CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Determination of reaction order of styrene epoxidation by m-chloroperbenzoic acid (mCPBA)

The characterization of the order of the reaction is based on how the reaction rate varies with the concentration of reactions. Due to the fact that there are only two main reactants in cluding styrene and mCPBA. Provided that only those two substances are involved, the general kinetic rate law can be written as:

$$\text{Rate (r)} = -d[\text{Styrene}]/dt = k\,[\text{Styrene}]^{m}\,[\text{mCPBA}]^{n}$$

Where

k = rate constant

[Styrene] = concentration of styrene solution

[mCPBA] = concentration of m-chloroperbenzoic acid solution

m = the reaction order of styrene

n = the reaction order of mCPBA

The reaction order of mCPBA and styrene can be calculated from the observed reaction rates. Changing the concentration of substances taking part in a reaction usually changes the rate of the reaction. The observed dependence of styrene oxide concentration on time with varied the concentration of styrene and mCPBA are shown in Figure 32 and 33 respectively. The styrene epoxidation rates (without catalyst) at the time 1 minute are summarized in Table 7.

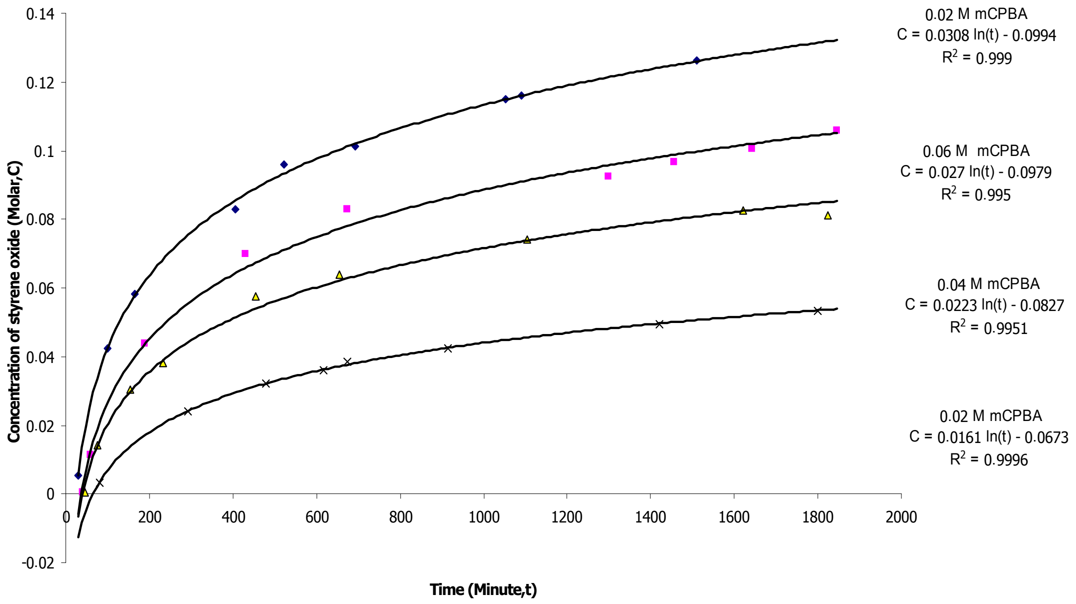

Figure 32 Plot of the increasing styrene oxide with time when vary the concentration of mCPBA (The concentration of styrene is 0.02 M)

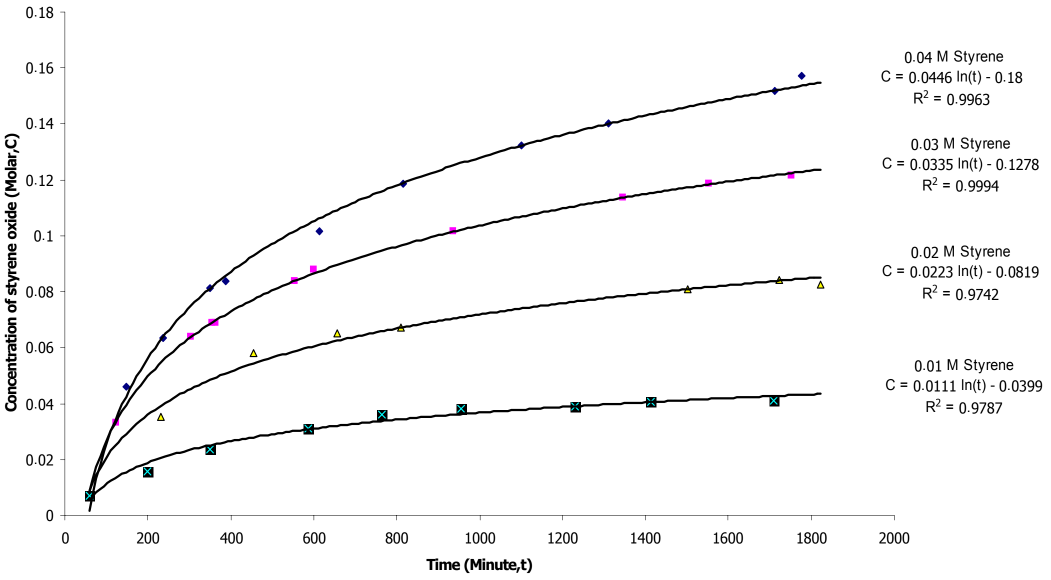

Figure 33 Plot of the increasing styrene oxide per time with varied the concentration of styrene (The concentration of mCPBA is 0.02 M)

Table 7 The styrene epoxidation rate (without catalyst) at the time 1 minute

Entry	Concentration of styrene (molar)	Concentration of mCPBA (molar)	Reaction rate (molar/minute)
1	0.02	0.02	0.0161
2	0.02	0.04	0.0223
3	0.02	0.06	0.0269
4	0.02	0.08	0.0308
5	0.01	0.04	0.0111
6	0.02	0.04	0.0223
7	0.03	0.04	0.0335
8	0.04	0.04	0.0446

Refer to Entry 1 and 2 in Table 13, the epoxidation rates with used the concentration of mCPBA 0.02 molar and 0.04 molar are 0.0161 molar/minute and 0.0223 molar/minute respectively. These values are added to the kinetic rate equations.

$$0.0161 = k\,(0.02)^m\,(0.02)^n \qquad (1)$$

$$0.0223 = k\,(0.02)^m\,(0.04)^n \qquad (2)$$

$(2) \div (1)$

$$1.3851 = 2^n$$

$$n = 0.46999$$

$$n \approx 0.5 \approx 1/2$$

From the Entry 5 and 6, the epoxidation rate when used the concentration of styrene 0.01 molar and 0.02 molar are 0.0111 molar/minute and 0.0223 molar/minute respectively. These values are added to the simple kinetic rate equation.

$$0.0111 = k\,(0.01)^m\,(0.04)^n \qquad (3)$$

$$0.0223 = k\,(002)^m\,(0.04)^n \qquad (4)$$

(4) ÷ (3)

$$2 = 2^m$$

$$m = 1$$

Refer to order of reaction was determined experimentally. The calculated results indicated that 1 as the order of reaction with respect to styrene and 1/2 as the order of reaction with respect to mCPBA. The overall order of the styrene epoxidation is the sum of the exponents, m + n, which is 3/2. The rate constants calculated from kinetic rate equation are shown in the Table 8.

Table 8 The rate constants of styrene epoxidation

Entry	Concentration of styrene (Molar)	Concentration of mCPBA (Molar)	Rate constants
1	0.02	0.02	5.06
2	0.02	0.04	5.06
3	0.02	0.06	5.05
4	0.02	0.08	5.05
5	0.01	0.04	5.05
6	0.02	0.04	5.06
7	0.03	0.04	5.07
8	0.04	0.04	5.06

The rate equation is therefore:

$$\text{Styrene epoxidation rate} = 5.06\ [\text{Styrene}]\ [\text{mCPBA}]^{1/2}$$

The goal of these rate law investigations is to determine that in the rate-determining step, which reactant is involved. This information is beneficial for the mechanism of the reaction. However, this is just apreliminary study. More investigations must be performed to confirm it. Furthermore, if the mechanism of the reaction with catalyst, the experiments can be conducted in the same way. It can be determined that the reactants get involved or not, which can be different from the mechanism without catalyst.

3.2 Catalysis study of styrene epoxidation

3.2.1 The Styrene epoxidation catalyzed by silver nitrate and various quinone compounds.

The percentage yields and conversions for styrene epoxidation in various cases of 5 categories are shown in Table 9.

Table 9 The results of styrene epoxidation catalysis by silver nitrate and various quinone compounds.

