ตัวเร่งปฏิกิริยาวานาเดียมสำหรับออกซิเดชันของแอลกอฮอล์

นางสาวปิยนุช หุ่นศาสน์

สถาบันวิทยบริการ
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

VANADIUM CATALYSTS FOR OXIDATION OF ALCOHOLS

Miss Piyanoot Hoonsart

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

A Thesis Submitted in Partial Fulfillment of the Requirements
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ปิยนุช หุ่นศาสน์ : ตัวเร่งปฏิกิริยาวานาเดียมสำหรับออกซิเดชันของแอลกอฮอล์ (VANADIUM CATALYSTS FOR OXIDATION OF ALCOHOLS) อ.ที่ปรึกษา : รศ.ดร. วิมลรัตน์ ตระการพฤกษ์; 74 หน้า.ISBN 974-14-2551-1

ในงานวิจัยนี้ได้ทำการเตรียมตัวเร่งปฏิกิริยาวานาเดียมออกไซด์และสารประกอบเชิงซ้อนวานาเดียม ได้แก่ *n*-Bu_4NVO_3 **(A)**, $[NBu_4][V(cat)_3]$ **(B)**, V-*L*-valine **(C)**, V-EDTA **(D)**, V-PCA **(E)**, $(VO)_2P_2O_7$ **(F)**, $VO(PO_4)(H_2O)_2$ **(G)**, $VO(HPO_4)(H_2O)_{0.5}$ **(H)** ได้ตรวจพิสูจน์เอกลักษณ์ของตัวเร่งปฏิกิริยาเหล่านี้ด้วยเทคนิค XRD, FT-IR, UV-vis และหาจุดหลอมเหลว ตัวเร่งปฏิกิริยาที่ได้นำไปเร่งปฏิกิริยาออกซิเดชันของแอลกอฮอร์ที่ 70 °C เป็นเวลา 24 ชั่วโมง สัดส่วนโดยโมลแอลกอฮอล์/สารออกซิไดซ์ = 2 สัดส่วนโดยโมลแอลกอฮอล์/ตัวเร่งปฏิกิริยา = 60 วิเคราะห์ผลิตภัณฑ์จากปฏิกิริยาด้วยเทคนิค GC

ผลการทดลองแสดงให้เห็นว่า ตัวเร่งปฏิกิริยาวานาเดียมสามารถเร่งปฏิกิริยาการออกซิเดชันของแอลกอฮอล์ไปเป็นอัลดีไฮด์หรือคีโตนในปริมาณที่สูง ในกรณีของออกซิเดชันของเบนซิลแอลกอฮอล์ผลิตภัณฑ์ขึ้นอยู่กับตัวทำละลายที่ใช้ ในทอลูอีน จะได้ผลิตภัณฑ์เบนซาลดีไฮด์ แต่ในอะซิโตไนไตรล์ปฏิกิริยาแสดงความเลือกจำเพาะต่อเบนโซอิกแอซิด (เปอร์เซ็นต์ความเลือกจำเพาะสูง 70 %) ออกซิเดชันของ 1-เฟนิลเอทานอล ให้ผลิตภัณฑ์เป็นอะซีโตฟีโนน ในขณะที่ไซโคลเฮกซะนอลให้ผลิตภัณฑ์เป็นไซโคลเฮกซะโนน

ความว่องไวในการเกิดปฏิกิริยาของแอลกอฮอล์ที่แสดงโดยตัวเร่งปฏิกิริยาทั้งหมดมีลำดับดังนี้ เบนซิลแอลกอฮอล์ > 1- เฟนิลแอลทานอล > ไซโคลเฮกซะนอล ลำดับความว่องไวในการเร่งปฏิกิริยาที่พบในงานวิจัยนี้ แสดงให้เห็นว่า สารประกอบเชิงซ้อนวานาเดียมที่มีลิแกนด์คีเลตดีกว่าตัวเร่งปฏิกิริยาที่มีวานาเดียมออกไซด์ และใกล้เคียงกับ V_2O_5 ที่ใช้ในการค้า

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ **ลายมือชื่อนิสิต**.....
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ **ลายมือชื่ออาจารย์ที่ปรึกษา**.....
ปีการศึกษา 2006 **ลายมือชื่ออาจารย์ที่ปรึกษาร่วม** -

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KEYWORD : VANADIUM/OXIDATION/ALCOHOLS

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In this thesis, some vanadium containing oxides and vanadium complexes were prepared. They are *n*-Bu_4NVO_3 **(A)**, $[NBu_4][V(cat)_3]$ **(B)**, V-*L*-valine **(C)**, V-EDTA **(D)**, V-PCA **(E)**, $(VO)_2P_2O_7$ **(F)**, $VO(PO_4)(H_2O)_2$ **(G)**, $VO(HPO_4)(H_2O)_{0.5}$ **(H)**). These were characterized by XRD, FT-IR, UV-Vis and melting point. They were used to catalyze the oxidation of alcohols at 70°C, 24 h using alcohol/oxidant mole ratio = 2, alcohol/catalyst mole ratio = 60. The reaction products were analyzed by GC technique.

The experimental results show that all vanadium catalysts catalyze the oxidation of alcohols to aldehyde or ketone with high yield. In the case of benzyl alcohol oxidation, the product depended on the solvent used, in toluene, benzaldehyde was obtained. But in acetonitrile, the reaction showed selectivity to benzoic acid (70% selectivity). The oxidation of 1-phenylethanol yielded acetophenone while cyclohexanol gave cyclohexanone .

The reactivity of alcohol demonstrated by all the catalysts is: benzyl alcohol > 1-phenylethanol > cyclohexanol. The reactivity order of the catalysts found in this work revealed that the vanadium complexes containing chelating ligand are better than the vanadium containing oxide catalysts, and the reactivity is comparable to the commercial V_2O_5.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Program.... Petrochemistry and Polymer Science... Student's signature.....
Field of study...Petrochemistry and Polymer Science Advisor's signature.....
Academic year.....2006..... Co-advisor's signature.....

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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

CONTENTS (CONT.)

LIST OF FIGURES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLE

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF SCHEMES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF ABBREVIATIONS

^{o}C	degree celcius
EA	elemental analysis
GC	gas chromatography
g	gram (s)
h	hour (s)
IR	infrared
m.p.	melting point
mL	milliliter (s)
mmol	millimole (s)
%	percentage
TBHP	*tert*-butyl hydroperoxide
cm^{-1}	unit of wavenumber
XRD	X-ray diffration
acac	acetylacetonate
PCA	pyrazine carboxylic acid
EDTA	ethylenediamine tetraacetic acid

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จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER I

Introduction

1.1 Introduction

Oxidation of hydrocarbons is a key process in industrial chemistry due to the large-scale applications of the ensuing functionalized compounds as raw materials and intermediates in industrial and pharmaceutical chemistry. In addition, for obvious environmental constraints, classical stoichiometric oxidants, such as dichromate or permanganate, should be replaced by new environmentally friendly catalytic processes using clean oxidants like molecular oxygen or hydrogen peroxide [1] .

The oxidation of primary and secondary alcohols to the corresponding carbonyl, is one of the widely used chemical transformations in organic synthesis as these products are important precursors or intermediates in the organic synthesis of many drugs, vitamins and fragrance represents a significant step in synthetic organic chemistry for both environmental and economical reasons [3-4].

Aldehydes and ketones are widely used industrial chemicals both as solvents and as chemical intermediates (ingredients for other chemicals). Most can be classified as volatile organic compounds meaning that their vapors may be easily inhaled or ignited. Many ketones and aldehydes are also flammable as liquids and solids. For example, formaldehyde is an industrially important aldehyde that is used on the billion ton scale. Glutaraldehyde is a "cold sterilent" used widely in the health care industry. Both are potent sensitizers. Exposure to either of these can make you hypersensitive to contact with other chemicals and carries definite health risks. Special rules and regulations have been developed to minimize formaldehyde exposure.

Benzaldehyde is used chiefly in the synthesis of other organic compounds, ranging from pharmaceuticals to plastic additives. It is also an important intermediate for the processing of perfume and flavouring compounds and in the preparation of certain aniline dyes.

Cyclohexanone is employed as an industrial solvent and as activator in oxidation reactions. It is also used in the production of adipic acid, cyclohexanone resins, caprolactam and nylon 6.

Acetophenone is a crystalline ketone that is used as a solvent for cellulose ethers and esters in the manufacture of alcohol-soluble resins. These in turn are used in perfume. Acetophenone is used to create fragrances that resemble almond, cherry, honeysuckle, jasmine, and strawberry. This chemical may be obtained by the dry distillation of a mixture of the calcium salts of acetic and benzoic acids. At one time it was used as a hypnotic under the name of hypnone.

Thus, much effort has been devoted to the development of oxidation catalyst with high selectivity and activity. The selective activation of particular varieties of bonds can be controlled after the desired substitution has been achieved.

Interest in vanadium coordination chemistry over the past decade has accelerated because of vanadium complexes play a very important role in catalytic organic chemistry [6-10] and also in living organisms [11-15]. Some of the vanadium compounds stimulate glucose uptake and inhibit lipid breakdown in a manner remarkably reminiscent of insulin effects.[16] Its complexes with certain amino acids have been proposed as anti-tumor and antileukemic agents [17-21], they initiate the photo-cleavage of DNA and are finally known as potent toxicants and carcinogens [22-27] which can act via generation of hydroxyl radicals. These radicals formed from molecular oxygen or hydrogen peroxide under the action of vanadium complexes in a living cell [28-31], attack various cell components leading to damage and induce aerobic peroxidation of liposomal membranes. In recent years, many papers have been published on the synthesis of biomimetic vanadium complexes and on their activity in various metabolisms [32-36].

Vanadium containing haloperoxidases catalyse the oxidation of halides in the presence of hydrogen peroxide to highly reactive intermediate, a hypohalous acid, which may react either with suitable nucleophilic acceptor.

Vanadium(V) peroxide complexes also are efficient and selective catalysts in the oxidation of prochiral dialkyl, arylalkyl or diaryl sulfides to the corresponding sulfoxides. These complexes are usually generated in situ from vanadium salts such as $VO(acac)_2$, sodium *meta*-vanadate ($NaVO_3$), or vanadium pentoxide (V_2O_5) and H_2O_2. The reactions are often nearly quantitative with respect to the peroxide. Two mechanisms may occur, dependent on the nature of the ligand. The reaction pathway proceeds either *via* heterolytic or homolytic cleavage of the peroxidic oxygen-oxygen bond.

In this research, several vanadium complexes were synthesized and characterized. Three types of alcohols were selected to be as substrate for oxidation reaction catalyzed by the vanadium complexes. The parameters influencing the oxidation reaction were studied.

1.2 Objectives of thesis

1.2.1 To synthesize and characterize vanadium complex catalysts.

1.2.2 To study parameters affecting the oxidation of alcohols using the vanadium complex catalysts.

1.3 The scopes of the thesis

The experiments were divided into following :

- Synthesis and characterization of vanadium complexes.
- Study of the optimum condition for oxidation of alcohols.
- Comparison of the catalytic activity of vanadium catalysts for the oxidation of benzyl alcohol, cyclohexanol and 1- phenylethanol.

CHAPTER II

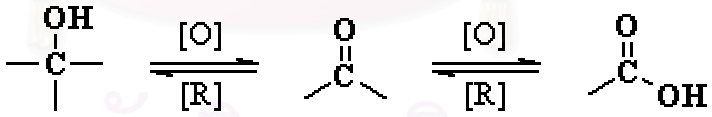
THEORY AND LITERATURE REVIEWS

Oxidation is the process of oxidizing; the addition of oxygen to a compound with a loss of electrons; always occurs accompanied by reduction**.**

Alcohols are the family of compounds that contain one or more hydroxyl (-OH) groups. Alcohols are represented by the general formula R-OH. Alcohols are important in organic chemistry because they can be converted to and from many other types of compounds. Reactions with alcohols fall into two different categories. Reactions can cleave the R-O bond or they can cleave the O-H bond.

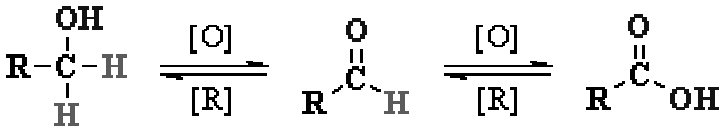
2.1 Oxidation of alcohols

Oxidation in organic chemistry always involves either the addition of oxygen atoms or the removal of hydrogen atoms. Whenever a molecule is oxidized, another molecule must be reduced. Therefore, these reactions require a compound that can be reduced. These compounds are usually inorganic. They are referred to as oxidizing reagants.



2.1.1 Oxidation of primary alcohols

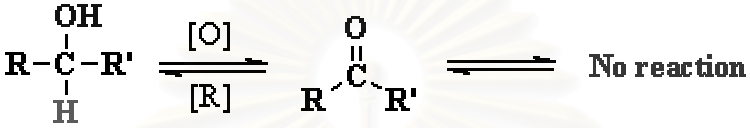
Primary alcohols can be oxidized to either aldehydes or carboxylic acids depending on the reaction conditions. In the case of the formation of carboxylic acids, the alcohol is first oxidized to an aldehyde which is then oxidized further to the acid.



1° alcohol aldehyde

2.1.2 Oxidation of secondary alcohols

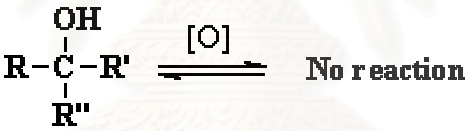
Oxidation of secondary alcohols can be oxidised to ketones, no further.



2° alcohol ketone

2.1.3 Oxidation of tertiary alcohols

Oxidation of tertiary alcohols cannot be oxidized (no carbinol C-H) .



3° alcohol

2.2 Catalysis

In chemistry and biology, catalysis is the acceleration of the reaction rate of a chemical reaction by means of a substance, called a catalyst, that is itself not consumed by the overall reaction. The biochemical equivalent is the enzyme unit. Catalysts work by changing the activation energy for a reaction, i.e., the minimum energy needed for the reaction to occur. This is accomplished by providing a new mechanism or reaction path through which the reaction can proceed. When the new reaction path has a lower activation energy, the reaction rate is increased and the reaction is said to be catalyzed.

If the activation energy for the new path is higher, the reaction rate is decreased and the reaction is said to be inhibited. Inhibitors can provide an interesting challenge to the chemist. For example, because oxygen is an inhibitor of free-radical reactions, many of which are important in the synthesis of polymers, such reactions must be performed in an oxygen-free environment under a blanket of nitrogen gas.

Two types of catalysts are generally distinguished:

- homogeneous catalysts
- heterogeneous catalysts

2.3 Homogeneous catalysts

In its widest sense homogeneous catalysis occurs when the catalyst and the reactants are both in the same phase. Either gas or liquid. In more recent years the term has come to be applied more specifically to the use of a solution of certain organometallic compounds in which a central metal atom is surrounded by a regular pattern of atoms or molecules, known as ligands, with which it is coordinated.

In the case of basic chemicals the chances for new catalytic processes are small, but they are better for higher value chemicals such as fine and specialty chemicals. Pharmaceuticals and agrochemicals are two areas where homogeneous catalysts have advantages.

Depending upon the nature of the ligands, the metal atom may be in a low-positive, zero, or low-negative state. Several different structures may exist in equilibrium in solution simultaneously, with different reactivities, but since the catalyst is dissolved in the reacting medium, each molecule of a particular structure acts like any other. There are systematic correlations of the structure, the nature of the ligands, and the catalytic activity of the catalyst complex.

Homogeneous catalysts have certain advantages: they contain only one type of active site and as a result are more specific. The selective ligand exchange, in contrast, thermal stability and suitable solvents. Then, they are often more selective, more active, and more reproducible, but are generally more difficult to remove after

the reaction; they also are more vulnerable to extraneous materials, have shorter catalyst life, and are thermally more unstable when compared to usual heterogeneous catalysts.

Mild homogeneous catalyst systems are easily examined along the reaction by nondestructive chemical analysis such as NMR, electron spin resonance (ESR), and infrared (IR) spectroscopy .The ease of investigation into the mechanism of homogeneous catalysis and the structure of homogeneous catalysts is a distinct advantage, opening rational easy to develop novel and intriguing catalysts.

2.4 Heterogeneous catalysts

A major problem associated with most homogeneous catalyst systems is the separation and recycling of the expensive catalyst. A possible solution to this problem is to “heterogenize” a homogeneous catalyst, either by anchoring the catalyst on a solid support or by using a liquid-liquid two-phase system.

Heterogeneous catalysts are present in different phases from the reactants (e.g. a solid catalyst in a liquid reaction mixture). A simple model for heterogeneous catalysis involves the catalyst providing a surface on which the reactants (or substrates) temporarily become adsorbed. Bonds in the substrate become weakened sufficiently for new to be created. The bonds between the products and the catalyst are weaker, so the products are released. One or more of the reactants are adsorbed on to the surface of the catalyst at active sites. An active site is a part of the surface which is particularly good at adsorbing things and helping them to react. There is interaction between the surface of the catalyst and the reactant molecules which makes them more reactive. This might involve an actual reaction with the surface, or some weakening of the bonds in the attached molecules. Both of the reactant molecules might be attached to the surface, or one might be attached and hit by the other one moving freely in the gas or liquid. The product molecules are desorbed. Desorption simply means that the product molecules break away. This leaves the active site available for a new set of molecules to attach to and react. A good catalyst needs to adsorb the reactant molecules strongly enough for them to react, but not so

strongly that the product molecules stick more or less permanently to the surface. Silver, for example, is not a good catalyst because it doesn't form strong enough attachments with reactant molecules. Tungsten, on the other hand, is not a good catalyst because it adsorbs too strongly. Metals like platinum and nickel make good catalysts because they adsorb strongly enough to hold and activate the reactants, but not so strongly that the products cannot break away.

