

CHAPTER III

RESULTS AND DISCUSSION

The oxidation of hydrocarbons is significant to the chemical industries because these oxidation reactions are normally used to convert petroleum hydrocarbon feedstocks into fine chemicals employed in the downstream polymer and petrochemical industries. This research was mainly focused on the selectivity study of the oxidation process of saturated hydrocarbons. Metal soluble complexes including chromium(III), manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) stearate complexes were employed to explore for their catalytic capability. The advantage of this type of catalyst is its ability to be homogenized with organic phase used [22, 23]. Cyclohexane was selected as a model substrate to observe the selectivity towards the formation of ketone and alcohol. Other substrates such as *tert*-butylcyclohexane, *n*-hexane, methylcyclohexane and adamantane were chosen for further regioselectivity study. In general, the conditions for the oxidation reaction examined were as follows: metal stearate 0.2 mmol, 70% TBHP 9.0 mmol, 70°C for 24 hr.

3.1 Syntheses and identification of metal stearate complexes

Six metal stearate complexes: chromium(III), manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) stearate complexes were synthesized employing known procedures reported in chemical literature [24]. Their identities were confirmed by IR technique [25]. Generally, the absorption bands of free carboxylic acid ligands are visualized at 1700-1725 cm^{-1} for C=O stretching and 1395-1440 cm^{-1} and 1210-1320 cm^{-1} for C-O stretching and OH deformation, respectively. In metal stearate complexes, the C=O and C-O stretching vibration bands were shifted to 1710-1750 cm^{-1} and 1540-1460 cm^{-1} , respectively due to increasing of bond strength. All infrared absorption signals of complexes appear at higher frequency than those of free carboxylic group [26].

The infrared spectrum of a selected metal stearate complex, Cr(III) stearate is presented in Fig 3.1.

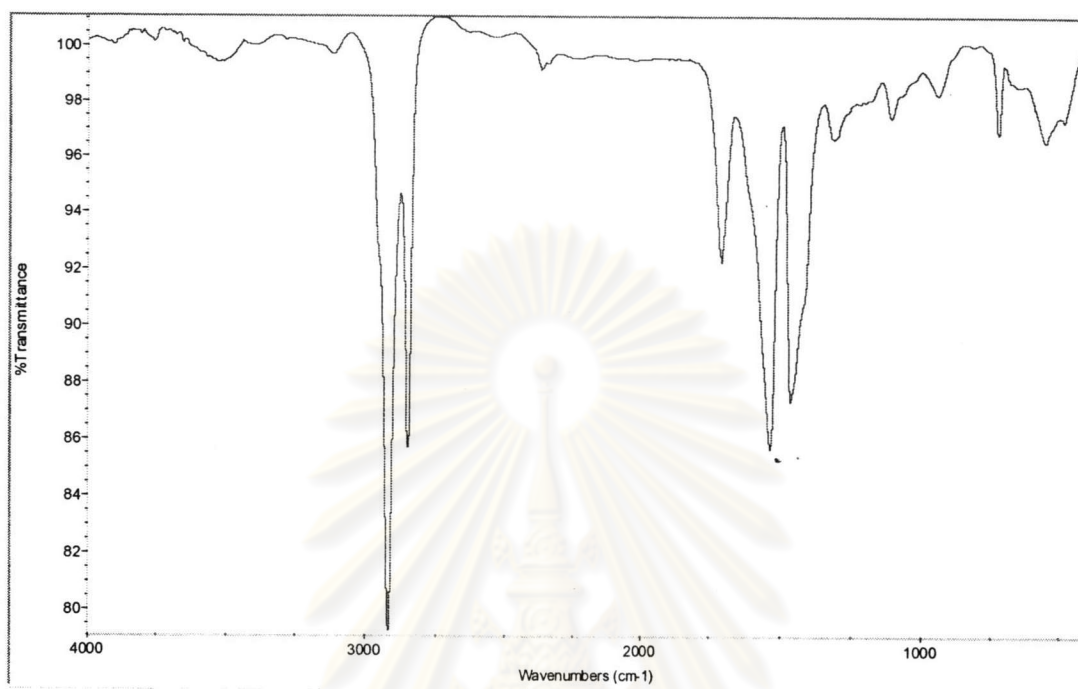


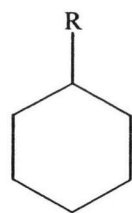
Fig 3.1 The IR spectrum of Cr(III) stearate

From Fig 3.1, chromium complex exhibited significant absorption peaks of C=O and C-O stretching around 1710 cm^{-1} and 1446 cm^{-1} , respectively which were well conformed with that previously reported [27].

3.2 Chemoselectivity study on cyclohexane oxidation

3.2.1 Effect of metal stearate complexes

Generally, the oxidation of cyclohexane catalyzed by metal complexes furnished cyclohexanone and cyclohexanol. In some rare cases, cyclohexane could also be transformed into adipic acid [14]. The type of metal complex is of significant factor affected on the formation of the desired products. The aim of this study was to observe the selectivity upon the conversion of cyclohexane to cyclohexanone and cyclohexanol using selected metal stearates as a catalyst. The results of the cyclohexane oxidation catalyzed by six metal stearate complexes are presented in Table 3.1 and Fig 3.2.



- (1) cyclohexane R = H
 (2) cyclohexanone R = O
 (3) cyclohexanol R = OH

Table 3.1 The effect of metal stearates on cyclohexane oxidation

Entry	Catalyst	Products (mmol)		Total (mmol)	Selectivity one/ol
		(2)	(3)		
1	Cr(III)stearate	1.551	0.373	1.924	4.16
2	Co(II)stearate	0.691	0.972	1.663	0.71
3	Mn(II)stearate	0.576	0.984	1.560	0.59
4	Ni(II)stearate	0.686	0.515	1.197	1.32
5	Cu(II)stearate	0.722	0.752	1.473	0.96
6	Fe(III)stearate	0.969	0.502	1.471	1.93

reaction conditions: cyclohexane 50 mmol, catalyst 0.2 mmol, TBHP 9.0 mmol, 24 hr at 70°C