Conditions	Percent conversions	Percent yields
1. Normal conditions		
1.1 Styrene 0.1 M in acetonitrile (Basic condition , BC)	0	0
1.2 BC + $AgNO_3$ (Condition A)	0	0
1.3 BC + mCPBA (Condition B)	88	62
1.4 BC + $AgNO_3$ + mCPBA (Condition C)	84	61
2. BC with 0.01 M ketones or quinones		
2.1 BC + Anthraquinone	0	0
2.2 BC + 1, 2-Dihydroxyanthraquinone	0	0
2.3 BC + 1, 4-Dihydroxyanthraquinone	0	0
2.4 BC + 1, 5-Dihydroxyanthraquinone	0	0
2.5 BC + 1, 8-Dihydroxyanthraquinone	0	0
2.6 BC + 2-(Hydroxymethyl)anthraquinone	0	0
2.7 BC + 2, 6-Dibromoanthraquinone	0	0

Table 9 (Continued)

Conditions	Percent conversions	Percent yields
2.8 BC + Anthraquinone - 2, 6 - disulfonic acid disodium	0	0
2.9 BC + 1, 4-Benzoquinone	0	0
2.10 BC + Tetrahydroxyquinone	0	0
2.11 BC + 1, 4-Naphtoquinone	0	0
2.12 BC + Benzophenone	0	0
2.13 BC + Anthrone	0	0
3. Condition A with 0.01 M ketones or quinones		
3.1 A + Anthraquinone	0	0
3.2 A + 1, 2-Dihydroxyanthraquinone	0	0
3.3 A + 1, 4-Dihydroxyanthraquinone	0	0
3.4 A + 1, 5-Dihydroxyanthraquinone	0	0
3.5 A + 1, 8-Dihydroxyanthraquinone	0	0
3.6 A + 2-(Hydroxymethyl)anhraquinone	0	0
3.7 A + 2, 6-Dibromoanthraquinone	0	0
3.8 A + Anthraquinone - 2, 6 - disulfonic acid disodium salt	0	0
3.9 A + 1, 4-Benzoquinone	0	0
3.10 A + Tetrahydroxyquinone	0	0
3.11 A + 1, 4-Naphtoquinone	0	0
3.12 A + Benzophenone	0	0
3.13 A + Anthrone	0	0
4. Condition B with 0.01 M ketones or quinones		
4.1 B + Anthraquinone	73	45
4.2 B + 1, 2-Dihydroxyanthraquinone	67	42
4.3 B + 1, 4-Dihydroxyanthraquinone	73	40

Table 5 (Continued)

Condition	Percent conversions	Percent yields
4.4 B + 1, 5-Dihydroxyanthraquinone	84	66
4.5 B + 1, 8-Dihydroxyanthraquinone	89	78
4.6 B + 2-(Hydroxymethyl)anhraquinone	92	92
4.7 B + 2, 6-Dibromoanthraquinone	89	73
4.8 B + Anthraquinone - 2, 6 - disulfonic acid disodium salt	91	84
4.9 B + 1, 4-Benzoquinone	85	81
4.10 B + Tetrahydroxyquinone	88	71
4.11 B + 1, 4-Naphtoquinone	63	29
4.12 B + Benzophenone	89	81
4.13 B + Anthrone	89	86
5. Condition C with 0.01 M ketones or quinones		
5.1 C + Anthraquinone	88	80
5.2 C + 1, 2-Dihydroxyanthraquinone	55	8
5.3 C + 1, 4-Dihydroxyanthraquinone	73	40
5.4 C + 1, 5-Dihydroxyanthraquinone	69	35
5.5 C + 1, 8-Dihydroxyanthraquinone	86	83
5.6 C + 2-(Hydroxymethyl)anhraquinone	92	87
5.7 C + 2, 6-Dibromoanthraquinone	88	67
5.8 C + Anthraquinone - 2, 6 - disulfonic acid disodium salt	92	81
5.9 C + 1, 4-Benzoquinone	77	67
5.10 C + Tetrahydroxyquinone	88	64
5.11 C + 1, 4-Naphtoquinone	80	56
5.12 C + Benzophenone	87	83
5.13 C + Anthrone	89	81

Generally the epoxidation of styrene can occur in the presence of oxidant. From the normal condition in Table 9, oxygen should not involve in the styrene epoxidation because there is no product. Similarly, silver nitrate does not help in the induction of oxygen addition. It is clear that mCPBA can act as oxidant. From entry 1.2 it is also obvious tht $AgNO_3$ does not help in the epoxidation. But in stead in inhibits the reaction

In the case catagories 2 and 3, the experiments were performed by adding ketone and quinones without $AgNO_3$. The % yields are all zero. Therefore, ketone and quinones have no role in epoxidation even if in the presence of silver species

According to the yields of category 4, the group with the yields higher than 62 (the yield of entry 1.3) and those with the yields are lower than 62. It can be inferred that, in the presence of mCPBA, ketones and quinones can either enhance or inhibit the epoxidation process. Due to the great variety of yields and structures, the group of dihydroxyanthraquinones is chosen for rate study

3.2.1.1 Proposed mechanism for epoxidation of styrene catalyzed by 2-(hydroxylmethyl)anthraquinone (without silver species)

From the result in Table 9, 2-(hydroxylmethyl)anthraquinone is the best catalyst (without adding any silver species) because it gave the highest percent yield (91.57%). This can be due to the fact that 2-(hydroxymethyl)anthraquinone is the best proton donor. It gave up to quantitative yields of anthraquinone-2-aldehyde. Work-up in the absence of air gave a product with an intense colour and aromatic NMR peak (in DMSO-d_6) including an aldehyde peak at δ 10.2. Introduction of oxygen to NMR sample converted these peaks to those of anthraquinone-2-aldehyde, with a characteristic sharp aldehyde peak at δ 10.1. The primary reaction step is benzylic C-H bond deprotonation by protic solvent to gave a highly resonance stabilized carbanion. In order to satisfy the unimolecular nature of the reaction, they propose that the next step involves protonation of the oxygen to give bisenol intermediate, which can readily transform to dihydroxyanthracene by keto-enol form tautomerization step (Lukeman M., Xu M. and Wan P., 2002).

Being proton donor, increase the yield by donating proton to the carbonyl group of mCPBA, this in turn gives away oxygen to styrene. The catalyst species can act as proton donor for many times. The proposed mechanism of styrene epoxidation catalysis by 2-(hydroxymethyl)anthraquinone is shown in Figure 34. The IR spectra and UV spectrum as shown in the Figure-35 - 45 support this. From Figure 36, it is clearly seen that the broad band of O-H stretching, observed in the range 3200-3600 cm^{-1}, is stronger than that recorded at the beginning as shown in Figure 35. It indicates that the carbonyl of 2-(hydroxymethyl)anthraquinone is reduced to hydroxyl. In addition (Figure 36), the pair of the C-H stretching of aldehyde peaks appears at 2730 and 2782 cm^{-1}. This confirming that the distal side chain benzylic alcohol is oxidized to the aldehyde.

The IR spectra of 2-(hydroxylmethyl)anthraquinone that detected by KBr pillet is shown in Figure 37, it was recorded in the range 4000-400 cm^{-1} which was helpful in the characterization of 2-(hydroxylmethyl)anthraquinone. The characteristic frequencies are -OH bonded stretching at 3446 cm^{-1},C=O stretching at 1675 cm^{-1}, C=C aromatic stretching at 1590 cm^{-1} and the pair of C-(C=O)-C at 1325 cm^{-1} and 1295 cm^{-1}.

The infrared spectra of some species that were recorded during the reaction are shown in Figure 38 - 43. The band intensity of C=C conjugated polyene is observed at 1,635 cm^{-1}. This peak increased when the time increased time but peaks of C-(C=O)-C was decreased. The UV spectrum in Figure 44 is the same species with IR spectra in Figure 40. It is clearly seen that the strong absorption band, observed in the range 360-460 nm. Figure 45 is shown the mixed reactant solution spectrum. The absorbtion band in the range 360-460 nm. was increased when the reaction time increased. These indicate that the polyene species was occurred in the solution. In addition, the polyene species can be support that 2-(hydroxymethyl)anthraquinone can act as proton acceptor in the catalytic system.