Over the past two decades, the studies of insoluble polymer-supported catalysts have attracted much attention. The isolation of products from the support catalyst is facilitated and the catalyst can be used repeatedly by a simple procedure. The advantages, apart from recovery and reuse, are isolation of catalytic sites and prevention of agglomeration leading to inactivation and coordinate unsaturation introduced by the polymeric matrix resulting in enhanced specificity.

Unfortunately, the use of insoluble polymer-supported catalysts suffered from lower catalytic activity and stereo selectivity due to the restriction of the polymer matrix which resulted in limited mobility and accessibility of the active sites. The leaching of the noble metal catalyst from the polymer support was also a significant problem.

The decomposition of hydrogen peroxide has been used as a model reaction for the investigation of the catalytic activity of various metal complexes. Although the catalytic mechanism has not been thoroughly elucidated, this decomposition of H_2O_2 is often employed as a standard reaction to determine the catalytic activity of a polymer metal complex.[34]

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Table 2.1 Major differences between homogeneous and heterogeneous catalysts

Characteristic	**Homogeneous catalyst**	**Heterogeneous catalyst**
1. Catalyst composition and nature of active site	Discrete molecules with will-defined site.	Nondiscrete molecular entities: active site not well-defined
2. Determination of reaction mechanism	Relatively straightforward using standard techniques.	Very difficult.
3. Catalyst properties	Easily modified, often highly selective, poot thermal stability and mild conditions.	Difficult to modify, relatively unselective, thermally robust and vigorous reaction conditions
4. Separation from product	Often difficult	Relatively easy.

2.5 History and occurrence of vanadium

Vanadium was discovered in 1831 by the Swedish chemist Nils Gabriel Sefström (1787-1845). He named the element vanadin, after the goddess of beauty, youth and love, Vanadis, referring to the beautiful multicoloured compounds.

Natural vanadium is a mixture of two isotopes, V (99.76%) and V (0.24%), the latter being slightly radioactive with a half-life of >3.9 x 1017 years. Important sources of the metal are the minerals carnotite [$K_2(UO_2)_2(VO_4)_2$] and vanadinite [$Pb(VO_4)_3Cl$]. It is also present in some crude oils in the form of organic complexes. Vanadium occurs with an abundance of 0.014% in the earth's crust and is widespread. The element is the second most abundant transition metal in the oceans. Some aquatic organisms are known to accumulate vanadium. For instance, members of an order of tunicates (Ascidiacea) concentrate vanadium to 0.15 M in specialised blood cells. However, the actual function of vanadium and the nature of the vanadium compounds present in these organisms remains unclear. In 1983, a naturally occurring vanadium-

containing enzyme, vanadium bromoperoxidase (V-BrPO), was discovered in the marine brown alga Ascophyllum nodosum. Since then, several vanadium haloperoxidases (vide infra) have been isolated and studied.

Vanadium can exist in eight oxidation states ranging from –3 to +5, but with the exception of –2.Only the three highest, *i.e.* +3, +4 and +5, are important in biological systems. Under ordinary conditions, the +4 and +5 oxidation states are the most stable ones. The majority of vanadium(IV) compounds contains the VO^{2+} unit (vanadyl ion). These complexes typically have square planar pyrimidal or bipyrimidal geometries with an axial oxo ligand. The coordination chemistry of vanadium(V) compounds is dominated by oxo complexes, containing the VO^{3+} or the VO^{2+} moiety. V^{4+} and V^{5+} ions are very small with radii of 0.61 Å and 0.59 Å, respectively.[18] Therefore these ions are even smaller than lithium (the radius of a Li^{+} ion is 0.78 Å).[18] Due to the d^1 configuration of V(IV) ions, vanadium(IV) species are easily identified by EPR spectroscopy. Typical eight-line patterns are observed due to hyperfine interaction of the V nucleus (I = 7/2). V(V) is EPR silent due to its d^0 state. Vanadium(V) complexes are therefore diamagnetic, which makes them appropriate for NMR analyses.

2.6 Vanadium complexes for oxidation chemistry

As a consequense of their low radius/charge ratio, vanadium(V) centres are usually strong Lewis acids, which makes them suitable for the activation of peroxidic reagents. Accordingly, vanadium(V) complexes have been found to act as catalyst precursors in various oxidation reactions like bromination reactions, epoxidations of alkenes and allylic alcohols, oxidations of sulfides to sulfoxides and sulfones, hydroxylations of alkanes and arenes, and oxidations of primary and secondary alcohols to the corresponding aldehydes and ketones (Figure 2.1). The active species has been identified in stoichiometric reactions as mononuclear oxoperoxovanadium(V) complexes, some of which have been structurally characterized. In all cases the peroxide is bound in an È2–manner in the equatorial plane relative to the axial oxo ligand. Vanadium(IV) complexes can also be used as

precursors in these oxidation reactions. In the presence of excess peroxide, they are readily converted to the oxoperoxovanadium(V) complexes.

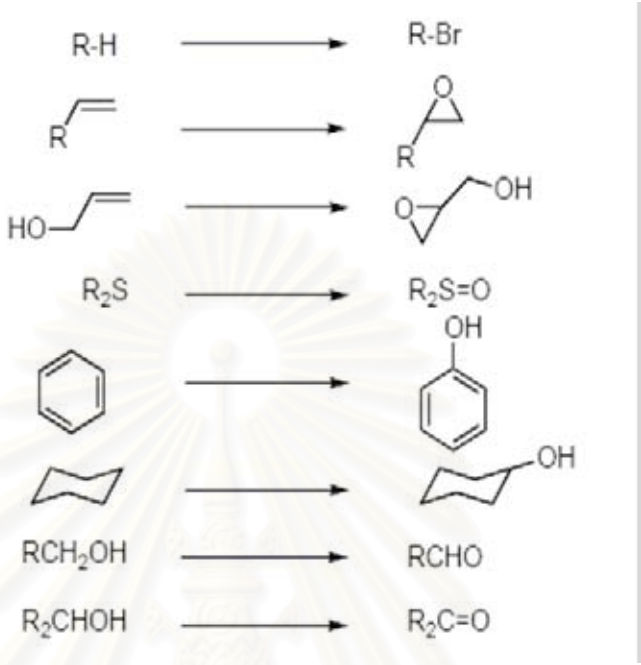

Figure 2.1 Examples of the reaction types mediated by peroxovanadium(V) complexes.

Several vanadium complexes are known to catalyse the oxidation of unfunctionalised olefins. It was proposed that when a vacant site on the vanadium centre is present, the olefins are able to coordinate to the vanadium centre, leading to the formation of epoxides with high selectivity. [30] However, when coordination of the olefin is not possible, one electron oxidation processes often play a role, which proceed in a non-stereoselective manner.

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2.6 Oxidizing agents [24]

Air, the cheapest oxidant, is used only rarely without irradiation and without catalysts. Examples of oxidations by air alone are the conversion of aldehydes into carboxylic acid (autoxidation).

Oxygen (O_2) exists in two states. Stable ground-state oxygen (triplet oxygen) has two odd electrons with parallel spins. It behaves like a diradical and is paramagnetic. In excited-state oxygen (singlet oxygen), the two odd electrons possess antiparallel spins. Such a molecule is unstable, with a half-life of 10^{-6} s , and is diamagnetic. Each form reacts differently with organic molecules.

Ozone (O_3), a blue gas or a dark blue liquid (bp.-106,-116 or-125 ◦C, depending on the source of data), is used in a mixture with oxygen. Ozonizations are carried out by passing ozone-containing oxygen through solution of organic compounds in solvent that do not react with ozone and liquid at low temperature. Cooling with dry ice-acetone bath (-78 ◦C) is frequently needed to prevent the decomposition of ozone, some of which are unstable at room temperature. The most common solvents are pentane, cyclohexane, dichloromethane, chloroform, methanol, acetic acid, and ethyl acetate.

Hydrogen peroxide (H_2O_2), an effective oxidant that could be used in many industrial processes. Because the only by-product of oxidation using hydrogen peroxide is water, it could become the ultimate green chemical for the manufacture of many oxygenated petrochemicals. However, the current method for producing is inefficient and too costly. It is commercially available in aqueous solutions of 30% or 90% concentration. The 30% hydrogen peroxide is a colorless liquid (*d* 1.110) and it is stabilized against decomposition, which occurs in the presence of traces of iron, copper, aluminum, platinum, and other transition metals. The 30% hydrogen peroxide does not mix with nonpolar organic compound. The 90% hydrogen peroxide is stable at 30◦C (The decomposition rate is 1%/year), it decomposed slowly at high temperatures and rapidly with boiling at140◦C. The pure hydrogen peroxide solution is stable with weak decomposition. However, when it comes in contact with heavy

metals or various organic compounds, or mixes with impurities, it produces oxygen gas and heat. When formic or acetic acid is used, the reacting species is the corresponding peroxy acid. Under such conditions, the products of oxidation by hydrogen peroxide resemble those obtained with peroxy acid.

***Tert*-butyl hydroperoxide** ($(CH_3)_3COOH$), a commercially available as a 70% or 90% solution containing water and *tert*-butyl alcohol. It must be handled with extreme care, because it may decompose violently in the presence of strong acid and some transition metals, especially manganese, iron, and cobalt. Oxidation with *tert*-butyl hydroperoxide consists of epoxidation of alkene in the presence of transition metals. In this way, α, β-unsaturated aldehyde and ketone are selectively oxidized to epoxide without the involvement of the carbonyl function. Other applications of *tert*-butyl hydroperoxide are the oxidation of lactam to imide, of tertiary amine to amine oxide, and of phosphite to phosphate. In the presence of a chiral compound, enantioselective epoxidation of alcohol is successfully accomplished with moderate to high enantiomeric excesses.

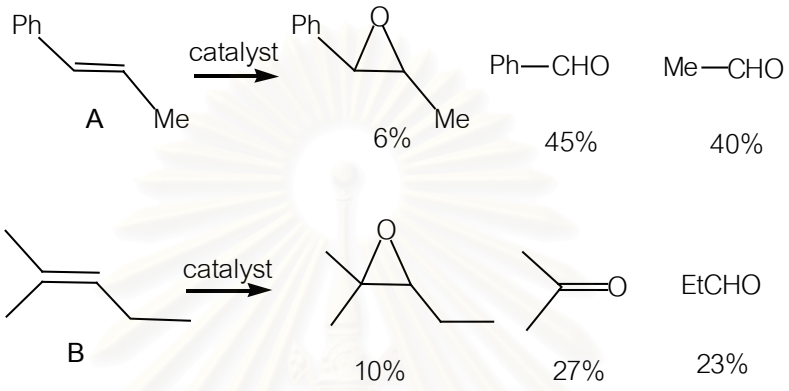
Peroxyformic acid (perfomic acid). HCO_3H, is always prepared *in situ* from hydrogen peroxide and formic acid. A much rare application of performic acid is the transformation of 2- or 4-dialkylaminoperhalopyridines into either amine oxides or N,N-dialkylhydroxylamines.

Peroxyacetic acid (peracetic acid), CH_3CO_3H, can be formed *in situ* from hydrogen peroxide with acetic acid. The most important applications of peroxyacetic acid are the epoxidation and antihydroxylation of double bonds, of tertiary amines to amine oxide, of sulfides to sulfoxide and sulfones, of iodo compounds to iodoso or iodoxy compounds, of alcohol to ketones, and of lactams to imides.

Sodium hypochorite, NaOCl. is a potent oxidizing agent that has been shown to transfer oxygen atom. However, the insolubility of hypochlorite salts in hydrocarbons and organic solvents has prevented the use of this material as a reagent for the selective oxidation of organic substrates.

2.7 Literature reviews

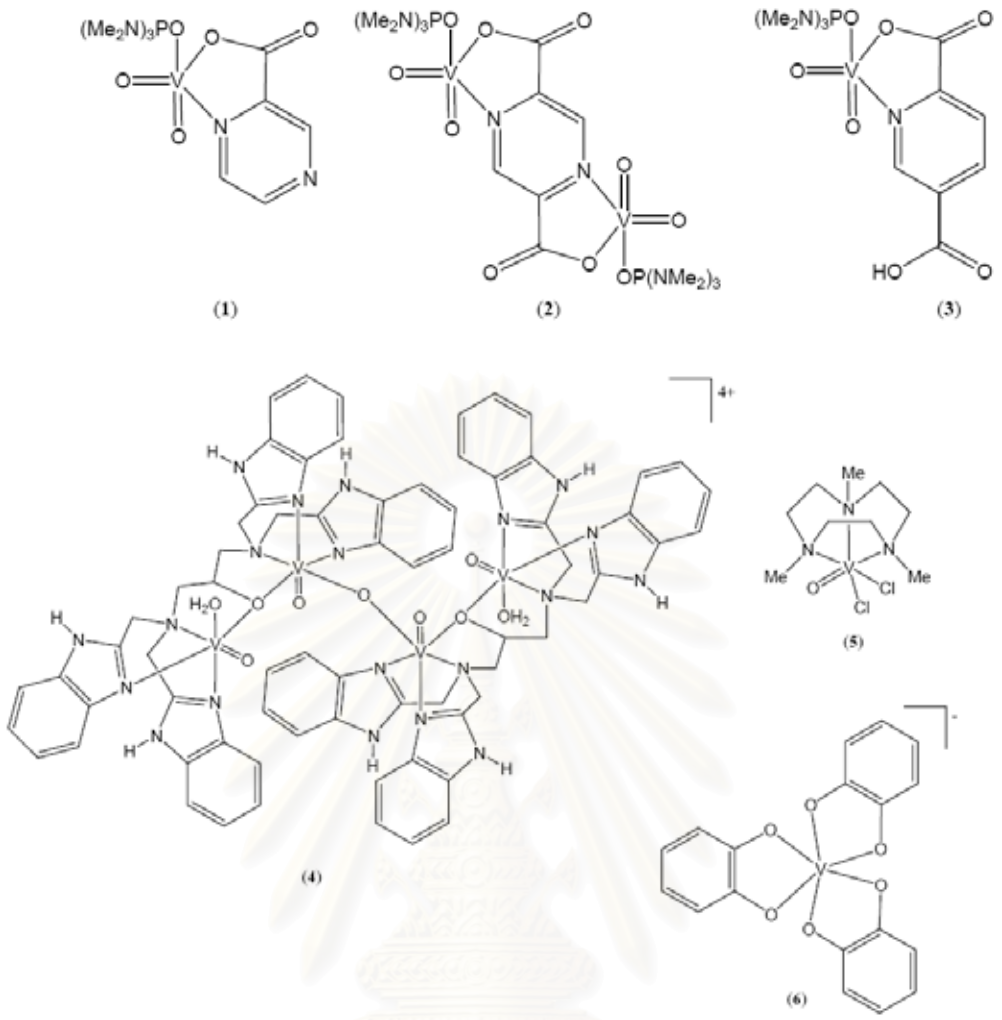
In 1982. Mimoun and coworker [34] synthesized vanadium (V) oxoperoxo catalyst by reacting picolinic acid with vanadium pentoxide (V_2O_5). It was used for oxidation of substrates A and B (scheme 2.1) using hydrogen peroxide as an oxidant in acetonitrile at 20 ◦C for 90 min.



Scheme 2.1 Products from oxidation with $[VO(O_2)(Pic).H_2O]$ catalyst.

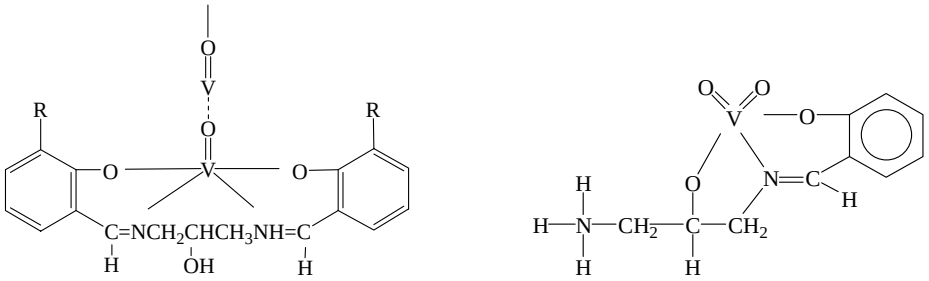
In 1997 Suss-Fink and coworkers [35] synthesized vanadium catalyst by reacting pyrazine-2-carboxylic acid with tetrabutyl-ammonium vanadate ($n\text{-}Bu_4NVO_3$). It was used for oxidation of methane using hydrogen peroxide as an oxidant in aqueous at 50◦C for 24 h under atmospheric pressure. The oxidation afforded acetic acid in 24% yield.

In 2003 Suss-fink and coworkers [4] prepared a series of mono and oligonuclear vanadium (V) and vanadium (IV) complexes containing various *N, O*–chelating ligands: $[VO_2(pca)(hmpa)]$ **(1)**, $[(VO_2)_2(pdca)(hmpa)_2]$ **(2)**, $[VO_2(pycaH)(hmpa)]$ **(3)**, $[(VO)_4(hptb)_2(\mu\text{-}O)]^{4+}$ **(4)**, $[VOCl_2(tmtacn)]$ **(5)** and $[V(cat)_3]^-$ **(6)**. These catalysts were used for oxidation of cyclohexane using hydrogen peroxide and air as oxidant in acetonitrile at 40 C◦ for 24 h. Pyrazine 2-carboxylic acid (pcaH) was also added as a cocatalyst (V/pcaH ratio 1:4) and found to accelerate the reaction. The complex **(1)** oxidizes cyclohexane to cyclohexanone, cyclohexanol and cyclohexyl peroxide in 3.6%, 17.3% and 8.6% respectively. Complex **(6)** catalyzes the oxidation with the highest initial rate. Structures of the catalysts are shown in scheme 2.2 .



Scheme 2.2 Mono and dinuclear vanadium (V) complexes containing *N, O*–chelating ligand.

