OXIDATION OF ETHYLBENZENE AND 1,6-HEXANEDIOL USING COBALT AND RUTHENIUM COMPLEXES

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Abstract

The oxidation of ethylbenzene and 1,6-hexanediol were investigated using catalysts including *bis*-(bipyridine)cobalt(II) chloride (*bis*-Co), *tris*-(bipyridine)cobalt(II) nitrate (*tris*-Co), *trans*-dichloro-*bis*-(ethylenediamine)cobalt(II) chloride (*trans*-Co), cobalt phthalocyanine (Co-Pc) and *bis*-dichloro(*p*-cymene)ruthenium(II) dimer (Ru-dimer). The reaction was carried out at various temperature and time. The oxidation of ethylbenzene yields acetophenone and 2-hydroxy-ethylbenzene as major and minor products, respectively. The results reveal that the activity increases in the order of : *trans*-Co > *tris*-Co > *bis*-Co > blank > Co-Pc > Ru-dimer. This is the result of narrow d-splitting energy gap and lower steric hindrance. The oxidation of 1,6-hexanediol, on the other hand, at 110 °C and 24 h, *bis*-dichloro(*p*-cymene)ruthenium(II) dimer is the most active catalyst producing ε-caprolactone and 6-hydroxyhexanal. Interestingly, Co-Pc gives the 100% selectivity towards ε-caprolactone even at 150 °C. Comparing the effect of ligands on the promising Ru-complexes (dichloro)(*p*-xymene) ,diphenyl phosphino-, and tert-butyl-pyridine, diphenylphosphino-Ru complex is the most active and has >98% selectivity towards ε-caprolactone at 110 °C, which could attribute to the better σ-donor/π-acceptor stabilizing the transition complexes and the steric effect enhancing the reductive elimination.

Keywords : Oxidation, ε-caprolactone and Metal-complex catalysts, Cobalt Compound Ruthenium Complex

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Last but not least, the authors would like to gracefully thank the parents and families, who give an encouragement. This thesis would not be possible without them.

The thesis dedicate for the world citizen, who want to be a technical and theoretical expert.

Miss. Narumon Yeamsantie
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CHAPTER 1

INTRODUCTION

1.1 Motivation

The oxidation is a significant reaction employing in organic synthesis for the preparation of alcohol, aldehyde, ketone and carboxylic compounds. These compounds are used as intermediates in industrial applications, such as pharmaceutical and polymer industries. Some of the interesting products from the oxidation are ethybenzene to acetophenone, hexanol to hexanal and diols to lactone. Acetophenone is mainly used in pharmaceutical as well-known "Hypnone", function as anesthesia in surgery. Hexanal has an antibiotic activity and can be used as a food additive for anti-fungi compound, which is accepted by Food and Drug Administration (FDA). Lactone is used as a monomer for the production of polylactone, which is widely used in suture, drug delivery and polymeric plasticizer.

The oxidation is normally catalyzed by metal complex such as Ru [1], Ni [2], Cu [3, 4] and Co complexes [5, 6]. However, the reaction releases toxic waste such as organic solvent and harmful oxidants. Moreover, the catalyst synthesis is complicated and economically inconvenient. Accordingly, it is interesting to adjust the reaction to be green and worthiness by using immediate strong oxidant such as air, inexpensive raw materials, non-air sensitive catalyst and simple catalyst preparation at low temperature and atmospheric pressure. With this view, Co complexes with schiff base 2,2′-bipyridine, ethylenediamine and phthalocyanine ligands are an attractive ligand. Due to the availability and widely use of 2,2′-bipyridine, this ligand forms complexes with most transition metal ions such as Ru [7], Fe [8], Os [9], Cu [10], Co [11], Cr [12] and Ni [12]. Metal with ethylenediamine as ligand are also studied for example, Co [13], Ni, Cr and Cu [14] has been reported. Metal with phthalocynine as ligand such as Al [15], Co [16, 17], Zn [18] and Cu [19] are also investigated.

Therefore, in this project, *bis*-(bipyridine)cobalt(II) chloride, *tris*-(bipyridine) cobalt(II) nitrate, *trans*-dichloro-bis-(ethylenediamine)cobalt(III) chloride and cobalt phthalocynine complexes were synthesied and used for the simple oxidation reaction of ethylbenzene and 1,6-hexandiol in non-crucial condition. The effect of temperature, amount of dissolved oxygen on the oxidation of ethylbenzene, residence time and oxidant were investigated.

1.2 Objective

1.2.1 To optimize the cobalt and ruthenium complexes for the oxidation reaction of ethybenzene and 1,6-hexandiol.

1.2.2 To understand parameters : reaction temperature, resident time and amount of ligands that affect on the oxidation reaction of ethylbenzene and 1,6-hexandiol.

1.3 Scopes of this study

1.3.1 Synthesis of *bis*-(bipyridine)cobalt(II) chloride, *tris*-(bipyridine)cobalt(II) nitrate, *trans*-dichloro-bis-(ethylenediamine)cobalt(III) chloride and cobalt phthalocyanine complexes as catalysts.

1.3.2 Characterization of the catalysts by Fourier-Transform Infrared Spectroscopy (FT-IR) and Ultraviolet–Visible Spectroscopy (UV)

1.3.3 Catalytic testing was carried out in glass type stirred-batch reactor.

1.3.4 The feasible parameters affect on catalytic performance are investigated sequentially:

1.3.4.1 Reaction temperature at 60, 90 and 110 °C for ethylbenzene and 60, 110 and 150 °C for 1,6-hexnandiol.

1.3.4.2 Residence time in range of 24 and 48 h for ethylbenzene and 24 h for 1,6-hexnandiol.

1.3.4.3 Amount of dissolved oxygen on the oxidation of ethylbenzene (closed and air-bubbling system).

1.3.4.4 Coordinated p-cymene, tert-butyl-pyridine and, diphenyl phosphino ligand of ruthenium complexes for the oxidation of 1,6-hexanediol.

1.3.5 Qualitative and quantitative analysis of the obtained products are determined on Gas Chromatography (GC), DB-wax and Nuclear magnetic resonance (^{1}H-NMR).

1.4 Expected results

1.4.1 Synthesis of *bis*-(bipyridine)cobalt(II) chloride, *tris*-(bipyridine)cobalt(II) nitrate, *trans*-dichloro-bis-(ethylenediamine)cobalt(III) chloride and cobalt phthalocyanine complexes for the oxidation of ethylbenzene and 1,6-hexanediol.

1.4.2 The synthesized acetophenone and caprolactone using a new cobalt complexes.

1.4.3 The optimum condition for the oxidation of ethylbenzene and 1,6-hexanediol oxidation such as temperature, amount of ligand in complex and residence time.

CHAPTER 2
LITERATURE REVIEWS AND THEORY

2.1 Catalysts

2.1.1 Type of Catalysts [20]

2.1.1.1 Heterogeneous Catalysts

Heterogeneous catalysts act in a different phase than the reactants. Most heterogeneous catalysts are solids that react with substrates in a liquid or gaseous reaction mixture. The diverse mechanisms for reactions on surfaces are known, depending on how the adsorption taking place. The total surface area of solid has the important effect on the reaction rate. The smaller the catalyst particle size, the larger the surface area for a given mass of particles.

A heterogeneous catalyst has active sites, the atoms or crystal faces where the reaction actually occurs. Depending on the mechanism, the active site may be either a planar exposed metal surface, a crystal edge with imperfect metal valence or a complicated combination of the two. Thus, not all the parts of the heterogeneous are active. Finding out the nature of the active site requires technically challenging research. Thus, empirical research for finding out new metal combinations for catalysis has been of many interests.

2.1.1.2 Homogeneous Catalysts

Homogeneous catalysts function in the same phase as the reaction mixture, but the mechanistic principles invoked in heterogeneous catalysis are generally applicable. Typically homogenous catalysts are dissolved in a solvent with the substrates. One example of the homogeneous catalysis involves the influence of H^+ on the esterification of acetic acid and methanol. Forming methyl acetate for inorganic chiteria, homogeneous catalysis is often synonymous of organometallic catalysts.

2.1.1.3 Eletrocatalysts

In the context of electrochemistry, specifically in fuel cell engineering, various metal-containing catalysts are used to enhance the rates of the half reactions that comprise the fuel cell. One common type of fuel cell electrocatalyst is based upon nanoparticles of platinum that are supported on slightly larger carbon particles. When in contact with one of the electrodes in a fuel cell, this platinum increases the rate of oxygen reduction either to water, hydroxide, or hydrogen peroxide.

2.1.1.4 Organocatalysis

Organocatalysis is a type of catalysis where the catalyst in the chemical reaction is an organic (non-metallic) compound. While transition metals sometimes attract most of the attention in the study of catalysis, organic molecules without metals can also exhibit catalytic properties, such as the catalysis reaction using phosphorous compounds on the synthesis [21].

2.1.1.5 Enzymes and Biocatalysts

In biology systems, enzymes are protein-based catalysts in metabolism and catabolism. Most biocatalysts are enzymes, but other non-protein-based classes of biomolecules also exhibit catalytic properties including ribozymes, and synthetic deoxyribozymes [22]. Biocatalysts can be thought of an intermediate between homogeneous and heterogeneous catalysts, although strictly speaking soluble enzymes are homogeneous catalysts and membrane-bound enzymes are heterogeneous. Several factors affect the activity of enzymes, including temperature, pH, concentration of an enzyme, and substrates. A particularly important reagent in enzymatic reactions is water which is the product of many bond-forming reactions and a reactant in many bond-breaking processes.

Some monoclonal antibodies, whose binding target is a stable molecule resembling the transition state of a chemical reaction, can function as weak catalysts for some chemical reactions by lowering the activation energy. Such catalytic antibodies are sometimes called abzymes.

2.2 Oxidation [23]

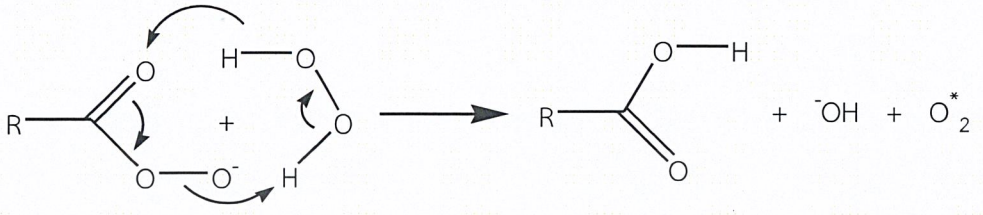
Some oxidation are defined as the interaction between oxygen molecules and all the different substances. A oxidation always comes together with an reduction, called redox reaction. The substance that acts as an electron donor is called a reducing agent, on the other hand, a substance that acts as an electron acceptor is called oxidizing agent.

2.2.1 Oxidation Agents

2.2.1.1 Air, Oxygen, Ozone and Electrolysis

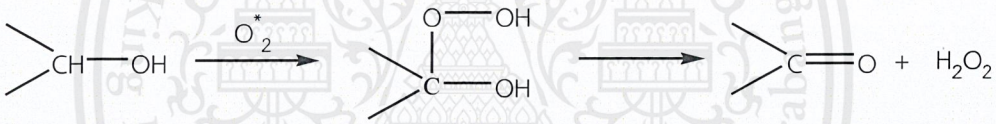
Air is the cheapest oxidant, used only rarely without photoirradiation and catalysts. The examples of oxidation involving an air are the conversion of aldehydes into carboxylic acids and the oxidation of acyloins to α-diketones. Oxygen exists in two states. Excited-state oxygen (singlet oxygen) is a name given to several higher-energy species of molecular O_2 in which all the electron spins are paired. It

reacts with organic compounds in the same way as singlet oxygen generated chemically by several reactions, such as the treatment of hydrogen peroxide in alkaline medium with sodium hypochlorite, bromine. Singlet oxygen can also be obtained by the decomposition of aromatic endoperoxides, such as organic peroxy acids (**Equation 2.1**).



(**Equation 2.1**)

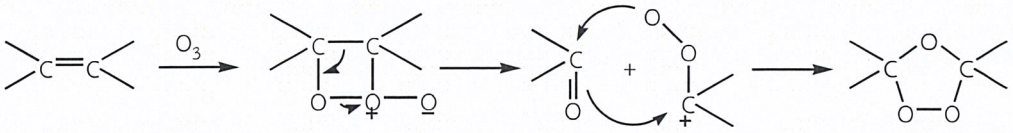
The illustration of the oxidation using a singlet oxygen are the conversions of alkenes into epoxides, secondary alcohol into ketones via alcohol hydroperoxides (shown in **Equation 2.2**), and the oxidative degradation of tertiary amines to secondary amines.



(**Equation 2.2**)

Ground-state oxygen rarely involves in the oxidation. However a classical example is the autoxidation of benzaldehyde to benzoic acid, usually yielding the undesirable products even in the absence of light. The oxidation by the combination of oxygen and catalysts are used for the conversion of alkanes into alcohol, ketones, or acids, the epoxidation of alkenes, and the oxidation of aromatic compounds to quinones or carboxylic acids.

Ozone is a blue gas or a dark blue liquid, used in a mixture of oxygen. Such mixture is commercially available but it is usually prepared in the laboratories. The oxidation using ozone as an oxidant is called " ozonization", carried out by passing ozone-containing oxygen through solutions of organic compounds in the solvent that does not react with ozone at low temperature. The most common reaction of ozone is with alkenes as shown in **Equation 2.3**.



(Equation 2.3)

The electrolytic oxidation takes place at the anode of an electrolytic cell, which may or may not contain a diaphragm to separate cathodic and anodic spaces. The anode must be made of a metal that resists oxidation reaction, such as lead and platinum [24]. The reported electrolytic oxidation are the epoxidation of alkenes, the synthesis of ketones from alkenes, and the conversion of primary alcohols and, secondary alcohol to carboxylic acids and ketones, respectively.

2.2.1.2 Hydrogen Peroxide and Its Derivatives

Hydrogen peroxide, H_2O_2, is commercially available in aqueous solutions with the concentration of 30% or 90%. The 30% hydrogen peroxide is a colorless liquid stabilized against the decomposition. The oxidation with hydrogen peroxide includes the oxidation of aldehydes to acids, carboxylic acids to peroxy acids, sulfides to sulfoxides or sulfones, primary amines to nitroso compounds, secondary amines to hydroxylamines and tertiary amines to amine oxides.