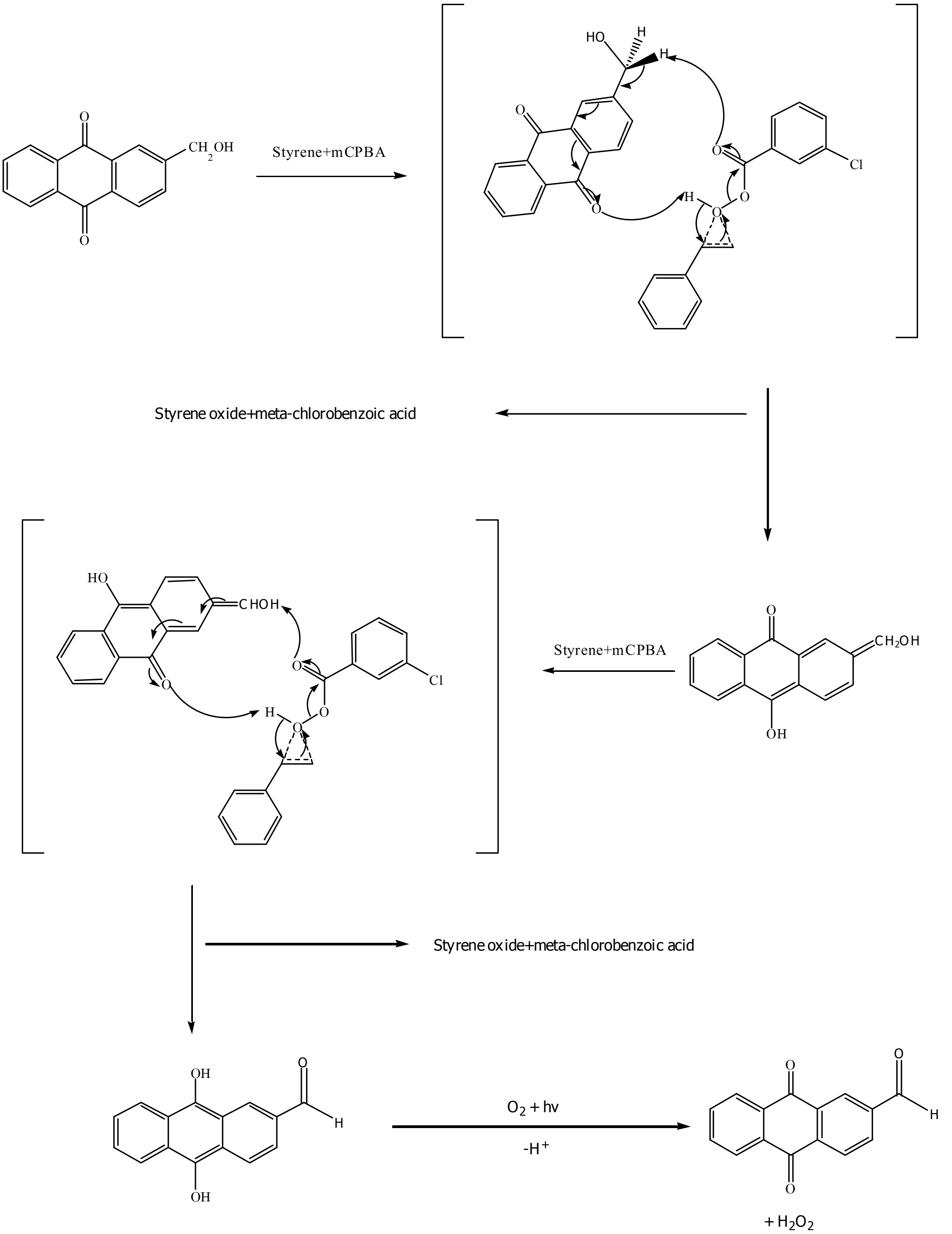

Figure 34 Proposed mechanism of styrene epoxidation catalyzed by 2-(hydroxyl methyl)anthraquinone

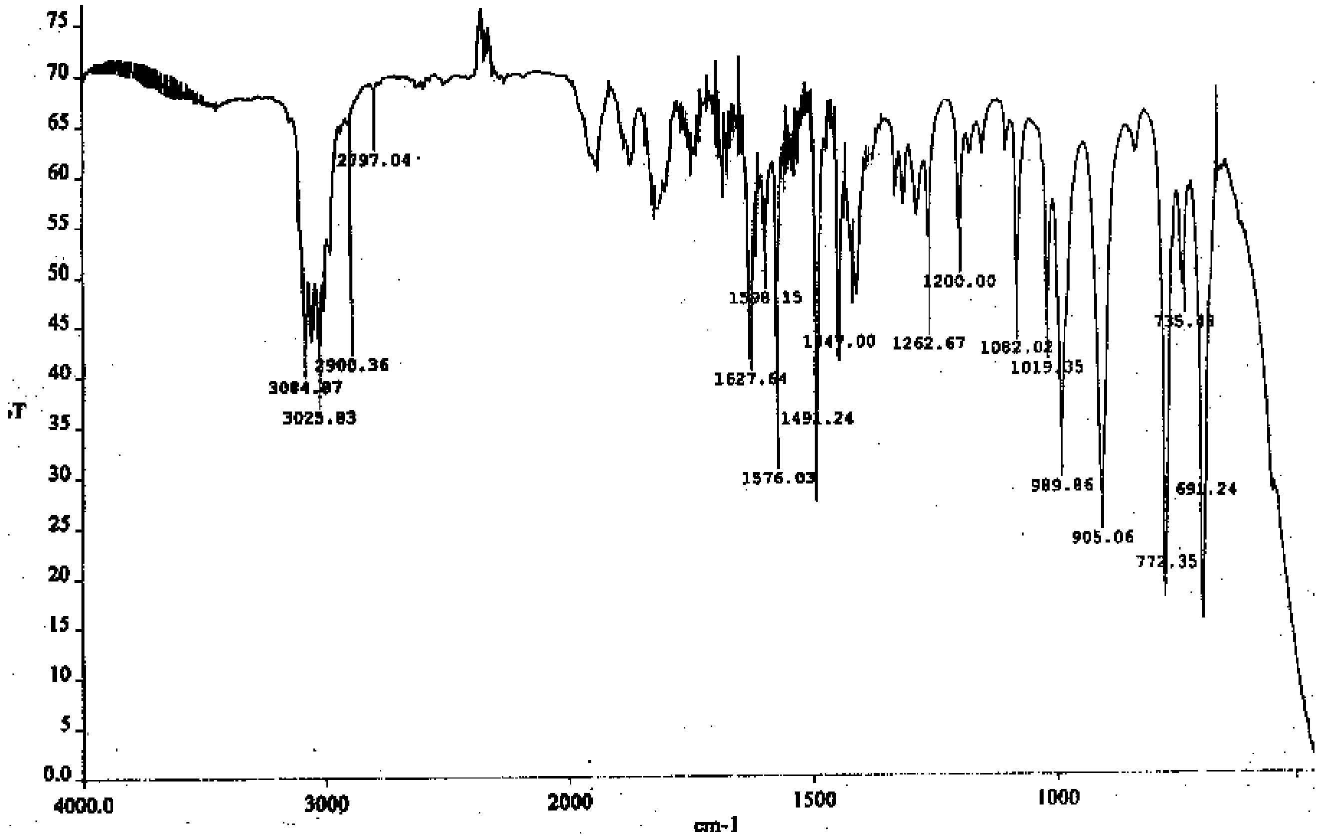

Figure 35 Infrared spectra of the mixed reactants and 2-(hydroxymethyl)anthraquinone at the reaction time of 30 minutes

