

CHAPTER 2

EXPERIMENTALS

2.1 Chemicals

The chemicals for the investigations and synthesis were the highest purity commercially available and were used without further purification. They are all shown in Table 2.

Table 2 Chemicals.

Entry	Chemicals	Source	Grade	Remark
1	Styrene	-	-	Department of polymer science , Prince of Songkhla University
2	Styrene oxide	Fluka	Chemika	Purum $\geq 97\%$ (GC)
3	m-chloroperbenzoic acid	Fluka	Chemika	$\sim 70\%$ (RT)
4	Silver nitrate	MERCK	Pro analysi	Switzerland
5	Acetonitrile	LAB-SCAN	Analytical Reagent	Ireland
6	Ammonium chloride	UNIVAR	Analytical Reagent	Assay 99.5 % min
7	Sodium sulfat	Fisher chemicals	Laboratory	$> 99\%$
8	1, 4-Naphtoquinone	Fluka	Chemika	Puriss 99.5%
9	Anthraquinone	BPH	Laboratory	England

Table 2 (Continued).

Entry	Chemicals	Source	Grade	Remark
10	2-(hydroxymethyl)anthraquinone	Fluka	Chemika	Purum 97% (HPLC)
11	1, 2-dihydroxyanthraquinone	Aldrich	Laboratory	Puriss 97% (USA)
12	1, 4-dihydroxyanthraquinone	Aldrich	Laboratory	Puriss 96% (USA)
13	1, 5-dihydroxyanthraquinone	Aldrich	Laboratory	~97 % (HPLC)
14	1, 8-dihydroxyanthraquinone	Aldrich	Laboratory	Puriss 97 % (USA)
15	Anthraquinone- 2, 6- disulfonic acid disodium salt	Fluka	Chemika	Purum \geq 97% (HPLC)
16	2, 6-dibromoanthraquinone	Fluka	Chemika	Purum 98%
17	α -Tetralone	Fluka	Chemika	Puriss 97 %
18	9-Xanthone	Fluka	Chemika	Puriss \geq 97% (Switzerland)
19	Anthrone	Aldrich	Laboratory	Puriss 97% (USA)
20	Benzophenone	Aldrich	Laboratory	Puriss 96 % (USA)
21	1, 4-Benzoquinone	Fluka	Chemika	Puriss \geq 99.5%
22	Tetrahydroxyquinone	Fluka	Chemika	Puriss 99.5%

2.2 Instruments

2.2.1 Gas Chromatography - Flame Ionization Detector (GC - FID)

The HEWLETT - PACKARD model 5890 SERIES II Gas Chromatography equipped with Flame Ionization Detector was used with capillary column: SP 1 [cross - linked methyl silicone gum (25 m x 0.32 mm i.d.)].



Figure 29 The HEWLETT - PACKARD model 5890 SERIES II Gas Chromatography

The high purity (99.999 %) gases including nitrogen gas, hydrogen gas and air zero gas were bought from TIG Thailand. The optimized conditions for product and reactant analyses are summarized in Table 3.

Table 3 The optimized GC conditions for analysis.

Parameters	Optimum values
Carrier gas flow rate	35 ml / min
Hydrogen gas flow rate	45 ml / min
Air zero gas flow rate	450 ml / min
Injector temperature	165 °C
Detector temperature	195 °C
Initial temperature	95 °C
Ramp I	5 °C/ min
Finish Ramp I	120 °C
Ramp II	1 °C/ min
Finish Ramp II	125 °C
Ramp III	25 °C/ min
Finish Ramp III	275 °C

2.2.2 Fourier Transform Infrared Spectrometry (FT-IR)

FT-IR is used to determine the functional group of catalyst species. The used instrument was PERKIN ELMER SPECTRUM GX FT - IR Spectrometer. The region of wave number under study was 4000 - 400 cm⁻¹.

**Figure 30** PERKIN ELMER SPECTRUM GX FT - IR Spectrometer

2.2.3 UV - Visible spectroscopy (UV-Vis)

The SPECCORD S 100 UV - Visible spectrometer was used in this study.



Figure 31 SPECCORD S 100 UV - Visible spectrometer

2.3 Procedure

2.3.1 Determination of reaction order of styrene epoxidation by m-chloroperbenzoic acid (without catalyst)

Reaction rates of styrene epoxidation were measured in the unit of concentration (molar) per time (hour, minute or second). The experiments were conducted as follows.

Stock 0.1 M styrene and 0.2 M mCPBA solutions in acetonitrile were mixed with the volumes as shown in Table 4. The solutions are adjusted to 5 ml with acetonitrile.

Table 4 The ratios of reactants for epoxidation rate investigation.

