.16 and Fig 3.13.

Table 3.16 Effect of various substituted hydroquinones in cyclododecane oxidation^a

Additive	% yield at 16 h			(45)/(46)	% Mass Balance
	(45)	(46)	(45)+(46)		
None	11.10	trace	11.10	-	99.17
Hydroquinone	6.29	7.64	13.93	0.8	100.79
2-Methylhydroquinone	5.28	9.24	14.52	0.6	100.73
2,3-Dimethylhydroquinone	5.14	11.21	16.35	0.5	100.64
<i>Tert</i> -Butylhydroquinone	6.37	10.75	17.12	0.6	102.74
2,5-di- <i>tert</i> -Butylhydroquinone	5.36	13.05	18.41	0.4	100.83

a. Reaction conditions: cyclododecane (5 mmol), (28) (0.25 mmol), additive (varied) pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT
 (45) cyclododecanone (46) cyclododecanol

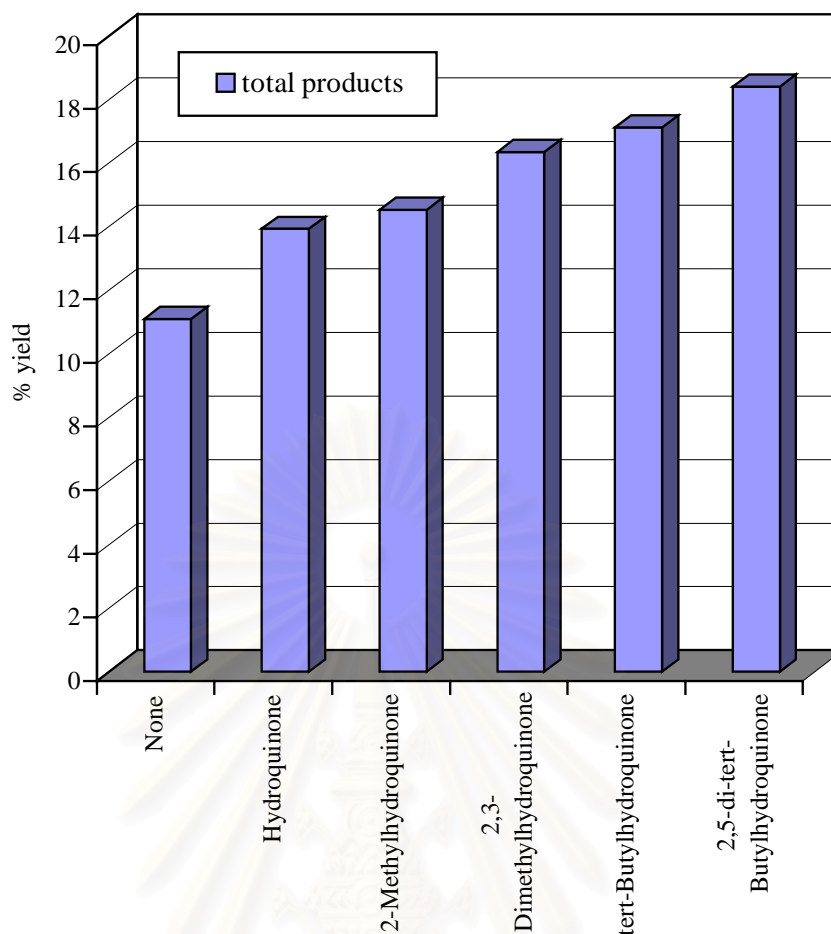


Fig 3.13 Effect of various substituted hydroquinones in cyclododecane oxidation

The effects of amines such as triethylamine, aniline, *N,N'*-dimethylaniline (entries 10-12, Table 3.14) were taken into consideration, the oxidation of cycloalkane was still took place. However, using *N,N'*-dimethylaniline as an additive seriously affects the oxidation process. It reduced the oxidation process of cyclododecane producing cyclododecanone only 3.31 percent while cyclododecanol could not be detected. The oxidation reaction in the presence of acetamide group such as *N,N'*-dimethylacetamide (entry 13, Table 3.14) could occur yielding ketone more or less the same as normal oxidation (entry 1, Table 3.14).