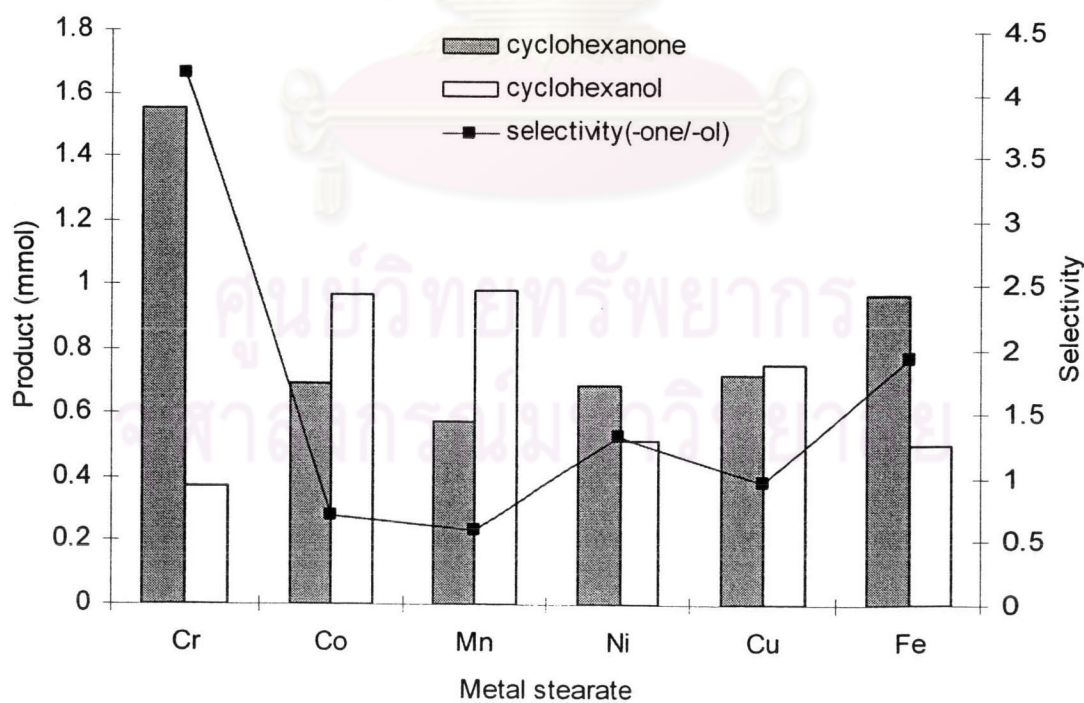


Fig 3.2 The effect of metal stearates on cyclohexane oxidation

From Table 3.1 and Fig 3.2, it was found that the selective oxidation of cyclohexane was proceeded with high efficiency crucially depending on type of transition metal. The use of Cr(III) stearate as a catalyst gave the highest yield of cyclohexanone with excellent selectivity for cyclohexanone and cyclohexanol formation, whereas other stearate complexes of Co(II), Mn(II), Cu(II) and Fe(III) gave comparatively good total yield; however with poor selectivity. It is interesting to note that Co(II) and Mn(II) stearates revealed the favor for the formation of cyclohexanol. With the aim to search for a good oxidation system providing intriguing selectivity, Cr(III) stearate will thus be utilized as a catalyst for the oxidation saturated hydrocarbons in this research.

3.2.2 Effect of bi- and tri- catalysts

3.2.2.1 Effect of the ratio of bicatalysts

In order to gain more insight to the role of metal stearate catalyst for the selectivity towards the formation of ketone and alcohol, the system consisted of a binary mixture of metal stearates was explored. Cr(III) and Co(II) stearates were selected as bicatalysts for this study since both of them provided high yield of the desired products. Thus, various ratios of Cr(III) and Co(II) stearates were examined and the results are shown in Table 3.2.

Table 3.2 The effect of various ratios of Cr(III) and Co(II) stearates on cyclohexane oxidation

Entry	Ratio of catalyst (Cr :Co)	Products (mmol)		Total (mmol)	Selectivity one/ol
		(2)	(3)		
1	1:0	1.551	0.373	1.924	4.16
2	1:1	0.584	0.917	1.501	0.64
3	2:1	0.690	0.937	1.626	0.74
4	3:1	1.234	1.351	2.585	0.91
5	4:1	0.974	0.739	1.713	1.32

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

From Table 3.2, it was observed that the oxidation of cyclohexane by the use of Cr(III) and Co(II) stearates gave lower selectivity for cyclohexanone/cyclohexanol formation than the system employing solely Cr(III) stearate. It was noteworthy that with the ratio of Cr(III):Co(II) stearate of 3:1 provided the highest total yield of the desired oxidized product. The total oxidation yield was improved approximately 34% based on the system employed Cr(III) stearate catalyst alone. Nevertheless, low selectivity of the formation of the desired products was observed.

3.2.2.2 Effect of type of bicatalysts

According to the outcome obtained previously, Cr(III) stearate was chosen as a main catalyst and other metal stearates (Co(II), Cu(II), Ni(II), Mn(II) and Fe(III) stearates) was substituted with the same ratio of 3:1 to catalyze the oxidation of cyclohexane. The results are displayed in Table 3.3 and Fig 3.3.

Table 3.3 The effect of bicatalysts on cyclohexane oxidation

Entry	Catalyst	Products (mmol)		Total (mmol)	Selectivity one/ol
		(2)	(3)		
1	Cr	1.551	0.373	1.924	4.16
2	Cr : Co	1.234	1.351	2.585	0.91
3	Cr : Mn	1.435	0.699	2.134	2.05
4	Cr : Ni	1.002	0.242	1.244	4.14
5	Cr : Cu	1.456	0.724	2.180	2.01
6	Cr : Fe	1.465	0.148	1.613	9.87

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

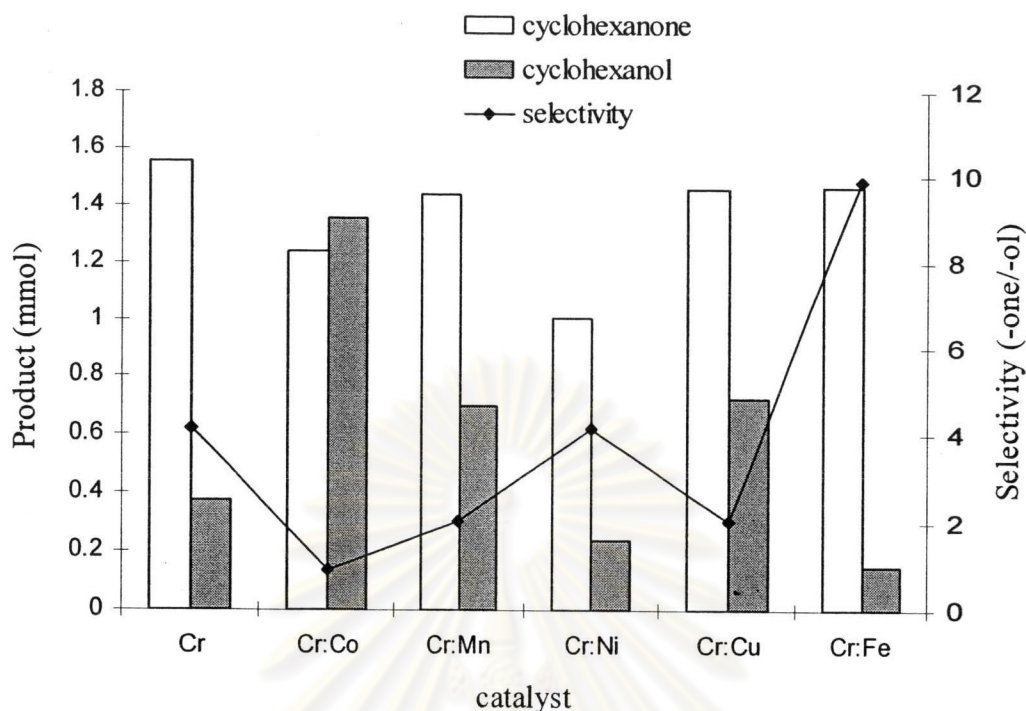


Fig 3.3 The effect of bicatalysts on cyclohexane oxidation

Table 3.3 and Fig 3.3 present the catalytic activities for the oxidation of cyclohexane using Cr(III) stearate coupled with other metal stearates as a dual catalyst. It was observed that the best selectivity of cyclohexanone/cyclohexanol was still gained when Cr(III) stearate was alone used as catalyst. Nevertheless, the total yield of the oxidation products was increased in the presence of bicatalysts such as Cr:Mn, Cr:Cu and Cr:Co systems. Interestingly, Cr:Co system gave higher yield of cyclohexanol than that of cyclohexanone.

Literature review revealed that recently, Can-Cheng *et al.* have reported the development of a new catalyst system for an aerobic oxidation of cyclohexane catalyzed by a simple μ -oxo dimeric ironporphyrin $(TPPFe^{III})_2O$ in the absence of solvent and cocatalyst. This reported system provided the selectivity of cyclohexanone/cyclohexanol as 2.41[28]. It should therefore be noted that the selectivity for cyclohexanone and cyclohexanol formation by this present work was far superior to the system of Can-Cheng.

3.2.2.3 Effect of tricycatalysts

The examination of the effect of tricycatalysts system for the selective oxidation of cyclohexane is shown in Table 3.4 and Fig 3.4 using the ratio of Cr(III) stearate and other two types of metal stearate as 2:1:1.