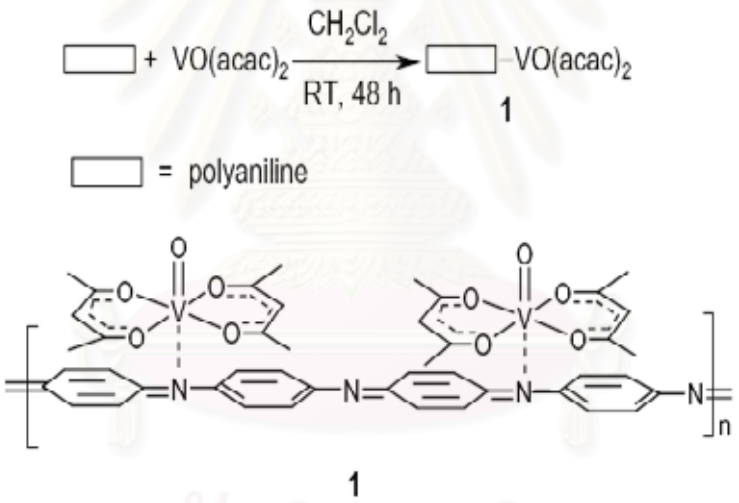
In 2003 Smith and coworkers [36] synthesized a Schiff base oxovanadium complexes of the salicyladimine ligand: $VO_2(C_{10}H_{13}N_2O_2)$ **(1)** and $VO(H_2O)(C_{19}H_{20}N_2O_5.2C_2H_4C_{l2})$ **(2).** They were used for oxidation of cyclohexene using *tert*-butyl hydroperoxide (TBHP) as oxidant in dichloromethane solvent. The reaction mixture was brought to reflux over a 30 min period. The product was cyclohexene oxide.



(1) (2)

Scheme 2.3 Proposed Schiff base oxovanadium complex structures.

In 2004, Reddy and coworkers [37] synthesized polymer-supported vanadium catalyst, by reacting polyaniline with $VO(acac)_2$. and used it for oxidation of benzyl alcohol at 80 °C for 15 h and atmospheric pressure of oxygen. When using acetonitrile solvent, the oxidation afforded benzaldehyde with 68% yield.



Scheme 2.4 $VO(acac)_2$ supported on polyaniline.

In 2004 Pillai and cowokers [38] synthesized vanadium phosphorus oxide (VPO) catalyst with a P/V of 1:1, and used it to catalyze oxidation of cyclopentanol using hydrogen peroxide at 65 °C for 4 h under nitrogen pressure. The oxidation took place and afforded cyclopentanone.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

The chemicals used were analytical grade.

Chemicals	Supplier
Ammonium (meta)vanadate	Fluka Chemie A.G., Switzerland
Acetonitrile	Merck, Germany
Acetone	Fluka Chemie A.G., Switzerland
Acetophenone	Fluka Chemie A.G., Switzerland
2- Butanol	Fluka Chemie A.G., Switzerland
Catechol	Fluka Chemie A.G., Switzerland
Dichloromethane	Lab Scans Co., Ltd., Ireland
Ethanol	Merck, Germany
Ethylenediamine tetraacetic acid	Fluka Chemie A.G., Switzerland
Methanol	Merck, Germany
Benzyl alcohol	Fluka Chemie A.G., Switzerland
Benzaldehyde	Fluka Chemie A.G., Switzerland
Cyclohexanol	Fluka Chemie A.G., Switzerland
Cyclohexanone	Fluka Chemie A.G., Switzerland
30 % Hydrogen peroxide	Merck, Germany
Nitric acid	Fluka Chemie A.G., Switzerland
1-Phenylethanol	Fluka Chemie A.G., Switzerland
Phosphoric acid	Fluka Chemie A.G., Switzerland
Sodium hydogen carbonate	Fluka Chemie A.G., Switzerland
Tert-butyl hydroperoxide (80%)	Merck, Germany
Tetabutylammonium hydroxide	Fluka Chemie A.G., Switzerland
Toluene	Lab Scans Co.,Ltd., Ireland
Tetabutylammonim hydroxide solution	Fluka Chemie A.G., Switzerland
Triethylamine	Fluka Chemie A.G., Switzerland
L- valine	Fluka Chemie A.G., Switzerland
Vanadium pentoxide	Fluka Chemie A.G., Switzerland
Vanadyl acetylacetonate	Fluka Chemie A.G., Switzerland

3.2 Equipment

- Heating oil bath
- Magnetic stirrer/hot plate
- Vacuum pump
- pH meter
- micropipette
- balance

3.3 Characterization methods

3.3.1 Fourier-transform infrared (FT-IR)

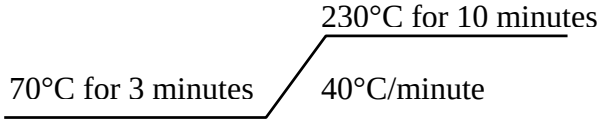
FTIR spectra were recorded on FTIR-8400-8900 at Department of Chemistry, Phetchaburi Rajabhat University. The samples were made into a KBr pellet. Infrared spectra were recorded between 400-4000 cm^{-1} transmittance mode.

3.3.2 Gas-liquid chromatography (GC)

Capillary column gas chromatography GC-14B, Shimadzu was used for the determination of products. The column is DB-1 and the detector is FID.

Programmed temperature for benzyl alcohol

Detetor temperature : 230 °C
Injector temperature : 230 °C
Carrier gas : Nitrogen

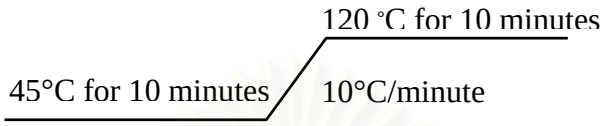


Programmed temperature for cyclohexanol

Detetor temperature : 180 °C

Injector temperature : 180 °C

Carrier gas : Nitrogen



Programmed temperature for 1-phenylethanol

Detetor temperature : 180 °C

Injector temperature : 180 °C

Carrier gas : Nitrogen

Isothermal temperature: 60 °C for 20 minutes

3.3.3 UV-visible spectrophotometry (UV-vis)

UV-visible spectra were recorded on UV-1601 Shimadzu in range of 200-700 nm.

3.3.4 X-ray diffraction (XRD)

The XRD patterns of catalysts were obtained on Rigaku, DMAX 2002 Ultima Plus X-ray powder diffractometer equipped with a monochromator and a Cu-target X-ray tube (40 kV, 30 mA).

3.3.5 Elemental analysis (EA)

Elemental analysis was carried out on CHNS/O ANALYSER (Perkin Elmer PE2400 Series II) at Scientific and Technological Research Equipment Center, Chulalongkorn University.

3.4 Synthesis of catalysts

A. *n*-Bu_4NVO_3, (tetabutylammonium vanadate) [35]

The compound was prepared by adding V_2O_5 (4.4 g) to 200 mL of aqueous *n*-Bu_4NOH solution (0.4 M). The contents were stirred for 18 h, then it was filtered off the small amount of insoluble material, and then evaporated to dryness at 60 °C.

B. [*n*-Bu_4N][V(cat) $_3$], (vanadium catecholate complex) [4]

To an acetonitrile solution (50 ml) of catechol (1.4204 g, 0.0129 mol) and triethylamine (10 ml) was added 1.4683 g (0.0043 mol) of *n*-Bu_4VO_3. The color of the solution immediately changed from colorless to blackblue. The reaction solution was refluxed for 5 h and the reaction mixture was evaporated to 1/3 of its volume, giving a dark blue precipitate of crystal which was filtered and washed five times with small amounts of acetonitrile.

C. V-*L*-valine, (vanadium-L-valine complex) [modified from 36]

To an aqueous solution (30 mL) of *L*-valine ($C_5H_{11}NO_2$) 0.47 g (4 mmol) and a hot solution of $VO(acac)_2$ 0.530g (2 mmol) in methanol (10 mL) . The reaction mixture was refluxed for 48 h. After that, the dark green compound was filtered and washed with water and dried.

D. V-EDTA, (vanadium ethylenediamine tetraacetate complex) [modified from 41]

To a rapidly stirred suspension of 11.17 g (30 mmol) of $Na_2H_2EDTA.2H_2O$ in 30 ml of water was added 3.51 g (30 mmol) of NH_4VO_3. The pH of the solution was adjusted to 7 by adding HCl or NaOH. A nearly clear yellow solution resulted after 1 h. The solution was filtered. Ethanol was added until a permanent turbidity was

obtained. The reaction mixture was reduced its volume, giving a shiny yellow crystal which was filtered and washed five times with acetonitrile.

E. V-PCA, (vanadium pyrazine carboxylate complex) [modified from 35]

A suspension of NH_4VO_3 (0.483 g) and pyrazine carboxylic acid ($C_5H_4N_2O_2$) (1.0415 g) was stirred in 30 mL of hot acetonitrile. The reaction solution was stirred for 24 h then it was reduced volume, giving a yellow powder which was filtered and washed with acetonitrile.

E. $(VO)_2P_2O_7$, (vanadyl pyrophosphate) [38]

V_2O_5 (10 g) was refluxed in a mixture of 2-butanol (30 mL) and benzyl alcohol (15 mL) for 14 h followed by addition of concentrated H_3PO_4 (1.93 mL, P/V = 1.1) and refluxed for further 6 h. The light green precipitate was filtered off, dried at 110°C overnight and then calcined in air at 400 °C for 4 h.

F. $VO(PO_4)(H_2O)_2$, (vanadyl phosphate dihydrate) [42]

The ground V_2O_5 0.96 g (6.28 mmol) was mixed with 5.3 mL of concentrated H_3PO_4, 11 mL of H_2O and 3 drops of concentrated HNO_3. The mixture was refluxed for 2 h. The bright yellow slurry was allowed to cool to room temperature. The yellow powder was filtered and then washed with water, acetone and dried.

G. $VO(HPO_4)(H_2O)_{0.5}$, (vanadyl monohydrogen phosphate hemihydrate) [42]

The above compound G, $VO(PO_4)(H_2O)_2$ 0.5 g (1.71 mmol) was refluxed in 10 mL of 2-butanol for 24 h. The mixture was allowed to cool to room temperature and the blue solid was filtered and dried.

3.5 The gerneral procedure for the oxidation of alcohols

In a round bottom flask, a catalyst (V-L-valine 0.0187 g , 0.063 mmol) was added to alcohol substrate (0.517 mL, 5 mmol), then an oxidant (10 mmol) and solvent (10 mL) were added. The mixture was stirred at 70 ◦C for 24 h. After that, it was worked up by taking 0.5 mL of the reaction mixture and acidified with 25% H_2SO_4 0.5 mL, then neutralized with saturated $NaHCO_3$ solution. For acetonitrile and dichloromethane as solvent: after acidified with 25% H_2SO_4, it was extracted with diethyl ether, followed by neutralized with saturated $NaHCO_3$ solution. The organic layer was analyzed by GC with the addition of exact amount of cyclohexanol (internal standard).

3.6 Study on the optimum conditions for the oxidation of benzyl alcohol with V- *L*-valine catalyst

Effect of solvent type

The oxidation reaction was performed using different solvent (dichloromethane, acetonitrile and toluene)

Effect of oxidant type

The oxidation reaction was performed using different oxidants (hydrogenperoxide, *tert*-butylhydroperoxide).

Effect of temperature

The oxidation reaction was performed at different reaction temperature (30◦C, and 70◦C)

Effect of time

The oxidation reaction was monitored at various reaction time.

Effect of oxidant/alcohol mole ratio

The oxidation reaction was performed using different oxidant/alcohol mole ratio.

Effect of alcohol/catalyst mole ratio

The oxidation reaction was performed using different alcohol/catalyst mole ratio.

3.7 Oxidation of various alcohols

The oxidation reaction was performed following the general procedure 3.5 using different types of alcohol: benzyl alcohol, cyclohexanol and 1-phenylethanol. The activity comparison of all prepared catalysts (as well as the commercially available catalysts, V_2O_5 and $VO(acac)_2$) was made at the same fixed reaction condition.

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CHAPTER IV

RESULTS AND DISCUSSION

Apart from the commercially available vanadium compounds: V_2O_5 and $VO(acac)_2$, some vanadium compounds and complexes were synthesized in this work They are:

n-Bu_4NVO_3 **(A)**

[*n*-Bu_4N][$V(cat)_3$]) **(B)**

V-*L*-valine **(C)**

V-EDTA **(D)**

V-PCA **(E)**

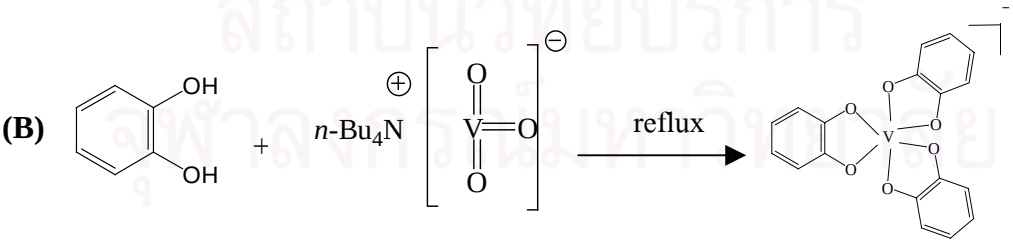
$(VO)_2P_2O_7$ **(F)**

$VO(PO_4)(H_2O)_2$ **(G)**

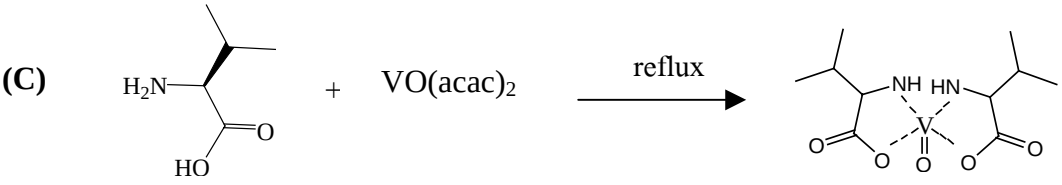
$VO(HPO_4)(H_2O)_{0.5}$ **(H)**

The reactions were shown below.

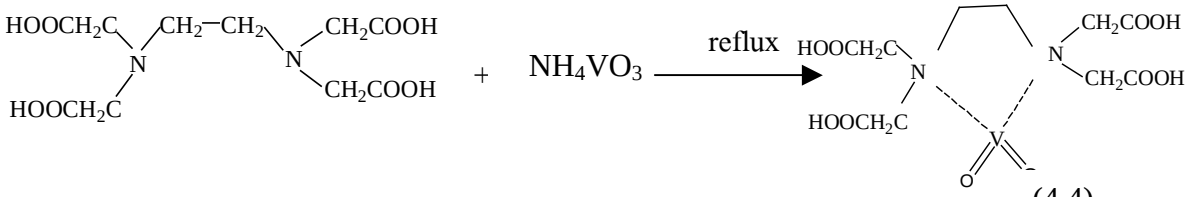
(4.1)



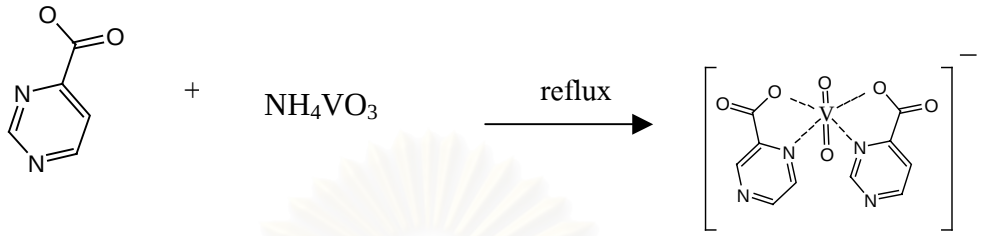
(4.2)



(4.3)

(D) 

(4.4)

(E) 

(4.5)

(F) V_2O_5 + 2butanol + benzyl alcohol + H_3PO_4 ⟶ $(VO)_2P_2O_7$

(G) $V_2O_5 + 2H_3PO_4 + H_2O$ ⟶ $2VO(PO_4)(H_2O)_2$

(H) $2VO(PO_4)(H_2O)_2 + CH_3CH_2CH(OH)CH_3$ ⟶ $2VO(HPO_4)(H_2O)_{0.5} + CH_3CH_2COCH_3 + 3H_2O$

4.1 Characterization of vanadium complexes

All prepared catalysts were characterized by X-ray diffraction (XRD), fourier transform infra-red, UV-visible and melting temperature. The data are shown below.

4.1.1. X-ray diffraction (XRD)

The crystalline characteristic of the prepared vanadium complexes was investigated by XRD technique. The XRD patterns are shown in Figure 4.1.