The cyclododecane oxidation reaction could still proceed especially, in the presence of certain sulfur compounds such as 2-mercaptoethanol, benzenethiol and diphenylsulfide. 2-Mercaptoethanol and benzenethiol showed a little effect on the oxidation process. In addition, diphenylsulfide had no effect on this oxidation reaction. It should also be noted that in the oxidation system with benzenethiol, the amount of alcohol increased. This clearly reinforced the presence of hydroperoxide which could be

reduced to the corresponding alcohol by benzenethiol. The results are presented in Table 3.14 (entries 14-16).

Refer to a test of a possible electron transfer mechanism, anisole and methyl benzoate (Table 3.14; entries 16-17) were used for this purpose. These compounds had slightly affected on the oxidation process. The oxidation of cyclododecane was still found to be prevailed, especially, in the presence of methyl benzoate the reaction still gave cyclododecanone in high yield (17.32 %).

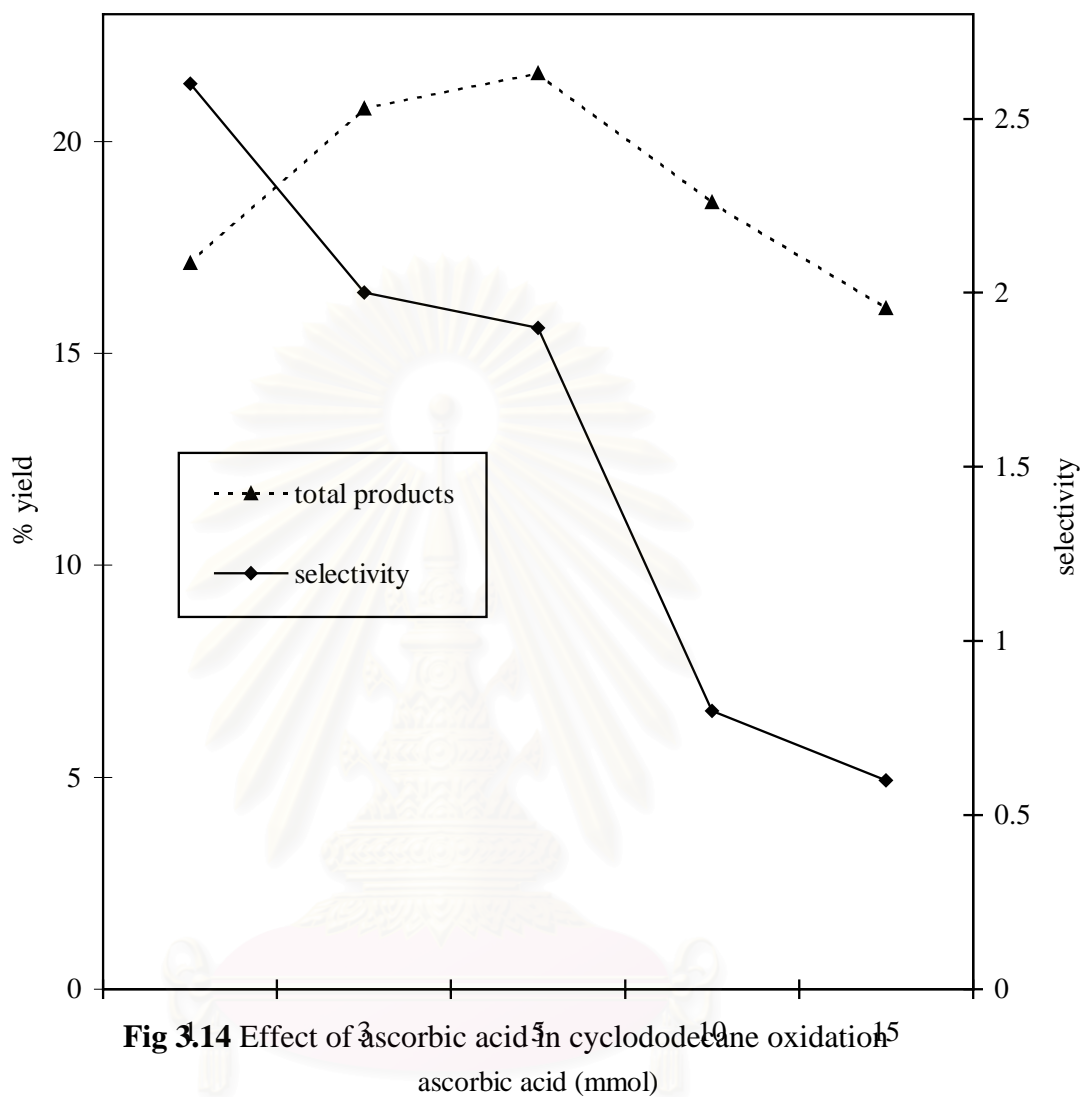
Ascorbic acid was a well-known biochemical reductant. Therefore in the presence of ascorbic acid, it was not surprised to observe the change of ketone to alcohol ratio selectively. The variation of the amount of ascorbic acid was further examined and the results are presented in Table 3.17 and Fig 3.14. When the amount of ascorbic acid was more than 10 mmol, the yield of the total products decreased a little bit. However, the ketone to alcohol selectivity decreased when the amount of ascorbic acid increased. This observation clearly showed that the excessive ascorbic acid had markedly effect to the oxidation process. The increasing amount of alcohol was manifestly derived from the transformation of hydroperoxide by ascorbic acid.