Potassium permanganate, $KMnO_4$, is a strong oxidizing agent. It dissolves in water to give intensely pink or purple solutions, the evaporation of which leaves prismatic purplish-black glistening crystals. The conversion of aldehydes to carboxylic acids as shown in **Equation 2.4** [25];

$$5\ C_6H_{13}CHO + 2\ KMnO_4 + 3\ H_2SO_4 \longrightarrow 5\ C_6H_{13}COOH + 3\ H_2O + K_2SO_4 + 2\ MnSO_4$$

(Equation 2.4)

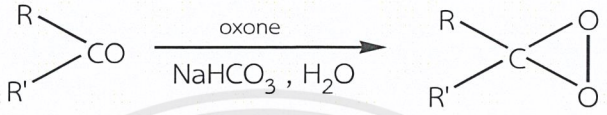
Sodium peroxide (Na_2O_2), a pale-yellow solid, is very rarely used. The conversion of aldoximes into carboxylic acids and the oxidation of ketones to esters are examples of this type of reactions.

Sodium perborate, $NaBO_3.4H_2O$, is used for the oxidation of primary aromatic amines to azo compounds or nitro compounds and of sulfides to sulfoxides and sulfones. This reagent does not have the effect on alcohols and only slightly effect on alkenes.

Persulfuric acid (sulfomonoper acid, peroxymonosulfuric acid), H_2SO_5, is prepared in situ either from hydrogen peroxide, potassium persulfate ($K_2S_2O_8$), or ammonium persulfate [$(NH_4)_2S_2O_8$]. The reagent can convert aldehydes into esters, primary aromatic amines into azoxy, nitroso, or nitro compounds, and iodo compounds

into iodoxy compounds. Currently, the use of persulfuric acid is very limited due to the toxicity.

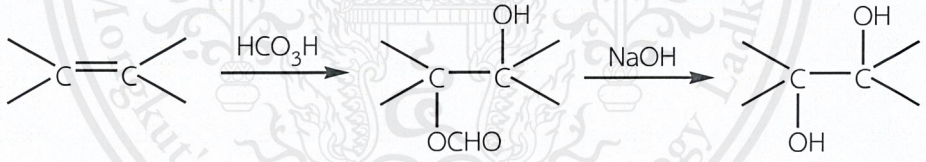
Dioxiranes, prepared from acetone and other aliphatic ketones mixtures treated with oxone, can accomplish the oxidation that are usually not achieved by oxone itself as shown in **Equation 2.5**. Examples of these applications are epoxidations of dioxiranes and the conversion of primary amines to nitro compounds, of tertiary amines to amine oxides, and of sulfides to sulfoxides.



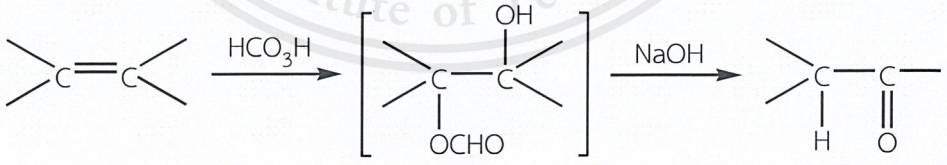
(Equation 2.5)

2.2.1.3 Organic Peroxy Acids

Peroxyformic acid (performic acid), HCO_3H, is always prepared in situ from the mixture of 25-30% hydrogen peroxide and 88 or 98-100% formic acid. In the case of alkenes, the reaction product are formyl esters of diols by heating with sodium or potassium hydroxide to give vicinal diols. Sometumes the formyl ester of the diol is directly converted into a ketone.



(Equation 2.6)



(Equation 2.7)

Benzeneperoxyseleninic acid, $C_6H_5Se(O)OOH$, is prepared in situ from benzeneseleninic acid and 30% hydrogen peroxide in tetrahydrofuran or methylene chloride. This reagent oxidizes cyclic ketones to lactones.

Peroxymaleic acid, *cis*-$HO_2CCH{=}CHCO_3H$, is prepared from 90% hydrogen peroxide and maleic anhydride, while peroxydichloromaleic acid, *cis*-$HO_2CCCl{=}CClCO_3H$, is prepared from 90% hydrogen peroxide and dichloromaleic

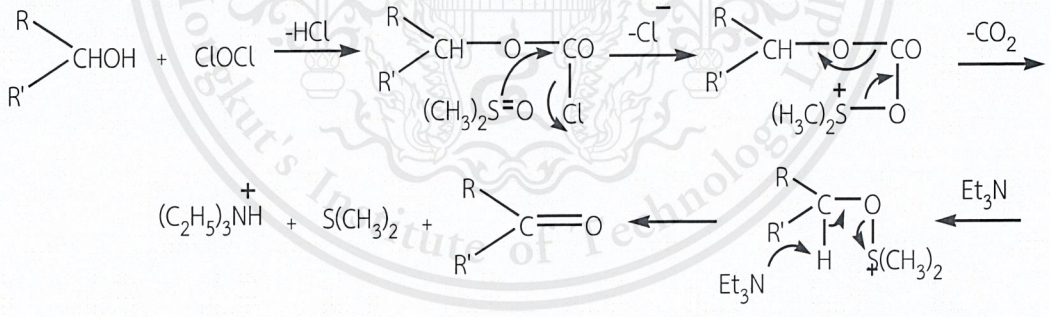
anhydric. Both oxidizing agents are used in dichloromethane solutions. Peroxymaleic acid oxidizes alkanes to epoxides, ketones to esters, primary aromatic amines to nitro compounds and sulfoxides to sulfones. Peroxydichloromaleic acid oxidizes 3-chloropyridazine to its 1-oxide.

2.2.1.4 Organic Oxidants

Carbon tetrachloride, CCl_4, is transformed primary alcohol into carboxylic acids, aryl methyl sulfones into arenesulfonic acids and methyl ketones in to acids with the same number of carbons or with one less carbon in the chain.

Acetone, cyclohexanone, benzophenone, cinnamaldehyde, and other carbonyl compounds are hydrogen acceptors in the oppenauer oxidationof alcohol to carbonyl compounds [26]. These dehydrogenations of alcohols to aldehydes or ketones require high temperature.

Dimethyl sulfoxide (DMSO), $(CH_3)_2SO$, is versatile reagent for the oxidation of alcohol to carbonyl compounds under mild conditions. In addition to the previously mentioned dehydrogenations, it is capable of other oxidation, such as acetylenes to α-diketones, alkyl halides to aldehydes, and phosphine sulfides or selenides to phosphine oxides. The reactions require the presence of acid catalysts such as acetic anhydride, phosphoric acid, sulfur trioxide hydrobromic acid, sulfur trioxide and carbonyl chloride (**Equation 2.8**).



(**Equation 2.8**)

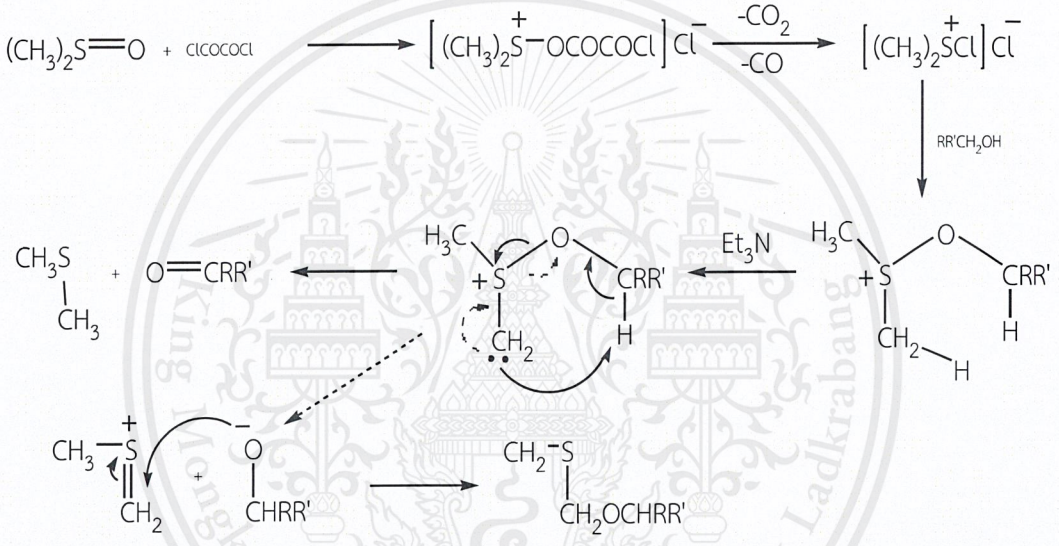
2.2.2 The Oxidation of Alcohols

Primary alcohols are oxidized to aldehydes or acids, and secondary alcohols are oxidized to ketones. On the other hand, tertiary alcohols are resistant to oxidation.

2.2.2.1 Primary Alcohols

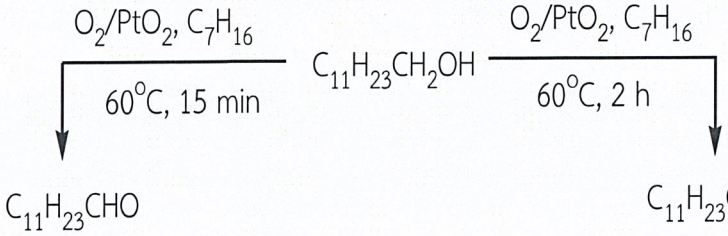
Primary alcohols can be oxidized to either aldehydes or carboxylic acids depending on the reaction conditions. In the case of the formation of carboxylic acids, the alcohol is first oxidized to an aldehyde, which is then oxidized further to the acid. The most common oxidizing agents for the oxidation of primary alcohols to aldehydes are dimethyl sulfoxide (DMSO), potassium permanganate ($KMnO_4$), dimethyl sulfide and chlorine or N-chlorosuccinimide (NCS).

The mechanism of alcohol oxidation using dimethyl sulfoxide as an oxidized agent is shown in **Equation 2.9**. DMSO is activated to form a complex with alcohol, and a base is required for proton abstraction from the complex to initiate its collapse to the aldehyde (or ketone).



(Equation 2.9)

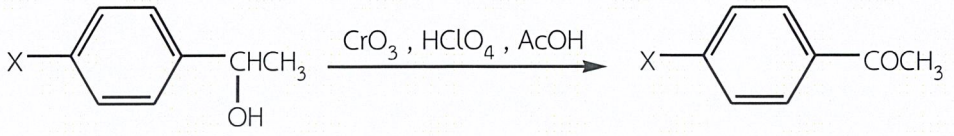
The oxidation of primary alcohol to carboxylic acid requires more harsh condition, higher temperature and/or longer reaction time. Furthermore, some catalysts can promote the reaction, platinum-on-charcoal with air or oxygen shown in **Equation 2.10**, for example.



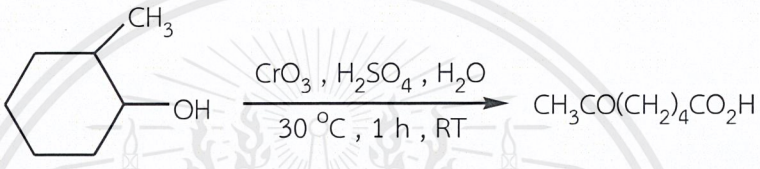
(Equation 2.10)

2.2.2.2 Secondary Alcohols

All oxidatants used for the oxidation of primary alcohols to aldehydes can be applied to secondary alcohols. Since, the products, ketones, are much less sensitive to overoxidation than aldehydes, more intensive reaction conditions, such as excess of the oxidant, higher temperature, or longer reaction time, can be used. **Equations 2.11, 2.12** are examples of the oxidation of secondary alcohols to ketones.



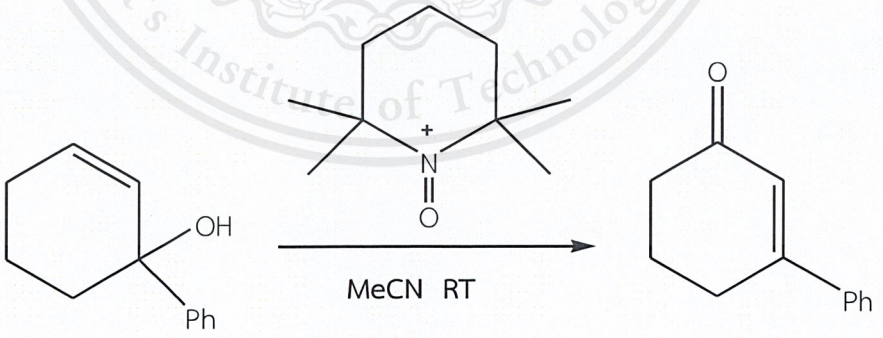
(Equation 2.11)



(Equation 2.12)

2.2.2.3 Tertiary Alcohol

Tertiary alcohols are resistant to an oxidation. However, some tertiary alcohols could be converted into tertiary hydroperoxides on treatment with hydrogen peroxide in sulfuric acid. Examples of the oxidation of tertiary alcohol are the conversion of 1-phenylcyclohex-2-en-1-ol into 3-phenylcyclohex-2-en-1-one by TEMPO-derived oxoammonium salts as shown in **Equation 2.13** [27].



(Equation 2.13)

2.2.3 Oxidation of Aromatic Compounds

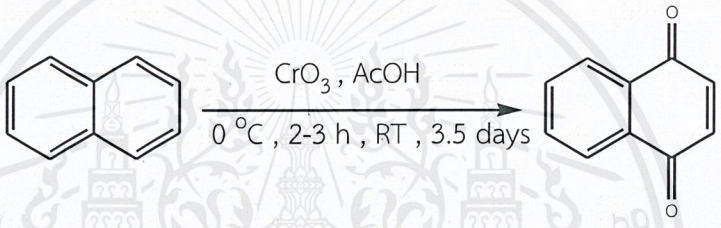
The oxidation of aromatic compounds will encompass the reactions of carbocyclic and heterocyclic aromatic compounds in which oxidation affects the aromatic rings and the attached side chains.