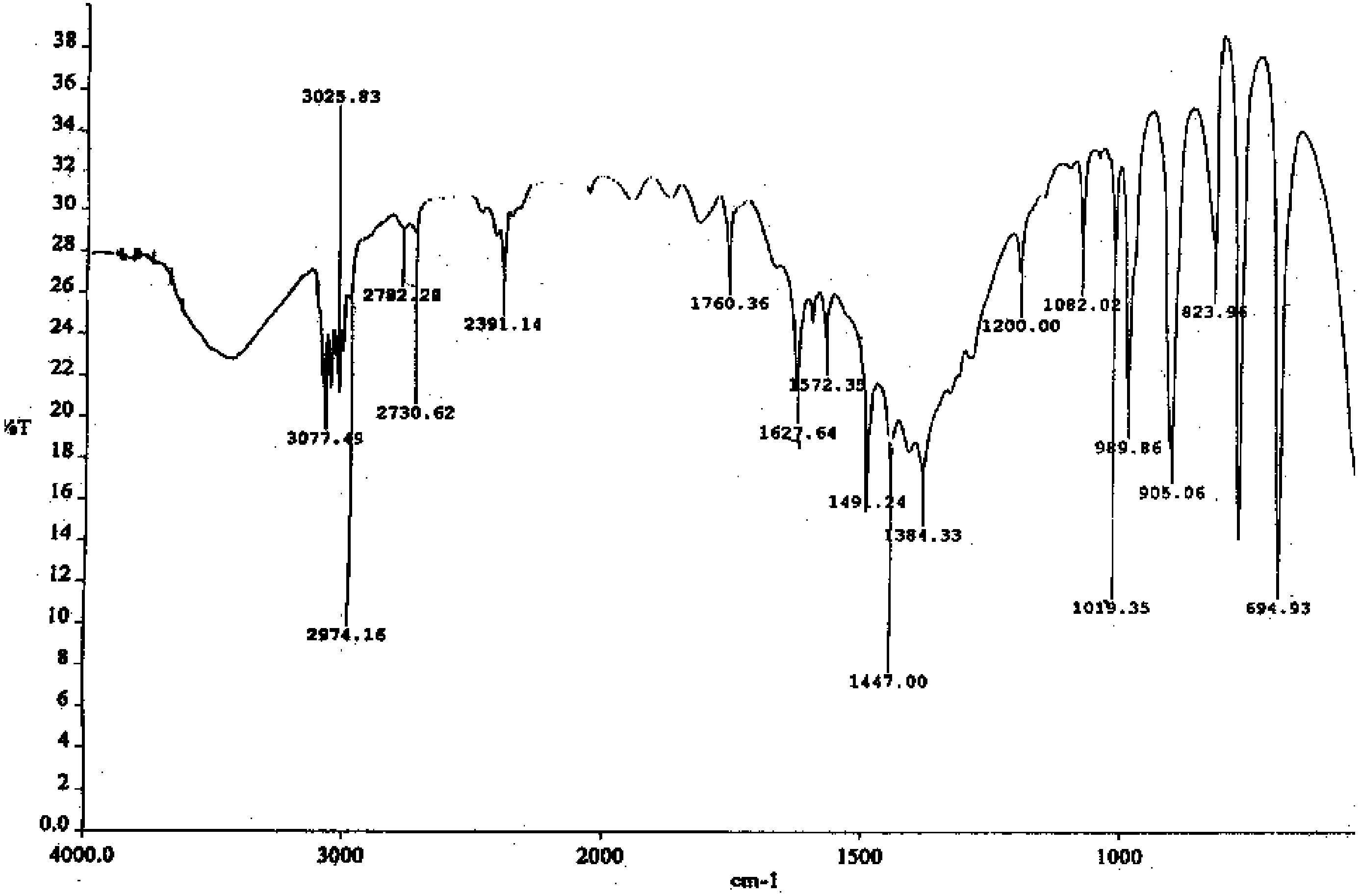

Figure 36 Infrared spectra of the mixed reactants and 2-(hydroxymethyl)anthraquinone at the reaction time of 2 hours