Table 3.17 Effect of ascorbic acid in cyclododecane oxidation^a

Additive	(mmol)	% yield at 16 h			(45)/(46)	% Mass balance
		(45)	(46)	(45)+(46)		
None		11.10	trace	11.10	-	99.17
Ascorbic acid	1	12.43	4.70	17.13	2.6	98.06
	3	13.86	6.91	20.77	2.0	97.84
	5	14.04	7.57	21.61	1.9	99.84
	10	8.20	10.37	18.57	0.8	99.34
	15	6.13	9.94	16.07	0.6	97.13

a. Reaction conditions: cyclododecane (5 mmol), (28) (0.25 mmol), ascorbic acid (varied), pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(45) cyclododecanone (46) cyclododecanol



Triphenylphosphine was another good reducing agent in this chemoselectivity study. From Table 3.18 and Fig 3.15, the yield of alcohol significantly increased when the amount of triphenylphosphine used increased.

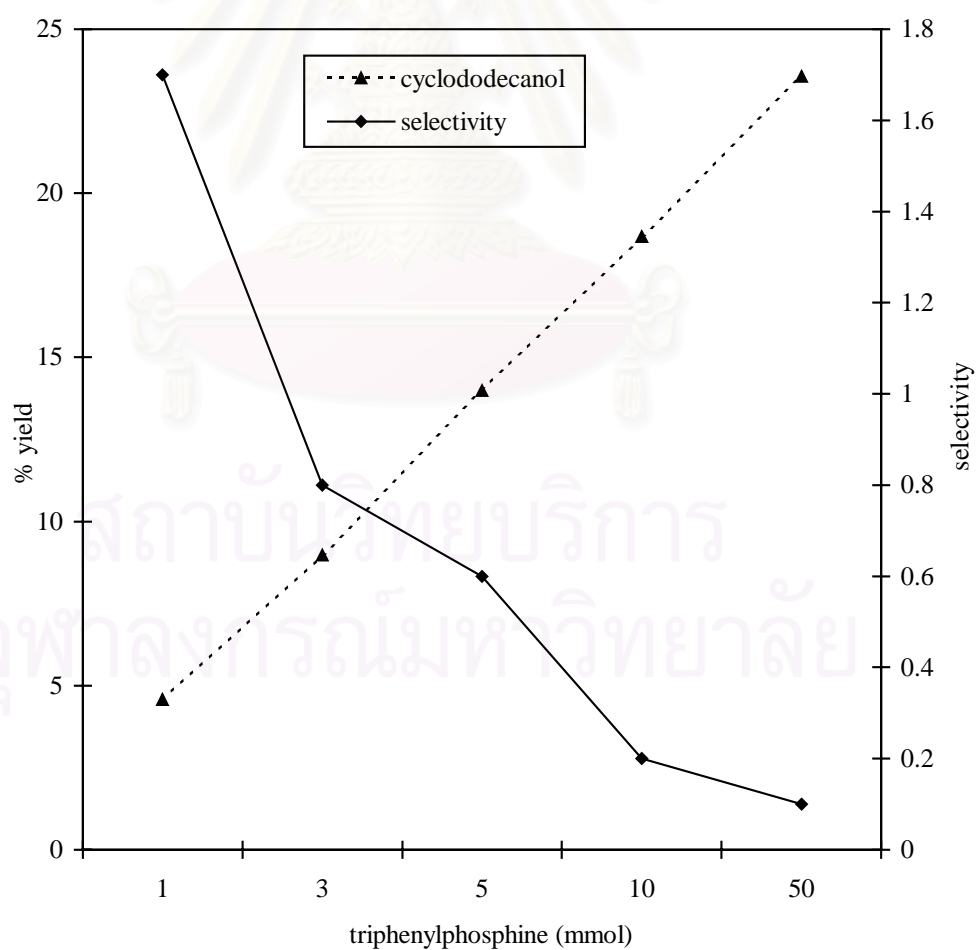
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Table 3.18 Effect of triphenylphosphine in cyclododecane oxidation^a