2.2.3.1 Hydroxylation of Aromatic Rings

The hydroxylation of aromatic compounds takes place when heating low electron density aromatic ring with solid potassium hydroxide. A historically important reaction is the hydroxylation of both α- and β-anthraquinonesulfonic acid by alkali fusion to yield alizarin (1,2-dihydroxyanthraquinone) [28].

2.2.3.2 Oxidation of Aromatic Compounds to Quinones

The oxidation of benzene to *p*-benzoquinone is impractical, because benzoquinone is obtained from other compounds. Condensed aromatic hydrocarbons are oxidized to quinones by many reagents, most frequently by the compounds of hexavalent chromium compounds [29].



(Equation 2.13)

2.2.3.3 Oxidative Cleavage of the Benzene Ring

The breakdown of the benzene ring to aldehydes is extremely rare and has been achieved only by ozone [30]. A historical and classical example is the disintegration of o-xylene to a mixture of glyoxal, methyl glyoxal, and diacetyl (butanedione) in the predicted ratios.

2.3 Literature Reviews

Liu, X., *et al.*, (1993), presented the oxidation of alcohols using the combination of *bis*-(bipyridine)copper(II) $[Cu^{II}(byp)_2]^{2+}$ complex with 2 equivalent of base and excess alcohol (e.g. benzyl alcohol) in an O_2-saturated acetonitrile solution. The results showed that benzyl alcohol was much more reactive than aliphatic primary alcohol and approached to the completion of 80% in 1 h. According to the rate expressions of benzyl alcohol formation, they indicate that the dehydrogenation process is first-order in each substrate, catalyst and oxygen concentration with an appearent the rate constant (k) for substrate of 68 $M^{-2}s^{-1}$. Additionally, the effect of ligand base and their stoichiometry relative to Cu(II) on the rate was studied, the $[Cu(II)(bpy)]^{2+}$ complex is the most effective catalyst in combination with 2 equivalent of HO^- or $HOC(O)O^-$. Excess base has a negative effect and usually induces precipitation of copper(II) oxide [31].

Sharma, B. V., *et al.*, (2003), studied cobalt(II) schiff base complexes as a catalyst for the oxidation of 4,4′-dimethylbenzoin with molecular oxygen bubbling and molecular sieve in acetonitrile. Among all catalysts, *bis*[2-[{(1-phenylethyl) imino}methyl] phenolato-N,O]-cobalt, (shown in **Figure 2.1**), is a most efficient catalyst. Moreover, alcohol having carbonyl moiety at their α-position was more reactive. The substituted aromatic alcohols were more rapidly yields corresponding ketones compared to substituted aliphatic alcohols. They also evaluated the catalytic parameter affecting the oxidation including catalyst concentration and reaction temperature. The results show that the reaction time decreases with increase in catalyst concentration. Moreover, the reaction rate was very slowly at high temperature feasibly ascribing to the involvement of reversible dioxygen-cobalt complexes which are favorably formed at low temperatures [32].

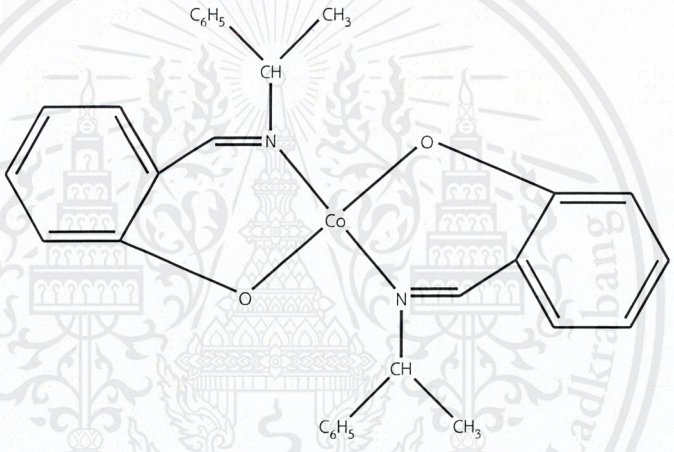


Figure 2.1 *bis*[2-[{(1-phenylethyl)imino}methyl] phenolato-N,O]-cobalt [32]

Shabaani, A., *et al.*, (2008), studied the aerobic oxidation of alkyl arenes and alcohols using cobalt(II) phthalocyanine as a catalyst in various ionic liquid. They conluded that the best ionic liquid is 1-butyl-3-methylimidazolium bromide ([bmim]Br), act as both phase transfer catalyst and non-coordinating polar solvent. Moreover, this liquid has advantages of green, suitable for various organic substance and gaining high reactivity. Moreover, the result showed that the oxidation of benzoin with various metallophthalocyanines in [bmim]Br, cobalt(II) phthalocyanine shows highest efficiency in oxidation of alkyl arenes and alcohol [17].

Kharat, A. N., *et al.*, (2011), studied cobalt(II) and cobalt(III) complexes of a terpyridine based ligand for the oxidation of alcohol with hydrogen peroxide. The effect of solvents, substrates, reaction temperatures counterion, nitrate or acetate, were investigated. It is noticeably shows that water is the suitable solvent that is low toxicity and promotes the oxidation. High temperature can break down the cobalt

complexes resulting on the suppressed productivity. Moreover, the more active cobaltous complex can possibly be oxidized to the cobaltic complex, deactivation was continually exhibited. Accordingly, the cobaltous complex, $[Co(L)_2](NO_3)_2 \cdot 2CH_3OH \cdot H_2O$, is more active than the cobaltic species, $[Co(L)_2](NO_3)_3 \cdot 2CH_3OH$, as a catalyst for oxidation [5].

Weiss, J. C., *et al.*, (2014) investigated nickel(II) diphosphine complexes oxidation of primary and secondary alcohols to aldehydes and ketones using triethylamine and decamethylferrocenium ($Cp^*_2Fe^+$; $Cp^* = Me_5C_5$) as the stoichiometric base and oxidant, respectively. The complexes were catalytically compared in this studies, the oxidation of diphenylmethanol to benzophenone represents a test reaction. The complexes with $P^R_2N^{Bn}_2$ (shown in **Figure 2.2**) were inefficient catalysts for the oxidation of alcohol, although being active for the oxidation of formate to carbon dioxide. Nonetheless, monodiphospine ligand complexes were enhanced turn over frequency, a 10-fold increase in rate is also noticed with the addition of basicity on pendent amine in the diphosphine ligand. Subsequently, the impacts of varying steric and electronic properties of the substrate were studied. The gigantic substituent on substrates reduces the rate of oxidation due to steric effect, hindered binding of Pr_2EtN [2].

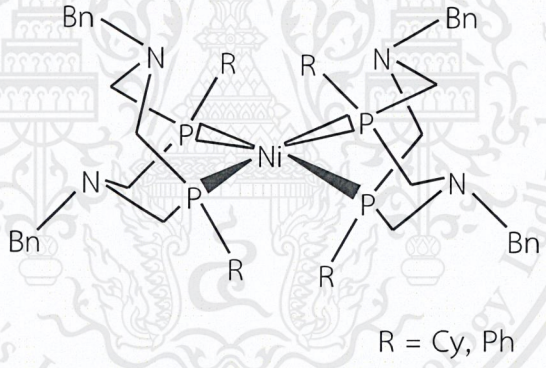


Figure 2.2 $[Ni(P^{Cy}_2N^{Bn}_2)_2]^{2+}$ $[Ni(P^{Ph}_2N^{Bn}_2)_2]^{2+}$ [2]

Noshiranzadeh, N., *et al.*, (2014), synthesized mononuclear complex of chromium(III), $[Cr(bp)(N_3)(CH_3OH)].2CH_3OH$ (shown in **Figure 2.3**), for the oxidation of primary alcohols to aldehydes with hydrogen peroxide as an oxidant. The effect of various parameters included the molar ratio of the oxidant to substrate, temperature and solvent were comparably employed at 25 to 80 °C for 5 h in atmospheric in oxidation of benzyl alcohol. This is achieved 10 to 80% of conversion of secondary alcohol when the ratio approach 3:1, temperature of 60 °C and the atmosphere has not affect on catalytic activity. In addition, they found at that the order of the solvent is acetonitrile > acetone > tetrahydrofuran > dichloromethane > chloroform > toluene > ethyl ether > dimethylsulfoxide [33].

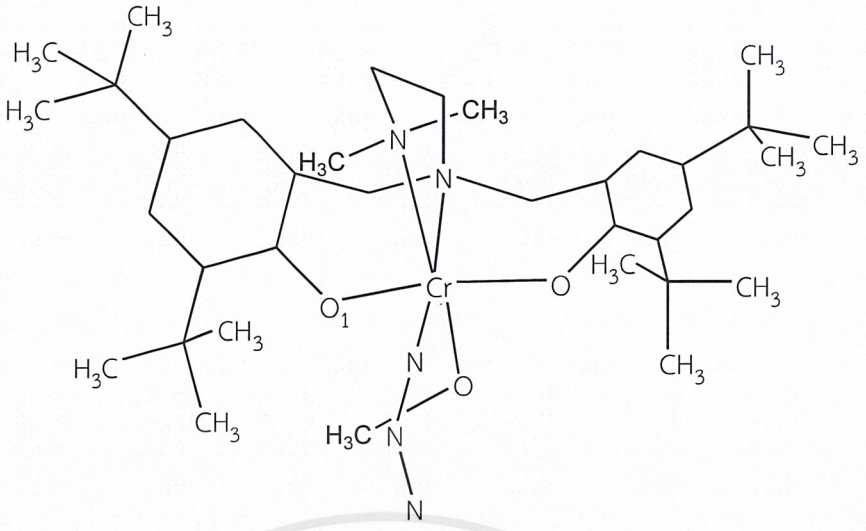


Figure 2.3 [Cr(bp)(N_3)(CH_3OH)].2CH_3OH [33]

Subarkhan, M. M. and Rames, R. (2015), report binuclear ruthenium(III) complexes containing bidentate thiosemicarbazone, halides and triphenylphosphine or triphenylarsine used as oxidant in oxidation of primary alcohols to aldehydes and secondary alcohols to ketones in the presence of co-oxidant N-methylmorpholine-N-oxide(NMO). In order to optimize reaction conditions, various substrate: catalyst ratios in presence of various co-oxidant were carried out. 1:100 of complex and substrate ratio increase the conversion of primary alcohol is over 91. It suggested that the complexes react with N-methylmorpholine-N-oxide to potentially obtain high valent Ru(V)=O species, favor oxygen atom transfer to alcohols [1].

Buntara, T., *et. al.*, (2011), studied the catalytic conversion of 5-hydromethylfurfural (HMF) into caprolactone using transition-based catalysts. Synthetic route for caprolactone production has been purposed at difference state in **Figure 2.4**. The catalytic conversion of the diols to lactone employing [{Ru(cymene)Cl_2}$_2$] and bis(diphenylphosphino)ferrocene with methyl isobuthylketone as a solvent under N_2 atmosphere reaches to the completion at 30 min [34].

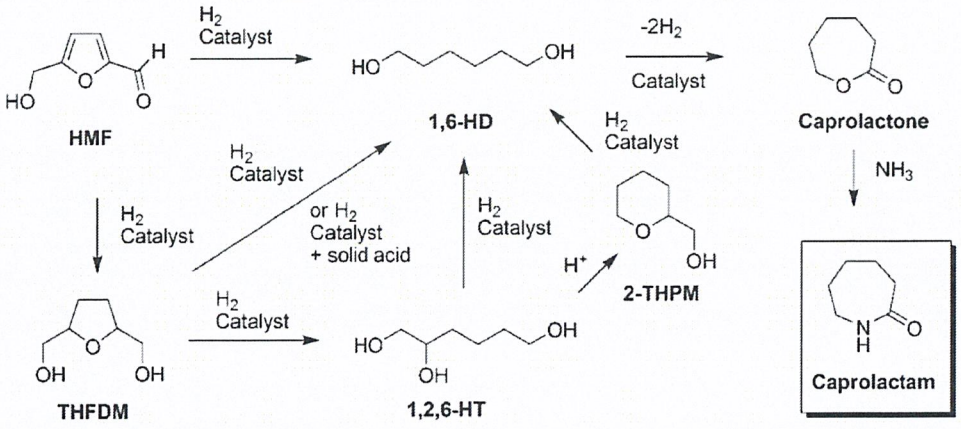


Figure 2.4. Synthetic routes for the conversion of HF into caprolactone [34]

CHAPTER 3

EXPERIMENTAL

3.1 Reagents

Chemicals	Grade of purity	Manufacturers
Acetone	100%	Zen point
Cobalt(II) chloride hexahydrate	98%	CARLO ERBA REAGENTS
Cobalt(II) nitrate hexahydrate	99%	Fluka Chemika
Dodecane	97%	ALDRICH
Ethybenzene	99.8%	Buksan
1,6-hexanediol	≥ 99%	Fluka Chemika
Methanol	≥ 99%	Fluka Chemika
2,2′-bipyridine	99.8%	FISONS
Dicyanobenzene	99.8%	CARLO ERBA REAGENTS
Diethyl ether	37%	CARLO ERBA REAGENTS
Toluene	> 99.8%	CARLO ERBA REAGENTS
Hydrochloric acid	1% v/v	ALDRICH
Nitrogen gas	99.999%	PRAXAIR
Deuterochloroform	99.8%	ALDRICH
Dichloromethane	99.99%	Fisher Scientific
Silica gel	100%	CARLO ERBA REAGENTS
Ru(*p*-cymene)(tbp)Cl_2	N/A	Assist. Prof. Dr. Nararak Leesakul
Ru(*p*-cymene)(dppm)Cl_2	N/A	Assist. Prof. Dr. Nararak Leesakul
Ru(*p*-cymene)Cl_2 dimer	N/A	Sigma-Aldrich

3.2 Apparatuses

1. Nuclear Magnetic Resonance (NMR),400 mHz
2. Beakers
3. Clamps
4. Condensers
5. Graduate pipettes
6. Gas Chromatography (GC-FID), Varians 3800
7. Hot Plate & Stirrer, IKA, RCT basic, 230 V, 50/60 Hz
8. Fourier-Transform Infrared Spectroscopy (FT-IR), Perkin Elmer, 400-4000 cm^{-1}
9. Ultraviolet–Visible Spectroscopy (UV), PG instruments limited, T60 U, 50-60 Hz, 150 W

10. Volumetric flasks
11. Vials
12. Thermometer
13. Buchner funnel
14. Desiccator
15. Round bottom flask 25 mL
16. Filter paper diameter 70 mm, MACHEREY-NAGEL
17. Nylon syringe filter, Verticlean , Membrane diameter 13 mm, 0.45 micron
18. Centrifuge, Centurion, 1000 Series
19. Micro pipette, pipet lite, SL1000, 100-1000 µL
20. Cooler and circulator, Heto, CBN 28-30
21. Air Balloons

3.3 Preparation and Characterization of Catalysts

3.3.1 Synthesis of *bis*-(bipyridine)cobalt(II) chloride

5.00 mmol of cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) was dissolved in 60.00 mL of acetone. 10.00 mmol of 2,2′-bipyridine ($C_{10}H_8N_2$) was dispersed in 60.00 mL of acetone [35]. Subsequently, the solutions were stirred at ambient temperature for 2 hours and left for crystallization for few hours. Afterwards, the pink crystals were filtrated by vacuum system and then washed with acetone. The crystals were collected and kept in non-moisture atmosphere.