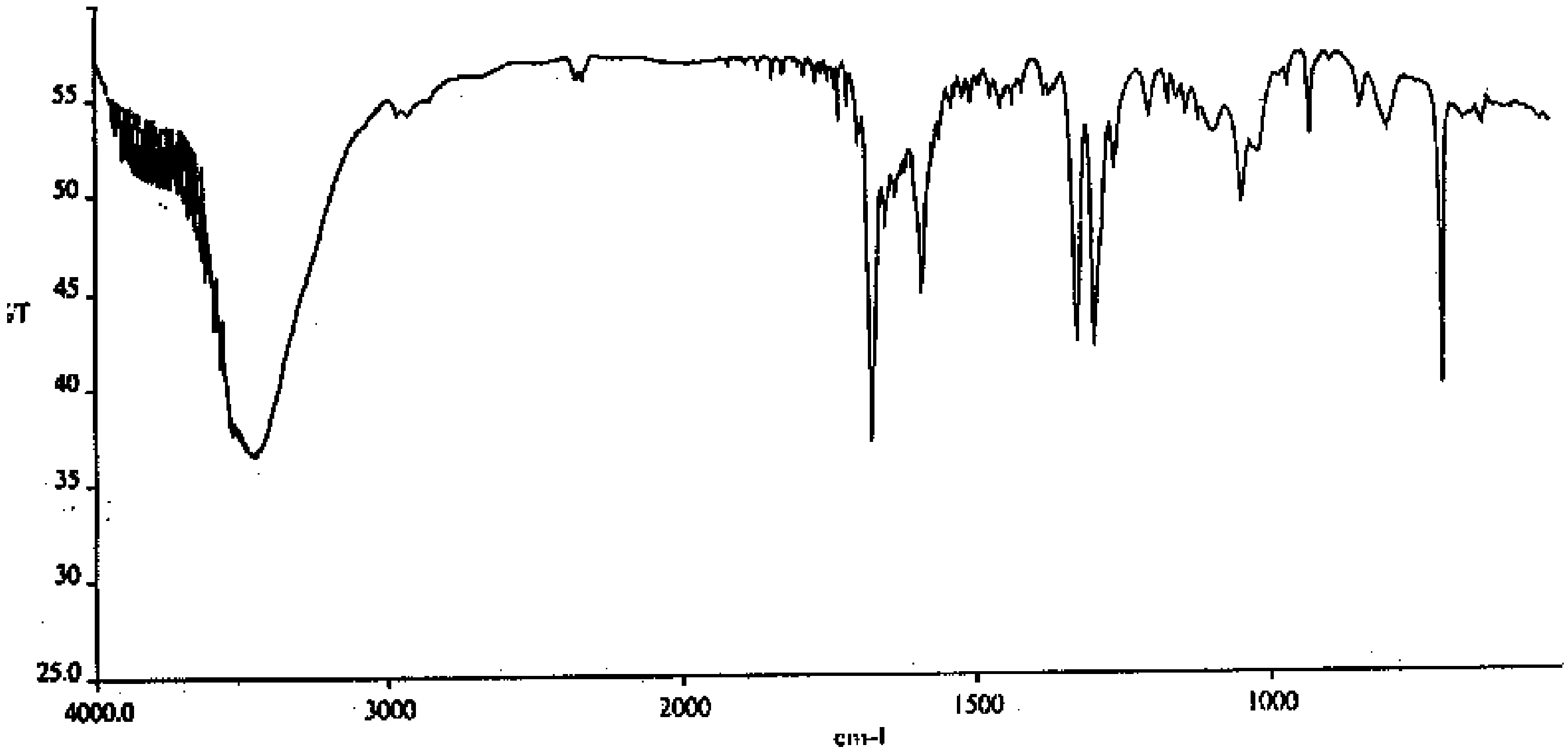

Figure 37 Infrared spectra of 2-(hydroxymethyl)anthraquinone

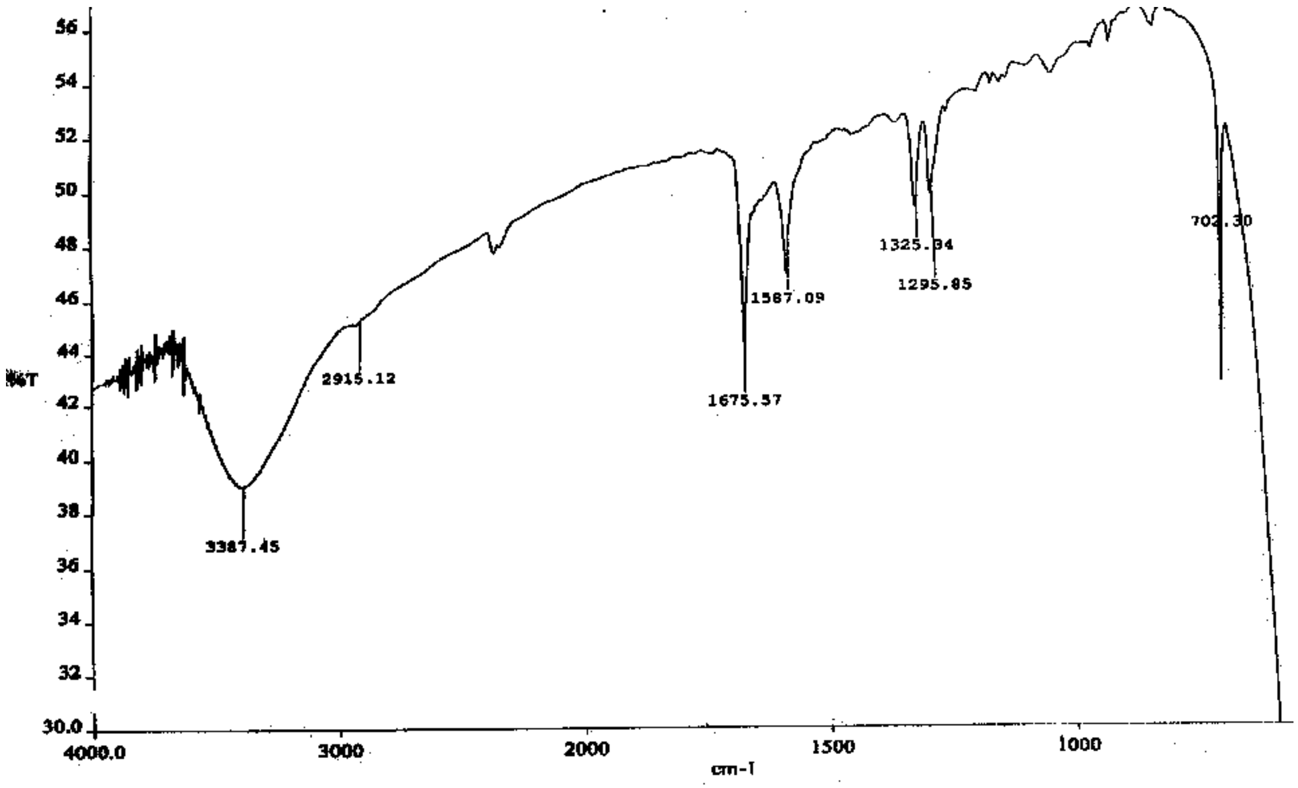

Figure 38 Infrared spectra of the catalyst species with the reaction time of 1 hour

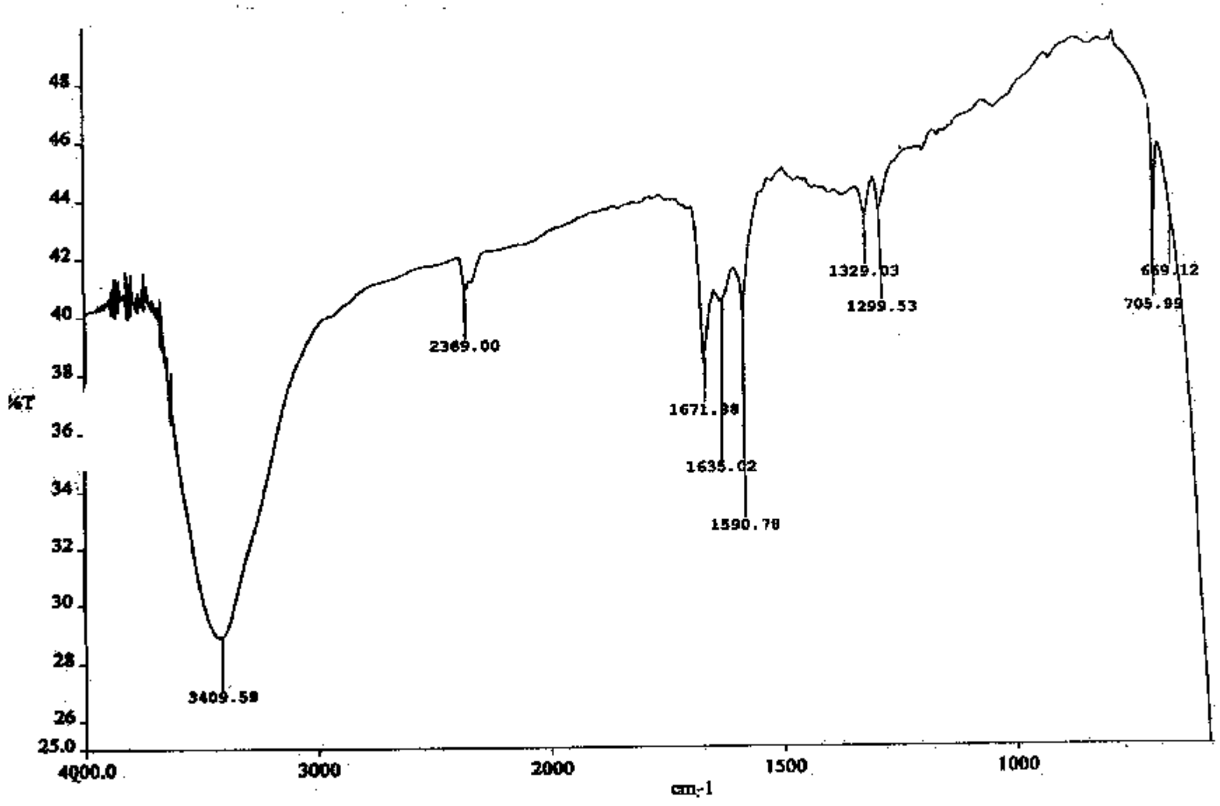

Figure 39 Infrared spectra of the catalyst species with the reaction time of 2 hours

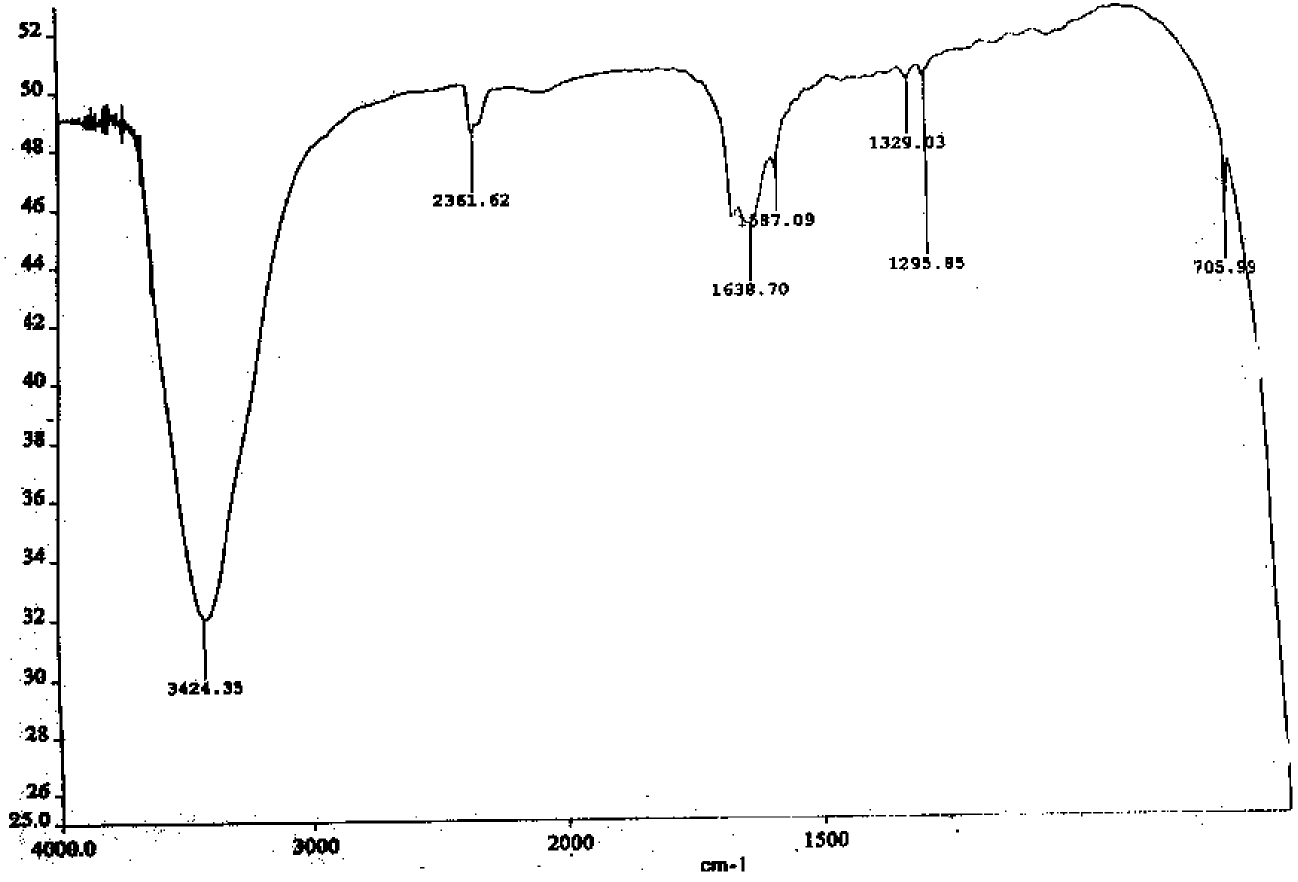

Figure 40 Infrared spectra of the catalyst species with the reaction time of 4 hours