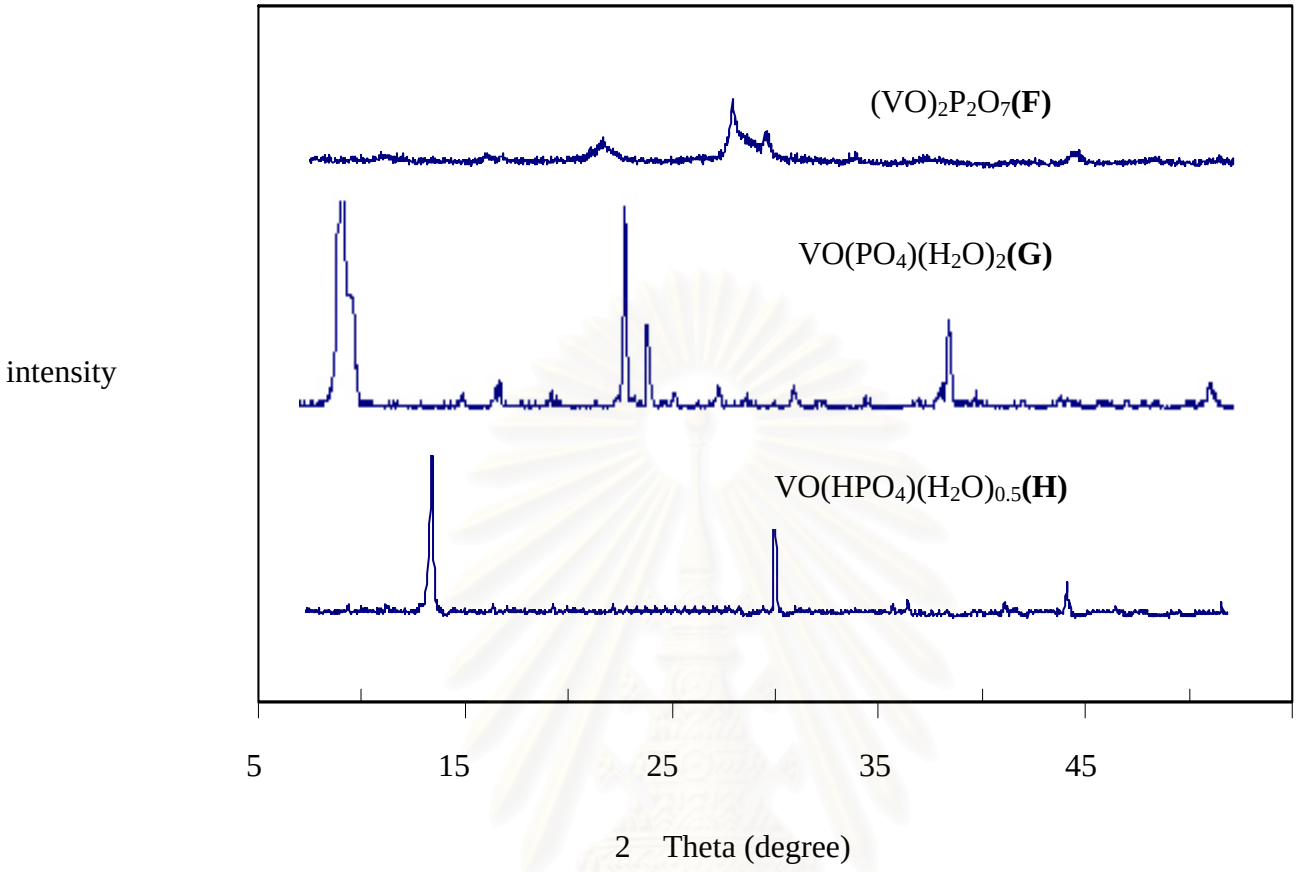


Figure 4.1 The XRD patterns of catalysts.

Table 4.1 The XRD technique was used to characterize structure of catalysts

Vanadiume complexes	**2 Theta (degree)**
n-Bu_4NVO_3**(A)**	7.4°, 15.0°, 22.7°
$[NBu_4][V(cat)_3]$**(B)**	9.3°, 21.8°
V-*L*-valine **(C)**	6.8°, 20.5°, 25.7°, 34.3°
V-EDTA **(D)**	8.6°, 9.0°, 15.9°, 17.2°, 18.5°
V-PCA **(E)**	12.3°, 22.4°, 22.6°, 27.9°
$(VO)_2P_2O_7$ **(F)**	23.0°, 28.4°, 29.9°. **ref. [38]**:23.1°, 28.4°, 29.9°
$VO(PO_4)(H_2O)_2$ **(G)**	11.88°, 23.9°, 37.8°. **ref. [42]** : 11.88°, 23.8°, 37.8°
$VO(HPO_4)(H_2O)_{0.5}$**(H)**	14.2°, 30.4°, 43.1°. **ref. [42]** : 14.3°, 30.5°, 43.1°

XRD patterns of the catalysts after calcination show characteristic peaks at 2θ values of 7.4°, 15.0° and 22.7° , characteristic of tetabutylammonium vanadate. For vanadium catechol complex, the peaks show at 9.3° and 21.8°.

4.1.2. Fourier transform infra-red (FT-IR)

The FT-IR spectra of vanadium complexes exhibited the characteristic absorption peaks as shown in Tables 4.2-4.7.

Table 4.2 The assignment for the FT-IR *n*-Bu_4NVO_3 **(A)**

Wave number (cm^{-1})	Assignment
850	V=O

In order to observe the coordination of metal to the ligand, the prepared tetra buthy complex was investigated by FT-IR technique. The peak at 850 cm^{-1} is the asymmetric of V=O stretching.

Table 4.3 The assignment for the FT-IR of vanadium-catechol **(B)**

Wave number (cm^{-1})		Assignment
Catechol ligand	Vanadium catecholate complexe	
2966	2966	C-H
1100	1150	C-O
-	874	V-O

In order to observe the coordination of metal to the ligand, the prepared vanadium-catechol complex was investigated by FT-IR technique. The results as given in Table 4.3. The appearance peak at 2966 cm^{-1} is assigned to C-H stretching.. The peak at 874 cm^{-1} is the asymmetric of V-O stretching. A band of C- O stretching at 1100 cm^{-1} positive shift to 1150 cm^{-1}. The results show that coordination of the ligand oxygen to the vanadium metal ion was occurred**.**

Table 4.4 The assignment for the FT-IR of *L*-valine and vanadium– *L*-valine complex **(C)**

Wave number (cm^{-1})		Assignment
L-valine ligands	Vanadium–*L*-valine complex	
2966	2966	C-H
1587	1587	C=O
1330	1326	C-O
1190	1200	C-N
-	836	V-O

In order to observe the coordination of metal to the ligand, the prepared vanadium –*L*-valine complex was investigated by FT-IR technique. The results as given in Table 4.3 the C-H stretching vibration appeared at 2966 cm^{-1}. The C=O stretching vibration appeared at 1587 cm^{-1}. The V-O stretching vibration appeared around 836 cm^{-1}. A band of C- O stretching at 1330 cm^{-1} negative shift to 1326 cm^{-1} and of C-N stretching at 1190 cm^{-1} position shift to 1200 cm^{-1} and The results show that coordination of the ligand nitrogen and oxygen to the vanadium metal ion was occurred**.**

Table 4.5 The assignment for the FT-IR (V-EDTA) **(D)**

Wave number (cm^{-1})		Assignment
EDTA ligands	Vanadium–EDTA complex	
3423	3423	O-H
1637	1637	C=O
1400	1400	C-O
1318	1308	C-N
-	831	V=O

In order to observe the coordination of metal to the ligand, the prepared vanadium EDTA complex was investigated by FT-IR technique. The results as given in Table 4. The O-H stretching vibration appeared at 3423 cm^{-1}. The C=O stretching vibration appeared at 1637 cm^{-1}. The V-O stretching vibration appeared around 831 cm^{-1}. The C-O stretching vibration appeared at 1400 cm^{-1}. A band of C-N stretching at 1318 cm^{-1} negative shift to 1308 cm^{-1}. The results show that coordination of the ligand nitrogen to the vanadium metal ion was occurred**.**

Table 4.6 The assignment for the FT-IR V-PCA **(E)**

Wave number (cm^{-1})		Assignment
PCA ligands	vanadium–PCA complex	
3068	3068	C-H
2650	2650	O-H
1700	1700	C=O
1400	1390	C-O
1180	1160	C-N
-	980	V-O

In order to observe the coordination of metal to the ligand, the prepared vanadium-PCA complex was investigated by FT-IR technique. The results as given in Table 4.6 the C-H stretching vibration appeared at 3068 cm^{-1}. The O-H stretching vibration appeared at 2650 cm^{-1}. The C=O stretching vibration appeared at 1700 cm^{-1}. The V-O stretching vibration appeared around 980 cm^{-1}. A band of C- O stretching at 1400 negative shift to 1390 and a band of C-N stretching at 1180 cm^{-1} negative shift to 1160 cm^{-1} and a The results show that coordination of the ligand nitrogen and oxygen to the vanadium metal ion was occurred**.**

The FT-IR spectra of vanadyl pyrophosphate ($(VO)_2P_2O_7$), vanadyl phosphate dihydrate ($VO(PO_4)(H_2O)_2$), vanadyl monohydrogenphosphate hemihydrate ($VO(HPO_4)(H_2O)_{0.5}$) were show in Table 4.6

Table 4.7 The assignment for the FT-IR $(VO)_2P_2O_7$ **(F),** $VO(PO_4)(H_2O)_2$ **(G),** $VO(HPO_4)(H_2O)_{0.5}$ **(H)**

Wave number (cm^{-1})			Assignment
$(VO)_2P_2O_7$	$VO(PO_4)(H_2O)_2$	$VO(HPO_4)(H_2O)_{0.5}$	
1081	1082	1055	P-O st.
962	952	920	V-O

From Table 4.5, the IR spectrum of FT-IR $(VO)_2P_2O_7$ **(F),** $VO(PO_4)(H_2O)_2$ **(G),** $VO(HPO_4)(H_2O)_{0.5}$ **(H)**. The peak at 1081-1055 cm^{-1} is assigned to P-O stretching. The peak at 962-920 cm^{-1} is the asymmetric of V-O stretching.

4.1.3 Ultraviolet – visible absorption spectroscopy

Vanadium complexes were characterized by UV-visible. Shows a representative UV-visible spectrum of catalysts, show in Tables 4.8

Table 4.8 The assignment for the UV-visible spectra of vanadium complexes

Entry	Vanadium complexes	Wavelength (nm)
1	*n*-Bu4NVO_3**(A)**.	307
2	$[NBu_4][V(cat)_3]$)**(B)**.	287
3	V-*L*-valine **(C)**	288
4	V-EDTA **(D)**	254
5	V-PCA **(E)**.	285
6	$(VO)_2P_2O_7$ **(F)**.	267
7	$VO(PO_4)(H_2O)_2$ **(G)**	292
8	$VO(HPO_4)(H_2O)_{0.5}$**(H)**	283

The absorption was originated from the ligand to metal charge transfer (LMCT) transition.

4.1.4 Melting temperature (T_m)

The melting temperatures of vanadium complexes : *n*-Bu_4NVO_3 **(A),** $[NBu_4][V(cat)_3]$ **(B)**, V-*L*-valine **(C)**, V-EDTA **(D)**, V-PCA **(E)**, $(VO)_2P_2O_7$ **(F)**, $VO(PO_4)(H_2O)_2$**(G)**, $VO(HPO_4)(H_2O)_{0.5}$ **(H)** were measured by differential temperture, shown in Table 4.9

Table 4.9 Melting temperature (°C) of vanadium complexes

Vanadium complexes	**Melting point (°C)**
n-Bu4NVO_3**(A)**.	120-121
$[NBu_4][V(cat)_3]$**(B)**.	330-332 (dec.)
V-*L*-valine **(C)**	330-333 (dec.)
V-EDTA **(D)**	114-116(dec.)
V-PCA **(E)**.	219-221
$(VO)_2P_2O_7$ **(F)**.	332-335 (dec.)
$VO(PO_4)(H_2O)_2$ **(G)**	330-332(dec.)
$VO(HPO_4)(H_2O)_{0.5}$**(H)**	114-116

4.2 Oxidation of alcohol

Various factors were evaluated to find the optimum conditions for the oxidation of alcohol. The representative catalyst, vanadium–*L*-valine was chosen as a representative compound and the results are shown in Tables 4.10-4.17

A. The effect of solvent type

The effect of solvent types was investigated in the oxidation of benzyl alcohol with acetonitrile, toluene and dichloromethane. The results were collected in Table 4.10

Table 4.10 The effect of solvent for the oxidation of benzyl alcohol by V-*L*-valine

Solvent	% benzyl alcohol (recovery)	%Yield	
		benzaldehyde	benzoic acid
acetonitrile	0	44.4	55.4
toluene	18.0	83.0	-
dichloromethane	8.1	42.0	48.1

Condition : Benzyl alcohol 5 mmol(0.517 mL), catalyst 0.0187 g, (0.063 mmol), TBHP 10 mmol(1.388 mL), solvent 10 mL, 70 ◦C, 24 h.

From the results obtained, benzaldehyde (83%)was formed as the only product when using toluene as solvent whereas both benzaldehyde and benzoic acid were formed when using more polar solvent: acetonitrile or dichloromethane. Both solvents gave comparable % aldehyde and acid (44% and 55%, respectively). This showed that solvent affects on the selectivity of product.

B. Effects of oxidant type

Two types of oxidant, tert-butyl hydroperoxide and hydrogen peroxide were compared and the results are shown in Table 4.11.

Table 4.11 The effect of oxidant type by V-*L*-valine

Oxidant	% benzyl alcohol (recovery)	% Yield (benzaldehyde)
70%TBHP	18.0	83.0
30%H_2O_2	48.9	53.0

Condition : Benzyl alcohol 5 mmol(0.517 mL), catalyst 0.0187 g, (0.063 mmol), oxidant 10 mmol, toluene 10 mL, 70 ◦C, 24 h.

The results under the same reaction conditions revealed that with regard to the nature of oxidants, it was found that TBHP and H_2O_2 were effective, the former is more effective (benzaldehyde 83%). The lower activity of H_2O_2 (benzaldehyde 53%) might be due to the too fast decomposition at 70 ◦C. Therefore, TBHP was chosen as oxidant for further experiments.

C. Effects of temperature

Temperature is another important parameter for the reaction. The results are collected in Table 4.10.

Table 4.12 The effect of temperature for oxidation of benzyl alcohol by V-*L*-valine.

Temp.	**% benzyl alcohol (recovery)**	**%Yield (benzaldehyde)**
30 ◦C	44.3	55.2
70 ◦C	18.1	83.0

Condition : Benzyl alcohol 5 mmol(0.517 mL), catalyst 0.0187 g, (0.063 mmol), TBHP 10 mmol (1.388 mL), toluene 10 mL, 24 h.

It can be seen that the oxidation of benzyl alcohol with TBHP at 70◦C gave superior yield of benzaldehyde to that performed at 30◦C (83% vs 55%). The %yield increased with increased temperatures, suggesting that the activation energy for TBHP decomposition is lower than the activation energy for the alcohol oxidation.

D. Effects of time

Oxidation of benzyl alcohol with TBHP was monitored with time, the results were shown in Table 4.11 and Figure 4.13

Table 4.13 The effect of time for oxidation of benzyl alcohol V-*L*-valine

Reaction time (h)	% benzyl alcohol (recovery)	% Yield (benzaldehyde)
4	36.1	63.0
8	28.2	72.9
12	22.9	77.3
16	19.3	80.0
20	17.1	82.2
24	18.0	83.0
32	15.3	85.3

Condition : Benzyl alcohol 5 mmol(0.517 mL), catalyst 0.0187 g, (0.063 mmol), TBHP 10 mmol (1.388 mL), toluene 10 mL.

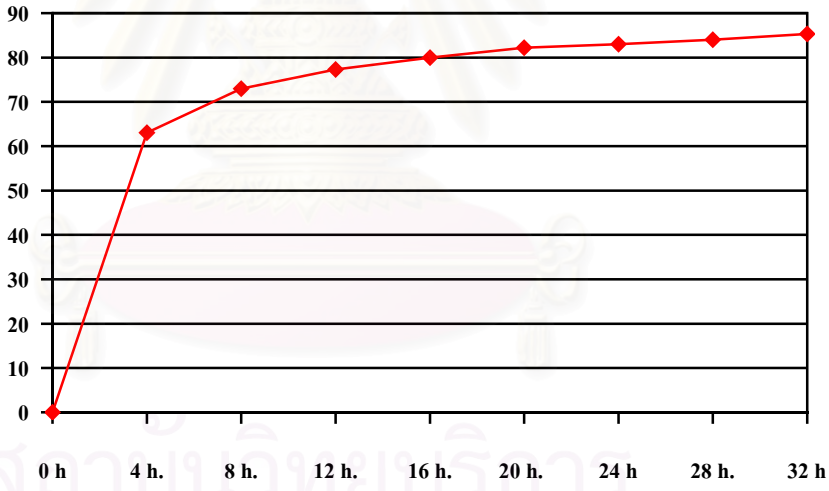


Figure 4.5 % Yield vs time.

The results indicate clearly that the yield of benzyl alcohol increased with reaction time. The rate increased rapidly in the initial stages, then remained almost constant after than 16 h. This result agrees with the previous reports [44-45].

E. Effects of oxidant/alcohol mole ratio

Mole ratio of oxidant/alcohol was varied, and the results were shown in Table 4.14.

Table 4.14 The effect of oxidant/alcohol mole ratio by V-*L*-valine

Mole ratio Oxidant/alcohol	**% benzyl alcohol (recovery)**	**% Yield** (benzaldehyde)
1	21.0	78.1
2	16.1	83.0
4	13.0	87.2

Condition : Benzyl alcohol 5 mmol(0.517 mL), catalyst 0.0187 g, (0.063 mmol), toluene 10 mL, 24 h.

The results showed increased product yield when oxidant/alcohol mole ratio was increased. At TBHP/benzyl alcohol mole ratio = 4, the obtained yield is 87.2%. This result agrees with the other report, the oxidation product of phenol increased when TBHP was increased. [10].

F. Effect of alcohol/catalyst mole ratio

Mole ratio of alcohol/catalyst: 60, 80, 100 were investigated. The results are presented in Table 4.15.

Table 4.15 The effect of alcohol/catalyst mole ratio by V-*L*-valine

Alcohol/catalyst Mole ratio	**% benzyl alcohol (recovery)**	**% Yield (benzaldehyde)**
60	21.0	84.2
80	16.1	83.0
100	13.0	73.4

Condition: Benzyl alcohol 5 mmol(0.517 mL), TBHP 10 mmol (1.388 mL), toluene 10 mL, 24 h.