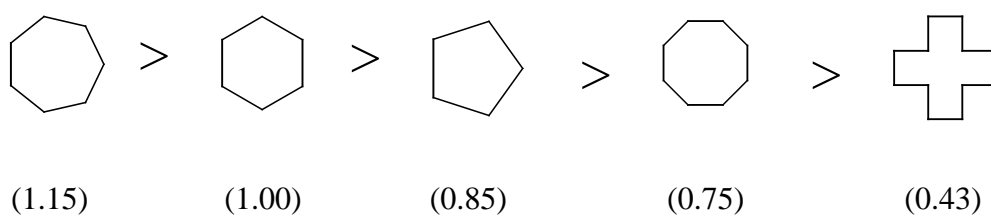
Additive	(mmol)	% yield at 16 h			(45)/(46)	% Mass balance
		(45)	(46)	(45)+(46)		
None		11.10	trace	11.10	-	99.17
Triphenylphosphine	1	7.93	4.57	12.50	1.7	98.61
	3	7.47	8.97	16.44	0.8	98.59
	5	7.83	13.98	21.36	0.6	100.46
	10	3.84	18.67	22.51	0.2	100.53
	15	3.62	23.56	27.18	0.1	99.97

a. Reaction conditions: cyclododecane (5 mmol), (28) (0.25 mmol), triphenylphosphine (varied), pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(45) cyclododecanone (46) cyclododecanol