3.3.2 Synthesis of *tris*-(bipyridine)cobalt(II) nitrate

3.00 mmol of cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and 11.00 mmol of 2,2′-bipyridine ($C_{10}H_8N_2$) were mixed together and dissolved in a minimum volume of methanol [36]. The solution was stirred at ambient temperature for 2 hours and left for 24 hours for precipitation. The yellowish crystals were collected and kept in a desiccator.

3.3.3 Synthesis of *trans*-dichloro-*bis*-(ethylenediamine)cobalt(III) chloride

5.00 mmol of cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) was dissolved in 9.50 mL of distilled water and added ethylenediamine ($C_2H_4(NH_2)_2$) solution (16%en in water) 2.50 mL. The solution was drop-wise added by 30% H_2O_2 1.20 mL, then, evaporated at relative low temperature to 2.00 mL of the solvent approximately, obtaining emerald green crystal. This crystal was washing with 16.00 mL of ethanol and 16.00 mL of diethyl ether (from inorganic laboratory).

3.3.4 Synthesis of cobalt phthalocyanine

4.00 mmol of cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and 21.00 mmol of dicyanobenzene ($C_6H_4(CN)_2$) were mixed and grinded together, putting in round bottom flask using sand bath as heating unit and N_2-filled balloon to restrict inert closed-system as shown in **Figure.3.2**. After that, the system was heated at 220 °C for 4 hours giving blue-green particles. To precipitate out unreacted $CoCl_2 \cdot 6H_2O$ and partially unreacted dicyanobenzene, 20.00 mL of toluene was added then filtrate in vacuum to obtain dark green particles. The particles was dispersed in diethyl ether to eliminate remained dicyanobenzene and un-impure cobalt phthalocyanine.

3.3.5 Catalyst characterization

3.3.5.1 Fourier-Transform Infrared Spectroscopy (FT-IR)

The powder of the sample was dispersed in potassium bromide (KBr). The mixture was pressed about 5 tons into a disc. Infrared spectra were collected using Spectrum GX (Perkin Elmer) at Scientific Instrument Service Centre, KMITL, from 400-4000 cm^{-1}. The IR signal was calibrated and corrected employing polystyrene film as a standard.

3.3.5.2 Ultraviolet–Visible Spectroscopy (UV)

The absorption spectra of the catalysts were determined by using UV-Vis spectrophotometer (PG instruments limited, T60 U, 50-60 Hz, 150 W). Methyl alcohol was used as solvent for baseline correction. The 0.10 mg of catalyst was diluted in methyl alcohol 8.00 mL. Subsequently, the solution was filled into quartz cuvette, to avoid self-interference in UV region, in scanning mode from 200 to 900 nm of wavelength.

3.4 Catalytic Testing

3.4.1 The Oxidation of Ethylbenzene

Ethylbenzene 5.00 mL and catalyst 0.20 mmol was mixed together in 0.50 mL of dodecane, using oil bath as a heating unit and the air was bubbled through the system as shown in **Figure.3.1**, then the mixtures were heated at various temperatures (60, 90, 110 °C) for 24 and 48 hours. Obtained solution 100.00 µL *was dispersed in solution of* 100.00 µL of HCl and 2.00 mL of diethylether, centrifuged at 3000 rpm for 15 min to separate the catalyst. The supernatant was quantitatively analyzed by gas chromatography (Varians 3800) equipped with a DB-wax column (30m×0.53 mm) and flame ionization detector (FID), injector 220 °C, N_2 flow 1.5 mL/min, column 70 °C hold

2 min to 180 °C rate 20 °C/min, detector 220 °C, pressure 16.4 psi, linear velocity 36.1 cm/sec.

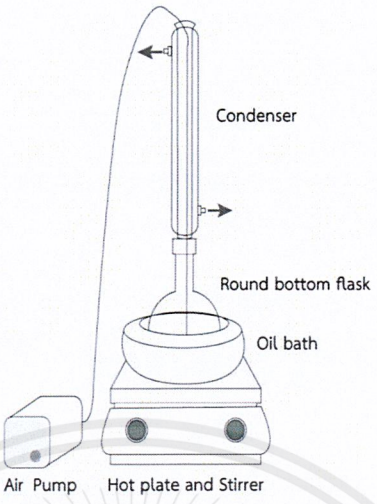


Figure. 3.1 Cataytic testing of ethylbenzene

3.4.2 The Oxidation of 1,6-Hexanediol

1,6-hexanediol 1.00 g and catalyst 0.20 mmol was mixed in a round bottom flask, using oil bath as heating unit and air-filled balloon to restrict closed-system as shown in **Figure.3.2**, then the mixtures were heated at 60 °C, 110 °C or 150 °C for 24 hours. 100.00 µL of the obtained mixture was mixed with 1 mL of dichloromethane, attached cobalt complex with 1.00 cm of silica bed then eluted with 3 mL of dichloromethane. The solution was purged in nitrogen gas to evaporate solvent and added into deuterochloroform 1 mL, perform on 400 mHz NMR.

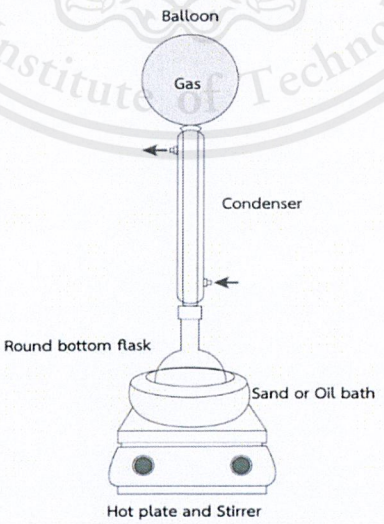


Figure. 3.2 Equipment for cobalt phthalocyanine synthesis and catalytic testing of 1,6-hexanediol

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Characterization of Catalysts

The characterization of the catalysts provides the information indicating the complex formation, composition, and stability of compounds. *bis*-(bipyridine)cobalt(II) chloride, *tris*-(bipyridine)cobalt(II) nitrate, *trans*-dichloro-*bis*-(ethylenediamine)cobalt(III) chloride, cobalt phthalocyanine and dichloro(*p*-cymene)ruthenium(III) dimer (designated as *bis*-Co, *tris*-Co, *trans*-Co, Co-Pc and Ru-dimer, respectively) used as catalysts, were initially characterized by the following method: Fourier Transform Infrared Spectroscopy (FTIR) and UV-Visible Spectroscopy (UV-Vis). Quantitative products analysis of ethylbenzene oxidation was measured by Gas Chromatography (GC) and 1,6-hexanediol oxidation was detected by ^{1}H NMR.

4.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra of 2,2′-bipyridine, *bis*-(bipyridine)cobalt(II) chloride, *tris*-(bipyridine)cobalt(II) nitrate are depicted in **Figure 4.1.**

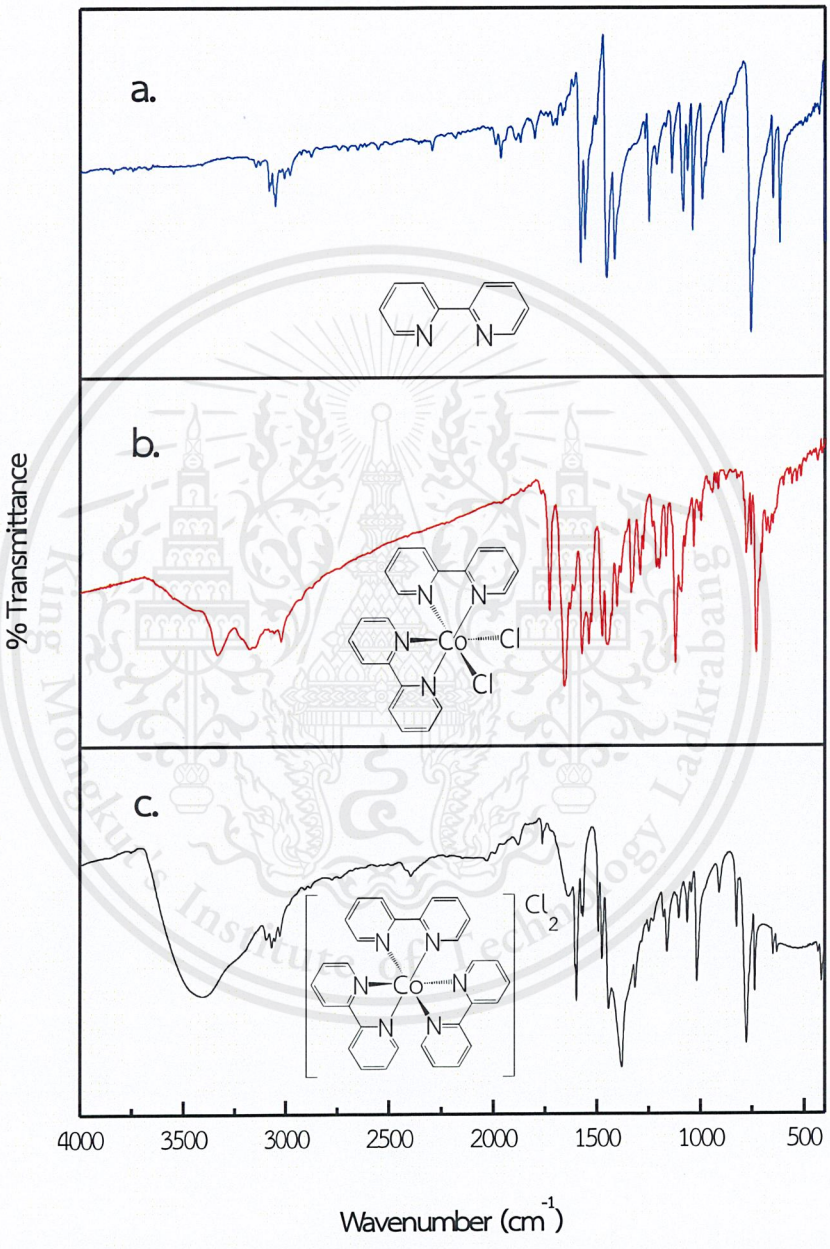


Figure. 4.1 FTIR spectra of a) 2,2′-bipyridine, b) *bis*-(bipyridine)cobalt(II) chloride and c) *tris*-(bipyridine)cobalt(II) nitrate

The comparative spectra shows that *bis*-Co and *tris*-Co have the pyridine moiety as compared to the free pyridine. However, peaks of the pyridine in *bis*-Co and *tris*-Co are shifted to the lower wavenuber indicating the bonding between pyridine and cobalt metal. All the peaks of the compounds are similar to the previously reported paper [37]. The vibration frequencies of each band are listed in **Appendix B**. It is noted that the broad band from 3715 to 3120 cm^{-1} is assigned to vibrational stretching mode of OH due to adsorbed atmospheric water. The intense peak at high wavenumber (3100 cm^{-1}) is ascribed to CH stretching from the coordinated ligand. Multiple peaks around 1940 cm^{-1} are overtones of aromatic and the intense peak at 1580 and 1558 cm^{-1} belong to C=N stretching. Considering the peak of C-N stretching of free pyridine, *bis*-Co, and *tris*-Co occur at 1415, 1422 and 1442 cm^{-1}, respectively. The vibration bands at 1416 cm^{-1}, 1300-900 cm^{-1} and 757 cm^{-1} are designated to be C-N stretching, C-H bending and C-N out-of-plane bending, respectively. Comparing *bis*-Co and *tris*-Co, the FTIR peaks of the bipyridine are relatively shifted to the higher wavenumber with respect to the number of the coordinated ligands. This effect could be attributed to higher affinity of Co as due to a higher ligand field of additional bipyridine, as compared to Cl^-.

The FTIR spectra of dicyanobenzene and cobalt phthalocyanine are depicted in **Figure 4.2**.