Entry	Stock styrene solution 0.1 M (ml)	Stock mCPBA solution 0.2 M (ml)	Concentration ratio (Styrene / mCPBA)
1	1.0	2.0	1:4
2	1.0	1.5	1:3
3	1.0	1.0	1:2
4	1.0	0.5	1:1
5	2.0	1.0	1:1
6	1.5	1.0	3:4
7	0.5	1.0	1:4

The concentrations of styrene oxide at various periods of time were analyzed by GC technique. Plot of the increasing styrene oxide with time and equations are made with Microsoft Excel program. The reaction rates are calculated from the slope of curve at 1 minute (considered to be initial rate). Rate constants (k) can be calculated from the simple kinetic rate equations.

2.3.2 Catalysis study of styrene epoxidation.

2.3.2.1 The styrene epoxidation catalyzed by silver nitrate and various quinone compounds

The investigation of styrene epoxidation catalyzed by silver nitrate and various ketone and quinone compounds were conducted with the same concentration of reactants (styrene and m-chloroperbenzoic acid) and catalysts.

Pipetting 0.1 M styrene stock solution 1 ml to the vial performed the experiments. When the reactions with mCPBA and silver nitrate were studied, the styrene solution was mixed with 0.2 M mCPBA 0.5 ml and 0.01 M silver nitrate 1 ml. 0.01 M of quinones and ketones were used. All solutions were

adjusted to 5 ml with acetonitrile. The solutions were stirred for 25 hours at room temperature. The chemical were mixed as follows:

Table 5 Various conditions for styrene epoxidation

Conditions	mCPBA 0.2 M (ml)	AgNO ₃ 0.01 M (ml)	Ketone or Quinone (Mole)
1. Normal conditions			
1.1 Styrene 0.1 M in acetonitrile (Basic condition, BC)	0	0	0
1.2 BC + AgNO ₃ (Condition A)	0	1	0
1.3 BC + mCPBA (Condition B)	0.5	0	0
1.4 BC + AgNO ₃ + mCPBA (Condition C)	0.5	1	0
2. BC with 0.01 M ketones or quinones			
2.1 BC + Anthraquinone	0	0	0.01
2.2 BC + 1, 2-Dihydroxyanthraquinone	0	0	0.01
2.3 BC + 1, 4-Dihydroxyanthraquinone	0	0	0.01
2.4 BC + 1, 5-Dihydroxyanthraquinone	0	0	0.01
2.5 BC + 1, 8-Dihydroxyanthraquinone	0	0	0.01
2.6 BC + 2-(Hydroxymethyl)anthraquinone	0	0	0.01
2.7 BC + 2, 6-Dibromoanthraquinone	0	0	0.01
2.8 BC + Anthraquinone - 2, 6- disulfonic acid disodium salt	0	0	0.01
2.9 BC + 1, 4-Benzoquinone	0	0	0.01
2.10 BC + Tetrahydroxyquinone	0	0	0.01
2.11 BC + 1, 4-Naphtoquinone	0	0	0.01
2.12 BC + Benzophenone	0	0	0.01
2.13 BC + Anthrone	0	0	0.01

Table 5 (Continued)

Conditions	mCPBA 0.2 M (ml)	AgNO ₃ 0.01M (ml)	Ketone or Quinone (Mole)
3. Condition A with 0.01 M ketones or quinones			
3.1 A + Anthraquinone	0	1	0.01
3.2 A + 1, 2-Dihydroxyanthraquinone	0	1	0.01
3.3 A + 1, 4-Dihydroxyanthraquinone	0	1	0.01
3.4 A + 1, 5-Dihydroxyanthraquinone	0	1	0.01
3.5 A + 1, 8-Dihydroxyanthraquinone	0	1	0.01
3.6 A + 2-(Hydroxymethyl)anthraquinone	0	1	0.01
3.7 A + 2, 6-Dibromoanthraquinone	0	1	0.01
3.8 A + Anthraquinone-2, 6-disulfonic acid disodium salt	0	1	0.01
3.9 A + 1, 4-Benzoquinone	0	1	0.01
3.10 A + Tetrahydroxyquinone	0	1	0.01
3.11 A + 1, 4-Naphtoquinone	0	1	0.01
3.12 A + Benzophenone	0	1	0.01
3.13 A + Anthrone	0	1	0.01
4. Condition B with 0.01 M ketones or quinones			
4.1 B + Anthraquinone	0.5	0	0.01
4.2 B + 1, 2-Dihydroxyanthraquinone	0.5	0	0.01
4.3 B + 1, 4-Dihydroxyanthraquinone	0.5	0	0.01
4.4 B + 1, 5-Dihydroxyanthraquinone	0.5	0	0.01
4.5 B + 1, 8-Dihydroxyanthraquinone	0.5	0	0.01

Table 5 (Continued)