**Fig 3.15** Effect of triphenylphosphine in cyclododecane oxidation

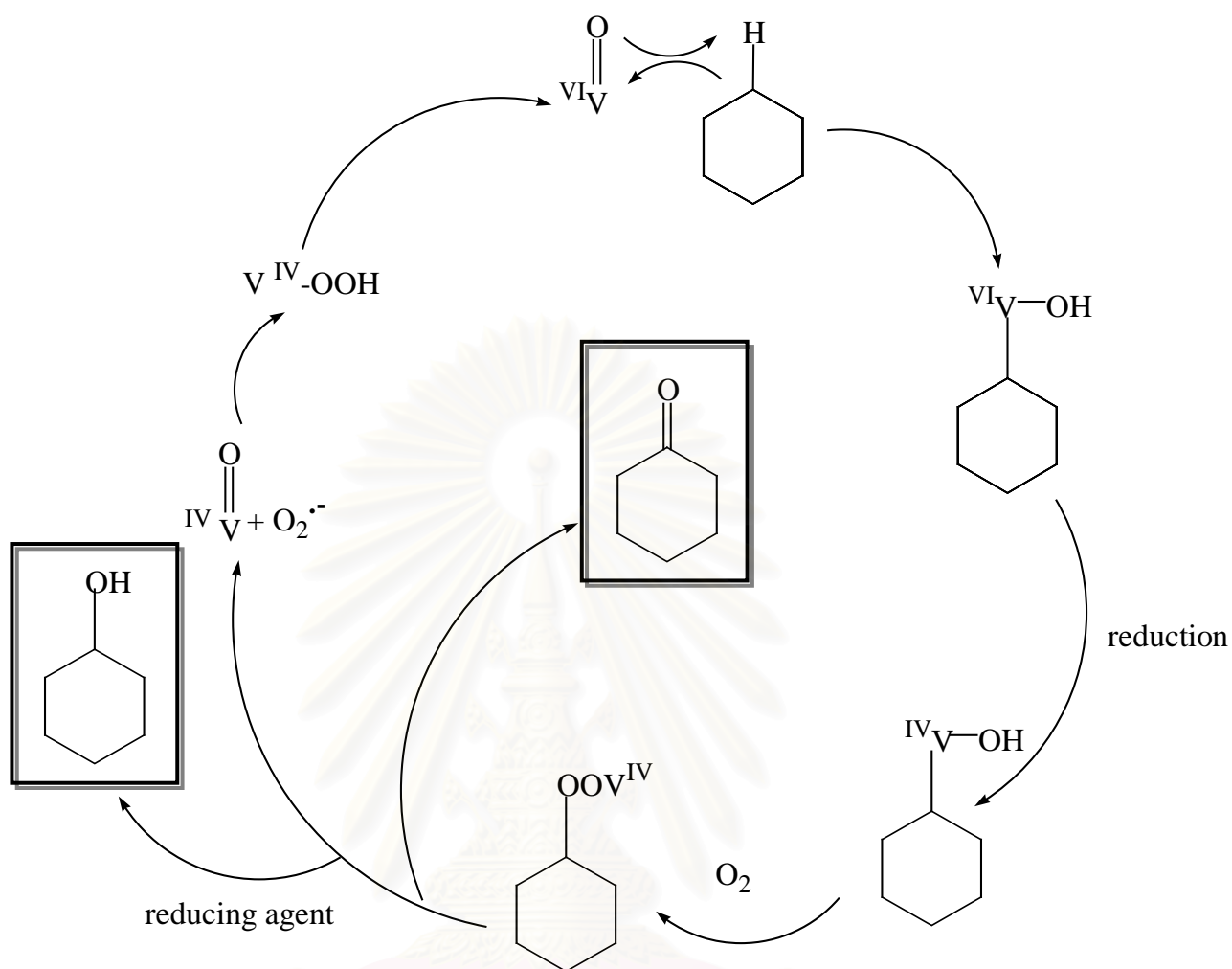
This reactivity was almost conformed to the comparison relative reactivity in the oxidation reaction of cycloalkanes catalyzed by iron catalyst⁶¹ (Gif-type system) :



Moreover, the relative reactivity of cyclopentane/cyclohexane in this study was less than 1.0. This data suggested that the mechanism of the oxidation of cycloalkanes catalyzed by oxovanadium (IV) complex catalysts in this study not occur *via* the radical pathway.

3.10 The proposed mechanistic pathway for oxovanadium (IV)-catalyzed cycloalkane oxidation

Besides the informative results guided of the mechanistic pathway derived from chemoselectivity study, the comparative study on reactivity of cycloalkane in oxidation (section 3.9) also indicated that this oxidation reaction proceeded *via* non radical reaction. The mechanism was thus proposed as that of Gif-type systems.¹¹



Scheme 4.1 Proposed mechanistic pathway for oxovanadium (IV)-catalyzed cycloalkane oxidation

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3.11 The oxidation reaction of cyclohexene

The oxidation of cyclohexene (**47**) by this developed system was investigated using Schiff's base oxovanadium (IV) complex (**28**) as a catalyst. The results are presented in Table 3.20.

Table 3.20 The oxidation of cyclohexene catalyzed by (**28**)

Substrate	Products (mmol)						
	2 h			16 h			
	(48)	(49)	(50)	(48)	(49)	(50)	(48)+(49)+(50)
(47)	0.623	0	0.139	1.143	0	0.253	1.396

a. Reaction conditions: substrates (15 mmol each), (**28**) (0.25 mmol), pyridine (28 mL) acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(**48**) cyclohexenone (**49**) cyclohexenol (**50**) cyclohexene oxide