Table 3.4 The effect of tricycatalysts on cyclohexane oxidation

Entry	Catalyst	Products (mmol)		Total (mmol)	Selectivity one/ol
		(2)	(3)		
1	Cr	1.551	0.373	1.924	4.16
2	Cr : Mn : Co	2.104	1.250	3.354	1.68
3	Cr : Co : Ni	1.453	0.582	2.035	2.46
4	Cr : Mn : Ni	0.926	0.652	1.578	1.42
5	Cr : Mn : Fe	0.942	0.565	1.507	1.67
6	Cr : Fe : Co	0.563	0.680	1.243	0.83

reaction conditions : cyclohexane 50 mmol, catalyst 0.2 mmol (Cr(III)stearate : other two metal stearates 2:1:1), TBHP 9.0 mmol, 24 hr at 70°C.

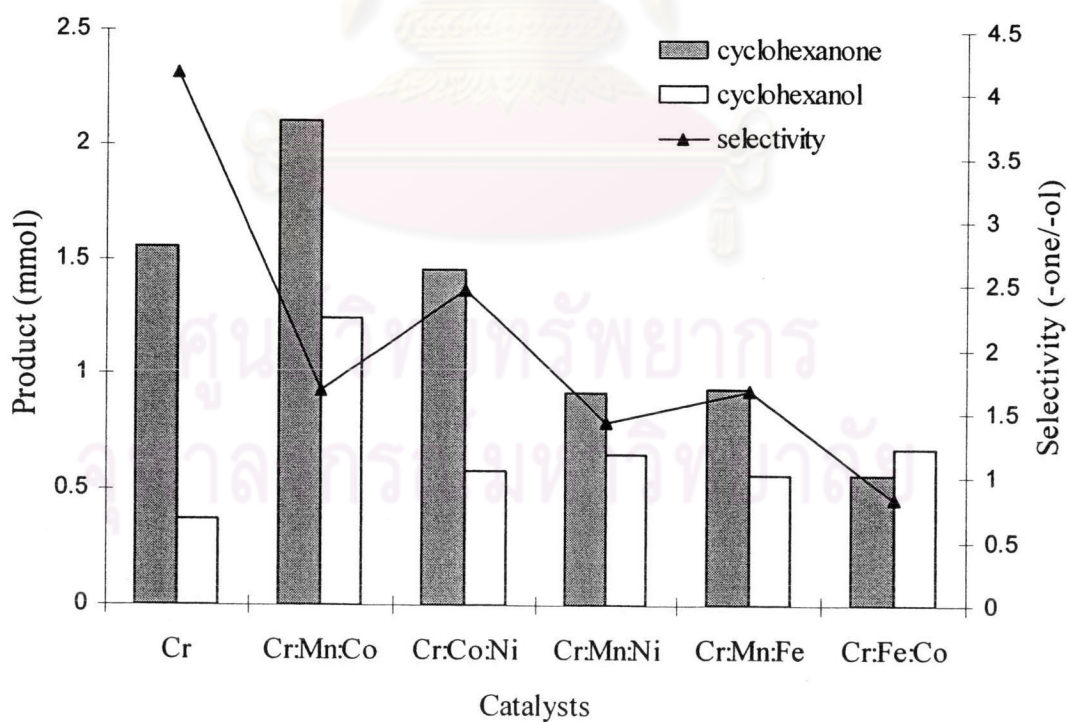


Fig 3.4 The effect of tricycatalysts on cyclohexane oxidation

Table 3.4 and Fig 3.4 reveal the yields of cyclohexane oxidation in presence of tricatalysts. It was found that the tricatalysts system composing of Cr(III):Mn(II):Co(II) stearates gave the highest total yield of product, approximately 74 % higher than the normal system using only Cr(III) stearate as catalyst. Nonetheless, lower selectivity for the formation of cyclohexanone over cyclohexanol was observed. It was noteworthy to the state at this point that the tricatalysts system had never been previously addressed and gave impressive results with the extent of the consideration of the total yield of the desired product.

3.3 Kinetic study on the reaction rate of cyclohexane oxidation

The kinetic study of the oxidation was performed in order to observe the progress of the reaction vs time. The rate of this reaction was generally slow and needed more time to complete. The rate of the oxidation of cyclohexane catalyzed by Cr(III) and Co(II) stearates and Cr:Co (3:1) system was compared. The kinetic analysis results are presented in Fig 3.5.

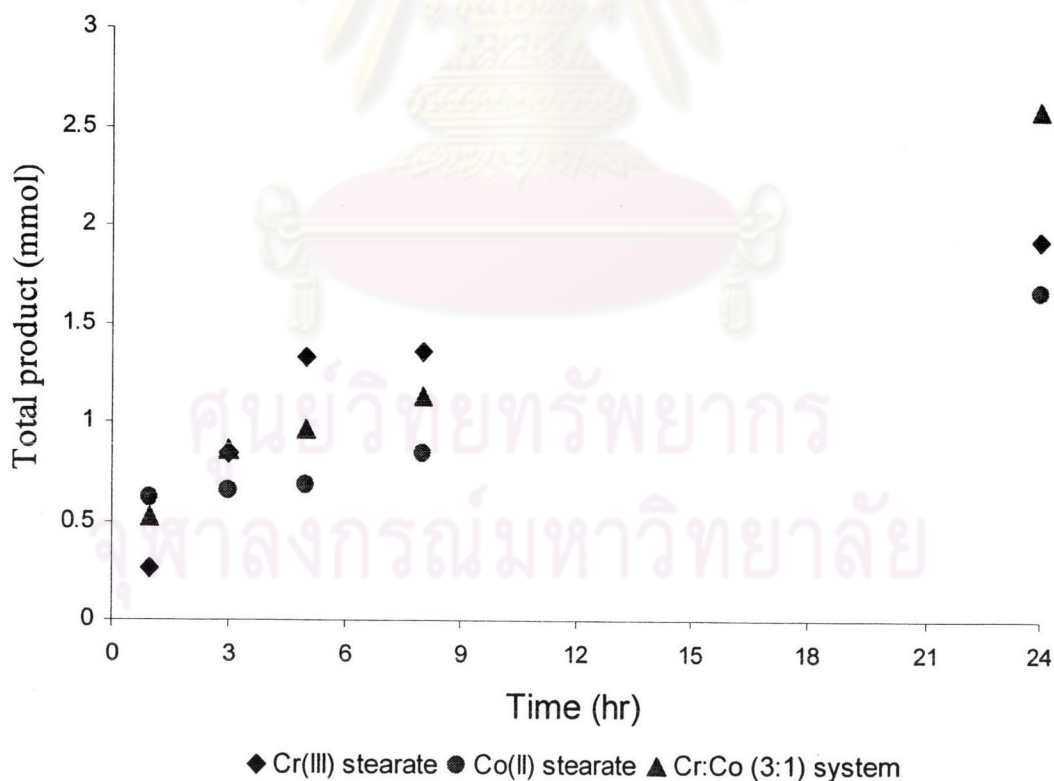


Fig 3.5 Kinetic analysis of cyclohexane catalyzed by Cr(III) and Co(II) stearates and Cr:Co (3:1) system

From Fig 3.5, two metal complexes: Cr(III) and Co(II) stearates and Cr-Co system were employed for kinetic study on the oxidation of cyclohexane. It was found that the rate of the oxidation reaction employing Co(II) stearate was clearly faster than that of Cr(III) stearate and Cr:Co system at the initial period of the reaction. Half-lives of the reaction were approximately 4, 8 and 8 hr for Cr(III), Co(II) stearates and Cr:Co (3:1) system, respectively. Considering in terms of total yield of the desired products, it was clearly observed that Cr(III) stearate could provide more significant amount of cyclohexanone than Co(II) stearate and Cr:Co (3:1) system.

3.4 The effect of the amount of Co(II) stearate on the oxidation of cyclohexane

Based upon the information gained from Table 3.1, Co(II) stearate was found to display a unique characteristic to provide cyclohexanol prevailing to cyclohexanone. The effect of various amounts of Co(II) stearate catalyst (0.1, 0.2, 0.3 and 0.5 mmol) was thus investigated. The results are presented in Table 3.5.