Condition	mCPBA 0.2 M (ml)	AgNO ₃ 0.01M (ml)	Ketone or Quinone (Mole)
4.6 B + 2-(Hydroxymethyl)anthraquinone	0.5	0	0.01
4.7 B + 2, 6-Dibromoanthraquinone	0.5	0	0.01
4.8 B + Anthraquinone - 2, 6-disulfonic acid disodium salt	0.5	0	0.01
4.9 B + 1, 4-Benzoquinone	0.5	0	0.01
4.10 B + Tetrahydroxyquinone	0.5	0	0.01
4.11 B + 1, 4-Naphtoquinone	0.5	0	0.01
4.12 B + Benzophenone	0.5	0	0.01
4.13 B + Anthrone	0.5	0	0.01
5. Condition C with 0.01 M ketones or quinones			
5.1 C + Anthraquinone	0.5	1	0.01
5.2 C + 1, 2-Dihydroxyanthraquinone	0.5	1	0.01
5.3 C + 1, 4-Dihydroxyanthraquinone	0.5	1	0.01
5.4 C + 1, 5-Dihydroxyanthraquinone	0.5	1	0.01
5.5 C + 1, 8-Dihydroxyanthraquinone	0.5	1	0.01
5.6 C + 2-(Hydroxymethyl)anthraquinone	0.5	1	0.01
5.7 C + 2, 6-Dibromoanthraquinone	0.5	1	0.01
5.8 C + Anthraquinone-2, 6-disulfonic acid disodium	0.5	1	0.01
5.9 C + 1, 4-Benzoquinone	0.5	1	0.01
5.10 C + Tetrahydroxyquinone	0.5	1	0.01
5.11 C + 1, 4-Naphtoquinone	0.5	1	0.01

Table 5 (Continued)

Condition	mCPBA 0.2 M (ml)	AgNO ₃ 0.01M (ml)	Ketone or Quinone (Mole)
5.12 C + Benzophenone	0.5	1	0.01
5.13 C + Anthrone	0.5	1	0.014

After 25 hours, the 1 ml of mixture of 0.01 M ammonium chloride and 0.0001 M hydrochloric acid were added to separate silver chloride by centrifugation. In some conditions that quinone compounds have high boiling point and melting point, the solutions were separated from the solid by evaporation. The separated solutions were analyzed using Gas - Chromatography.

2.3.2.2 Reaction rates of styrene epoxidation using 1, 2- Dihydroxyanthraquinone, 1, 8- Dihydroxyanthraquinone and silver nitrate as catalyst

From the results of dihydroxyanthraquinone catalysts in the Table 5, 1, 2-dihydroxyanthraquinone was not suitable catalyst whereas 1, 8 - dihydroxyanthraquinone is satisfactory. They therefore have been chosen for the examination of catalytic activity. Even though the presence of AgNO₃ in category 5 seem to have less effect to the percentage yields, in the case of 1, 2-DHAQ, it significantly inhibits the reaction, resulting in much lower yield. This is an additional reason to choose this compound as a representative for the rate study.

All vials were added 0.1 M styrene 1 ml and 0.2 M mCPBA 0.5 ml with varied concentrations of quinone. All solutions were adjusted to 5 ml with acetonitrile. The conditions for this investigation were summarized in Table 6.

Table 6 Conditions for styrene epoxidation rate study

Entry	Weight of quinone	0.1 M AgNO ₃ (ml)
1. Condition RA 0.1 M styrene 1 ml+0.2 M mCPBA 0.5 ml+1, 8-dihydroxyantheraquinone (varied weights)		
1.1	0.0011	0
1.2	0.0047	0
1.3	0.0082	0
1.4	0.0114	0
1.5	0.0147	0
2. Condition RB 0.1 M styrene 1 ml+0.2 M mCPBA 0.5 ml+1, 2-dihydroxyantheraquinone (varied weights)		
2.1	0.0022	0
2.2	0.0048	0
2.3	0.0073	0
2.4	0.0104	0
2.5	0.0160	0
2.6	0.0223	0
3. Condition RC 0.1 M styrene 1 ml+0.2 M mCPBA 0.5 ml+1, 2-dihydroxyantheraquinone (constant weight)+ AgNO ₃		
3.1	0.022	0.2
3.2	0.022	0.4
3.3	0.022	0.6
3.4	0.022	0.8
3.5	0.022	1.0

Table 6 (Continued)

Entry	Weight of quinone	0.1 M AgNO ₃ (ml)
4. Condition RD		
0.1 M styrene 1 ml+0.2 M mCPBA 0.5 ml+1, 2-dihydroxyantheraquinone (constant weight)+ AgNO ₃		
4.1	0.022	0.2
4.2	0.022	0.4
4.3	0.022	0.6
4.4	0.022	0.8
4.5	0.022	1.0