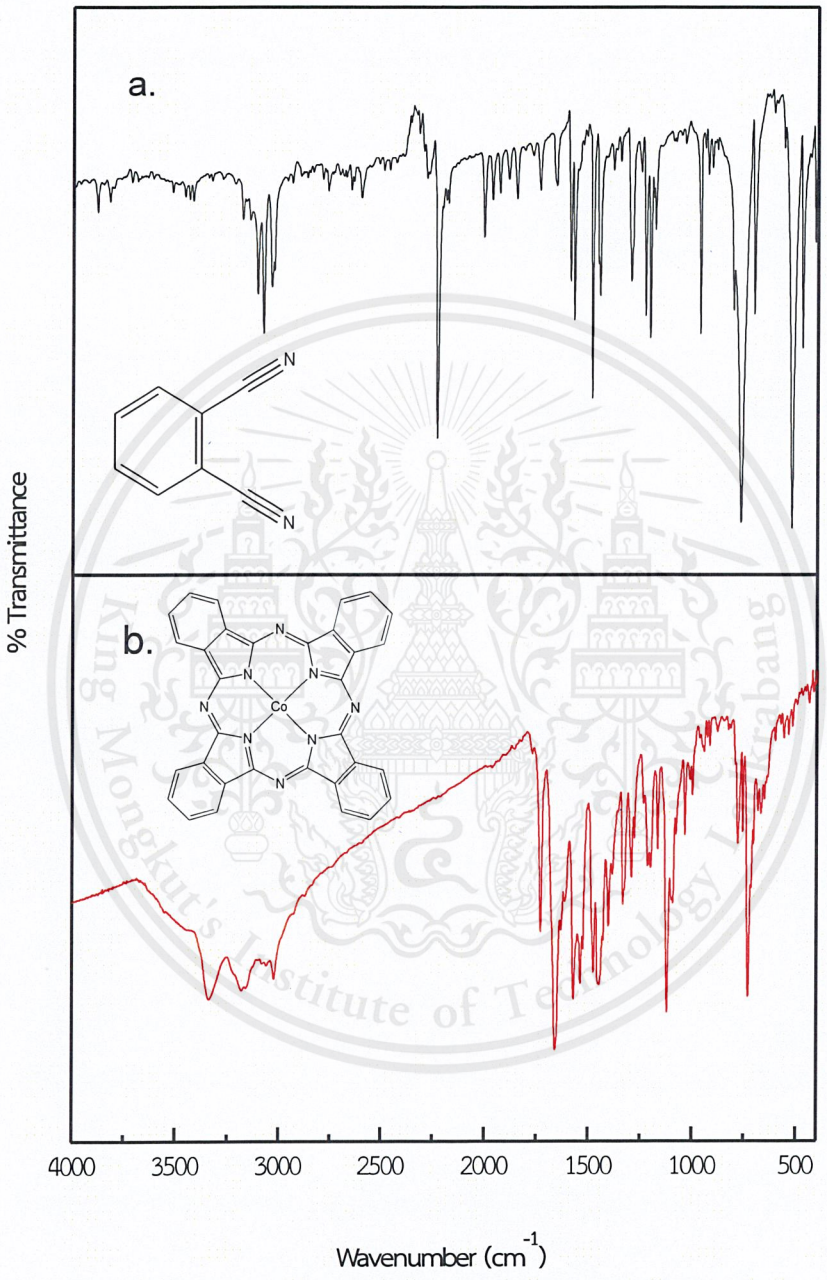


Figure. 4.2 FTIR spectra of a) dicyanobenzene b) cobalt phthalocyanine

The spectra of the Co-Pc is clearly different from the dicyanobenzene, a starting material. The disappearance of C≡N in this complex describing from the formation of phorphyrin ring induced by cobalt center. In addition, the C-CN bonds

(527 and 770 cm^{-1}), wherein the free ligand, are also absent in the product indicating the pure synthesized compound. The exact absorption band shows in **Appendix B**. Vibration bands at 3150-3020 cm^{-1} are C-H stretching, and 1730-1290 cm^{-1} are the couple of C-H and C-N stretching. The peak at 1120 cm^{-1}, 1090 cm^{-1} and 730 cm^{-1} are designated to C-H in-plane bending, C-N stretching, and C-H out of plane bending, respectively. The FTIR spectrum of Co-Pc has a similarity to the previously reported by Enokida *et. al.* [38].

The FTIR spectrum of *trans*-dichloro-*bis*-(ethylenediamine)cobalt(III) chloride is shown in **Figure 4.3**.

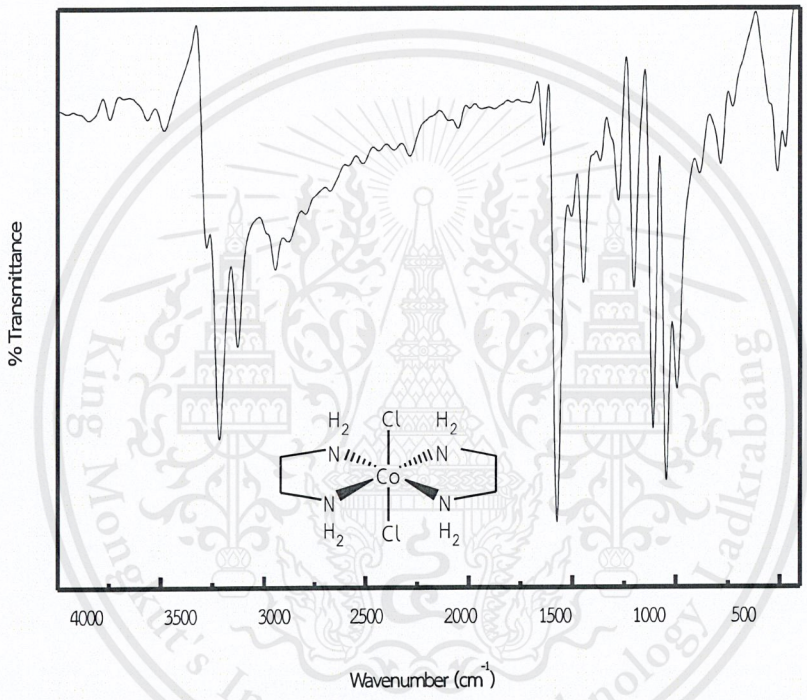


Figure. 4.3 FTIR spectra of *trans*-dichloro-*bis*-(ethylenediamine)cobalt(III) chloride

It is noted that at 3217 cm^{-1} is attributed to –OH stretching and 2943 cm^{-1} is C-H stretching. The peaks at 1573, 1446, 1200-1040 and 480 cm^{-1} belong to N-H bending, C-H bending, C-N stretching and Co-N, respectively [39].

4.1.2 UV-Visible Spectroscopy (UV-Vis)

The UV-Visible adsorption spectra of all complexes scanning from 400 to 800 nm are shown in **Figure 4.4.**

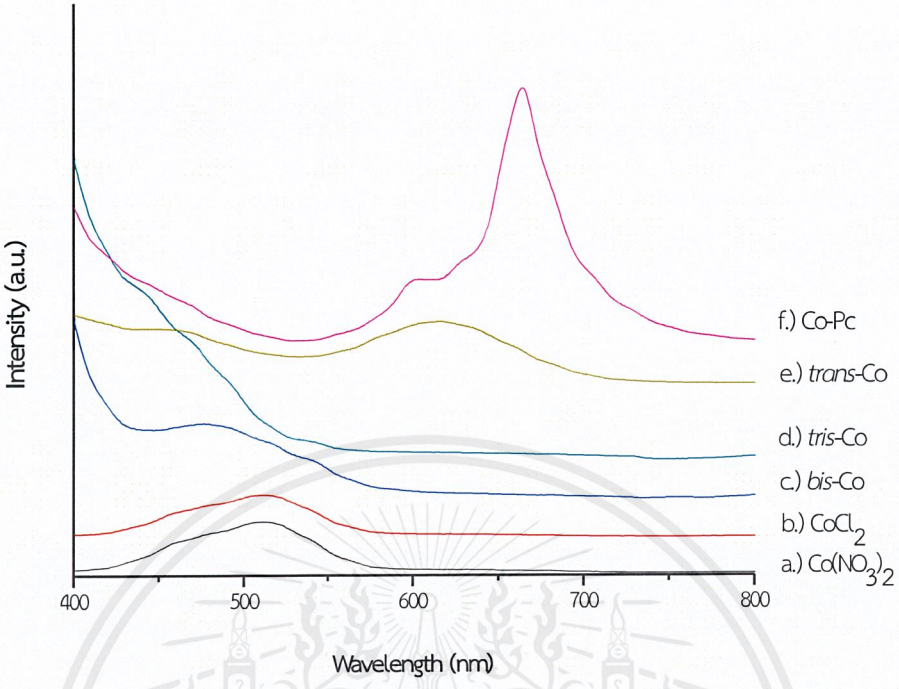


Figure. 4.4 UV-VIS spectra of a) cobalt(II) nitrate hexahydrate, b) cobalt(II) chloride hexahydrate, c) *bis*-(bipyridine)cobalt(II) chloride, d) *tris*-(bipyridine)cobalt(II) nitrate, e) *trans*-dichloro-*bis*-(ethylenediamine)cobalt(III) chloride and f) cobalt phthalocyanine

Cobalt(II) nitrate hexahydrate and cobalt(II) chloride hexahydrate, which are used as a metal precursor, show the absorption peak at 510 nm [40 and 41]. Both are dissolved in water forming six-coordinated cobalt hydrate. The absorption peak of all complexes is shifted as compared to the precursor, which dues to the electronic effect induced by the coordinated ligands. *bis*-(bipyridine)cobalt(II) chloride absorbs at 474 nm, corresponding to a pink crystalline; whereas, *tris*-(bipyridine) cobalt (II) chloride, yellow crystalline, is positioned at 438 nm. *trans*-dichloro-*bis*-(ethylenediamine) cobalt(III) chloride, depicts an absorption at 615 nm resulting an emerald green sample [42]. Cobalt phthalocyanine shows the doublet spectra around 664 and steep shoulder at 606 nm of cobalt center d-d transition and π - π^* transition of the ligand. All absorption peaks of all complexes are similar to those previously reported [43]. These results indicate the degree of the ligand field affecting of the d-d orbital splitting. The higher the energy (lower wavelength), the wider the d-d energy gap. Thus, in general, the degree of the ligand field would be Cl^- <en < bipyridine.

4.2 Catalytic Testing

4.2.1 Oxidation of Ethylbenzene

4.2.1.1 Effect of Chemical Potential of Oxygen for the Oxidation of Ethylbenzene

The comparison of the oxidation of ethylbenzene without the catalysts (blank) in closed- and air-bubbling systems is shown in **Figure 4.5.**

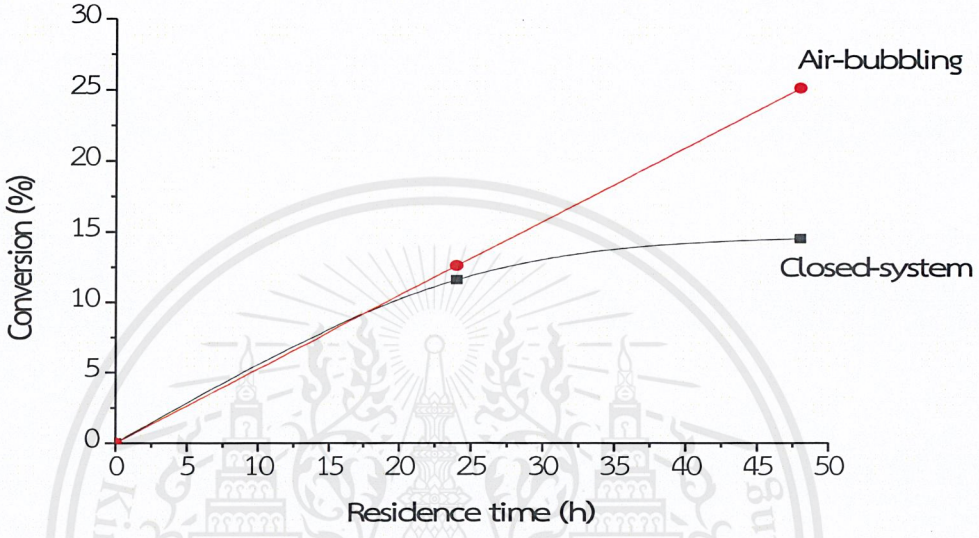


Figure 4.5 Conversion of ethylbenzene in closed- (■) and air-bubbling (●) systems without a catalyst (blank) at 110 °C

Closed-system was performed by filling oxygen into the balloon and restricted at the end of the condenser; on the other hand, the bubbling system is carried out by gently pumping oxygen flow. The time-dependent conversion were considered at 24 and 48 h. The oxidation without catalysts could be spontaneously activated. At 24 h both systems give relatively the same activity. In the air-bubbling system, the conversion increases linearly with the time, suggesting that the oxidation of ethylbenzene can take places homogeneously. Moreover, the air-bubbling also increases the interface of oxygen contact. In contrary, the conversion in the closed-system is declined after 24 h. This could be reasoned of the limited chemical potential of the oxygen in the closed-system.

The yields of products from the oxidation of ethylbenzene in closed-system and air-bubbling system are shown in **Figure 4.6**.

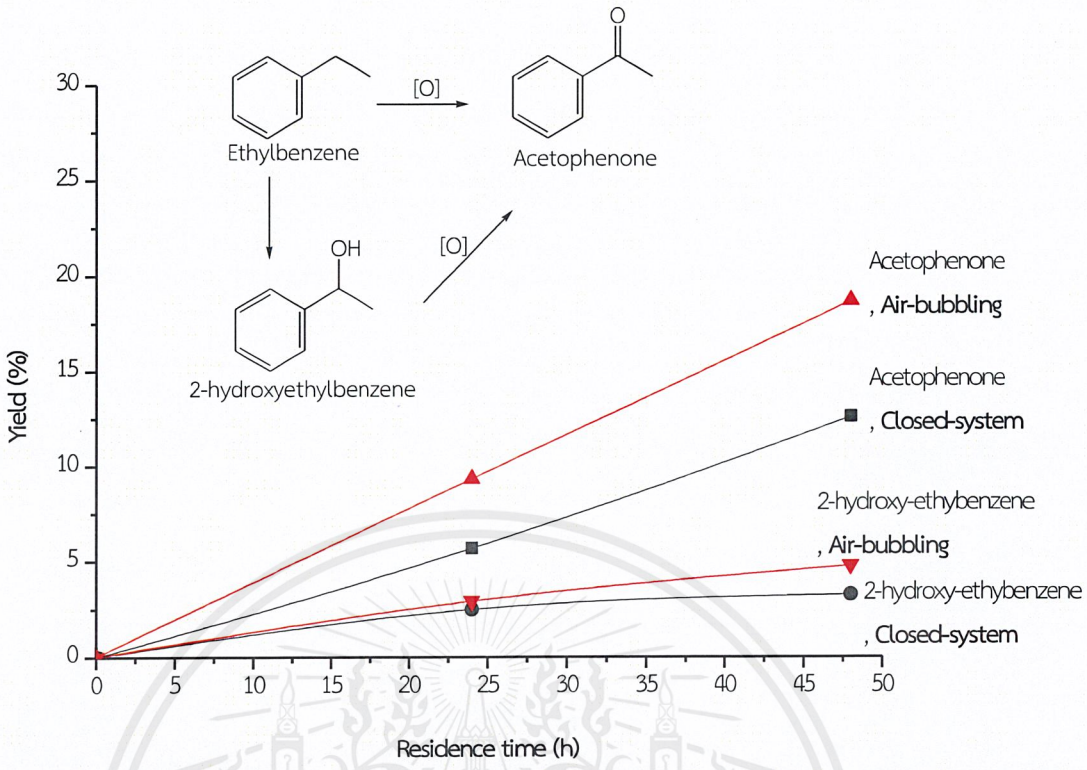


Figure 4.6 Yield of acetophenone (▲ Air-bubbling and ■ Closed-system) and 2-hydroxy-ethylbenzene (▼ Air-bubbling and ● Closed-system) in blank at 110 °C

Both systems produce acetophenone as a main product and 2-hydroxy-ethylbenzene as a minor product. The yield of 2-hydroxy-ethylbenzene is not significantly changed with time; while, the yield of acetophenone keeps increasing. This is presumably because 2-hydroxy-ethylbenzene could be an intermediate for the formation of acetophenone.