Table 3.5 The oxidation of cyclohexane catalyzed by Co(II) stearate

Entry	Catalyst (mmol)	Products (mmol)		Total (mmol)	Selectivity one/ol
		(2)	(3)		
1	0.1	0.428	0.569	0.997	0.752
2	0.2	0.691	0.972	1.663	0.711
3	0.3	0.368	0.545	0.913	0.675
4	0.5	0.163	0.264	0.427	0.617

reaction conditions : cyclohexane 50 mmol, Co(II) varied, TBHP 9.0 mmol, 24 hr at

70°C

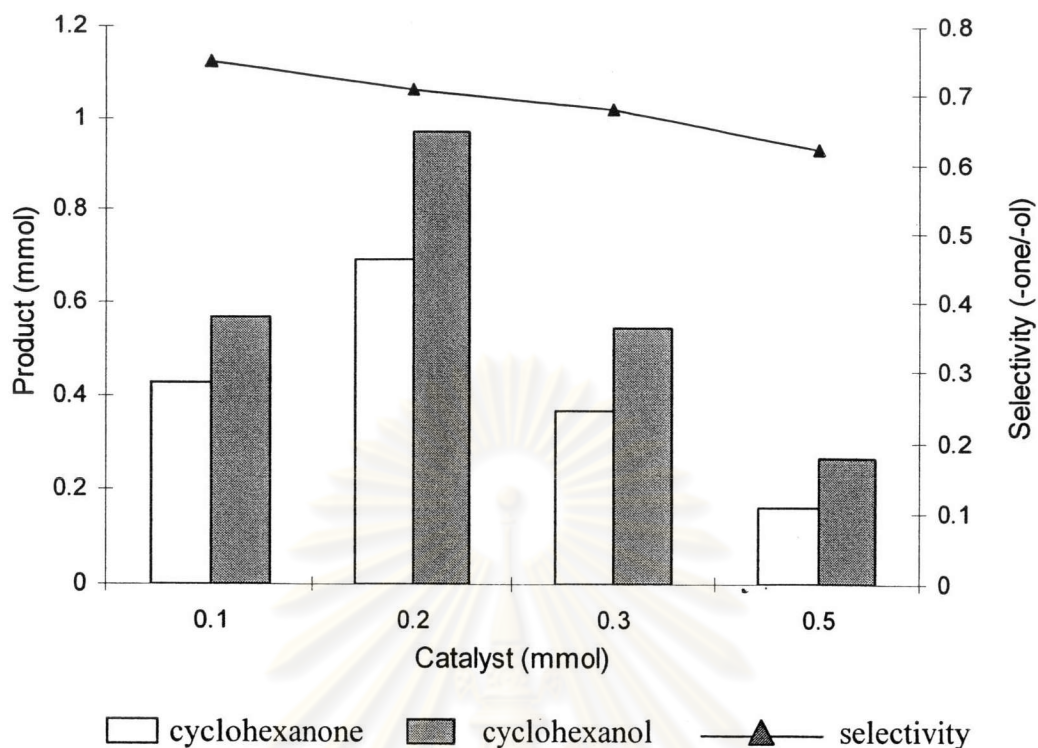


Fig 3.6 The oxidation of cyclohexane catalyzed by Co(II) stearate

The amount of catalyst clearly influenced the yields of the reaction; however, not much affected on the selectivity of ketone to alcohol ratio as presented in Table 3.5 and Fig 3.6. The catalytic effect of the system with 0.2 mmol gave the highest yield of the oxidized product. The more catalyst used, the lower yields obtained. This may be because the rapid interaction of the reaction species taken place and may compete the desired oxidation route and eventually yield unwanted side reaction products. When 0.1 mmol catalyst was used, the reaction gained a lower yield though the selectivity increased a little. Table 3.5 also showed that the amount of catalyst has little influence on the selectivity of the products.

3.5 The oxidation of other selected organic substrates

Cyclohexanone, cyclohexyl acetate and cyclohexanol were selected in order to investigate the scope of this oxidation system. The results are displayed in Table 3.6.

Table 3.6 Chromium(III)stearate-catalyzed oxidation reaction of cyclohexanone, cyclohexyl acetate and cyclohexanol

Entry	Substrate	Product (%)	% Substrate (recovery)	Mass balance (%)
1	cyclohexanone	0	95	95
2	cyclohexyl acetate	0	97	97
3	cyclohexanol	cyclohexanone (90%)	6	96

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

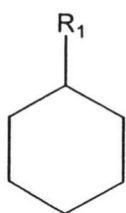
Table 3.6 exhibits that this developed oxidation system was selective. Among three distinct functional groups tested, *i.e.*, ketone, acetate ester and hydroxyl group, only the hydroxyl group could be cleanly transformed into the corresponding carbonyl compound in good yield (entry 3). Unlike, other reported systems, for example Besson *et al.* developed that the new catalyst carbon derived from phenolic resins were used as catalyst for the aqueous phase oxidation of cyclohexanone. The selectivity for adipic acid was found to be 33% [29]. Crezee *et al* reported the selective of cyclohexanone using carbon coated monolithic as catalysts. It was found the reaction gave five products such as 2-hydroxycyclohexanone, adipic acid, succinic, glutaric acid and fumaric acid. Adipic acid was a major product 16% [30]. This developed system may therefore be utilized to selectively oxidized alcohol in the presence of other functional groups such as ketone and ester.

3.6 Effect of additives

The addition of a trapping agent to the reaction was examined in order to get some informative clues for mechanistic pathway of this system. Two trapping agents were chosen to investigate, *i.e.*, carbon tetrachloride (CCl₄) and bromotrichloromethane (BrCCl₃).

3.6.1 Effect of CCl₄

CCl₄ was the first additive examined. The outcomes from the reaction are presented in Table 3.7.