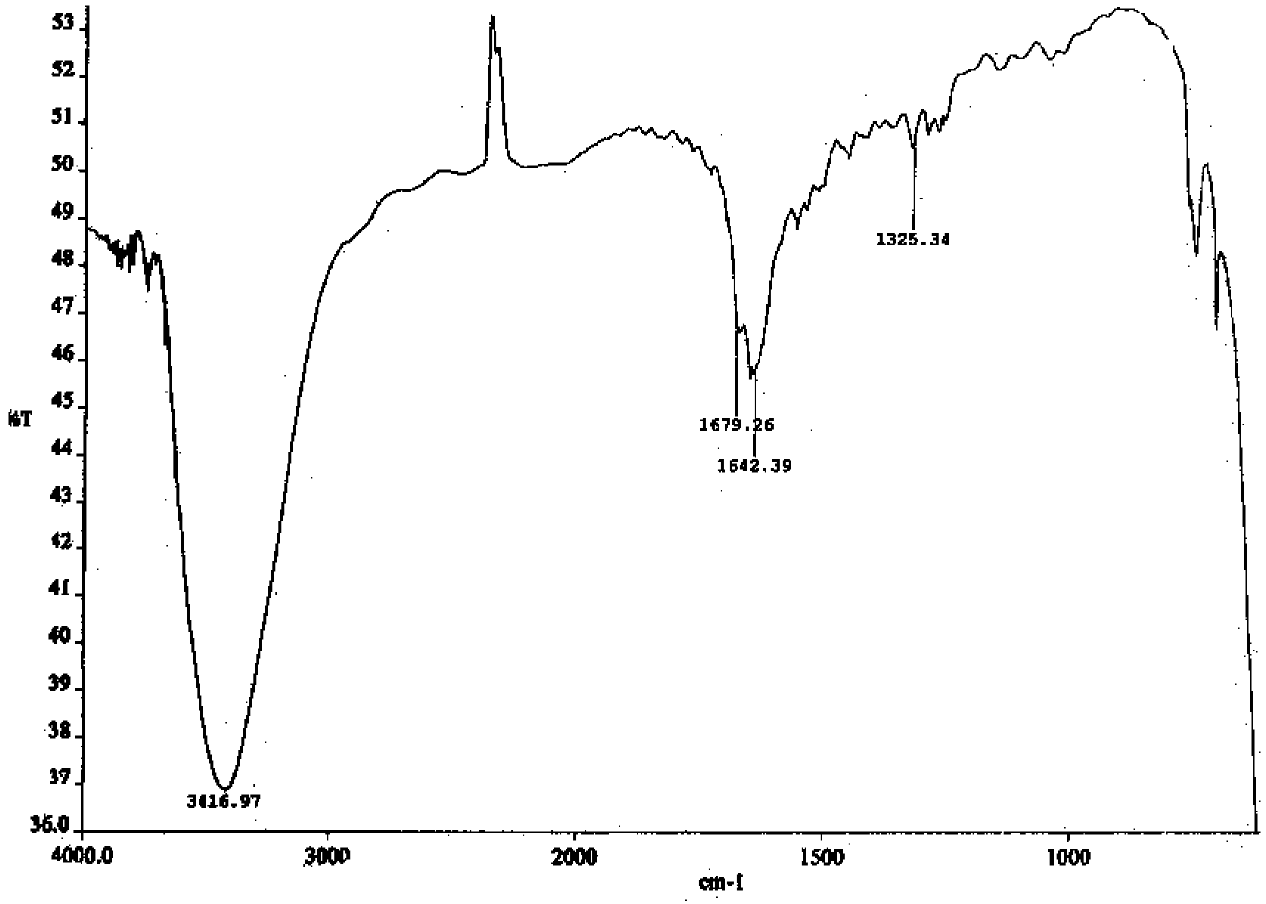

Figure 41 Infrared spectra of the catalyst species with the reaction time of 6 hours

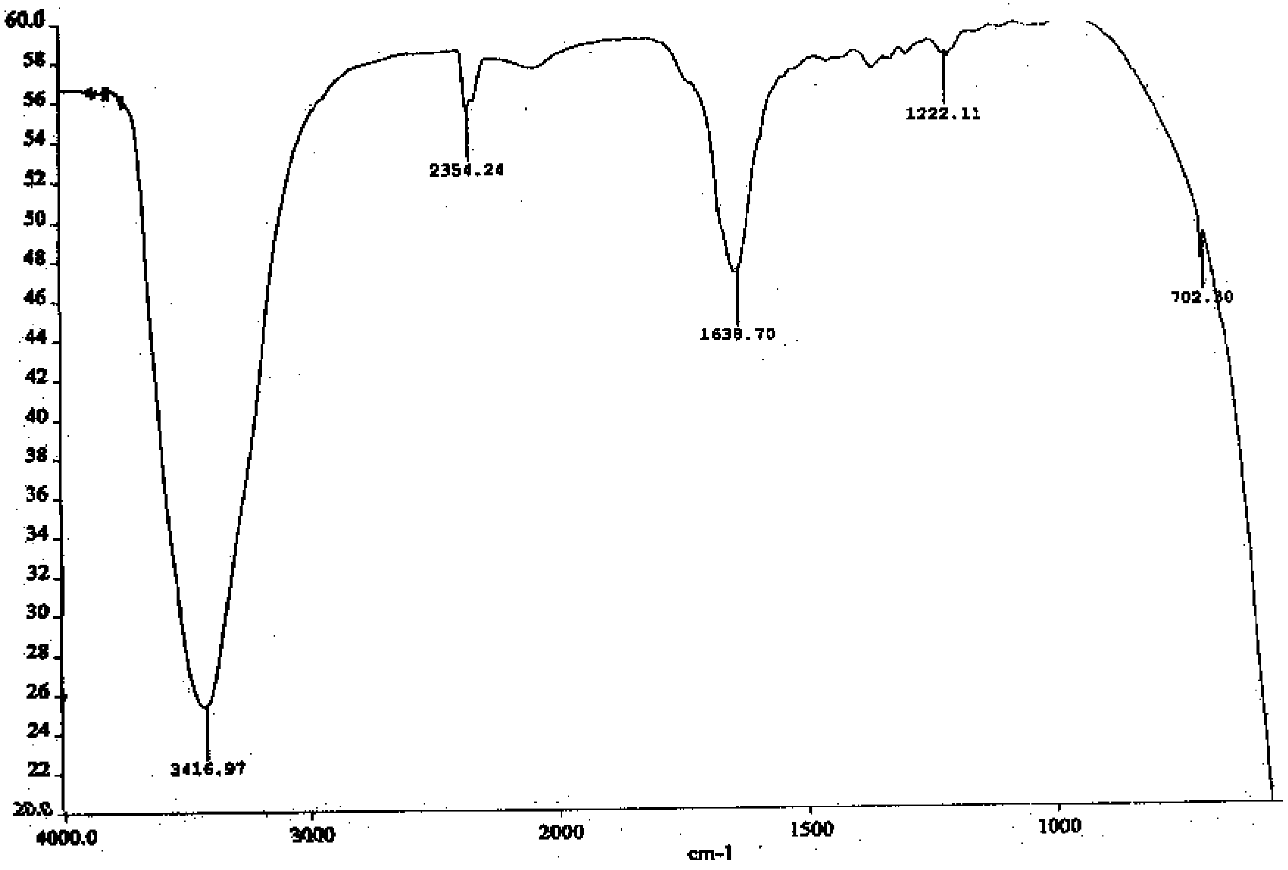

Figure 42 Infrared spectra of the catalyst species with the reaction time of 8 hours