When mole ratio of alcohol/catalyst = 60, the highest yield of benzaldehyde was obtained. It was generally found that oxidation product (e.g. of phenol) increased when creasing the amount of catalyst [13].

Oxidation of various alcohols with various catalysts

The oxidation of various alcohols was performed using different catalysts, a comparison was also made between the prepared catalysts and the commercially available ones: V_2O_5 and $VO(acac)_2$. Besides, activities of the catalysts in toluene and acetonitrile solvents were also compared. The results were summarized in Tables 4.14 - 4.15.

Table 4.16 Oxidation of various alcohols using toluene as solvent

Catalyst	**benzyl alcohol**	**1-phenylethanol**	**cyclohexanol**
	%benzaldehyde	**% acetophenone**	**%cyclohexanone**
V_2O_5	79.3	76.1	66.0
$VO(acac)_2$	65.5	54.5	45.5
nBu_4VO_3 **(A)**	63.0	53.2	46.5
$[NBu_4][V(cat)_3]$ **(B)**	81.4	73.8	63.7
V-L-valine **(C)**	83.0	74.1	64.3
V-EDTA **(D)**	46.1	38.2	28.1
V-PCA **(E)**	87.4	76.4	69.4
$(VO)_2P_2O_7$ **(F)**	60.1	52.1	42.1
$VO(PO_4)(H_2O)_2$ **(G)**	65.1	57.3	47.0
$VO(HPO_4)(H_2O)_{0.5}$ **(H)**	60.1	52.2	42.2

Conditions: catalyst 0.063 mmol, alcohol 5 mmol; TBHP 10 mmol; toluene 10 mL; 70 °C; 24 h.

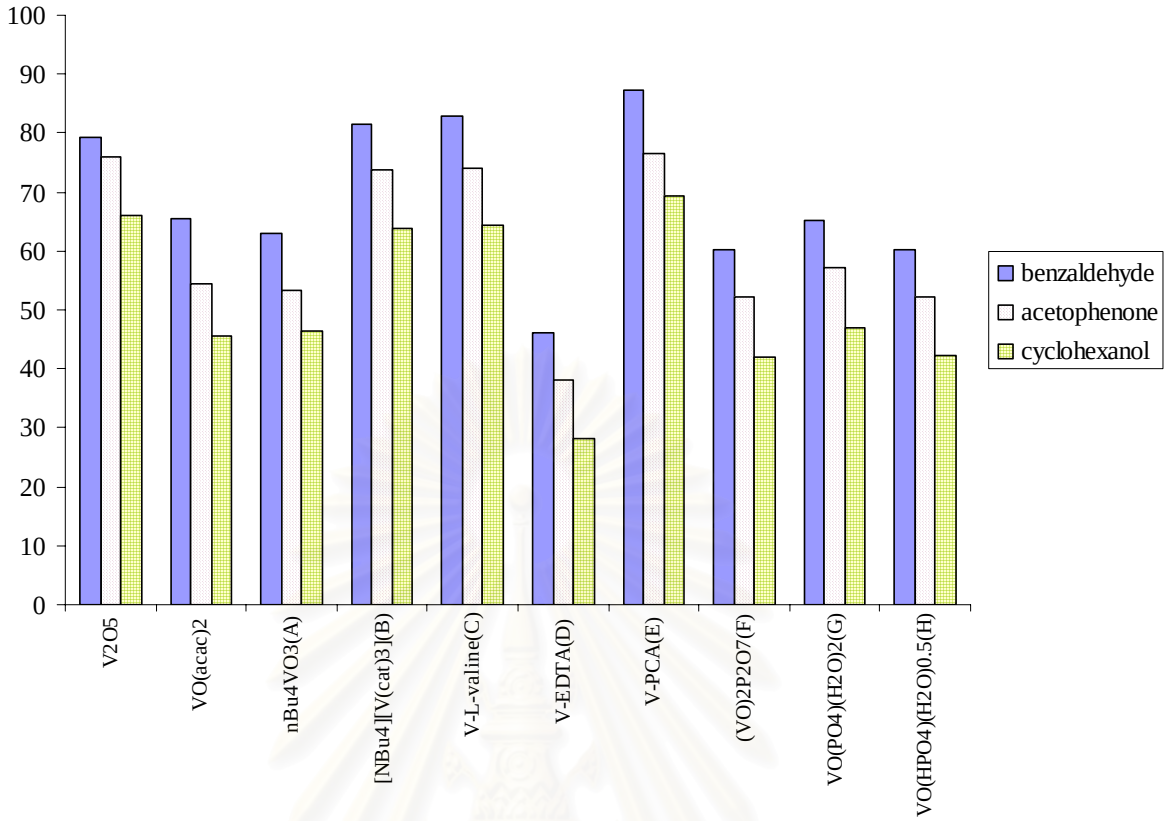


Figure 4.2 % Yield when using various of catalyst when using toluene as solvent.

Considering each type of catalyst, the oxidation of different alcohols resulted in different results. Using toluene solvent, it was found that the oxidation of benzyl alcohol, 1-phenylethanol and cyclohexanol afforded benzaldehyde, acetophenone and cyclohexanone, respectively. The order of reactivity is: benzyl alcohol > 1-phenyl ethanol > cyclohexanol. This result agrees with the previous reported [46-47]. Oxidation of alcohols the reactivity commonly found is with the following order: secondary benzylic > primary benzylic > secondary acyclic > primary acyclic.

From this result, it was demonstrated that primary alcohol was oxidized faster than secondary alcohol. It should be mentioned that for benzyl alcohol, it was oxidized to aldehyde, with no further oxidation to benzoic acid.

Considering the type of catalysts, for each substate, it was noticed that the catalysts containing chelating ligand: catalyst, V-PCA **(E)**, V-L-valine **(C)**, $[NBu_4][V(cat)_3]$ **(B)** showed higher activity than simple vanadium oxide, vanadium

phosphorus oxide or vanadate. However, for V-EDTA, the yield is quite low, this might be due to the impured compound.

It was reported that the ligand containing O-N, i.e. pyrazinecarboxylic and picolinic acid was good complexing ligand to interact with vanadium ion.

In this work, the catalyst containing L-valine ligand showed good activity (83%), this is better than that reported using polymer-supported copper(II)-L-valine complex, which the oxidation reaction of benzyl alcohol was performed at 45 ˚C for 24 h, using TBHP oxidant and yield 72% benzaldehyde product [39].

From Table 4.8, it was shown that both acetonitrile and dichloromethane gave similar results. Therefore, in order to determine the yield of the oxidation product with various catalysts, acetonitrile was selected for the study. The results are summarized in Table 4.15.

Table 4.17 Oxidation of various alcohols using acetonitrile as solvent

Catalyst	Benzyl alcohol		1-Phenylethanol	Cyclohexanol
	%benzaldehyde	%benzoic acid	%acetophenone	%cyclohexanone
V_2O_5	28.7	71.0	89.0	86.5
$VO(acac)_2$	43.0	56.0	70.7	65.5
nBu_4VO_3 **(A)**	29.9	70.1	87.0	85.2
[NBu4][V(cat)3] **(B)**	29.7	70.3	86.0	82.0
V-L-valine **(C)**	30.4	69.4	80.0	75.5
V-EDTA **(D)**	61.6	38.3	49.8	44.3
V-PCA **(E)**	26.0	73.1	95.0	89.4
$(VO)_2P_2O_7$ **(F)**	28.0	72.1	91.9	86.9
$VO(PO_4)(H_2O)_2$ **(G)**	26.1	73.0	93.2	88.2
$VO(HPO_4)(H_2O)_{0.5}$ **(H)**	30.0	70.1	89.4	84.4

Conditions: catalyst 0.063 mmol, alcohol 5 mmol; oxidant 10 mmol; acetonitrile 10 mL; 70 ˚C; 24 h.

From the results, it was found that acetonitrile gave different results from toluene. For benzyl alcohol, not only benzaldehyde was detected, but also benzoic acid product, selectivity to benzoic acid = 70-73% (except for V-EDTA, selectivity to benzoic acid = 38%) . This illustrated that the solvent has an effect on the reaction.

It was known that acetonitrile also activated H_2O_2 by forming a perhydroxyl anion (OOH^-) that nucleophilically attacks the nitrile to generate a peroxy-carboximidic acid intermediate [37]. This intermediate is a good oxygen transfer agent. Therefore, benzyl alcohol was oxidized further to benzoic acid. [48]

When performing oxidation of 1-phenylethanol using acetonitrile as solvent, it turned out that all catalysts showed higher activity than using toluene. This is quite interesting. Generally, acetonitrile was a preferred solvent for many reactions. [49]

For the oxidation of cyclohexanol, the results obtained are similar to that of 1-phenyl ethanol, all the catalysts gave high yield of product.

When compare the results obtained from this work with others, it should be mentioned that in the literature, it was reported that oxidation of benzyl alcohol, 1-phenyl ethanol and cyclohexanol with Fe(3+)/K10 catalyst using H_2O_2 and acetonitrile gave 95%, 86% and 35% conversion, respectively. [50] In the case of benzyl alcohol, benzoic acid was also obtained (selectivity to benzoic acid = 68).

Compared among the various catalysts tested in this work, at the fixed reaction conditions: the results reveal that V- PCA, V-L-valine gave better activity than others.

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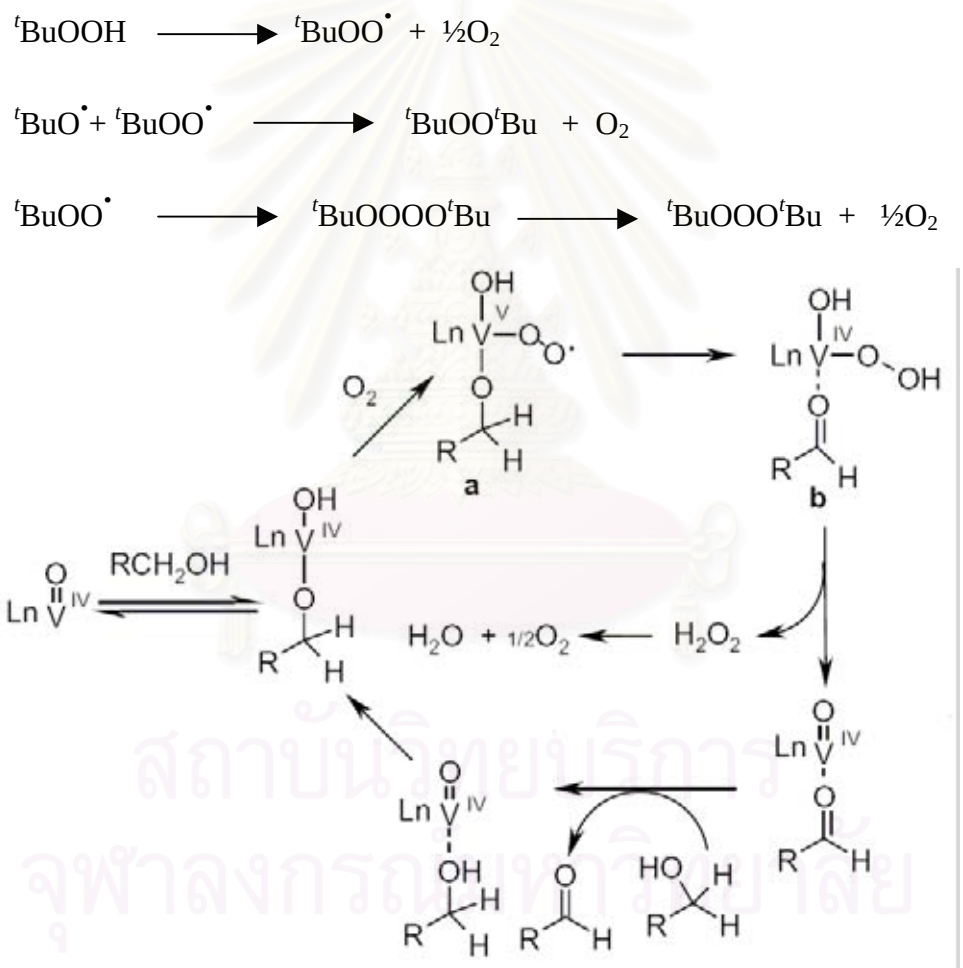
Proposed mechanism

The oxidation of alcohol to ketone and aldehyde compounds can take place via free radical. The active sites of vanadium catalysts might be derived from hydroxyl groups associated to the vanadium cations. Alcohol attacks on a hydroxyl group on the vanadium, and then a ligand-exchange reaction between the hydroxyl and alcohol gives a vanadium species, which further undergoes elimination to afford an aldehyde product. Presumably, the hydroxyl groups (OH-) with strong basicity promote the ligand exchange between alcohol and hydroxyl; a basic hydroxyl group abstracts a proton from alcohol to form a water molecule and a vanadium species [17,47].



Scheme 4.1 Proposed mechanism for vanadium catalyzed oxidation of alcohols.

CHAPTER V

CONCLUSION AND SUGGESTION

From the proceeding results and discussions, the main focus of this research is to synthesize and utilize vanadium catalysts for the oxidation of different type of alcohols. Vanadium complexes were prepared with several kinds of ligands: *L*-valine, ethylene diamine tetraacetic acid (EDTA), catechol, pyrazine-2-carboxylic acid. .The structures of the complexes were confirmed by X-ray diffraction, Fourier transform infrared spectroscopy, UV-visible spectrometry.

It was found that the solvent system, temperature, time, alcohol/oxidant mole ratio, alcohol/catalyst mole ratio affected % yield of product. The optimum condition was found to be at 70 °C for 24 h and alcohol/TBHP mole ratio = 2. Benzyl alcohol was oxidized to benzaldehyde and benzoic acid in the presence of acetonitrile as solvent whereas only benzaldehyde was detected when using toluene. 1-phenylethanol and cyclohexanol gave ketone product.

Suggestion for the future work

As the activity of the catalysts in this work is comparable to the commercial V_2O_5, but lower amount of oxidant is used. Therefore, the catalytic system found should be applied to a larger scale.

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APPENDICES

สถาบันวิทยบริการ
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APPENDIX A

สถาบันวิทยบริการ
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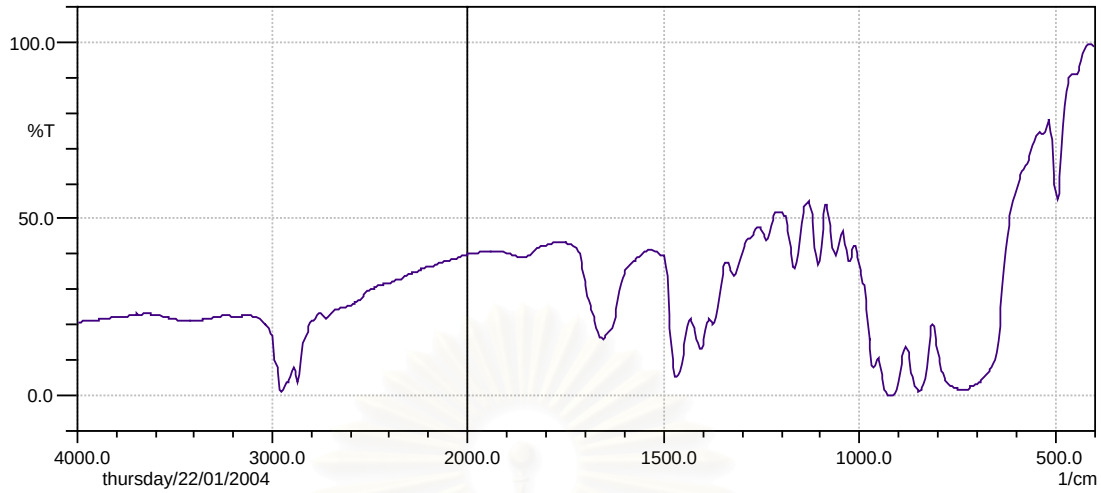

Figure 4.1 FT-IR spectram of *n*-Bu_4NVO_3.

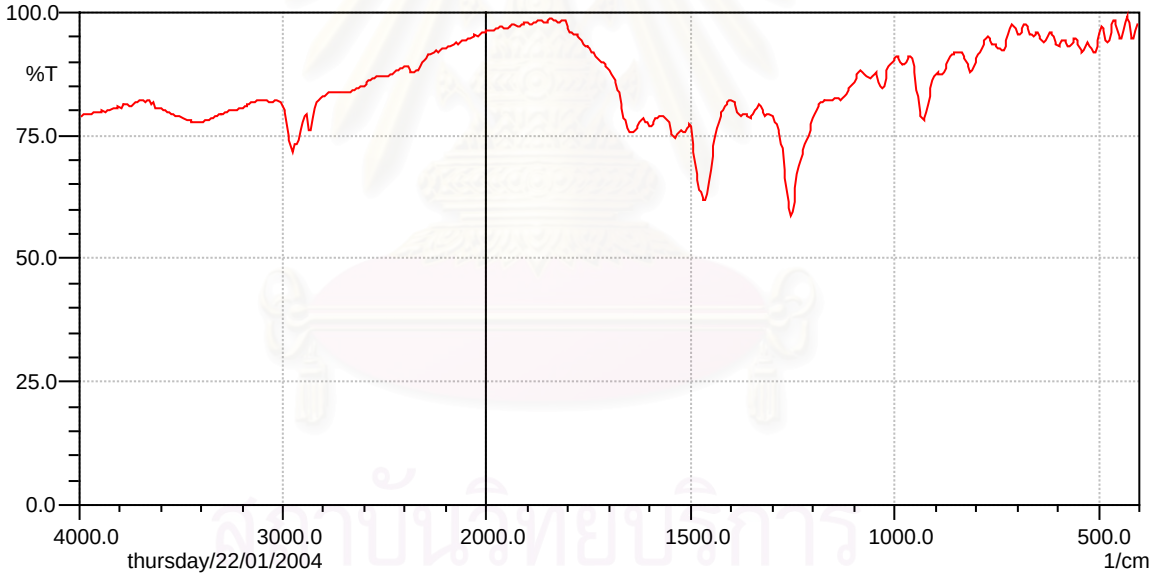

Figure 4.2 FT-IR spectram of V-catechol.