(2) Cyclohexanone

 $R_1 = O$

(3) Cyclohexanol

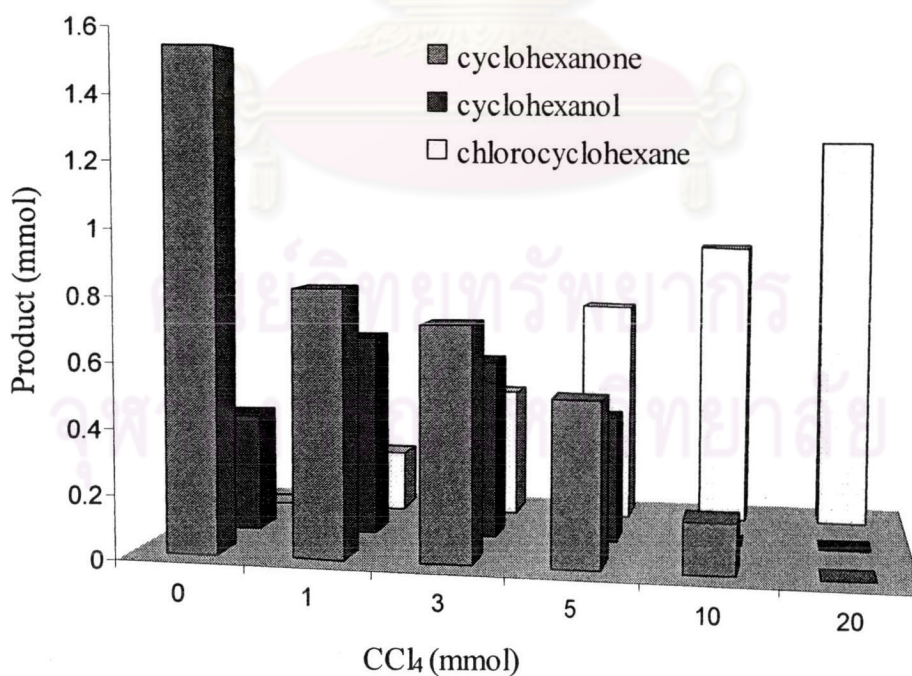
 $R_1 = OH$

(4) Chlorocyclohexane

 $R_1 = Cl$ **Table 3.7** Effect of CCl_4 on the oxidation of cyclohexane

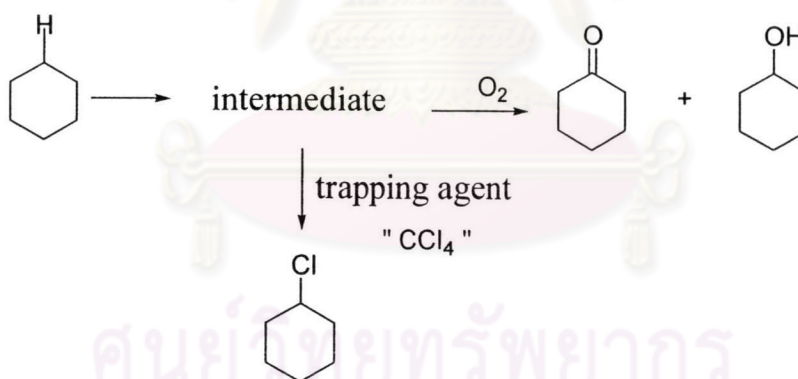
Entry	CCl_4 (mmol)	Product (mmol)			Total product (mmol)	Ratio one+ol/-Cl
		(2)	(3)	(4)		
1	0	1.551	0.373	-	1.924	-
2	1	0.821	0.636	0.196	1.653	4.07
3	3	0.720	0.566	0.418	1.694	3.08
4	5	0.508	0.398	0.719	1.625	1.26
5	10	0.158	trace	0.925	1.083	0.17
6	20	-	-	1.274	1.274	0

reaction conditions : cyclohexane 50 mmol, Cr(III) stearate 0.2 mmol, TBHP 9.0 mmol, 24 hr at $70^\circ C$

**Fig 3.7** The effect of CCl_4 on the oxidation of cyclohexane

From Table 3.7 and Fig 3.7, it was found that the amount of oxidized products: cyclohexanone and cyclohexanol was decreased, while the amount of chlorocyclohexane was increased when the amount of CCl_4 in the reaction was increased. With 20 mmol of CCl_4 , the oxidation reaction was completely suppressed and diverted to yield cyclohexyl chloride. Therefore, this system could be another alternative way to be used for the synthesis of alkyl chloride which was much convenient than the chlorination using Cl_2 in conventional way. Alkyl chlorides themselves are very important in organic synthesis as alkylating agents [21].

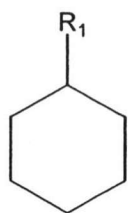
The outcome from this study was useful to postulate that CCl_4 may trap the intermediate present in the reaction and transform into chlorocyclohexane with the suppression of the formation of oxidized products. This trapping reaction is rationalized in terms of a competition between O_2 and CCl_4 for cyclohexyl radical [31]. This derived information implied that the mechanism of this reaction may take place *via* the radical pathway. The proposed conceptual mechanism for the interception the intermediate with CCl_4 on cyclohexane oxidation is shown in Scheme 3.1.



Scheme 3.1 The proposed conceptual mechanism on cyclohexane oxidation upon the addition of CCl_4

3.6.2 Effect of BrCCl_3

BrCCl_3 was another well-known radical trapping reagent. The effect of BrCCl_3 on the oxidation of cyclohexane is shown in Table 3.8.



(2) cyclohexanone

 $R_1 = O$

(3) cyclohexanol

 $R_1 = OH$

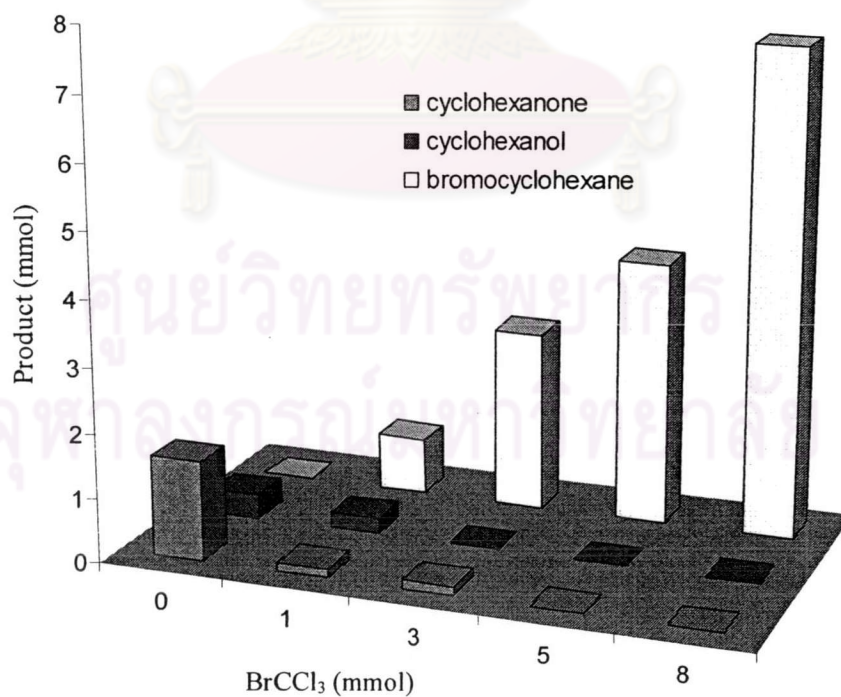
(5) bromocyclohexane

 $R_1 = Br$ **Table 3.8** Effect of $BrCCl_3$ on the oxidation of cyclohexane

Entry	$BrCCl_3$ (mmol)	Product (mmol)			Total Product (mmol)	Ratio one+ol/-Br	% efficiency of TBHP
		(2)	(3)	(5)			
1	0	1.551	0.373	-	1.924	-	0
2	1	0.134	0.240	0.878	1.252	0.426	9.75
3	3	0.128	-	2.798	2.926	0.045	31.09
4	5	-	-	4.074	4.074	0	45.27
5	8	-	-	7.518	7.518	0	83.53

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

*based on TBHP

**Fig 3.6** The effect of $BrCCl_3$ on the oxidation of cyclohexane

From Table 3.8 and Fig 3.6, the addition of BrCCl_3 to this system diverted the formation of oxygenated products in favor of bromocyclohexane. With BrCCl_3 5 mmol was added to the reaction, bromocyclohexane (**5**) was only the product detected. Thus, this process was another suitable procedure for synthesis of alkyl bromide more than a classical route employing using Br_2 . The ratio of oxygenated products to bromocyclohexane was decreased when the amount of BrCCl_3 in the reaction was increased. The overall of % efficiency of TBHP in this process was increased. Compared with the results of the additive CCl_4 (Table 3.7, Entry 4) under the same conditions, it was found that the oxygenated products still remained in the reaction, while the use of BrCCl_3 gave the only product of bromocyclohexane. This could be seen that BrCCl_3 was a better trapping agent than CCl_4 in this system.

The outcome from the addition of BrCCl_3 supported the results obtained from the experiment employing of CCl_4 . To illustrate this both CCl_4 and BrCCl_3 acted as a radical trap. Therefore, the possible the mechanism for this reaction should occur *via* a free radical pathway.

3.7 Regioselectivity study

The study on regioselectivity is often the case that chemical reaction may, in principle, proceed to yield more than one product. *tert*-Butylcyclohexane (**6**), methylcyclohexane (**13**), *n*-hexane (**17**) and adamantane (**24**) were selected as model substrates on the oxidation reaction.

3.7.1 The oxidation of *tert*-butylcyclohexane

The oxidation of *tert*-butylcyclohexane (**6**) catalyzed by Cr(III) stearate was carried out under optimal conditions. The results are shown in Table 3.9.

