

## CONTENTS

	<b>Page</b>
CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
CHAPTER	
1. INTRODUCTION	1
1.1 Introduction	1
1.1.1 Synthesis of epoxides	1
1.1.1.1 Epoxidation with peracids	2
1.1.1.2 Epoxidation with hydroperoxide and alkyl hydroperoxides	3
1.1.1.3 Epoxidation with dioxiranes	4
1.1.1.4 Epoxidation with molecular oxygen	5
1.1.1.5 The other methods for epoxide preparations	5
1.1.1.5.1 Conversion of halohydrins	5
1.1.1.5.2 Reaction of carbonyl compounds and sulfur ylides	6
1.1.2 Quinones	7
1.1.2.1 Structure and characteristic of quinone	7
1.1.2.2 Role of quinones	7
1.1.2.3 Acid–base and redox properties of quinones	11
1.2 Literature review	16
1.2.1 Heterogeneous olefin epoxidation catalysis	17
1.2.2 Homogeneous olefin epoxidation catalysis	23
1.3 Objectives	26
2. EXPERIMENTALS	27

## CONTENTS (CONTINUED)

	<b>Page</b>
2.1 Chemicals	27
2.2 Instruments	29
2.2.1 Gas Chromatography - Flame Ionization Detector (GC - FID)	29
2.2.2 Fourier Transform Infrared Spectrometry (FT-IR)	30
2.2.3 UV - Visible spectroscopy (UV-Vis)	31
2.3 Procedure	31
2.3.1 Determination of reaction order of styrene epoxidation by mCPBA	31
2.3.2 Catalysis study of styrene epoxidation	32
2.3.2.1 The styrene epoxidation catalyzed by silver nitrate and various quinone compounds	32
2.3.2.2 Concentration effect of silver nitrate, 1, 2 - DHAQ, 1, 8- DHAQ on styrene epoxidation rate	36
3. RESULTS AND DISCUSSIONS	39
3.1 Determination of reaction order of styrene epoxidation by mCPBA	39
3.2 Catalysis study of styrene epoxidation	44
3.2.1 The Styrene epoxidation catalyzed by silver nitrate and various quinones compounds	44
3.2.1.1 Proposed mechanism for 2-(hydroxymethyl)anthraquinone catalyst (Without silver species)	47
3.2.1.2 Proposed mechanism of acid dissociation of dihydroxy anthraquinone (Without silver species)	61

## CONTENTS (CONTINUED)

	<b>Page</b>
3.2.2 Concentration effect of silver nitrate, 1, 2 - DHAQ, 1, 8-DHAQ on styrene epoxidation rate	78
3.2.2.1 Concentration effect of 1, 2 - DHAQ, 1, 8-DHAQ	78
3.2.2.2 Concentration effect of silver nitrate when used the constant concentration of 1, 2-DHAQ, 1, 8-DHAQ	78
4. CONCLUSION	89
BIBLIOGRAPHY	91
VITAE	98

## LIST OF TABLES

<b>Tables</b>	<b>Page</b>
1. Acid dissociation and logarithms of homoconjugation constants of the three anthraquinones investigated and the acid dissociation constant of water in the non - aqueous solvents under study and 298 K	16
2. Chemicals	27
3. The optimized GC condition for analysis	30
4. The ratio of reactant for epoxidation rate investigation	32
5. Various conditions for styrene epoxidation	33
6. Conditions for styrene epoxidation rate study	37
7. The styrene epoxidation rate (without catalyze) at the time 1 minute	41
8. The rate constant of styrene epoxidation	43
9. The results of styrene epoxidation catalysis by silver nitrate and various quinone compounds	44

## LIST OF FIGURES

Figures	Page
1. The structure of oxirane ring (epoxide ring)	1
2. The general mechanism of alkene epoxidation by peracids	2
3. Proposed mechanism for the $\text{Al}_2\text{O}_3$ - catalyzed alkene epoxidation	3
4. The structure of some dioxiranes	4
5. Catalytic cycle for epoxidation with dioxirane	4
6. Epoxide preparation by halohydrin	6
7. Epoxide preparation by sulfur ylides	6
8. Two basic structures of quinones	7
9. The structure of phylloquinone (Vitamin $\text{K}_1$ )	8
10. The structure of menaquinone (Vitamin $\text{K}_2$ )	8
11. The structure of menadione (Vitamin $\text{K}_3$ )	8
12. The structure of mepron (atovaquone)	9
13. The structure of 2 - hydroxyl - 1, 4- naphthoquinone (Lawsone)	9
14. The Z scheme in the photosynthesis	10
15. $\text{H}_2\text{S}$ suppression mechanism of anthraquinone in the sulfate- reducing bacteria	11
16. Redox reaction of anthraquinone	11
17. The relationship of redox potential between metals and quinone	12
18. Tautomeric structures resulting from proton transfer in 1, 4 – dihydroxy anthraquinone, and structures bearing no hydrogen bond	13
19. Tautomeric structures resulting from proton transfer in 1, 5 – dihydroxy anthraquinone, and structures bearing no hydrogen bond	14