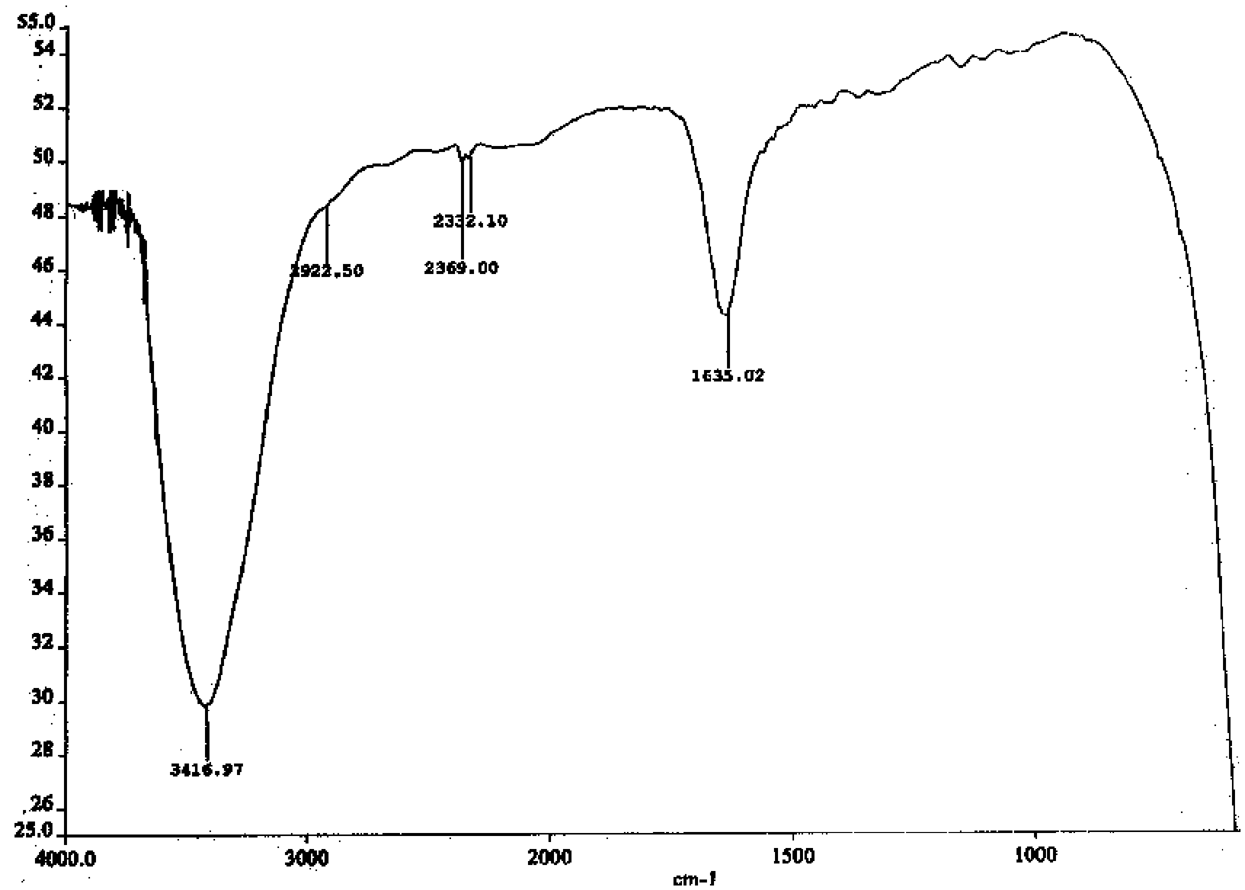

Figure 43 Infrared spectra of the catalyst species with the reaction time of 10 hours