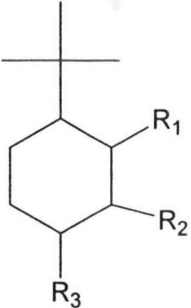
	(6) <i>tert</i> -butylcyclohexane	$\text{R}_1=\text{H}, \text{R}_2=\text{H}, \text{R}_3=\text{H}$
	(7) 2- <i>tert</i> -butylcyclohexanone	$\text{R}_1=\text{O}, \text{R}_2=\text{H}, \text{R}_3=\text{H}$
	(8) 3- <i>tert</i> -butylcyclohexanone	$\text{R}_1=\text{H}, \text{R}_2=\text{O}, \text{R}_3=\text{H}$
	(9) 4- <i>tert</i> -butylcyclohexanone	$\text{R}_1=\text{H}, \text{R}_2=\text{H}, \text{R}_3=\text{O}$
	(10) 2- <i>tert</i> -butylcyclohexanol	$\text{R}_1=\text{OH}, \text{R}_2=\text{H}, \text{R}_3=\text{H}$
	(11) 3- <i>tert</i> -butylcyclohexanol	$\text{R}_1=\text{H}, \text{R}_2=\text{OH}, \text{R}_3=\text{H}$
	(12) 4- <i>tert</i> -butylcyclohexanol	$\text{R}_1=\text{H}, \text{R}_2=\text{H}, \text{R}_3=\text{OH}$

Table 3.9 The oxidation of *tert*-butylcyclohexane catalyzed by Cr(III) stearate

Substrate	Product (mmol)						Selectivity 2-one:3-one:4-one
	(7)	(8)	(9)	(10)	(11)	(12)	
6	0.030	0.496	0.299	trace	trace	trace	1 :16 :10

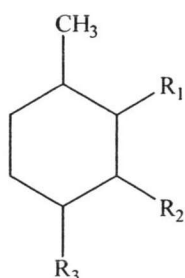
reaction condition : *tert*-butylcyclohexane 15 mmol, Cr(III)stearate 0.2 mmol, TBHP 9.0 mmol, 24 hr at 70°C

tert-Butylcyclohexane was another interesting model for regioselectivity study because it consists of 4 hydrogen atoms at 2- and 3- position and 2 hydrogen atoms at 4-position. The statistically of the oxidation of *tert*-butylcyclohexane at 2-, 3- and 4-position was 2:2:1. From Table 3.9, it was found that at positions 3- and 4- in *tert*-butylcyclohexane the oxidation was preferentially taken place. The little oxidation occurred at the 2-position. The selectivity of ketone formation: 2-one: 3-one: 4-one was 1: 16 : 10. The reason of this may be due to the steric effect of *tert*-butyl group in cyclohexane to cause the 2-position difficult to be attacked by active species.

The oxidation system using iron porphyrin as a catalyst which was previously studied³² provided similar results and gave the ratio of 2-one : 3-one : 4-one as 1 : 32 : 14. This observation displayed that *tert*-butyl substituent on cyclohexane had a profound effect on the oxidation reaction and induced the oxidation to take place preferentially at 3-position.

3.7.2 The oxidation of methylcyclohexane

Methylcyclohexane was selected as the next target substrate for studying the effect of substituents on cyclohexane oxidation. The postulation that the size of substituent on cyclohexane may have a profound effect on regioselectivity for the oxidation reaction would be verified. The results of the oxidation of methylcyclohexane are presented in Table 3.10.



- (13) Methylcyclohexane R₁= H, R₂= H, R₃= H
 (14) 2-Methylcyclohexanone R₁= O, R₂= H, R₃= H
 (15) 3-Methylcyclohexanone R₁= H, R₂= O, R₃= H
 (16) 4-Methylcyclohexanone R₁= H, R₂= H, R₃= O

Table 3.10 The oxidation of methylcyclohexane catalyzed by Cr(III) stearate

Substrate	Product (mmol)			Total product (mmol)	Selectivity 2-one:3-one:4-one
	(14)	(15)	(16)		
(13)	0.228	0.454	0.116	0.798	2 : 4 : 1

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

From Table 3.10, the oxidation of methylcyclohexane gave three main products. 2- and 3-methylcyclohexanes were observed as a main product. The little oxidation occurred at the 4- position. The ratio of 2-position : 3-position : 4-position was 2:4:1 which similar to the statistic value. But methyl group had an affect on the reaction at 2-position. Compared with the oxidation of *tert*-butylcyclohexane under the same conditions (Table 3.9), it was found that the oxidation of methylcyclohexane gave the ratio of 2-one : 3-one : 4-one (2 : 4 : 1) higher than the oxidation of *tert*-butylcyclohexane (1 : 16 : 10). Interestingly, the reaction of methylcyclohexane gave the product yield at 2- position higher than the reaction of *tert*-butylcyclohexane, which indicated that steric hindrance could affect to regioselectivity for reaction.

Sarneski *et al.* have recently reported the alkyl hydroperoxide oxidation of methylcyclohexane with $[\text{Mn}_3\text{O}_4(\text{dipy})_4(\text{OH}_2)_2](\text{ClO}_4)_4$ in CH_3CN , claiming an initial C^3/C^2 selectivity per bond on a basis of 1.6 at low conversion, rising to 2.1 in the presence of excess oxidant [8].

A series of experiments conducting on the oxidation of *tert*-butylcyclohexane and methylcyclohexane manifestly displayed that the substituent on cyclohexane had profound effect of the oxidation reaction. The size of the substituent on cyclohexane stipulated the position for the reaction.

3.7.3 The oxidation of *n*-hexane

The regioselective oxidation of aliphatic hydrocarbon was studied using *n*-hexane as a model substrate. The results of the oxidation of *n*-hexane are shown in Table 3.11.

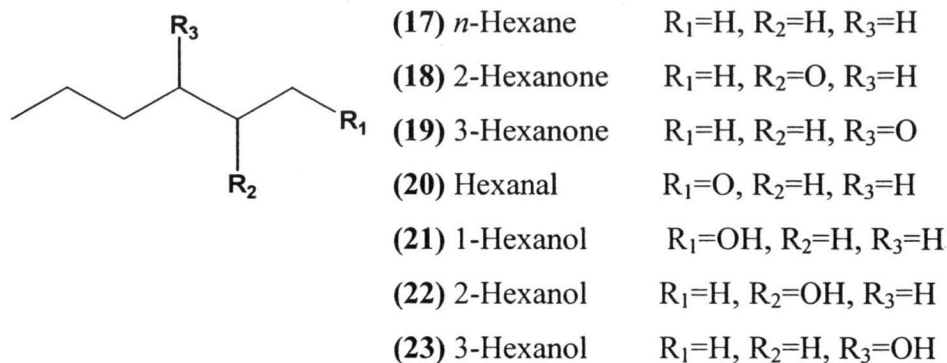


Table 3.11 The oxidation of *n*-hexane catalyzed by various metal stearates

Entry	Catalyst	Product (mmol)				Total (mmol)	Selective 2- : 3- position
		(18)	(19)	(22)	(23)		
1	Cr(III)stearate	0.654	0.501	0.109	0.047	1.311	1.39
2	Co(II)stearate	0.138	0.107	0.177	0.100	0.522	1.52
3	Mn(II)stearate	0.306	0.218	0.163	0.197	0.884	1.13
4	Cu(II)stearate	0.396	0.314	0.338	0.222	1.269	1.37

reaction conditions: *n*-hexane 50 mmol, catalyst 0.2 mmol, TBHP 9.0 mmol, 24 hr at 70°C

From Table 3.11, the oxidation of *n*-hexane catalyzed by various metal stearates was carried out. Four distinct products were detected. The yield of product taken place at 2-position (2-hexanol and 2-hexanone) were significantly prevailed to the other products could be detected at 3-position (3-hexanol and 3-hexanone). No reaction at primary carbons was taken place. Cr(III) and Cu(II) stearates revealed good capability as catalyst for the reaction. The 2-position: 3-position ratio was 1.39 and 1.37, respectively. Whereas those stearate complexes of Co(II) and Mn(II) stearates did not behave well as oxidation of *n*-hexane catalysts regarding the yield of the obtained products.