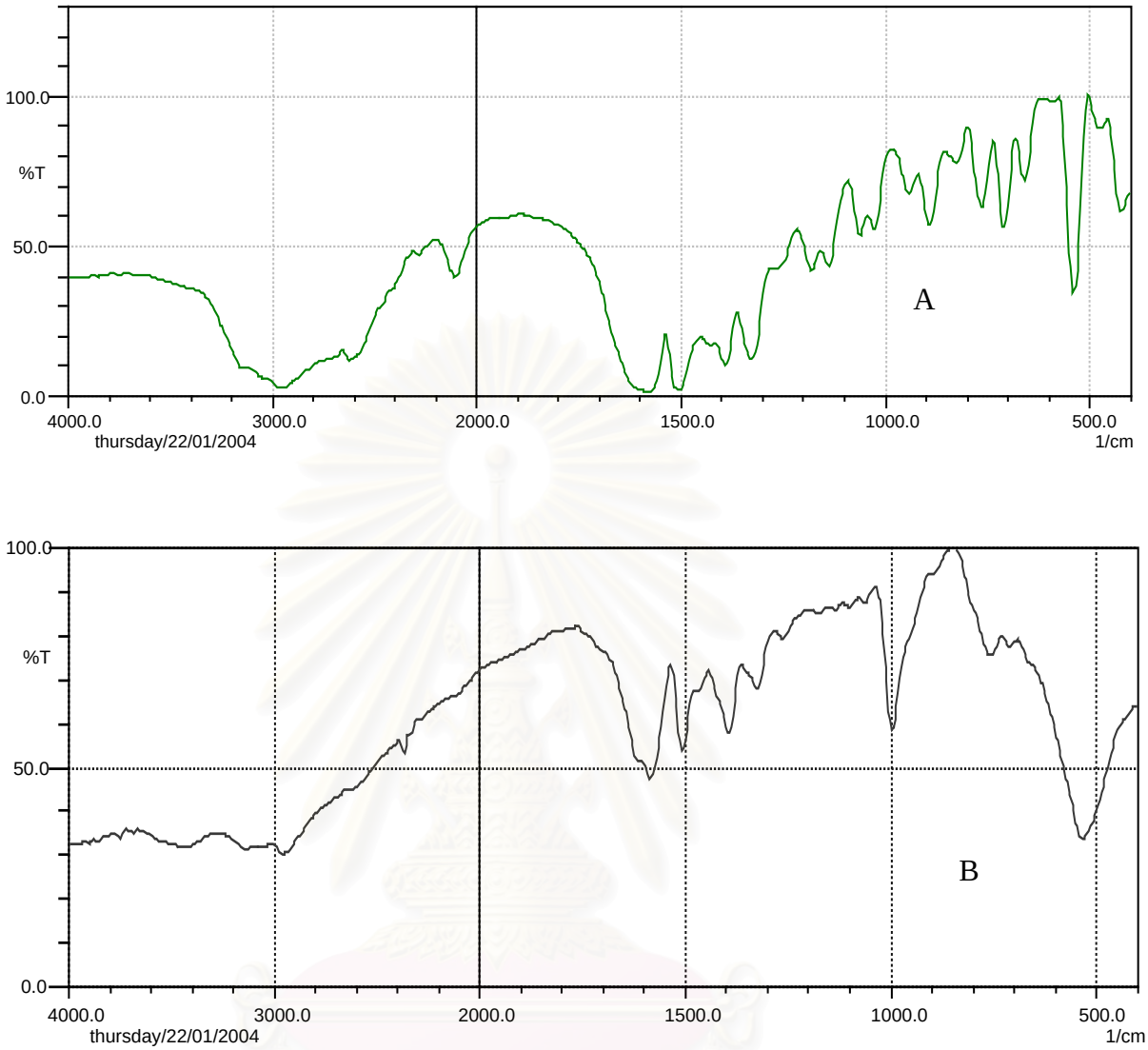

Figure 4.3 FT-IR spectra of *L*- valine ligand (A) and V-*L*- valine complex (B).

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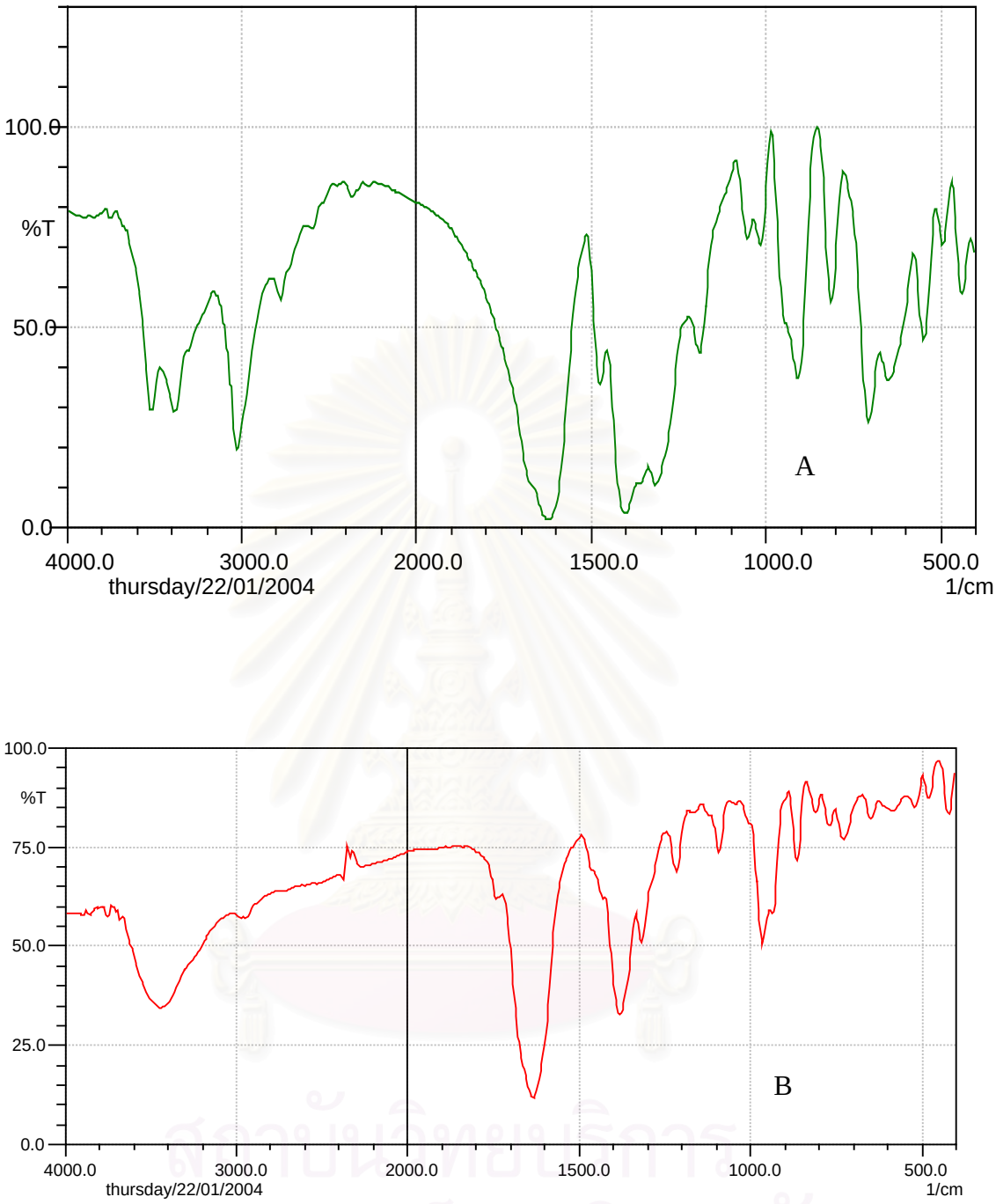

Figure 4.4 FT-IR spectra of EDTA ligand (A) and V-EDTA complex (B).

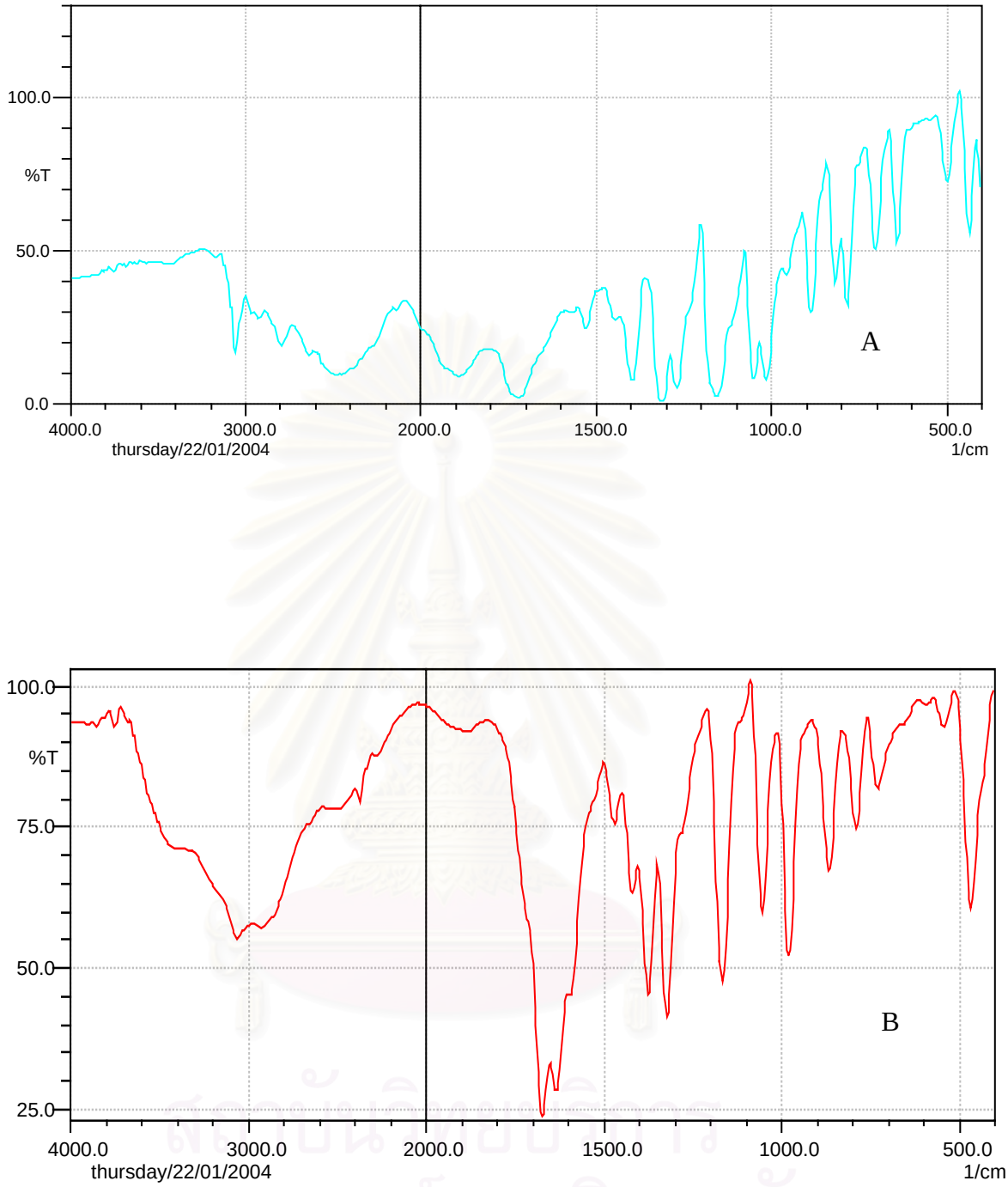

Figure 4.5 FT-IR spectra of pyrazine carboxylic acid (PCA) ligand (A) and vanadiume pyrazine carboxylic acid (V-PCA) (B).

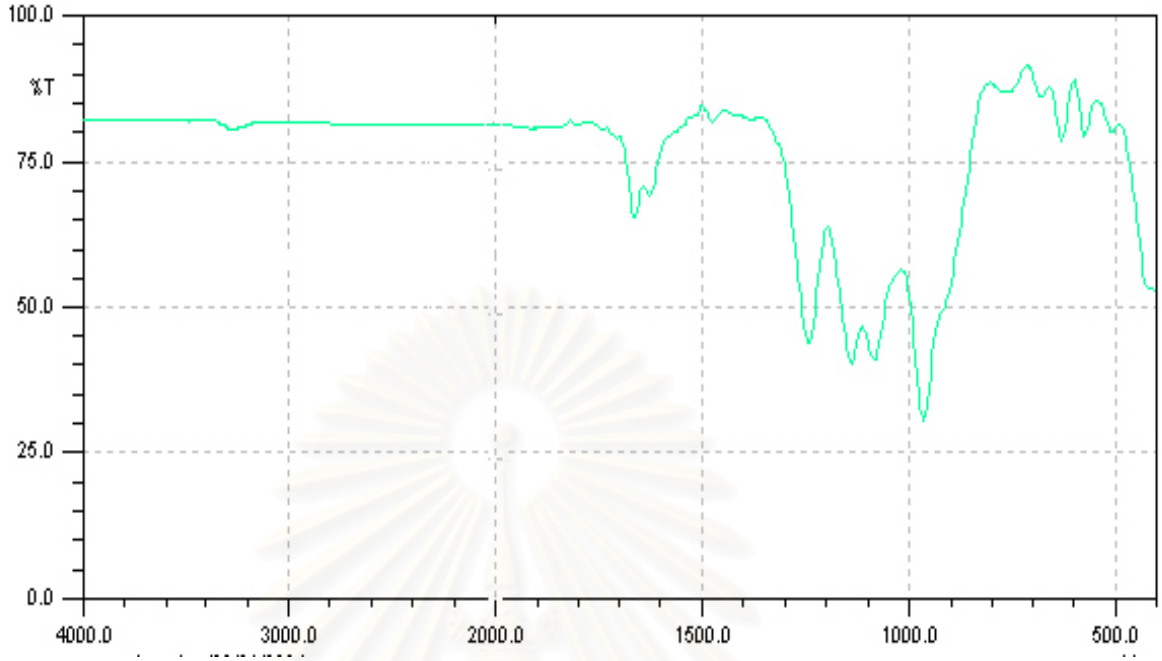

Figure 4.6 FT-IR spectram of $VO2(P_2O_7)$ **(F)**.

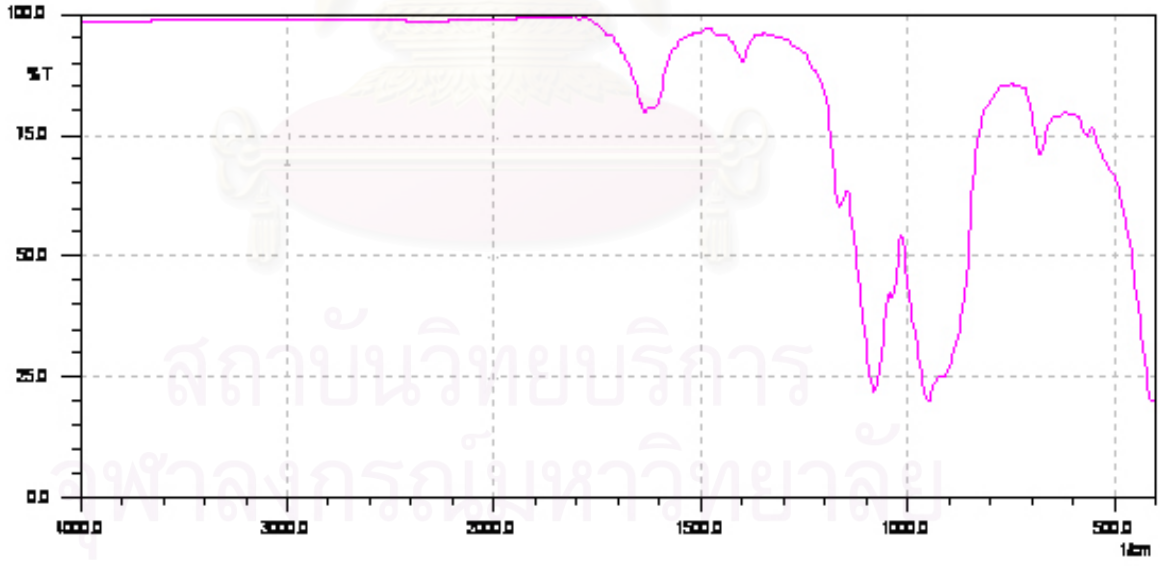

Figure 4.7 FT-IR spectram of $VO(PO_4)(H_2O)_2$ **(G)**.

