

# CHAPTER I

## INTRODUCTION

During the last decade, petrochemical industries have been widely developed in Thailand. Hydrocarbons are discovered to be the largest group in petroleum products. Although saturated hydrocarbons are the biggest component in total hydrocarbons, they are mostly used as an energy supplier or as a fuel source. Functionalization of saturated hydrocarbons to other organic compounds is in fact not simple or easy task. That mainly stemmed from their inertness of C-H bond in saturated hydrocarbons. Their bond dissociation energies (BDE) range from 85-91 kcal/mol for tertiary, to 90-95 kcal/mol for secondary and 97-104 kcal/mol for primary C-H bonds.<sup>1</sup> The breaking of these bonds usually requires drastic conditions, *e.g.* high pressure, high temperature, basic or acidic conditions, or extremely strong and unselective reagents, *etc.* For example, the oxidation of cyclohexane yielding a mixture of cyclohexanone and cyclohexanol could proceed employing an oxidation catalyst such as cobalt naphthenate at 180-250<sup>0</sup>C, 10 atm, with low conversion.<sup>2</sup> Due to these vigorous conditions, the chemical reaction is unselective and many products are invariably produced.

In the traditional autoxidation procedures the first C-H bonds to cleave and functionalize would be tertiary ones because of their weakness compared with secondary and primary C-H bonds. This often leads to a subsequent C-C bond cleavage at tertiary and formation of various kinds of free radicals, which can abstract atoms from other molecules or rearrange to form more stable radicals and so on. The outcome of these oxidations is usually a multitude of products, with the most of them being in high oxidation levels, since functionalization makes neighboring C-H bonds even more vulnerable to attack by free radicals.

Therefore, it is clear for the needs of catalysts that would selectively activate particular varieties of C-H bonds and reduce the activation energy of the oxidation process to a great enough extent so that the process can be controlled and stopped after

the desired substitution has been achieved. Transition metal complexes have been recognized as being among promising catalysts for such processes: the relative stability of a variety of their oxidation and spin states makes them excellent candidates to bridge the spin differences and lower the activation energy of the reaction between hydrocarbons and dioxygen, a cheap, convenient and environmentally friendly oxidizing agent.

The different solubilities and reactivities of hydrocarbons and transition metal complexes, however, require careful consideration of the reaction conditions. Heterogeneous and homogeneous catalysts are both used in practical applications, although homogeneous processes offer certain advantages in predictability, reproducibility and control of the reaction.

Several biological systems particularly those found in mammals have been reported to be able to transform saturated hydrocarbons to hydroxylated products under mild conditions<sup>3</sup> such as at room temperature or slightly above and at atmospheric pressure. The oxidation systems catalyzed by Cytochrome P-450 enzymes and that catalyzed by peroxidases are two important examples. With their remarkable abilities, several chemical models have been later developed. Working towards the main aim to carry on the reaction at lower temperature is very promising idea because one can reduce the capital cost that is the main objective in petrochemical industries.

In this research, the oxidation of cyclohexane to cyclohexanone and cyclohexanol, one of the most important oxidation process in industry, was chosen to examine. The major advantages in this industry are the production of adipic acids and hexamethylene diamine for nylon 66, and caprolactam for nylon 6.<sup>4</sup> However, in industry, the oxidation of cyclohexane proceeded under vigorous conditions. Thus, the optimum conditions for the oxidation of cyclohexane and relevant hydrocarbons catalyzed by copper salts and copper complexes were investigated. In addition, the kinetic study and chemoselectivity of the developed reaction were explored. The suitable conditions for the functionalization of cyclohexane would also be investigated, for example, the production of bromocyclohexane, chlorocyclohexane, and cyclohexyl azide.