From the previous report, in 1999 Masahiro and his co-workers used soluble titanium complexes to catalyze the oxidation of *n*-hexane by TBHP as oxidant. *n*-Hexane could be oxidized to the corresponding ketone and alcohol.¹⁷ The ratio of the products occurred at 2-position (2-hexanol and 2-hexanone): 3-position (3-hexanol and 3-hexanone) was approximately 1:1 which simply similar results were observed by this system.

3.7.3.1 The effect of the amount of TBHP on Cr(III) stearate oxidation of *n*-hexane

The amount of TBHP in the reaction was varied from 3 to 18 mmol in order to find the most appropriate amount of TBHP that provided the highest yield of the desired product. The results are presented in Table 3.12.

Table 3.12 The effect of the amount of TBHP in *n*-hexane oxidation

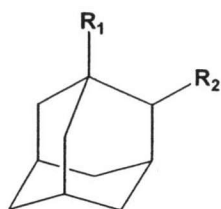
Entry	TBHP (mmol)	Product (mmol)				Total (mmol)	Selectivity 2- : 3- position
		(18)	(19)	(22)	(23)		
1	3	0.579	0.426	0.029	trace	1.034	1.43
2	9	0.654	0.501	0.109	0.047	1.311	1.39
3	18	0.290	0.208	0.112	0.042	0.652	1.61

reaction conditions: *n*-hexane 50 mmol, Cr(III) stearate 0.2 mmol, TBHP varied, 24 hr at 70°C

From Table 3.12, it is interesting to note that when employing TBHP 3.0 mmol the desired product was produced lower than the former condition employing TBHP 9.0 mmol. When the amount of TBHP was increased (18.0 mmol), the yield was decreased. It might be explained that the reaction was obstructed by H₂O in TBHP. Nevertheless, the increasing of TBHP was not effect to selectivity.

3.7.4 The oxidation of adamantane

Another selected saturated hydrocarbon to be examined is adamantane. Adamantane has been used by numerous researchers to investigate the activation process of saturated hydrocarbon. This may be because it is a non-volatile substrate, experimentally more convenient to use than lighter saturated hydrocarbons. With 12 equivalent secondary carbons and four equivalent tertiary carbons, it is a potential probe for regioselectivity study. Although, the interpretation of that selectivity is a matter of continuing controversy. The results of the oxidation of adamantane are shown in Table 3.13.



- (24) adamantane $R_1=H, R_2=H$
 (25) 1-adamantanol $R_1=OH, R_2=H$
 (26) 2-adamantanol $R_1=H, R_2=OH$
 (27) 2-adamantanone $R_1=H, R_2=O$

Table 3.13 The oxidation of adamantane catalyzed by various metal stearate complexes

Entry	Catalyst	Recovered adamantane (%)	Product (%)			Total Product (%)	C^2/C^3
			(25)	(26)	(27)		
1	Cr(III)stearate	74.42	14.30	trace	4.18	18.48	0.29
2	Co(II)stearate	77.40	9.10	1.16	1.72	11.98	0.32
3	Mn(II)stearate	78.26	11.24	1.04	2.30	14.58	0.30
4	Ni(II)stearate	84.66	7.76	0.66	2.40	10.82	0.39
5	Fe(III)stearate	90.20	2.12	0	0	2.12	-

reaction condition : adamantane 5 mmol, Cr(III) stearate 0.2 mmol, TBHP 9.0 mmol, isooctane 10 mL, 24 hr at 70°C

Table 3.13 shows the oxidation of adamantane catalyzed by various metal stearate complexes. Adamantane was oxidized mainly to 1-adamantanol, 2-adamantanone and 2-adamantanol. It was found that the oxidation of adamantane proceeded with high efficiency crucially depending on type of transition metal complex. Cr(III) stearate could provide the highest yield for the oxidation reaction (1-adamantanol (14.30%), 2-adamantanone (4.18%)). The adamantane selectivity C^2/C^3 value derived from this system was found to be approximately 0.29. The C^2 and C^3 are defined as the total oxidized products observed at the secondary and tertiary positions, respectively.

From the literature of the oxidation of adamantane, A C^2/C^3 value of 0.15 has been reported for alkoxy radical attack on adamantane [33]. The C^2/C^3 ratios obtained for hydrogen abstraction by a oxoferryl porphyrins species [34] and by the cobalt catalyzed autooxidation were 0.21 and 0.53 respectively [35]. Furthermore, the oxidation of adamantane with CrO_3 and TBHP in benzene at 60°C led to 1-adamantanol with a low yield (10%) while the use of $(n-Bu_3SnO)_2CrO_2$ instead of

CrO₃ afforded 1-adamantanol and 2-adamantanone with respectively 19% and 6% yield. C²/C³ ratio was 0.23 and 0.54 [10]. These systems were concluded to occur *via* radical pathway. Therefore, the possible mechanism for the oxidation of adamantane using Cr(III) stearate as catalyst and TBHP as oxidant should occur *via* radical pathway.

3.7.4.1 The study of adamantane oxidation catalyzed by bicatalysts of metal stearate complexes

Cr(III) stearate was used as a main catalyst in the presence of other metal stearates (Co(II) Mn(II), Ni(II) and Fe(III) stearates) in the ratio of 3:1 to catalyze the oxidation of adamantane. The results are shown in Table 3.14.

Table 3.14 The oxidation of adamantane catalyzed by bicatalysts

Entry	Catalyst	Recovered (%)	Product (%)			Total Product (%)	C ² /C ³
			(25)	(26)	(27)		
1	Cr	74.42	14.30	trace	4.18	18.48	0.29
2	Cr : Co	67.86	12.78	0.72	3.88	17.38	0.36
3	Cr : Ni	80.6	13.32	0	3.74	17.06	0.28
4	Cr : Mn	82.04	11.90	1.02	3.66	16.58	0.39
5	Cr : Fe	69.62	12.84	0	4.02	16.86	0.31

reaction conditions: adamantane 5 mmol, catalysts 0.2 mmol (Cr(II) stearate and other metal stearate as 3:1), TBHP 9.0 mmol, isooctane 10 mL, 24 hr at 70°C

Table 3.14 presents a series of the utilization of co-catalyst in Cr(III) stearate catalyzed oxidation of adamantane. It was observed that the oxidation of adamantane catalyzed by bicatalysts system gave almost the same amount of the desired product as the Cr(III) stearate alone was used as a catalyst. Cr:Co and Cr:Fe systems were another intriguing catalyst since it gave the best selectivity.

3.8 The oxidation of cyclohexane catalyzed by Cr(III) stearate in the large scale

The aim of the present study was to extend the scope of the oxidation of cyclohexane by increasing the amount of cyclohexane, catalyst and TBHP. The results are shown in Table 3.15.

Table 3.15 The oxidation of cyclohexane in large scale

Entry	Time (hr)	Product (mmol)		Total yield (mmol)	Selectivity -one/-ol
		(2)	(3)		
1	6	1.514	1.181	2.695	1.28
2	12	3.286	2.296	5.582	1.43
3	18	5.739	4.249	9.988	1.35
4	24	7.342	5.012	12.354	1.46
5	30	9.766	5.136	14.902	1.46
6	30*	10.239	3.714	13.953	2.76

reaction conditions: cyclohexane 500 mmol, Cr(III) stearate 1.0 mmol, TBHP 36.0 mmol (add four times with 9.0 mmol every 6 hr), 24 hr at 70°C
* TBHP 36.0 mmol

Table 3.15 exhibits that cyclohexane could be converted to cyclohexanone and cyclohexanol in high yield. The cyclohexanone/cyclohexanol ratio was 2.22. In the case when 36.0 mmol of TBHP was added at the initial stage of the reaction (entry 6), it was found that the total yield was decreased. Compared with other catalytic systems referred, this process is more suitable for industrial use.