## LIST OF FIGURES (CONTINUED)

<b>Figures</b>	<b>Page</b>
20. Possible tautomeric structures of 1, 8- dihydroxyanthraquinone	14
21. Titration curves of the dihydroxyanthraquinonate/ dihydroxyanthraquinone systems in acetonitrile	15
22. Synthesis of poly (S-DVB) – supported aminoacid–Ru(III) complex	19
23. Possible mechanism of styrene epoxidation that catalyst by hydrotalcite	21
24. Pathway for electrochemical and peroxide–driven catalysis of styrene epoxidation by cyt P450s	22
25. Epoxidation of thermally degraded poly(vinyl chloride) with m-chloro peroxybenzoic acid	23
26. Molecular structure and dimensions of the (a) CAT1 and (b) CAT2 homogeneous catalysts	24
27. Structure and labeling of the copper(II) schiff–base complexes	25
28. The principle of micellar catalysis	26
29. The HEWLETT – PACKARD model 5890 SERIES II Gas Chromatography	29
30. PERKIN ELMER SPECTRUM GX FT–IR SPECTROMETER	30
31. SPECORD S 100 UV–Visible spectrophotometer	31
32. Plot of the increasing styrene oxide per time when vary the concentration of mCPBA	40
33. Plot of the increasing styrene oxide per time when vary the concentration of styrene	40
34. Proposed mechanism of styrene epoxidation catalyzed by 2–(hydroxymethyl)anthraquinone	49

## LIST OF FIGURES (CONTINUED)

<b>Figures</b>	<b>Page</b>
35. Infrared spectra of the mixed reactant and 2 - (hydroxymethyl)anthraquinone at the reaction time of 30 minutes	50
36. Infrared spectra of the mixed reactant and 2 - (hydroxymethyl)anthraquinone at the reaction time of 2 hours	51
37. Infrared spectra of 2 - (hydroxymethyl)anthraquinone	52
38. Infrared spectra of the catalyst species at the reaction time 1 hour	53
39. Infrared spectra of the catalyst species at the reaction time 2 hours	54
40. Infrared spectra of the catalyst species at the reaction time 4 hours	55
41. Infrared spectra of the catalyst species at the reaction time 6 hours	56
42. Infrared spectra of the catalyst species at the reaction time 8 hours	57
43. Infrared spectra of the catalyst species at the reaction time 10 hours	58
44. UV - spectrum of the catalyst species at the reaction time 4 hours	59
45. UV - spectrum of the extracted catalyze at the reaction time 0, 0.5, 1, 1.5, 2, 2.5, 3 hour	60
46. The proposed mechanism of acid dissociation of 1, 2-dihydroxyanthraquinone	61
47. Acid dissociation of 1, 4-dihydroxyanthraquinone	62
48. Acid dissociation of 1, 8-dihydroxyanthraquinone	63
49. Acid dissociation of 1, 5-dihydroxyanthraquinone	64
50. UV - spectrum of 1, 4- dihydroxyanthraquinone in catalytic system	66

## LIST OF FIGURES (CONTINUED)

Figures	Page
51. UV – spectrum of 1, 4– dihydroxyanthraquinone in catalytic system (Added 0.001M NaOH 0.05 ml)	67
52. UV – spectrum of 1,4– dihydroxyanthraquinone in catalytic system (Added 0.001M HNO <sub>3</sub> 0.05 ml)	68
53. UV – spectrum of 1, 2– dihydroxyanthraquinone in catalytic system	69
54. UV – spectrum of 1, 2– dihydroxyanthraquinone in catalytic system (Added 0.001M NaOH 0.05 ml)	70
55. UV – spectrum of 1, 2– dihydroxyanthraquinone in catalytic system (Added 0.001M HNO <sub>3</sub> 0.05 ml)	71
56. UV – spectrum of 1, 8– dihydroxyanthraquinone in catalytic system	72
57. UV – spectrum of 1, 8– dihydroxyanthraquinone in catalytic system (Added 0.001M NaOH 0.05 ml)	73
58. UV – spectrum of 1, 8– dihydroxyanthraquinone in catalytic system (Added 0.001M HNO <sub>3</sub> 0.05 ml)	74
59. UV – spectrum of 1, 5 – dihydroxyanthraquinone in catalytic system	75
60. UV – spectrum of 1, 5– dihydroxyanthraquinone in catalytic system (Added 0.001M NaOH 0.05 ml)	76
61. UV – spectrum of 1, 5– dihydroxyanthraquinone in catalysis system (Added 0.001M HNO <sub>3</sub> 0.05 ml)	77



## LIST OF FIGURES (CONTINUED)

Figures	Page
62. Styrene epoxidation catalysis by various concentration of 1, 8-dihydroxy anthraquinone	79
63. Styrene epoxidation catalysis by various concentration of 1, 2-dihydroxy anthraquinone	80
64. Plot of epoxidation rate versus concentration of 1, 8-dihydroxyanthraquinone	81
65. Plot of epoxidation rate versus concentration of 1, 8-dihydroxyanthraquinone	82
66. The Infrared spectra of styrene	83
67. The Infrared spectra of the mixed styrene and silver nitrate	84
68. Styrene epoxidation catalysis by various concentration of silver nitrate and 0.0022 g of 1, 8-dihydroxyanthraquinone	85
69. Styrene epoxidation catalysis by various concentration of silver nitrate and 0.0022 g of 1, 2-dihydroxyanthraquinone	86
70. Plot of styrene epoxidation rate that used 0.0022 g of 1, 8-dihydroxyanthraquinone versus various concentration of silver nitrate	87
71. Plot of styrene epoxidation rate that used 0.0022 g of 1, 2-dihydroxyanthraquinone versus various concentration of silver nitrate	88