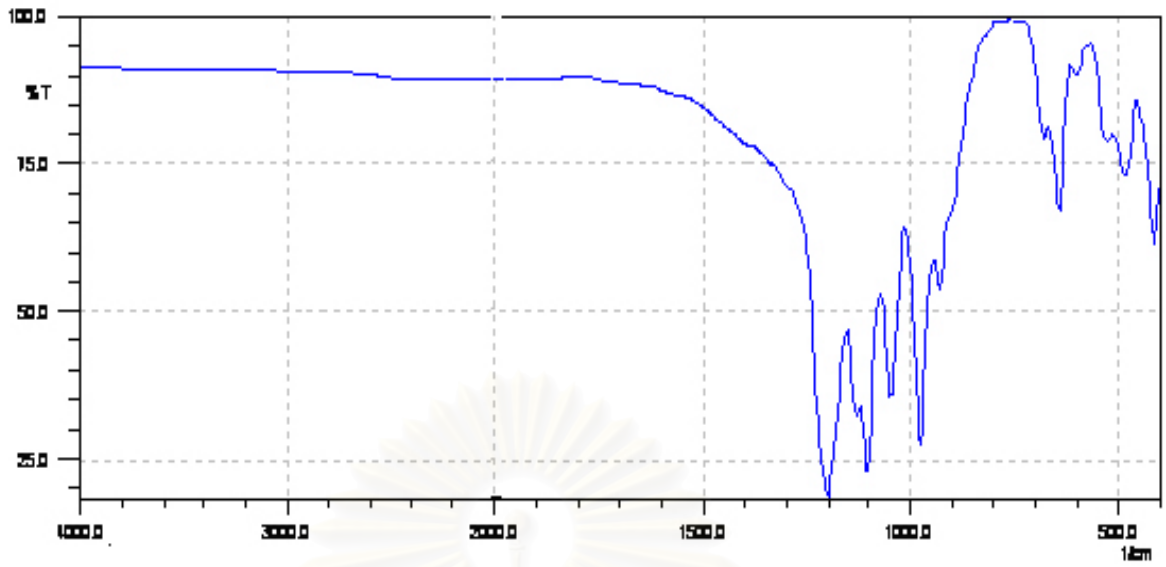

Figure 4.8 FT-IR spectram of $VO(HPO_4)(H_2O)_{0.5}$ **(H)**.

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APPENDIX B

สถาบันวิทยบริการ
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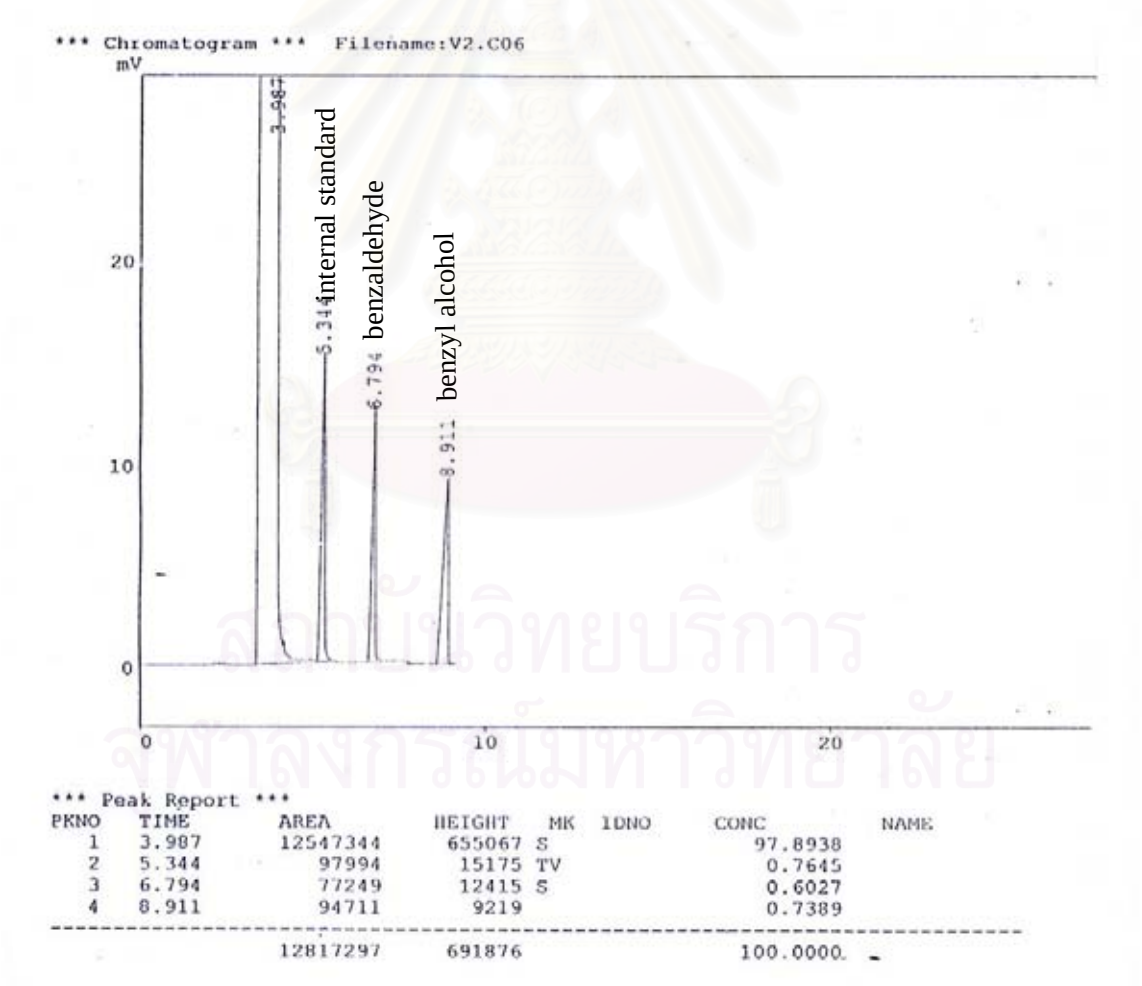
APPENDIX B

Product determination using gas chromatography

The reactant and product: benzyl alcohol and benzaldehyde were identified using internal standard method. The procedure for correction factor determination is done as follows:

Benzyl alcohol (0.1 mL) and benzaldehyde (0.1 mL) were pipetted into a 10 mL volumetric flask, volume made with toluene. From this solution, 1 mL was taken and acidified with 25% H_2SO_4 (1 mL), then neutralized with saturated $NaHCO_3$ solution. The upper organic layer was analyzed by GC with the addition of exact amount of 0.01 mL of cyclohexanol (as internal standard). From gas chromatogram, the peak area of each compound was used in the calculation for correction factor.



*** Peak Report ***

PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	3.987	12547344	655067	S		97.8938	
2	5.344	97994	15175	TV		0.7645	
3	6.794	77249	12415	S		0.6027	
4	8.911	94711	9219			0.7389	
		12817297	691876			100.0000	

Figure B-1 A gas chromatogram of benzyl alcohol and benzaldehyde for correction factor calculation.

Calculation of the correction factor

The correction factor was calculated based upon the results obtained from gas chromatographic analysis (see also the experimental section). Cyclohexanol was used as internal standard.

A : exact amount of benzyl alcohol prepared = 0.970 mmol (0.1 mL)

B : exact amount of benzaldehyde prepared = 0.980 mmol (0.1 mL)

C : exact amount of internal standard was added =0.094 mmol (0.01mL)

D : peak area of 1 benzyl alcohol prepared = 94711

E : peak area of benzaldehyde prepared = 71249

F : peak area of internal standard = 97994

G : total volume of the reaction = 10 mL

The calculation of the correction factor can be described as follows:

correction factor of benzyl alcohol:

The amount of of benzyl alcohol from the reaction mixture.

= (C x D/F) = H

= 0.094 x 94711)/97994

= 0.091 mmol

amount of of benzyl alcohol in G mL (total volume of the reaction)

= H x G =I

= 0.091 x 10

= 0.91 mmol

Thus, the correction factor of benzyl alcohol can be calculated as :

= A/I

= 0.97/0.91

= 1.06

correction factor of benzaldehyde:

The amount of of benzaldehyde from the reaction mixture.

= (C x E/F) = K

= (0.094 x 71249)/ 97994

= 0.074 mmol

amount of of benzaldehyde in G mL (total volume of the reaction)

= K x G =L

= 0.074x 10

= 0.74 mmol

Thus, the correction factor of benzaldehyde can be calculated as :

= B/L

= 0.98/ 0.074

= 1.32

The correction factors of chemicals are listed as follow:

benzyl alcohol = 1.06
benzaldehyde = 1.32

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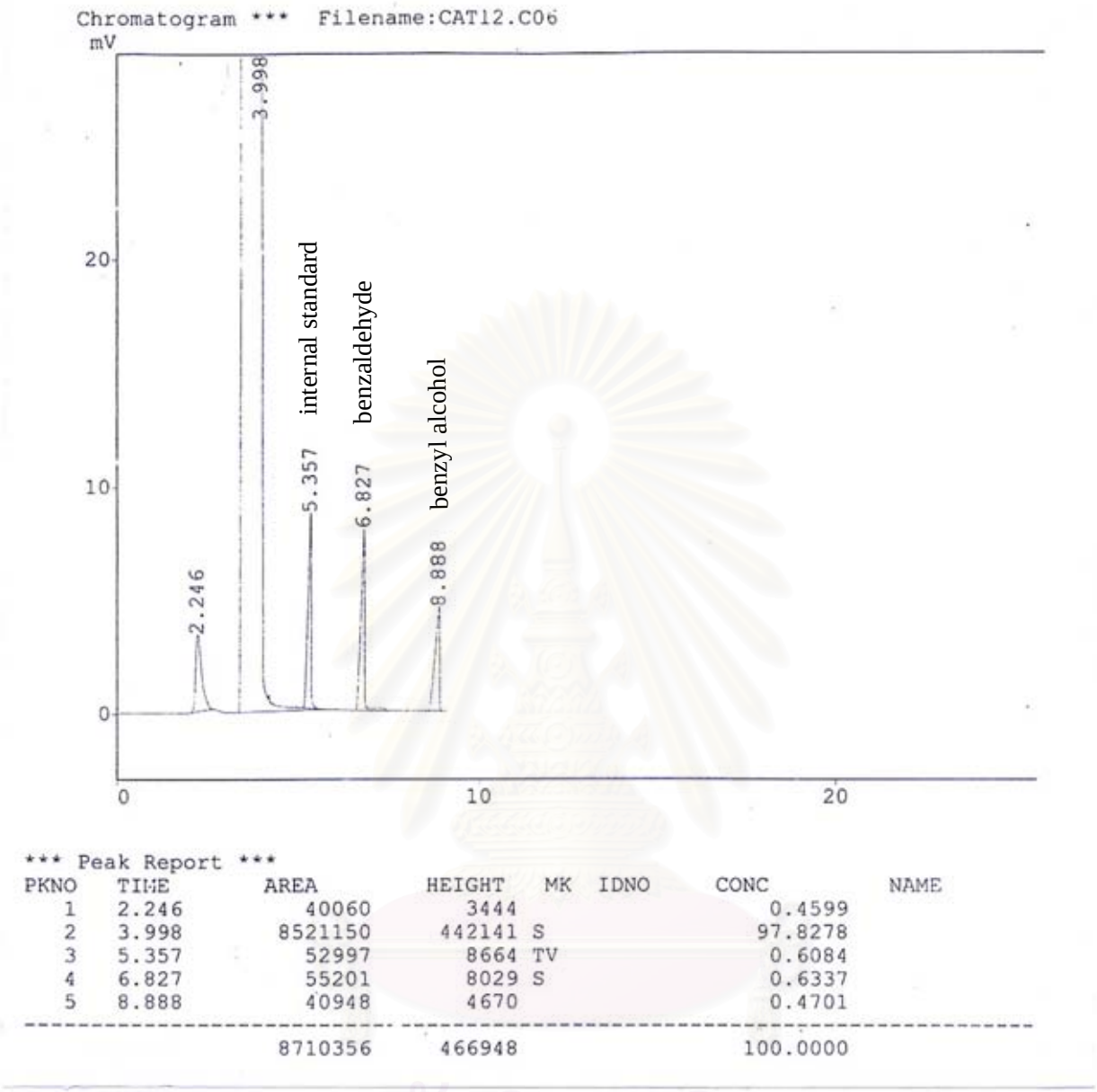

*** Peak Report ***

PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2.246	40060	3444			0.4599	
2	3.998	8521150	442141	S		97.8278	
3	5.357	52997	8664	TV		0.6084	
4	6.827	55201	8029	S		0.6337	
5	8.888	40948	4670			0.4701	
		8710356	466948			100.0000	

Figure B- 2 A gas chromatogram of products from reaction mixture of oxidation of benzyl alcohol.

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Calculation of the amount of the chemicals in the reaction mixture

A_{rxn} : exact amount of benzyl alcohol (substrate) = 5 mmol

B_{rxn} : exact amount of internal standard was added = 0.094 mmol

C_{rxn} : peak area of benzaldehyde = 55201

D_{rxn} : peak area of benzyl alcohol = 40948

E_{rxn} : peak area of the internal standard = 52997

F_{rxn} : total volume of the reaction = 11.91 mL

G_{rxn} : total volume of analyzing = 0.5 mL

Calculation of %yield of benzaldehyde :

Mole of benzaldehyde

$= (B_{rxn} \times C_{rxn})/ E_{rxn}$

$= (0.094 \times 55201)/52997$

$= 0.098$ mmol

In 0.5 mL mole of benzaldehyde 0.098 mmol

total volume the reaction 11.91 mL $= (11.91 \times 0.098)/0.5$

$= 2.33$

2.33 x correction factor

2.33 x 1.32

= 3.08 mmol

Thus, %yield of benzaldehyde

$= 3.08./ A_{rxn} \times 100$

$= (3.08/5) \times 100$

= 61.6 %

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Calculation of % conversion of benzyl alcohol:

Mole of benzyl alcohol

$= (B_{rxn} \times D_{rxn})/ E_{rxn}$

$= (0.094 \times 40948)/52997$

$= 0.073$ mmol

In 0.5 mL mole of benzyl alcohol 0.073 mmol

total volume the reaction 11.91 mL $= (11.91 \times 0.073)/0.5$

$= 1.73$ mmol

1.73 x correction factor

11.73 x 1.06

= 1.83 mmol

Thus, %conversion

$=(A_{rxn} – 1.83)/ A_{rxn} \times 100$

$= (5 – 1.83)/5 \times 100$

= 63.4 %

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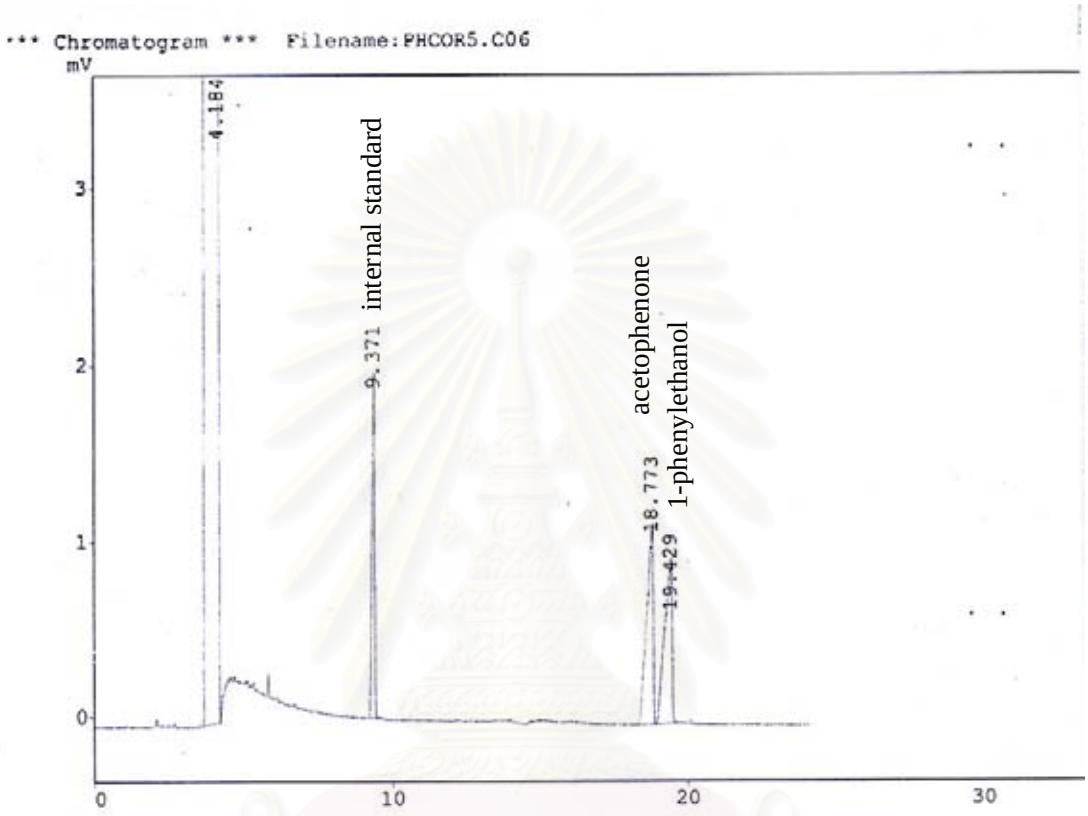
Corection factor of 1-phenylethanol and acetophenone

Gas chromatography determined product of 1-phenylethanol oxidation. Acetophenone product was indentified using benzaldehyde as internal standard addition method.



*** Peak Report ***

PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
	4.184	4554941	274972			99.0023	
	9.371	11684	1927			0.2540	
3	18.773	17668	1106			0.3840	
4	19.429	16552	917	V		0.3597	
		4600845	278922			100.0000	

Figure B-3 A gas chromatogram of 1- phenylethanol and acetophenone for correction factor calculation.

Calculation of the correction factor

The correction factor was calculated based upon the results obtained from gas chromatographic analysis (see also the experimental section). Benzaldehyde was used as internal standard.

A : exact amount of 1- phenylethanol prepared = 0.830 mmol (0.1 mL)

B : exact amount of acetophenone prepared = 0.860 mmol (0.1 mL)

C : exact amount of internal standard was added =0.098 mmol (0.01mL)

D : peak area of 1- phenylethanol prepared = 16552

E : peak area of acetophenone prepared = 17668

F : peak area of internal standard = 11684

G : total volume of the reation = 10 ml.

The calculation of the correction factor can be described as follows:

correction factor of 1- phenylethanol:

The amount of of 1- phenylethanol from the reaction mixture.