4.2.1.2 Effect of Complex Catalysts

The time-dependent oxidation of ethylbenzene using various catalysts in air-bubbling system is shown in **Figure 4.7**.

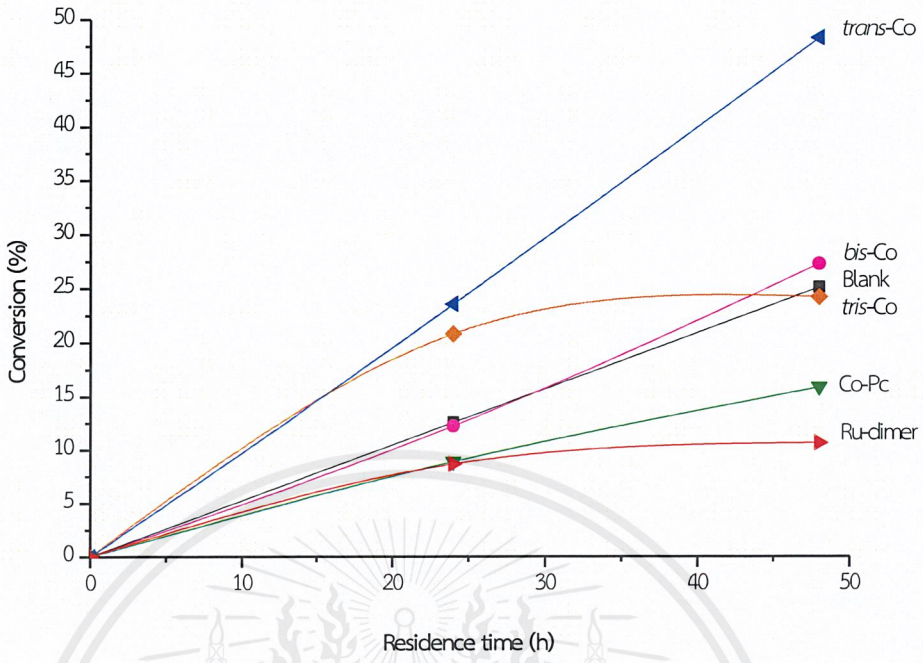


Figure 4.7 Conversion of ethylbenzene in air-bubbling system with blank (■), *bis*-Co (●), *tris*-Co (◆), Co-Pc (▼), *trans*-Co (◀) and Ru-dimer (▶)

tris-Co, *trans*-Co and *bis*-Co possess high activity but Co-Pc and Ru-dimer give the low conversion, even lower than that of the blank. Since the oxidation commonly promoted with singlet electron and unsaturated coordinate complexes, *trans*-Co shows the best catalyst to accelerate oxidation of ethylbenzene. In support manner, *trans*-Co shows the lower steric hindrance and narrower energy gap, as evaluated by UV-Vis absorption shown in **Table 4.1**

Table 4.1 Electronic properties of Co-complex catalysts

Samples	Conversion* (%)	Co state	Electronic structure	Energy gap** (eV)	Isomer	π Backbonding
trans-Co	23.55	3+	O_h	2.01	trans	✗
tris-Co	20.80	2+	O_h	2.80	✗	✓
bis-Co	12.23	2+	O_h	2.62	cis	✓
Co-Pc	8.90	2+	S_q	1.86	✗	✓
Ru-dimer	8.68	2+	-	2.87	cis	✗

* Conversion at 110 °C for 24 h.

** Determine from UV-Vis spectra

Although *bis*-Co also possesses a narrow energy gap, the activity is lower than *tris*-Co. This is due to the presence of Cl^- as coordinated ligands. This ligand is categorized as a high electronic withdrawing group, inducing the electronic field away from Co-center. In contrast, the higher activity of *tris*-Co, is presumably due to its high degree of σ–donor and π-backbonding despite of it high energy gap. This results of the bipyridine may act as a radical center with unclear oxidation state of metal. The radical might directly activate reactant. Unfortunately, *tris*-Co is unstable overtime observing from the deactivation after 24 h. This could be contributed to the exchange, oxidization or/and decomposition of the complex. In general, if the catalysts are not available, the activity must be equivalent to the blank. In contrast, comparing the conversion of Co-Pc, and Ru-dimer with the blank, they show the lower activity. These catalysts should be considered as an antioxidant [44] or participated metal complex mechanism [45, 46]. The concept of the antioxidant is realized from d-orbital splitting diagram in **Figure 4.8**.

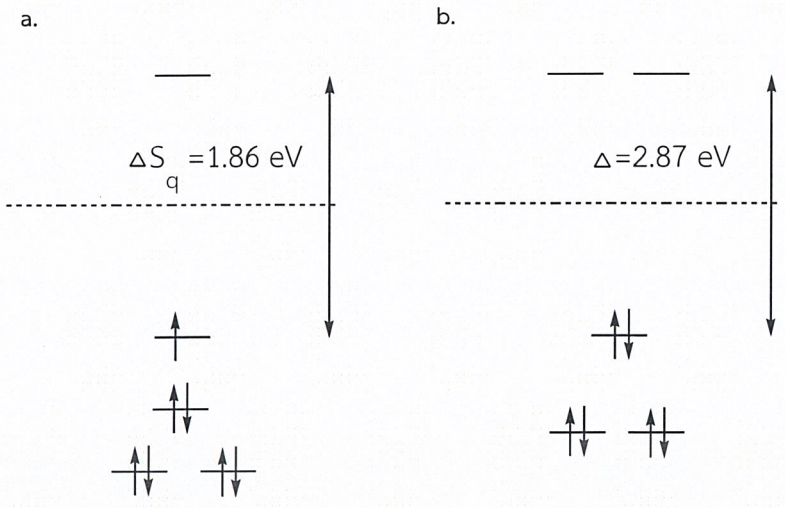


Figure 4.8 The orbital splitting diagram of a) square planar and b) half-sandwich pseudo-tetrahedral

Co-Pc is an electronic structure of a square planar having Pc ligand. This ligand is a sigma donor and strong π-acceptor. Therefore, rather than donating electron to form triplet state, it could traps an electron. Ru-dimer also has a high energy gap that electron in ground state could not be activated. Moreover, it can dissociate to form mono-Ru complexes as a half sandwich resulting the capture of an electron.

The oxidation of ethylbenzene comprises of two main products, acetophenone as a majority and 2-hydroxy-benzene as a minority, shown in **Figure 4.9.**

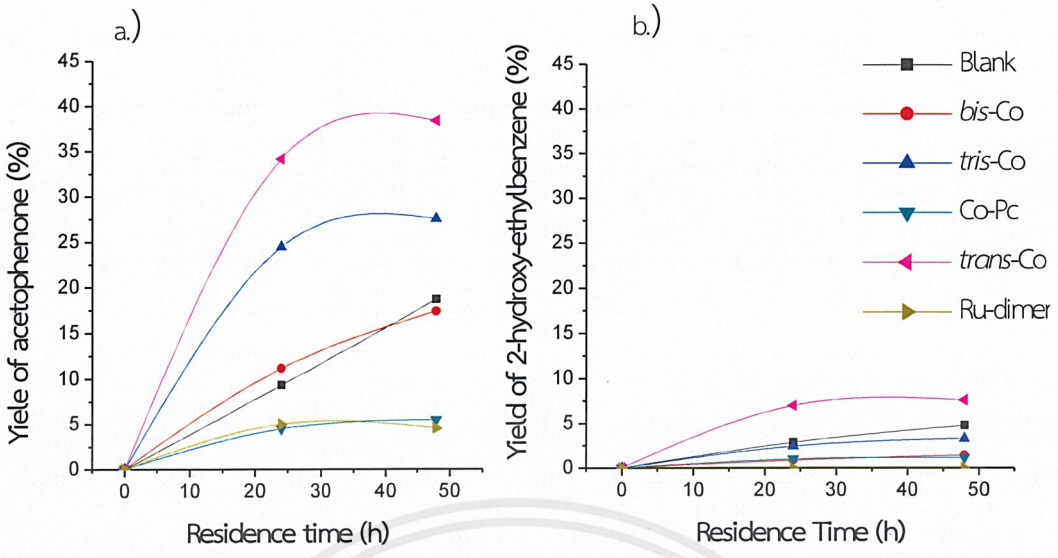


Figure 4.9 a.) yield of acetophenone and b.) yield of 2-hydroxy-ethylbenzene in air-bubbling system at 110°C

Table 4.2 TOF of acetophenone and 2-hydroxy-ethylbenzene

Catalysts	yield of acetophenone	TOF* (h^{-1})	yield of 2-hydroxy-ethylbenzene	TOF** (h^{-1})
trans-Co	34.13	2.84	7.00	0.58
tris-Co	24.43	2.04	2.44	0.20
bis-Co	11.10	0.93	0.88	0.07
Co-Pc	4.50	0.37	1.00	0.08
Ru-dimer	4.97	0.41	0	0

* TOF based on yield of acetophenone

** TOF based on yield of 2-hydroxy-ethylbenzene

GC-MS chromatogram additionally show small peaks at 7.583, 14.126, and 17.728 min. corresponding to benzaldehyde, butane-2,3-diyldibenzene, and benzoic acid, respectively. The chromatogram is demonstrated in **Figure 4.10**. Butane-2,3-diyldibenzene could result from the oxidative coupling of ethylbenzene radical fragments.

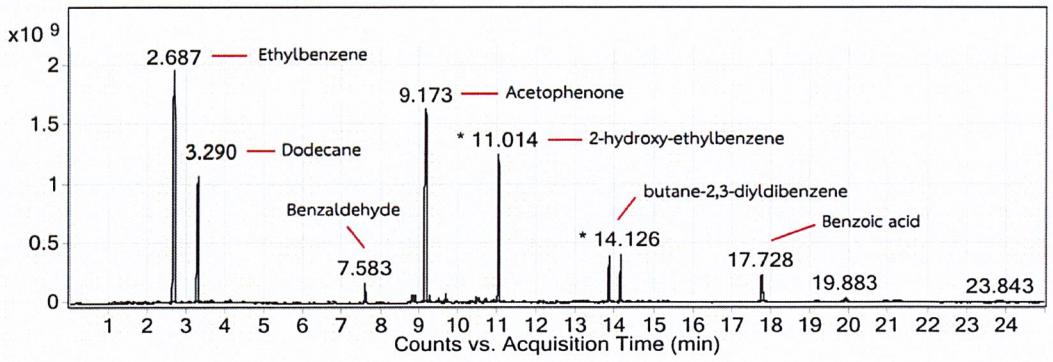


Figure 4.10 GC-MS Chromatogram

The proposed oxidation pathways of ethylbenzene are demonstrated in **Figure 4.11.**

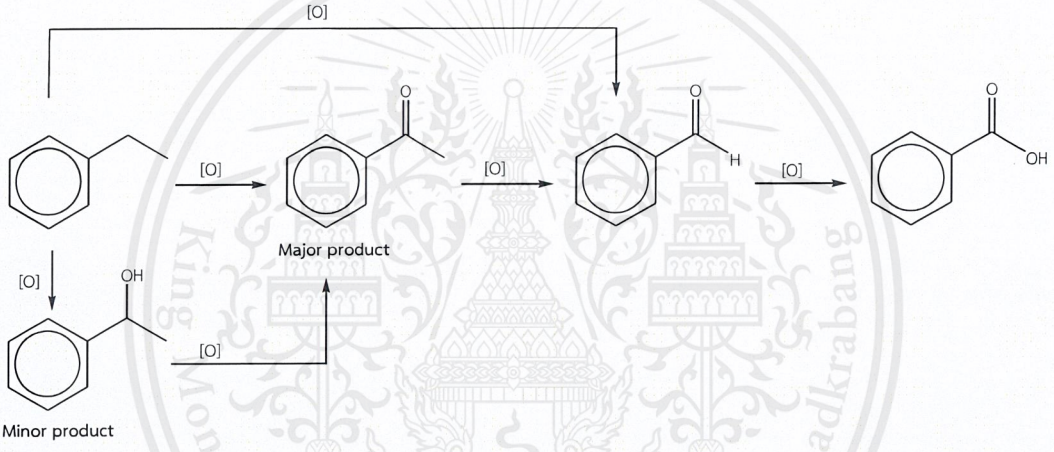


Figure 4.11 The proposed oxidation pathways of ethylbenzene to acetophenone

Accordingly to the GC-MS results, 2-hydroxyethylbenzene may be an intermediate of this reaction. The acetophenone might be further activated to higher oxidation level product, benzaldehyde and benzoic acid. The paradox of the reaction participated to nucleophilic aromatic substitution and condensation of acetophenone etc.

4.2.1.3 Effect of Temperature

The temperature is another key factor governing the reaction occurrence. According to the previous mentioned section, the effect of temperature on *trans*-Co and *tris*-Co is investigated since they show the promising result, as shown in **Table 4.3**

Table 4.3 Temperature effect on the oxidation of ethylbenzene

Temperature (°C)	Activity	Catalysts		
		blank	*tris*-Co	*trans*-Co
60	**Conversion**	**0**	**0**	**0**
	Yield of acetophenone	0	0	0
	Yield of 2-hydroxy-ethylbenzene	0	0	0
90	**Conversion**	**9.71**	**12.66**	**19.99**
	Yield of acetophenone	6.70	7.46	13.94
	Yield of 2-hydroxy-ethylbenzene	1.52	1.32	6.07
110	**Conversion**	**13.32**	**18.79**	**21.43**
	Yield of acetophenone	10.09	13.52	15.87
	Yield of 2-hydroxy-ethylbenzene	4.51	0.58	3.66

* air-bubbling system and residence time 24 h

From **Table 4.3**, there is no conversion at 60 °C for all catalysts. At this temperature, the system may not provide enough kinetic energy to activate the reactant with observable rate. The oxidation of ethylbenzene with various catalysts including blank has confirmed that the reaction is favorable at high temperature [46]. The activity of the catalysts for this reaction is in the order of blank, *tris*-Co, *trans*-Co, respectively. Moreover, the depletion of 2-hydroxy-ethylbenzene at high temperature of *tris*-Co and *trans*-Co reveals the promotion of 2-hydroxy-ethylbenzene to acetophenone by such catalyst as shown in Figure 4.11.