From Table 3.20, it was found that cyclohexenone was produced as a major product, while cyclohexene oxide being a minor one and cyclohexenol did not occur in this oxidation reaction. This result was different from other reported systems, for example the epoxidation of cyclohexene could be catalyzed by VO(SAP), VO(HNED), VO(ACEN), VO(SAC), VO(SALPHEN), VO(SALEN), VO(HAED), VO(HNOPD), VO(ANAC) and VO(HATRIEN) using 70% TBHP to give epoxide as a major product, cyclohexene oxide and small amount of cyclohexenol.⁶² Another example of cyclohexene oxidation was achieved in the VO(acac)₂-AIBN system. This catalytic system was efficient for epoxidation of cyclohexene, methylcyclohexene and cyclododecene yielding the corresponding epoxy alcohol in good yield.⁶³

3.12 Comparative studies on the oxidation of cycloalkane and cycloalkene

In this experiment, the competitive studies on the oxidation between cyclohexane (**41**) and cyclohexene (**47**) or *vice versa* were investigated. The results are shown in Table 3.21.

Table 3.21 Competitive studies on the oxidation of **(41)** and **(47)**^a

R¹H	R²H	Products (mmol)							
		2 h				16 h			
		(42)	(43)	(48)	(50)	(42)	(43)	(48)	(50)
(41)	(47)	0.433	0.159	0.507	trace	0.810	0.247	0.824	0.154

a. Reaction conditions: substrates (20 mmol each), **(28)** (0.25 mmol), pyridine (28 mL) acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(42) cyclohexanone **(43)** cyclohexanol **(48)** cyclohexenone **(50)** cyclohexene oxide

From Table 3.21, it was found that the amount of cyclohexenone occurred almost the same as that of cyclohexanone (cyclohexenone : cyclohexanone = 1 : 1). Generally, the relatively weak C-H bond energy as that in cyclohexene should be easily oxidized compared with inert C-H bond in cyclohexane. This study was another intriguing characteristic of this particular system that still called for further investigation.

3.13 Competitive studies on the oxidation of cycloalkane and alcohol

The competitive studies on the oxidation between cyclohexane **(41)** and cyclooctanol **(53)** and *vice versa* between cyclooctane **(51)** and cyclohexanol **(43)** were examined. The results are summarized in Table 3.22.

Table 3.22 Competitive studies on the oxidation of **(41)** and **(53)** and between **(51)** and **(43)**^a

Substrates	Product (mmol)							
	2 h				16 h			
	(42)	(43)	(52)	(53)	(42)	(43)	(52)	(53)
(41) + (53)	0.458	trace	1.233	14.665	0.808	0.282	1.710	14.776
(51) + (43)	0.664	13.537	0.325	trace	0.776	15.426	0.396	trace

a. Reaction conditions: substrates (15 mmol each), **(28)** (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), zinc grit (1.31 g) at RT

(42) cyclohexanone **(43)** cyclohexanol **(52)** cyclooctanone **(53)** cyclooctanol

From Table 3.22, it was shown that cyclohexane and cyclooctane were still alternatively oxidized. These observation confirmed the aforementioned results that the high valent $V^{VI}=O$ intermediate responsible for oxidation of alkanes should have a preference to oxidize saturated hydrocarbons to ketone.

3.14 The use of *tert*-butyl hydroperoxide as an oxidant

tert-Butyl hydroperoxide (TBHP) has been well-known to be employed in metal-catalyzed process in the past mostly dealt with the epoxidation of olefins.⁶⁴ However TBHP, a useful oxidizing agent in metal-catalyzed oxidations of saturated hydrocarbons has also turned out during the last decade, such as saturated hydrocarbons can be selectively converted into the corresponding ketones or olefins in the absence of solvent using a combination of TBHP and catalytic amounts of Fe (III) and Cu (II) complexes.⁶⁵ In this experiment, TBHP was used as an oxidizing agent in cyclooctane (**51**) oxidation reaction instead of Zn (grit) employing Schiff's base (**28**) and 1,3-dicarbonyl (**40**) oxovanadium (IV) complexes as comparative catalysts at atmospheric pressure around 60°C in pyridine-acetic acid solvent system. The results are tabulated in Table 3.23.