= (C x D/F) = H

= 0.098 x 16552)/17668

= 0.092 mmol

amount of of 1- phenylethanol in G mL (total volume of the reaction)

= H x G =I

= 0.092 x 10

= 0.92 mmol

Thus, the correction factor of 1- phenylethanol can be calculated as :

= A/I

= 0.83/0.92

= 0.91

correction factor of acetophenone:

The amount of of acetophenone from the reaction mixture.

= (C x E/F) = K

= (0.098 x 17668)/ 11684

= 0.10 mmol

amount of of acetophenone in G mL (total volume of the reaction)

= K x G =L

= 0.10 x 10

= 1.00 mmol

Thus, the correction factor of acetophenone can be calculated as :

= B/L

= 0.86/ 1.0

= 0.86

The correction factors of chemicals are listed as follow:

1-phenylethanol = 0.90
acetophenone = 0.86

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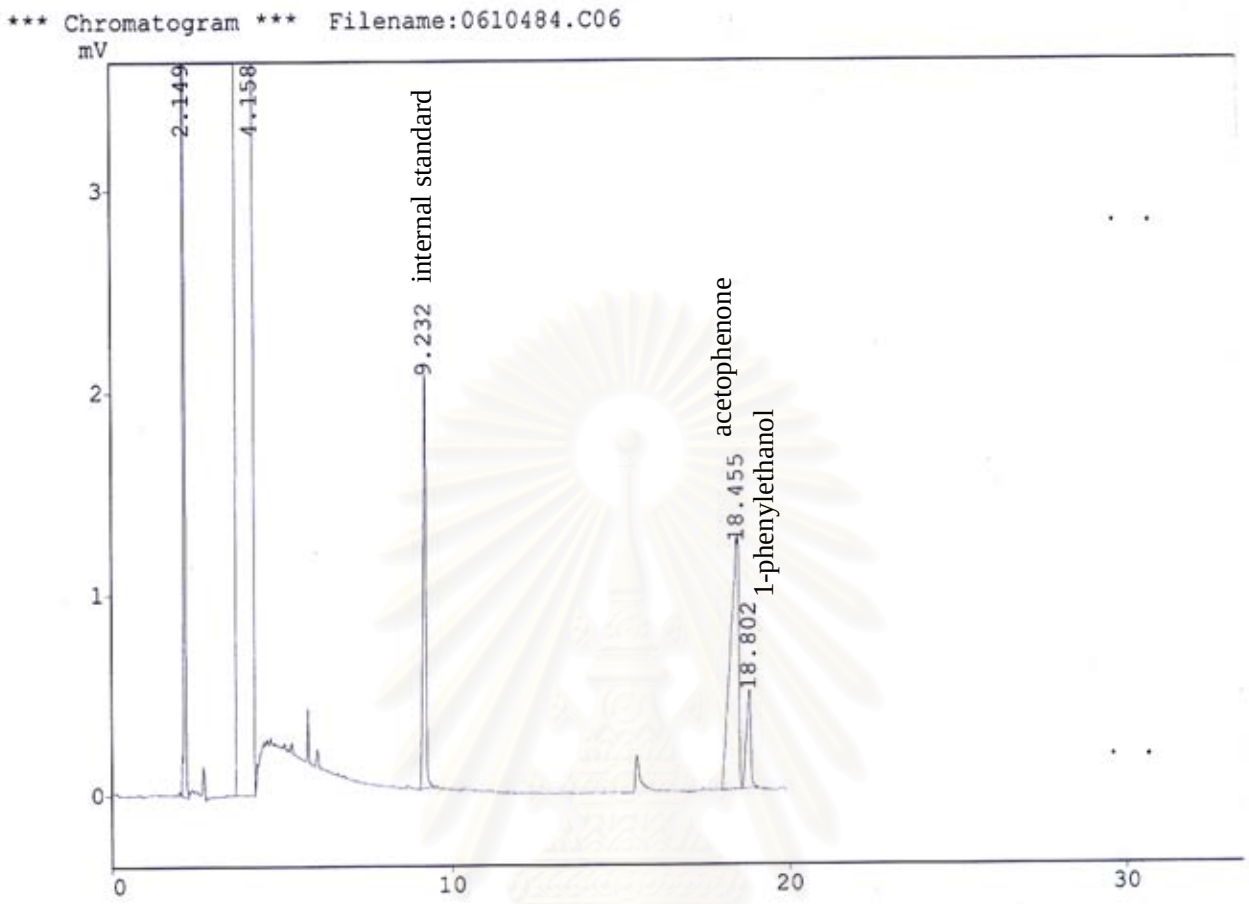

*** Peak Report ***

PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2.149	21328	7873	V		0.4233	
2	4.158	4978976	295344			98.8173	
3	9.232	12109	2055			0.2403	
4	18.455	24526	1234			0.4266	
5	18.802	7500	497	V		0.0925	
		5044439	307003			100.0000	

Figure B-4 A gas chromatogram of products from reaction mixture of oxidation of 1-phenylethanol.

Calculation of the amount of the chemicals in the reaction mixture

A_{rxn} : exact amount of 1- phenylethanol (substrate) = 5 mmol

B_{rxn} : exact amount of internal standard was added = 0.098 mmol

C_{rxn} : peak area of acetophenone = 24526

D_{rxn} : peak area of 1- phenylethanol = 7500

E_{rxn} : peak area of the internal standard = 12109

F_{rxn} : total volume of the reaction = 11.99 mL

G_{rxn} : total volume of analyzing = 0.5 mL

Calculation of %yield of acetophenone :

Mole of acetophenone

$= (B_{rxn} \times C_{rxn})/ E_{rxn}$

$= (0.098 \times 24526)/12109$

$= 0.18$ mmol

In 0.5 mL mole of acetophenone 0.18 mmol

total volume the reaction 11.99 mL $= (11.99 \times 0.18)/0.5$

$= 4.29$ mmol

4.29 x correction factor

4.29 x 0.86

= 3.69 mmol

Thus, %yield of acetophenone

$= 3.69./ A_{rxn} \times 100$

$= (3.69/5) \times 100$

= 73.8 %

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Calculation of % conversion of 1- phenylethanol :

Mole of 1- phenylethanol

$= (B_{rxn} \times D_{rxn}) / E_{rxn}$

$= (0.098 \times 7500)/12109$

$= 0.06$ mmol

In 0.5 mL mole of 1- phenylethanol 0.06 mmol

total volume the reaction 11.99 mL = $(11.99 \times 0.06)/0.5$

= 1.45 mmol

1.45 x correction factor

1.45 x 0.90

= 1.31 mmol

Thus, %conversion

$=(A_{rxn} - 1.31)/ A_{rxn} \times 100$

$= (5 - 1.31)/5 \times 100$

= 74 %

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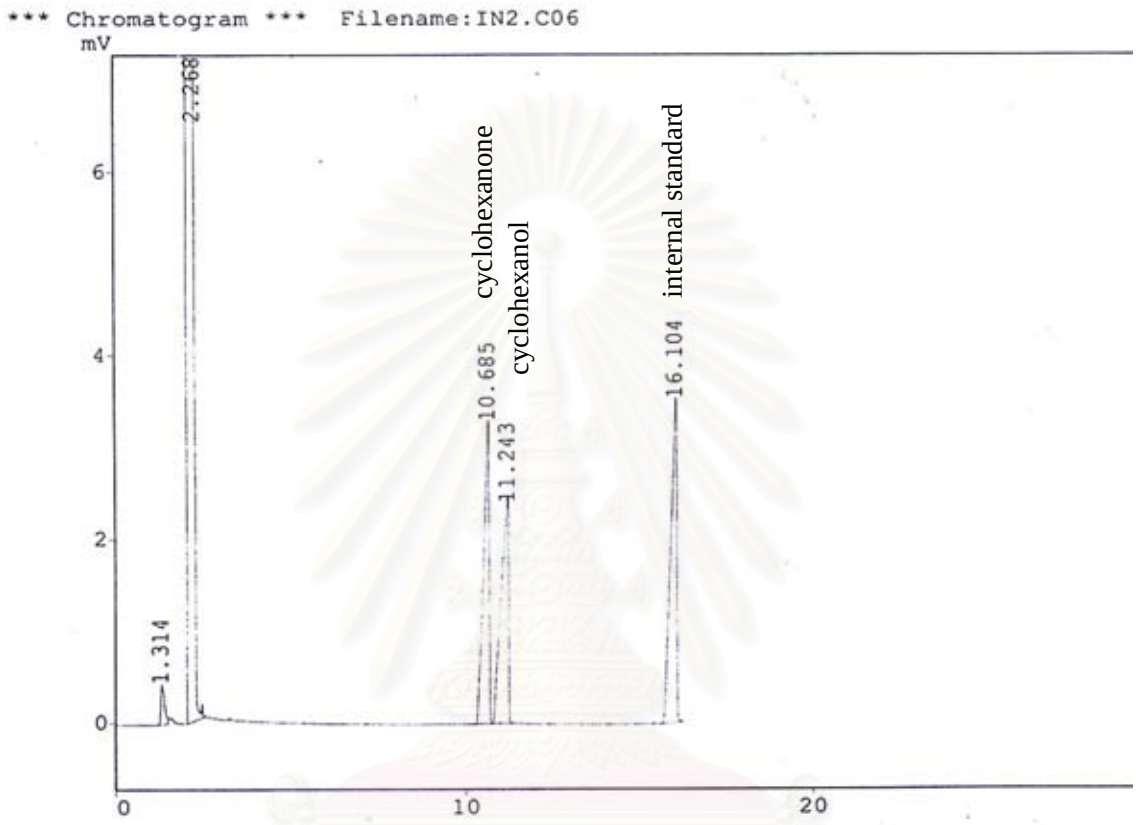
Corection factor of cyclohexanol and cyclohexanone

Gas chromatography determined product of cyclohexanol oxidation. Cyclohexanone product was indentified using benzaldehyde as internal standard addition method.



*** Peak Report ***

PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1.314	3307	452			0.1371	
2	2.268	2292213	273522	S		95.0505	
3	10.685	36836	3300			1.5275	
4	11.243	37107	2503	V		1.5387	
5	16.104	42110	3527			1.7462	
		2411574	283304			100.0000	

Figure B-5 A gas chromatogram of cyclohexanol and cyclohexanone for correction factor calculation.

Calculation of the correction factor

The correction factor was calculated based upon the results obtained from gas chromatographic analysis (see also the experimental section). Benzaldehyde was used as internal standard.

A : exact amount of cyclohexanol prepared = 0.940 mmol (0.1 mL)

B : exact amount of cyclohexanone prepared = 0.960 mmol (0.1 mL)

C : exact amount of internal standard was added =0.098 mmol (0.01mL)

D : peak area of cyclohexanol prepared = 37107

E : peak area of cyclohexanone prepared = 36836

F : peak area of internal standard = 42110

G : total volume of the reation = 10 ml.

The calculation of the correction factor can be described as follows:

correction factor of cyclohexanol:

The amount of of cyclohexanol from the reaction mixture.

= (C x D/F) = H

= 0.098 x 37107)/42110

= 0.086 mmol

amount of of cyclohexanol in G mL (total volume of the reaction)

= H x G =I

= 0.086 x 10

= 0.86 mmol

Thus, the correction factor of cyclohexanol can be calculated as :

= A/I

= 0.96/0.86

= 1.12

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correction factor of cyclohexanone:

The amount of of cyclohexanone from the reaction mixture.

= (C x E/F) = K

= (0.098 x 36836)/ 42110

= 0.086 mmol

amount of of cyclohexanone in G ml (total volume of the reaction)

= K x G =L

= 0.086 x 10

= 0.86 mmol

Thus, the correction factor of cyclohexanone can be calculated as :

= B/L

= 0.094/ 0.086

= 1.09

The correction factors of chemicals are listed as follow:

cyclohexanol = 1.12
cyclohexanone = 1.09

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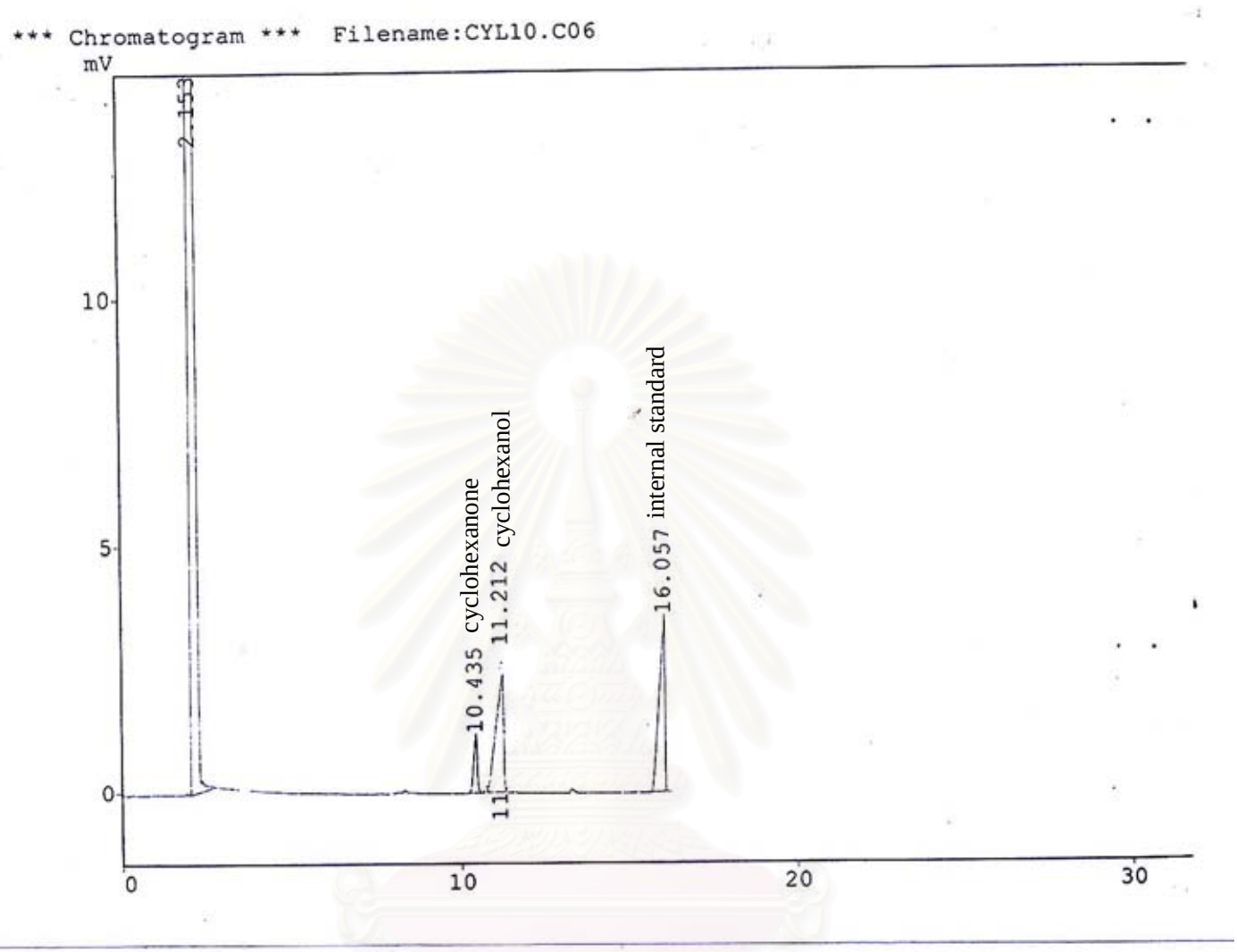

*** Peak Report ***

PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2.153	4132697	1094656	S		97.8397	
2	10.435	22366	1218			0.2117	
3	11.212	55808	5464			0.9849	
4	16.157	40815	3592			0.9637	
		4251686	1104930			100.0000	

Figure B- 6 A gas chromatogram of products from reaction mixture of oxidation of cyclohexanol.

Calculation of the amount of the chemicals in the reaction mixture

A_{rxn} : exact amount of cyclohexanol (substrate) = 5 mmol

B_{rxn} : exact amount of internal standard was added = 0.098 mmol

C_{rxn} : peak area of cyclohexanone = 22366

$_{Drxn}$: peak area of cyclohexanol = 55808

E_{rxn} : peak area of the internal standard = 40815

F_{rxn} : total volume of the reaction = 11.92 mL

G_{rxn} : total volume of analyzing = 0.5 mL

Calculation of %yield of cyclohexanone :

Mole of cyclohexanone

$= (B_{rxn} \times C_{rxn})/ E_{rxn}$

$= (0.098 \times 22366)/40815$

$= 0.057$ mmol

In 0.5 mL mole of cyclohexanone 0.057 mmol

total volume the reaction 11.92 mL = $(11.92 \times 0.057)/0.5$

= 1.28 mmol

1.28 x correction factor

1.28 x 1.09

= 1.40 mmol

Thus, %yield of acetophenone

$= 1.40/ A_{rxn} \times 100$

$= (1.40/5) \times 100$

= 28.1 %

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Calculation of % conversion of cyclohexanol**:**

Mole of cyclohexanol

$= (B_{rxn} \times D_{rxn})/ E_{rxn}$

$= (0.098 \times 55808)/40815$

$= 0.13$ mmol

In 0.5 mL mole of cyclohexanol 0.13 mmol

total volume the reaction 11.92 mL $= (11.92 \times 0.13)/0.5$

$= 3.21$ mmol

3.21 x correction factor

3.21 x 1.12

$= 3.60$ mmol

Thus, %conversion

$=(A_{rxn} – 1.31)/ A_{rxn} \times 100$

$= (5 – 3.60)/5 \times 100$

$= 28.0$ %

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VITAE

Miss Piyanoot Hoonsart was born on March 8, 1980 in Phetchaburi, Thailand. She received a Bachelor Degree of Education Science, major in Chemistry from Sinakarinwirot University in 2002. Since 2003 she has been a graduate student in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University.

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