The ratios of acetophenone: 2-hydroxy-ethylbenzene yield are illustrated in **Table 4.4**.

Table 4.4 The ratio of acetophenone: 2-hydroxy-ethylbenzene

trans-Co	*tris*-Co	*bis*-Co	blank	Co-Pc	Ru-dimer
4.88	10.01	12.57	3.21	4.48	4.97 (No alcohol)

* air-bubbling system at 110 °C, 24 h

The products from the oxidation of ethylbenzene over each catalyst yield higher ketone/alcohol ratio as compared to the blank. This again supports the oxidation of 2-hydroxy-ethylbenzene to acetophenone, especially, by bipyridine-complexes (*bis*-Co, *tris*-Co).

4.2.2 The Oxidation of 1,6-Hexanediol

4.2.2.1 Effect of Temperature for the Oxidation of 1,6-Hexanediol

The catalysts used for the oxidation of ethylbenzene are also investigated for 1,6-hexanediol oxidation. The various reaction temperatures including 60, 110, and 150 °C were studied in all catalysts. The results are shown in **Table 4.5.**

Table 4.5 Conversion of 1,6-hexanediol

Temperature (°C)	% Conversion in each catalyst				
	Ru-dimer	*tris*-Co	Co-Pc	*bis*-Co	*trans*-Co
60	0	2.54	1.02	1.23	2.85
110	28.11	21.22	11.25	1.22	N/A
150	14.71	8.22	2.77	5.58	9.68

According to **Table 4.4**, in general, the conversion increases as a function of temperature, consistent with temperature-dependent Arrhenius equation ($k= A_0 e^{-Ea/RT}$). *bis*-Co shows the better activity as the temperature raised from 60 to 150 °C. Similarly, others have the same trend as the temperature increased from 60 to 110 °C. Considering the conversion of the reaction at 110 °C, the activity of the catalysts is in the order of Ru-dimer > *tris*-Co > Co-Pc. On the other hand, at this temperature, *bis*-Co and *trans*-Co are not as active as the others which could be due to the insufficient energy for the catalyst complexes to overcome the reaction activation energy. Raised up the reaction temperature to 150°C shows unexpectedly low for Ru-dimer, *tris*-Co, and Co-Pc. This is presumably explained by the decomposition of complexes and ligand-dissociation at high temperature [5].

The conversion of 1,6-hexanediol yields both of ε-caprolactone and 6-hydroxy-hexanal as shown in **Table 4.6.**

Table 4.6 Selectivity of ε-caprolactone and 6-hydroxy-hexanal

Temperature (°C)	Selectivity (%)	Catalysts				
		Ru-dimer	*tris*-Co	Co-Pc	*bis*-Co	*trans*-Co
60	ε-caprolactone	0	100	100	100	100
	6-hydroxy-hexanal	0	0	0	0	0
110	ε-caprolactone	97.76	10.79	100	100	N/A
	6-hydroxy-hexanal	2.34	89.21	0	0	N/A
150	ε-caprolactone	54.93	27.00	100	89.25	72.46
	6-hydroxy-hexanal	45.07	73.00	0	10.75	27.54

The results reveal that Ru-dimer and Co-Pc are selective to ε-caprolactone; while, *tris*-Co is selective to 6-hydroxy-hexanal. It is predicted that the high degree of steric hindrance inhibited the intra-molecular cyclization of 6-hydroxy-hexanal. Surprisingly, although *trans*-Co is active for the oxidation reaction of ethylbenzene, there is no conversion for 1,6-hexanediol at 110 °C. From these results, it is assumed that the oxidation participates metal-complex mechanism as depicted in **Figure 4.12.**

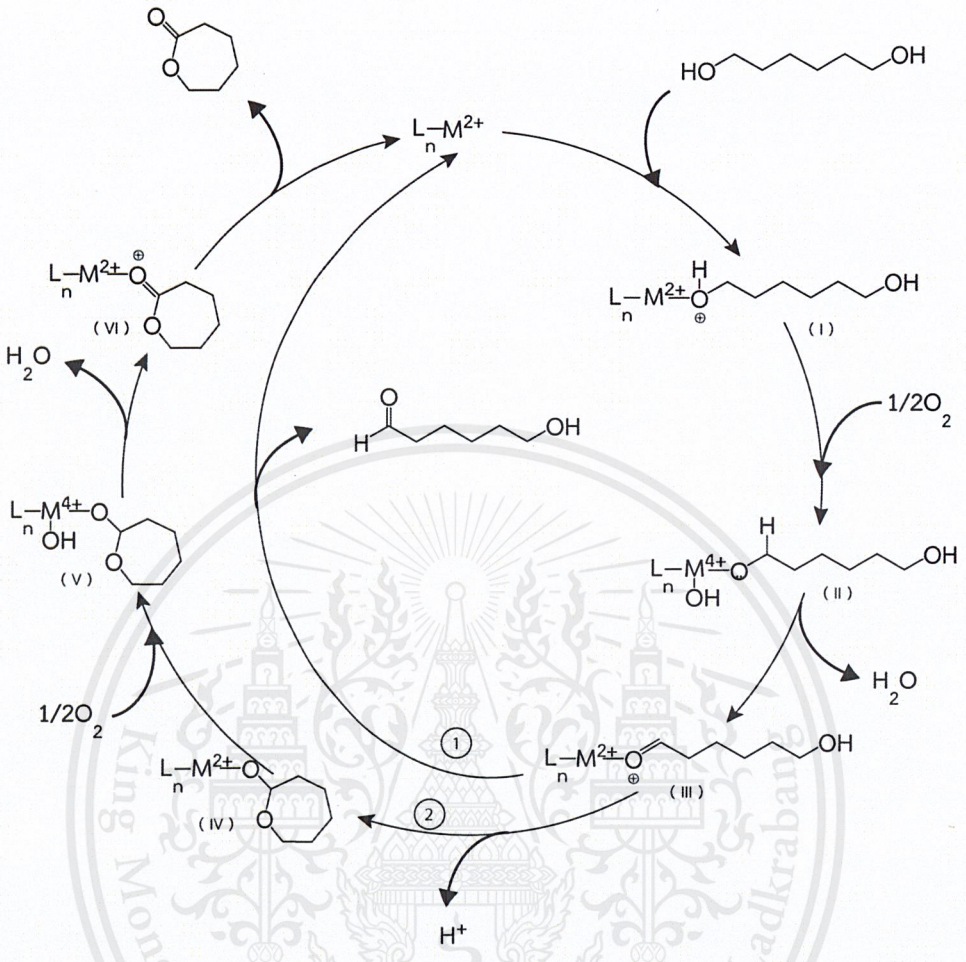


Figure 4.12 Proposed catalytic cycle of the 1,6-hexanediol oxidation

The ligand base association of 1,6-hexanediol to the metal center occurs first, followed by the oxidative addition oxygen generating the coordinated hydroxo complex (**II**). The next step is the reductive elimination of hydroxo complex by the abstraction of the α-carbon hydrogen by the hydroxyl ligand. This results the elimination of water and the generation of the oxonium compound (**III**). After forming the oxonium complex (**III**), it can simply dissociate giving 6-hydroxy-hexanal as a product (pathway **1**). This process is favorable at the high temperature since the percent selectivity of the aldehyde products dramatically increases at 110 °C compared to 60 °C, except for *tris*-Co. Coordinated bipyridene of *tris*-Co might be distorted at high temperature providing a large space for cyclization. Alternatively, the oxonium complex can proceed via intra-molecular cyclization (pathway **2**) by the nucleophilic attack at the acyl group with its hydroxyl group forming cyclic lactol complex (**IV**). This complex then takes up another half of molecular oxygen forming

the hydroxyl complex (**V**) via the oxidative addition, which can further eliminate water as the reductive elimination as previously mention. The last step is the dissociation of ε-caprolactone ligand yielding the cyclic ester. However, Co-Pc shows the constant ε-caprolactone selectivity at all temperature because the square planar structure aligns in two-dimensional axes accommodating the 6-hydroxyhexanal for cyclization.

4.2.2.2 Effect of the Ligands on the Ru Complexes for the Oxidation of 1,6-hexanediol.

Since Ru-dimer shows both the high reaction activity and high selective product at 110°C, the effect of the ligands on the Ru complexes was, thus, investigated. The modified Ru-dppm and Ru-tbp complexes having diphenyl phosphino- and *tert*-butylpyridine are shown in **Figure 4.13**, respectively.

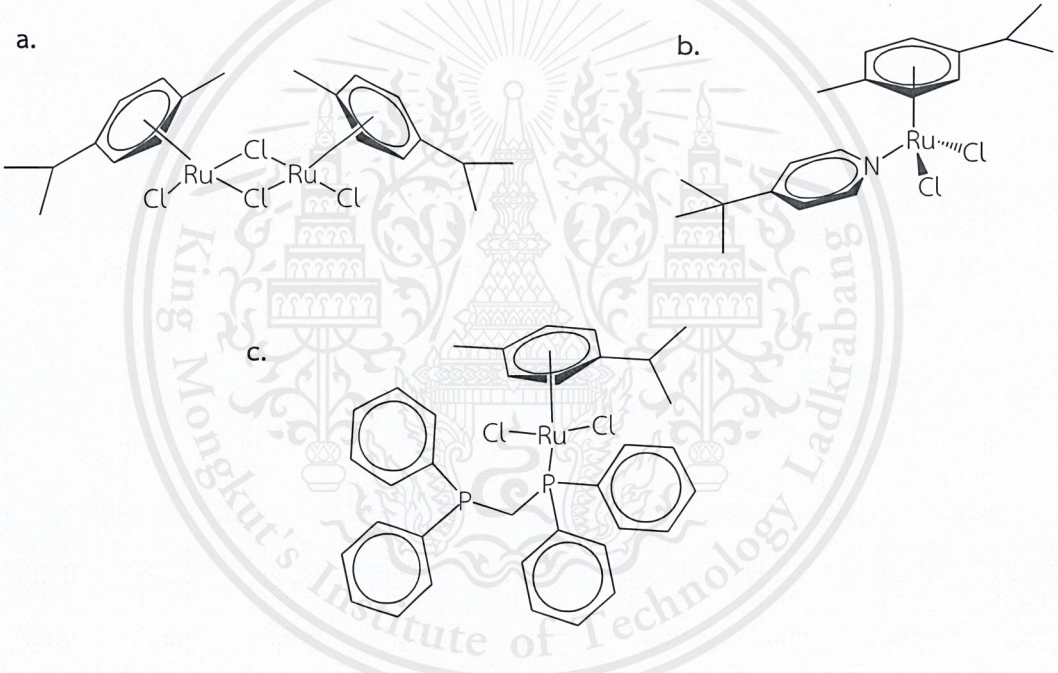


Figure 4.13 Structure of a. Ru-dimer, b. Ru-tbp and Ru-dppm

In comparison, all Ru complexes have the similar numbers of chloride and *p*-cymene. However, the two modified complexes are initially a monomeric structure forming a half-sandwich pseudo-tetrahedral complex while, the Ru-dimer has a dimeric pseudo-tetrahedral structure. **Table 4.7** shows the comparative studies of 1,6-hexanediol oxidation reaction using those three ruthenium complexes.

Table 4.7 Effect of ligand for the oxidation of 1,6-hexanediol

Catalysts	Amount of catalyst (mmol)	Conversion* (%)	Selectivity of ε-caprolactone (%)	Selectivity of 6-hydroxy hexanal (%)	TOF** (h^{-1})	TOF** (g/mol·h)
Ru-dimer	0.16	28.11	97.65	2.35	0.59	66.46
Ru-dppm	0.03	10.65	94.65	5.35	1.07	121.45
Ru-tbp	0.05	20.71	60.41	39.59	0.85	96.11

* Reaction at 110 °C for 24 h, using 1,6-hexanediol 8.46 mmol

** TOF : determined from yield of ε-caprolactone basis (turnover frequency, is calculated from their conversion per metal site per time.)

According to **Table 4.7**, the turn over frequency (TOF) of the ruthenium complexes for 1,6-hexanediol oxidation increases in the order of Ru-dppm, Ru-tbp, and Ru-dimer, respectively. Ru-dppm possesses the bulky phosphine ligand which is a strong σ-donor and fair π-acceptor. Relating to the electron donor ability of phosphine, it thus promotes the oxidative addition process. This ligand could further stabilize the complex as well as the transition states of complexes. Moreover, the steric hindrance of dppm could enhance the reductive elimination. In the comparison of tbp to dppm, tbp is a poorer σ-donor/ π-acceptor and also possesses less steric hindrance. It, hence, shows lower activity as compared to Ru-dppm. For the Ru-dimer, it initially exists as a dimer that is more steric. Since it is a dimer, all Ru-dimer complexes in solution might not be active. Moreover, if the dissociation takes place in Ru-dimer, it will form a three coordinated monomeric structure. This monomeric compound is not stable due to the electron deficiency, the low occupied sphere, and the high vacancy site. It thus reasons that Ru-dimer shows the lowest TOF of the three.