Table 3.23 Comparative study on the oxidation of cyclooctane using Schiff's base (**28**) and 1,3-dicarbonyl (**40**) oxovanadium (IV) complexes and *tert*-butyl hydroperoxide^a

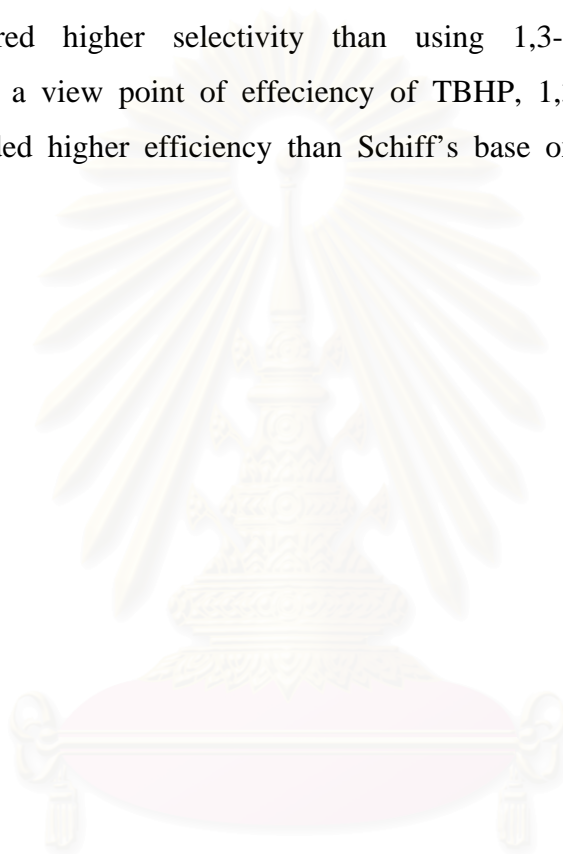
Oxovanadium (IV) complex	time h	Products (mmol)			(52)/ (53)	%Efficiency of TBHP ^b	%Mass balance
		(52)	(53)	(52)+(53)			
(28)	24	2.831	0.572	3.403	4.9	68.06	101.17
	48	2.839	0.560	3.399	5.1	67.98	99.32
	72	2.931	0.583	3.514	5.0	70.28	99.26
(40)	24	1.990	0.941	2.931	2.1	58.62	99.99
	48	3.324	0.985	4.309	3.4	86.18	99.91
	72	3.489	1.003	4.492	3.5	89.94	97.62

a. Reaction conditions: cyclooctane (20 mmol), oxovanadium (IV) complexes (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), *tert*-butyl hydroperoxide (10 mmol) at 60 °C

b. %Efficiency of TBHP = $\frac{2 \times \text{total amount of products (mmol)}}{\text{TBHP (mmol)}} \times 100$

(52) cyclooctanone (53) cyclooctanol

From Table 3.23, it could clearly be seen that the alkane oxidation catalyzed by Schiff's base oxovanadium (IV) complex proceeded faster than 1,3-dicarbonyl oxovanadium (IV) complex. The reaction was almost finished within 24 h. While using 1,3-dicarbonyl oxovanadium (IV) complex, the reaction was mostly finished within 48 h. Considering from the amount of kinetic and alcohol as total yield, using 1,3-dicarbonyl oxovanadium (IV) complex gave higher yield than using Schiff's base oxovanadium (IV) complex. However, in term of reaction selectivity, using Schiff's base oxovanadium (IV) complex offered higher selectivity than using 1,3-dicarbonyl oxovanadium (IV) complex. From a view point of efficiency of TBHP, 1,3-dicarbonyl oxovanadium (IV) complex provided higher efficiency than Schiff's base oxovanadium (IV) complex as a catalyst.