3.9 The kinetic study of the effect of triphenylphosphine on cyclohexane oxidation

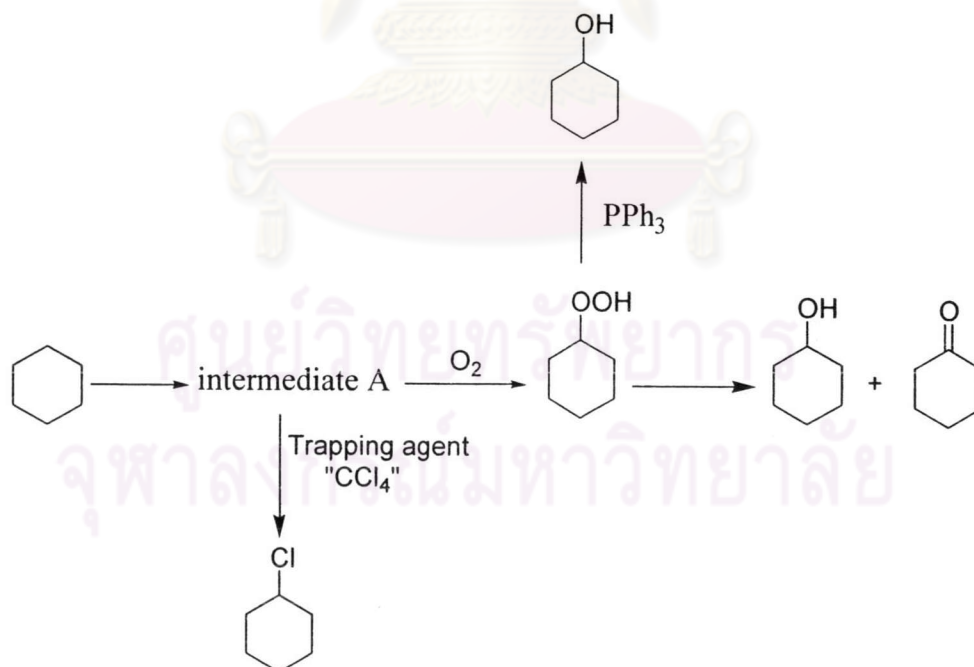
As reported earlier in the literature, the alkyl hydroperoxides could be quantitatively determined by *in situ* reduction to the corresponding alcohol. Thus, when a variable amount of PPh₃ was added to work up for cyclohexane oxidation, the resulting product distributions are obtained as shown in Table 3.16

Table 3.16 The kinetic study of the effect of PPh₃ on cyclohexane oxidation

Entry	Time (hr)	Product (mmol)		Ratio -one/-ol	Worked up with PPh ₃		Ratio -one/-ol
		(2)	(3)		(2)	(3)	
1	1	0.223	0.040	5.58	0.754	0.225	3.35
2	3	0.732	0.112	6.54	1.006	0.372	2.70
3	5	1.115	0.208	5.36	1.573	0.596	2.64
4	8	1.220	0.137	8.91	2.120	0.786	2.70

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

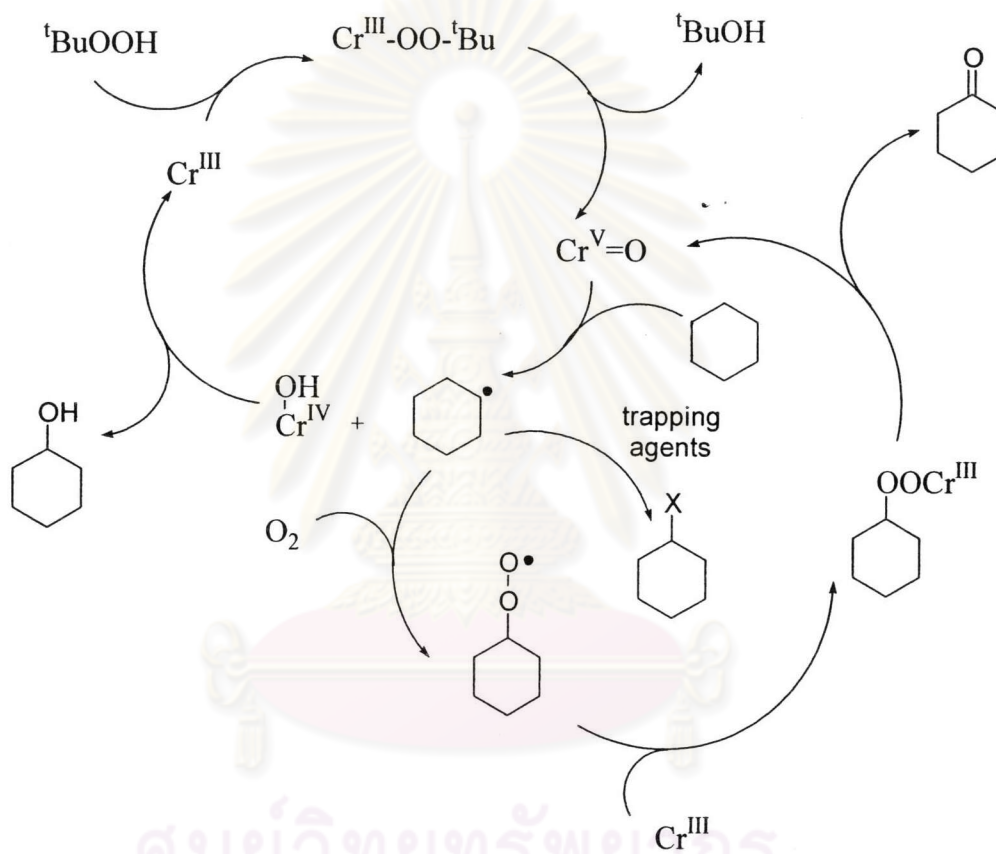
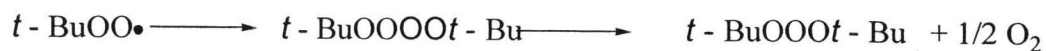
From Table 3.16, the addition of PPh₃ on cyclohexane oxidation clearly revealed the effect of reducing agent on this system. It was found that the amount of cyclohexanol was increased markedly. This could interpret that PPh₃ reduced an intermediate, possibly in this process, ROOH occurring which then convert to cyclohexanone and cyclohexanol. The possible conceptual mechanism could be drawn below.

**Scheme 3.2** The proposed conceptual mechanism on cyclohexane oxidation upon the addition of PPh₃

3.10 The proposed mechanistic pathway for Cr(III) stearate catalyzed on cyclohexane oxidation

From the regioselectivity study, the comparative study on the relative reactivity of saturated hydrocarbons and the results of the kinetic study on cyclohexane catalyzed by Cr(III) stearate, Co(II) stearate and co-catalyst (Fig 3.2) could be indicated that the mechanism of this oxidation may involve a free radical reaction. This proposed mechanism was based on the similar oxidation which presented by Muzart [22]. It was proposed that superoxide species from TBHP was transferred to Cr^{III} and the reaction was carried on by hyper-valent Cr^V oxo species. After that, the hyper-valent Cr^V oxo species might abstract hydrogen from cyclohexane and produced alkyl radicals. Cr^V was transformed to Cr(IV)-OH and then reacted with cyclohexyl radical giving cyclohexanol. In addition, oxygen may react with the produced carbon radical to form cyclohexyl hydroperoxide which then collapsed to cyclohexanone. At the temperature of 70°C, TBHP may homolytic cleaved and produce *t*-butyl peroxy radical (*t*-BuOO•). This radical might abstract hydrogen from cyclohexane and hence produced cyclohexyl radicals. Oxygen may then react with the produced carbon radical to form cyclohexyl hydroperoxide which then collapsed to the final products. The proposed mechanism on the oxidation cyclohexane catalyzed by Cr(III) stearate using TBHP as oxidant is shown in Scheme 3.3.

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Scheme 3.3 The proposed mechanism on the oxidation cyclohexane catalyzed by Cr(III) stearate using TBHP as oxidant