Considering the selectivity of ε-caprolactone, the order is in Ru-dimer ≈ Ru-dppm > Ru-tbp. This results from the eletonic deficiency of ruthenium center of Ru-dimer complex III as shown in Figure 4.12 which is 18 electrons. The dissociation of aldehyde is less after forming favorable then cyclization. Similarly, Ru-dppm has the strong π-backbonding ligand which then stabilize complex III and suppress the dissociation of complex III. Ru-tbp, on the other hand, has the lower σ-donor/π-acceptor. It, thus, less favorable to cyclization and yields more aldehyde products.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

In this work, the oxidation of ethylbenzene and 1,6-hexanediol using *bis*-Co, *tris*-Co, *trans*-Co, Co-Pc, and Ru-dimer were studied. *bis*-Co, *tris*-Co, *trans*-Co and Co-Pc were characterized and referenced with the previous reported papers using UV-Visible, and FTIR techniques confirming the formation of such complex. The activity for the oxidation reaction of ethylbenzene at 110 °C for 24 h, increases in the order of *trans*-Co > *tris*-Co > *bis*-Co > blank > Co-Pc > Ru-dimer. Hence, *trans*-Co, *tris*-Co and *bis*-Co are the effective catalysts; while, Co-Pc and Ru-dimer are the antioxidant. This results suggests that the dominant impacts are the energy gap and steric hindrance. The narrow energy gap and low steric hindrance are favorable to generate an singlet electron, which is a reactive molecule influencing the radical oxidation mechanism.

Similarly to the ethylbenzene oxidation, 1,6-hexandiol oxidation was also determined using the resemble catalysts. The reactivity of the investigated catalysts generating ε-caprolactone is in the order of Ru-dimer > *tris*-Co > Co-Pc > *bis*-Co > *trans*-Co. Noteworthy, the catalysts, that is reactive toward ethylbenzene oxidation, which long been known occurring via the radical mechanism, does not active in the oxidation reaction of 1,6-hexanediol. Thereafter, the later reaction mechanism is referred to the metal-complex mechanism. The effect of the ligand enhancing both electron donating and steric hindrance was studied at the reaction condition of 110 °C 24 h. TOF shows that the activity of ruthenium catalysts follows Ru-dppm, Ru-tbp, and Ru-dimer, respectively. These results correlates to the electron donor/acceptor ability and steric hindrance to stabilize the complexes during the reaction.

5.2 Suggestions

5.2.1 It is interesting to anchor the complexes into metal support for using as heterogeneous catalyst.

5.2.2 In order to increase the activity, the oxidation should be carried out in the high pressure of oxygen.

5.2.3 It is interesting to change ligand for others application such as olefins metathesis, hydrogenation and reduction.

5.2.4 It is expected that some of Co-complexes can be used as an antioxidant.

5.2.5 Further characterization of the stability of spent complexes can be provided by UV-Visible analysis.

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APPENDICES

APPENDIX A

CALCULATION

A1. Calculation of ethybenzene oxidation from gas chromatography

In order to evaluate the activity of each catalysts the information in Table A1 and A2 were calculated.

Table A1 The summation of reactants without the oxidation

Reactants	Peak area
Ethylbenzene (initial Feed)	88903
Dodecane (Internal standard)	7570

Table A2 The summation of the peak area for products.

Product	Peak area
Acetophenone	8302
2-hydroxyethyl benzene	561
Ethylbenzene (Feed at time)	76614
Dodecane (Internal standard)	7461
Total	92938

- *** Typical information of *tris*-Co in ethylbenzene, in air-bubbling system at temperature 110°C for**

  - **Conversion** can be calculated from the following equation :

$$\%\text{Conversion} = \left(\frac{\text{Corrected area of feed}_0 - \text{Corrected area of feed}_t}{\text{Corrected area of feed}_0}\right) \times 100$$

Initial feed ; feed_0

Feed at time ; feed_t

* Corrected area is the area divided by area of internal standard

For example;

$$\%\text{Conversion} = \left(\frac{\left(\frac{88903}{7570}\right) - \left(\frac{76614}{7461}\right)}{\left(\frac{88903}{7570}\right)}\right) \times 100$$

$$= 12.56\ \%$$

- **Yield**

Yield of each products are calculated from corrected area, area of product divided by area of internal standard as expressed by:

$$\%\text{Yield of each product} = \frac{\text{Corrected area of product}}{\text{Corrected area of feed}} \times 100$$

For example;

$$\%\text{Yield of Acetophenone} = \left(\frac{\frac{8302}{7461}}{\frac{88903}{7570}} \right) \times 100$$

$$= 9.47\ \%$$

- **Selectivity**

%Selectivity can be obtained from the following equation:

$$\%\text{Selectivity in each product} = \frac{\%\text{Yield of each product} \times 100}{\%\text{Conversion}}$$

For example;

$$\%\text{Selectivity of acetophenone} = \frac{9.47 \times 100}{12.56}$$

$$= 75.40\ \%$$

A2. The calculation for 1,6-hexanediols oxidation by ^{1}H NMR

The oxidation of 1,6-hexanediols was evaluated by ^{1}H NMR, the patterns were depicted by :

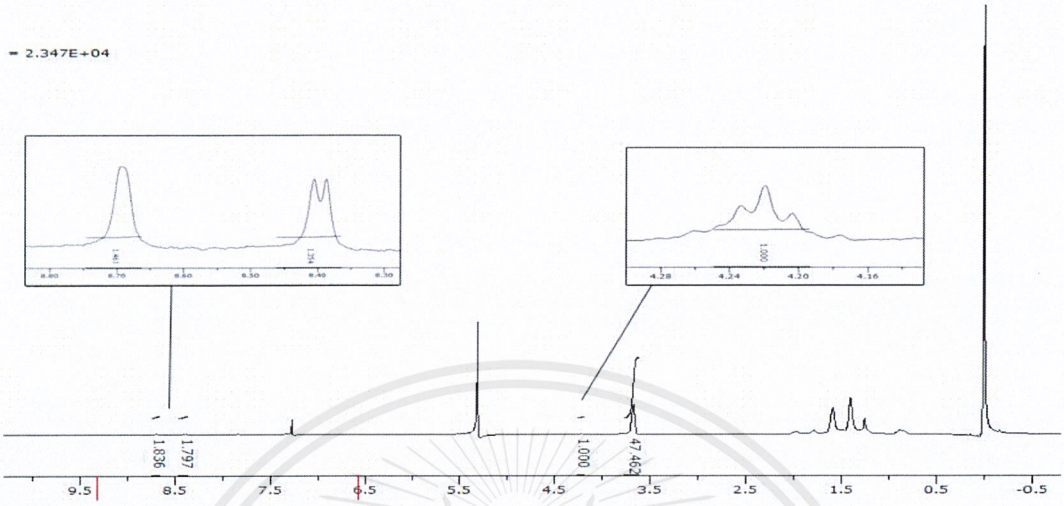


Figure A1. typical ^{1}H NMR pattern for the oxidation of 1,6-hexanediols

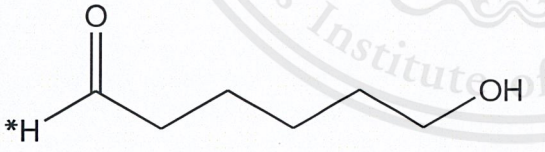
Prior to evaluate the characteristic NMR peaks was transformed in a unit per 1 molecular hydrogen:

Feed : 1,6-hexanediols

Integration value for H* : 40.298

or

Integration **value** $\frac{40.298}{4}$ per H*

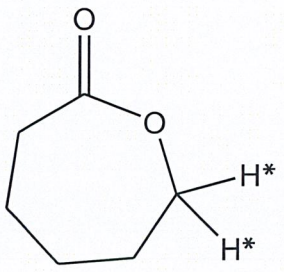


Products : 6-hydroxy-hexanal

Integration value for H* : 1.944

or

Integration **value** $\frac{1.944}{1}$ per H*



Products : ϵ-caprolactone

Integration value for H* : 0.500

or

Integration value $\frac{0.500}{2}$ per H*

Due to the pattern of protons in 1,6-hexane diols partially overlap with 6-hydroxyhexanal, the actual integration data of 1,6-hexanediols is :

$$\frac{40.298-(1.944\times2)}{4} \text{ or } 9.1025$$

and expressed total integration value : 9.1025 + 00.25 + 1.944 = 11.547

The calculation was determined by the normalization method

- **Conversion**

$$\%\text{Conversion} = \left(\frac{\text{Integration value of Remained feed}}{\text{total integration value}}\right)\times100$$

For example;

$$\%\text{Conversion} = \left(\frac{11.547 - 9.1025}{11.547}\right)\times100$$

$$= 21.17\ \%$$

- **Yield**

$$\%\text{ yield of 6-hydroxy-hexanal} = \left(\frac{\text{Integration value of 6-hydroxy-hexanal}}{\text{total integration value}}\right)\times100$$

For example;

$$\%\text{ yield of 6-hydroxy-hexanal} = \left(\frac{1.944}{11.547}\right)\times100$$

$$= 16.84\ \%$$

A3. Calculation of turn over frequency (TOF)

In order to calculate TOF, 0.05 grams of Ru-dimer must be transformed to molar unit (0.041 mmol). Nonetheless, the complex composed of 2 molecular Ru, so it can be 0.163 mmol.

TOF for the conversion of 1,6-hexanediols 1g equivalent to 8.46 mmol, was expressed by :

Thus, from conversion 28.11 %, the diols was equal to :

$$\text{Mole conversion} = \frac{28.11 \times 8.46}{100}$$

$$= 2.38 \text{ mmol}$$

Divide by mole of the catalysts

$$= \frac{2.380}{0.163}$$

$$= 14.60$$

Normalize by unit of time (24 h)

$$\text{TOF} = \frac{14.60}{24}$$

$$= 0.61 \ h^{-1}$$

Transverse to mass unit

$$= 0.613 \times 118.16$$

$$= 71.88 \text{ g/mol·h}$$

Table A2 Turn Over Frequency

Catalyst	$TOF_{conversion}$ (g/ mol·h)	TOF ε-caprolactone (g/mol·h)	$TOF_{6\text{-hydroxy hexanal}}$ (g/mol·h)
Ru-dimer	71.88	66.46	1.78
Ru-tbp	165.43	96.11	64.57
Ru-dppm	134.27	121.45	7.33

APPENDIX B

INFARED SPECTRA REFERENCE

Table B1. IR spectra of bipyridine complexes [37].

bipyridine	*bis*-Co	*tris*-Co	Vibration mode
652	650	652	C-C out-of-plane deformation
739	735	735	C-H out-of-plane deformation
755*	-	766*	C-N out-of-plane bending
-	774	774	
892	-	889	C-H out-of-plane bending
992	-	964	C-H out-of-plane bending
-	1017	1021	C-H in-plane bending
1041	1038	1045	C-H in-plane bending
1065	1073	1072	C-H in-plane bending
1085	-	1085*	C-H bending
1140	1149	1158	C-H bending
-	1173	1172	C-H bending
-	1224	1218	C-H bending
1252	1248	1248	C-H bending
-	1312	1317	C-H bending
1421	1438*	1446*	C-N stretching
-	1470	1474	C-N stretching
1560	1561	1566	C-N stretching
1583	-	1576	C=N stretching
-	1597	1604*	C=N stretching
-	3561	3399	O-H stretching

Table B2. IR spectra of Cobalt Phthalocyanine [38].

dicyanobenzene	Co-Pc	Vibration mode
524	-	C-CN bending
-	634	C-C out-of-plane bending
-	721	C-H out-of-plane bending
-	730	C-H out-of-plane bending
769	-	C-CN bending
-	771	C-H out-of-plane bending
-	781	C-N in-plane stretching
-	878	C-H in-plane bending
-	911	Metal-ligand
965	1069	N-H in-plane bending
-	1087	C-H in-plane deformation
-	1117	C-H in-plane bending
1189	1162	C-N in-plane bending
1297	1287	C-N stretching
1349	1329	C-C stretching
-	1424	C-C stretching
1484	1456	C-H in plane bending
1572	1521	C=N stretching
1590	1606	C=C ring deformation
2232	-	C≡N stretching
3042	3021	C-H stretching
-	3333	O-H stretching

Table B3. IR spectra of *trans*-dichloro-*bis*-(ethylenediamine)cobalt(II) chloride [39]

trans-Co	Vibration mode
480	Metal-N
1044	C-N stretching
1110	C-N stretching
1201	C-N stretching
1446	C-H bending
1573	N-H stretching
2942	C-H stretching
3216	O-H stretching

APPENDIX C

Gas Chromatogram

C.1 Analysis of product from gas chromatography

The quantitative analysis of each products was detected by GC-FID (gas chromatography with flam ionization detector) with the condition in **Table C1**

Table C1 The GC condition for quantitative analysis

Column	DB-WAX, 30 m, 0.25 m, 0.25 m
Temperature program	70 °C (2min hold) to 180°C at 20°C/min
Carrier gas	Nitrogen at 1.5 mL/min
Injaction	220 °C
Detector	FID

The chromatogram of products were identified using reference standard for comparison in **Table C2**

Table C2 Chromatogram data of standard product distribution and feed

Product or feed	Retention time of standard (min)
Diethyl ether	1.44
Ethylbenzene	3.05
Dodecane	3.47
Acetophenone	6.97
2-hydroxy ethylbenzene	7.90

APPENDIX D

Reaction Data

Table D1 Product yields after oxidation at temperature 110 °C

Catalysts	Time (h)	Conversion (%)	Yield (%)	
			Acetophenone	2-hydroxy ethylbenzene
Blank	24	10.69	9.54	2.97
	48	23.49	19.10	4.89
bis-Co	24	10.33	11.34	0.90
	48	25.67	17.74	1.47
tris-Co	24	20.80	24.43	2.44
	48	24.23	27.52	3.27
Co-Pc	24	6.92	4.58	1.02
	48	14.04	5.56	1.17
trans-Co	24	23.55	34.13	7.00
	48	48.26	38.34	7.61
Ru-dimer	24	8.67	4.97	0.00
	48	10.68	4.52	0.00

Table D2 Effect of temperature after oxidation over blank, *tris*-Co and *trans*-Co

Temperature (°C)	Catalysts	Time (h)	Conversion (%)	Yield (%)	
				Acetophenone	2-hydroxy ethylbenzene
90	Blank	24	9.71	6.70	1.52
		48	6.65	10.80	2.49
	tris-Co	24	12.66	7.46	1.32
		48	12.94	11.91	2.69
	trans-Co	24	20.00	13.94	6.07
		48	22.90	32.60	6.35
110	Blank	24	13.32	10.09	4.51
		48	21.58	21.51	5.69
	tris-Co	24	18.79	13.52	0.58
		48	25.22	27.33	3.16
	trans-Co	24	21.42	15.87	3.66
		48	26.40	19.32	3.84