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CHAPTER IV

CONCLUSION AND SUGGESTION FOR FURTHER WORK

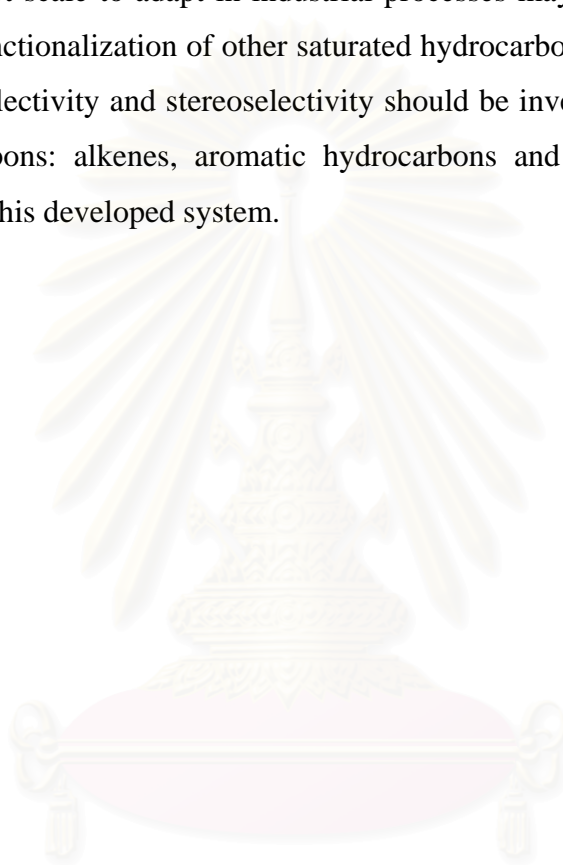
Methodology to functionalize saturated hydrocarbons to yield superior amount of the desired products with high selectivity of reactions compared with other classical methods reported is the aim of this research. Two types of catalysts: Schiff's base and 1,3-dicarbonyl complexed with oxovanadium (IV) were thoroughly investigated for cycloalkane oxidation reaction using zinc-pyridine-acetic acid-O₂ system at room temperature and atmospheric pressure. Cyclohexane 20 mmol, pyridine 28 mL, acetic acid 2.3 mL, zinc grit 1.31 g and oxovanadium (IV) complex 0.25 mmol were found to be the most appropriate optimized conditions. The use of co-solvent such as substituted picolines, acetone, dimethylsulfoxide and acetonitrile was also examined. Among various co-solvents tried to avoid using only pyridine, a mixture of pyridine and acetonitrile (1: 1) was observed to be another alternative to carry out this oxidation reaction. Under optimized conditions, Schiff's base oxovanadium (IV) complexes **(26)**, **(27)**, **(28)**, **(32)** and **(34)** provided good yields of desired products. In addition, 1,3-dicarbonyl oxovanadium (IV) complexes **(35)**-**(40)** gave a little better yield than aforementioned Schiff's base complexes.

In terms of rate of reaction, using Schiff's base oxovanadium (IV) complexes **(26)**, **(28)** and **(34)**, the oxidation reaction rate was faster than using 1,3-dicarbonyl oxovanadium (IV) complexes **(35)** and **(40)**, expect for **(38)** in cyclohexane oxidation reaction. Considering of catalytic turnover, bis(salicylaldehyde)*N,N'*-*o*-phenylenediimine-vanadium (IV) **(28)** provided the best catalytic turnover (about 295). The utilization of either VO (IV)-Schiff's base or VO (IV)-1,3-dicarbonyl complexes as a catalyst in alkane oxidation using Zn-AcOH-O₂ system has never been reported in chemical literature. The products observed and selectivity of the system were found to be unique and be similar to iron-catalyzed oxidation reactions, so-called "Gif-type" systems. The mechanism of cycloalkane oxidation was believed to occur by non radical reaction. The oxidation reaction was proved to proceed *via* alkyl hydroperoxide as an intermediate. The supporting information was derived from comparison of relative reactivity towards cyclic saturated hydrocarbons and chemoselectivity study. Furthermore, the use of TBHP as an

oxidizing agent in this developed oxidation reaction provided another choice of functionalization of alkanes. The efficiency of TBHP was found to be in a good range (59-90 %).

Suggestion for further work

The modification of this catalytic system to the larger scale experiments that could be applied in a pilot scale to adapt in industrial processes may be of important to carry out. In addition, functionalization of other saturated hydrocarbons to see the selectivity of the system: regioselectivity and stereoselectivity should be investigated. Moreover, other types of hydrocarbons: alkenes, aromatic hydrocarbons and alcohols should also be investigated under this developed system.



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