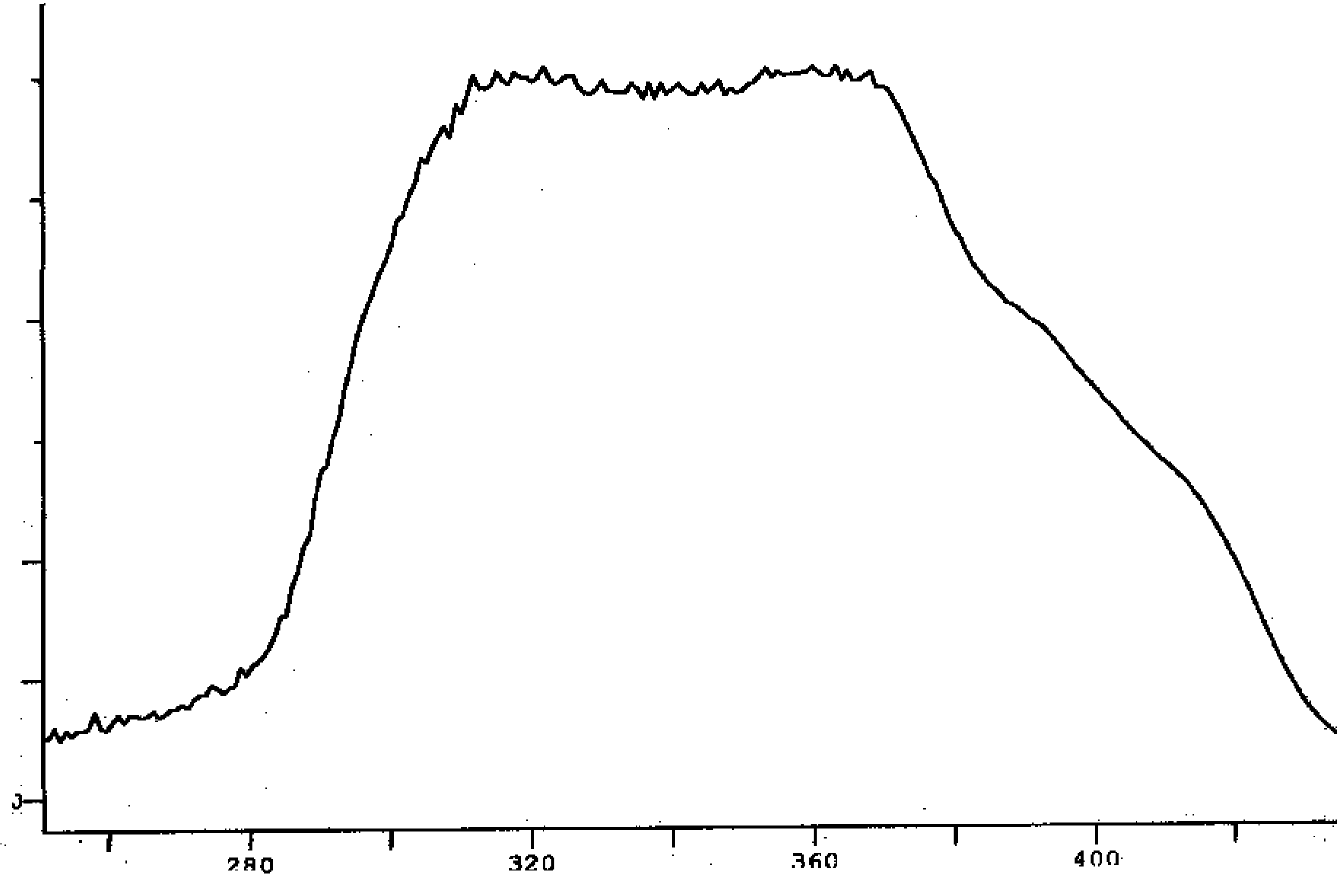

Figure 44 UV- spectrum of the catalyst species with the reaction time of 4 hours

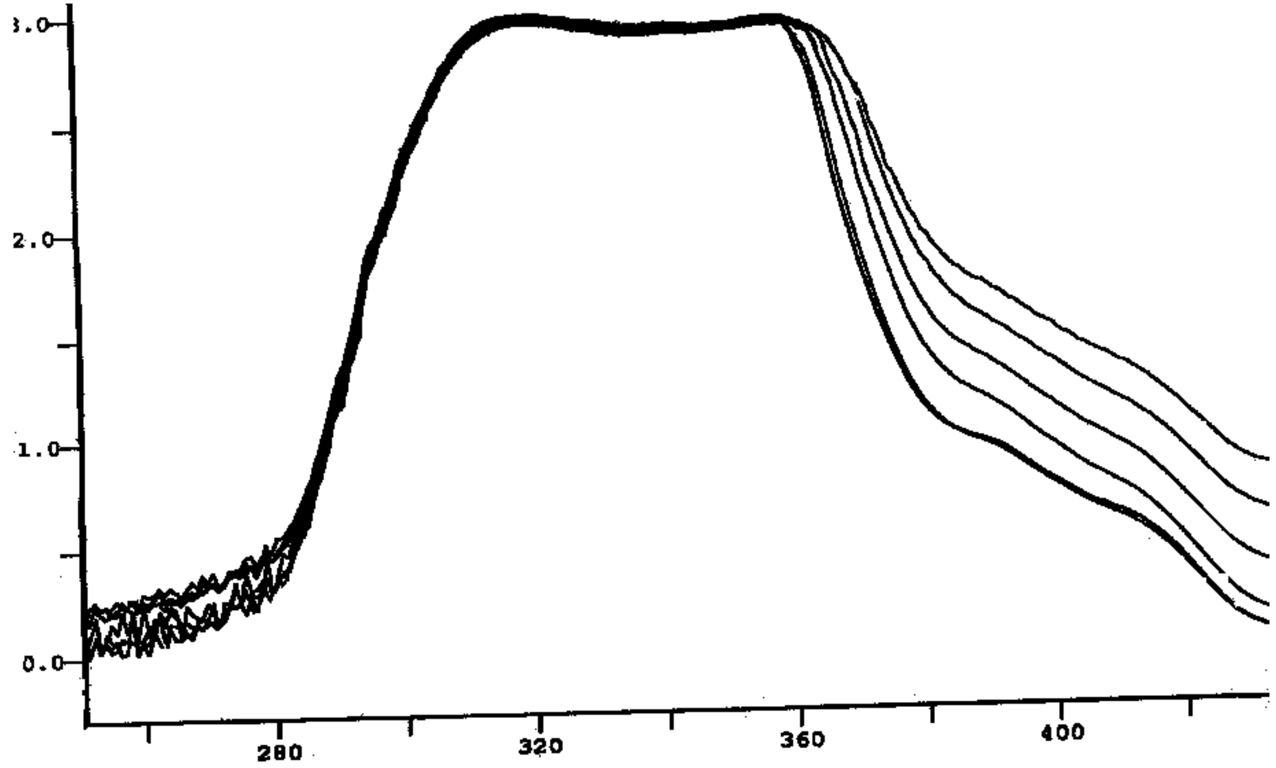

Figure 45 UV- spectrum of the catalyst species with the reaction time of 0,0.5, 1, 1.5, 2, 2.5, 3 hours

3.2.1.2 Propose mechanism of acid dissociation of dihydroxyanthraquinone (without silver species)

Dihydroxyanthraquinone have two hydroxyl functional groups as acidic group. They can be used as a proton donor for styrene epoxidation catalysis by m-chloroperbenzoic acid. This character is very strongly connected with their acid-base properties. In addition, acid dissociation depend on the stability of anion. The proposed mechanism of acid dissociation of 1, 2-dihydroxanthraquinone is shown in Figure 46.

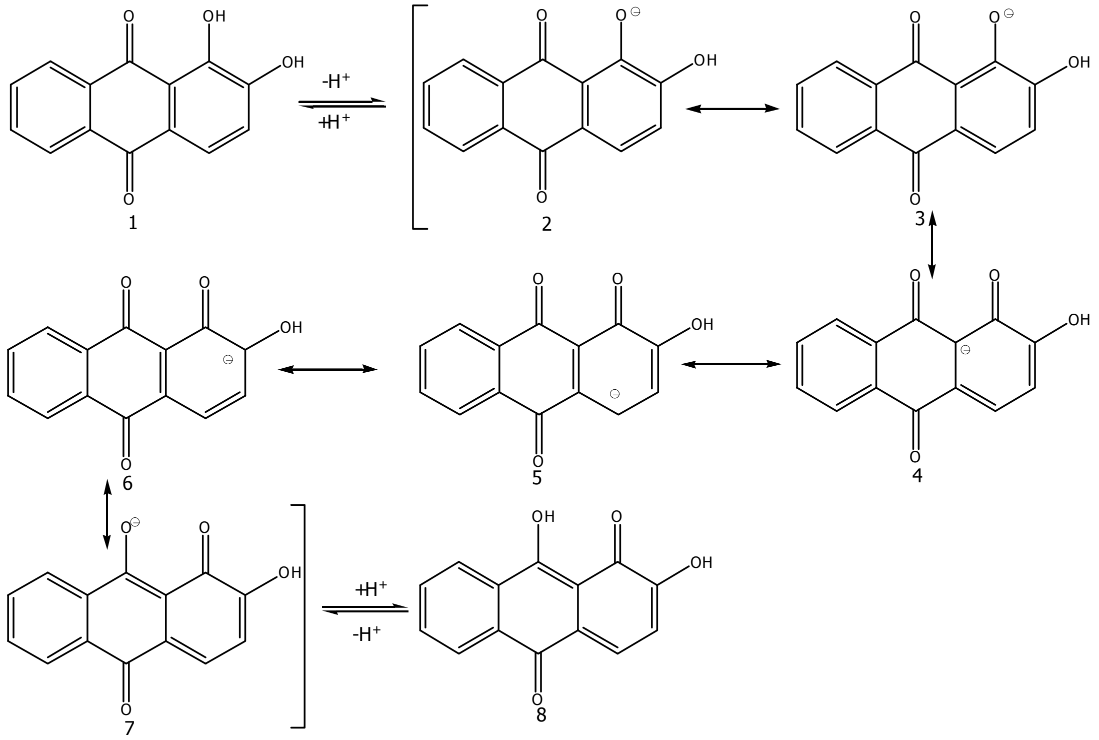

Figure 46 The proposed mechanism of acid dissociation of 1, 2-dihydroxy anthraquinone

Anion of 1, 2-dihydroxyanthraquinone (Figure 46) and 1, 4-dihydroxyanthraquinone (Figure 47) were not stable when they loss proton to the oxidant molecule. Some resonance structures of 1, 2-dihydroxyanthraquinone and 1, 4-dihydroxyanthraquinone the negative charge is located on the carbon atom to which - OH is attached. Although - OH releases electron to all position of the ring, it does so most strongly to the carbon atom nearest it; consequently, These resonance structures are particularly not stable structures.

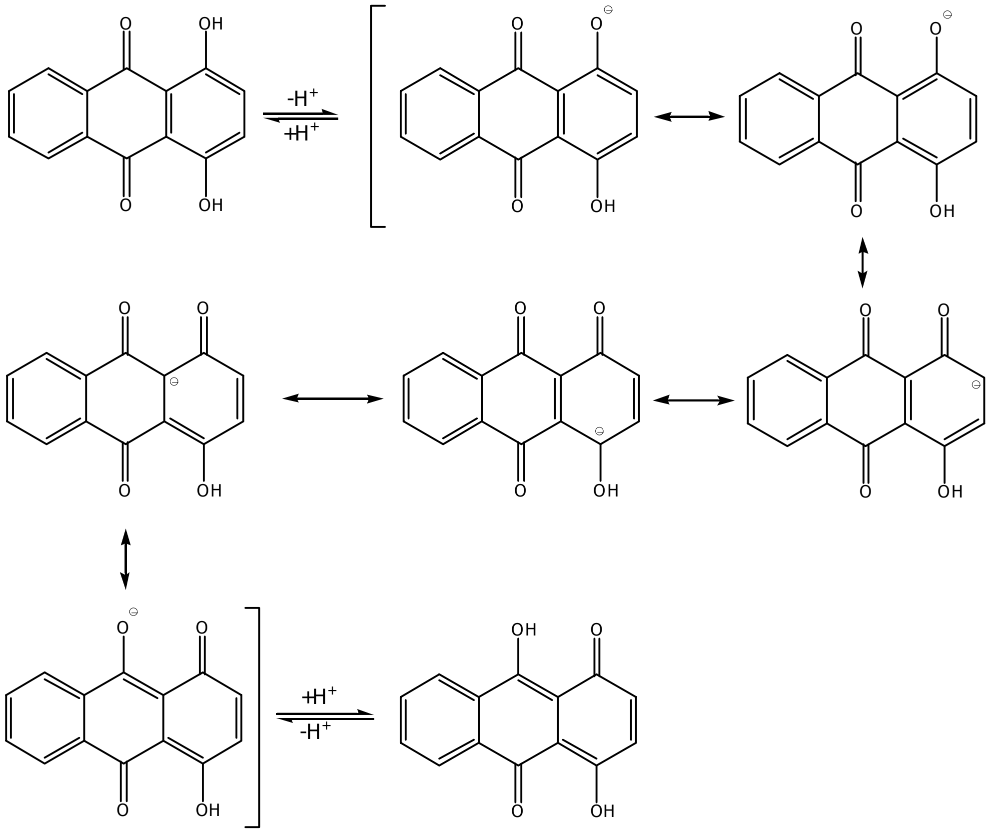

Figure 47 Acid dissociation of 1, 4-dihydroxyanthraquinone

The protons were difficult to dissociate but 1, 5- hydroxyanthra - quinone and 1, 8 - dihydroxyanthraquinone do not have this effect because the negative charge is not located on the carbon atom to which - OH is attached. Their anions were more stable than 1, 2 - dihydroxyanthraquinone and 1, 4 - dihydroxyanthraquinone when they loss proton to mCPBA; however 1, 5-dihydroxyanthraquinone has less efficient than 1, 8-dihydroxyanthraquinone. 1, 5-dihydroxyanthraquinone has five resonance structures. Nagative change can be delocalized to carbon atoms and it destroyed by the original carbonyl group to from new hydroxyl group. The species of quinone were studied by UV-Visible spectroscopic technique. The UV spectra of them were shown in Figure 50-61.

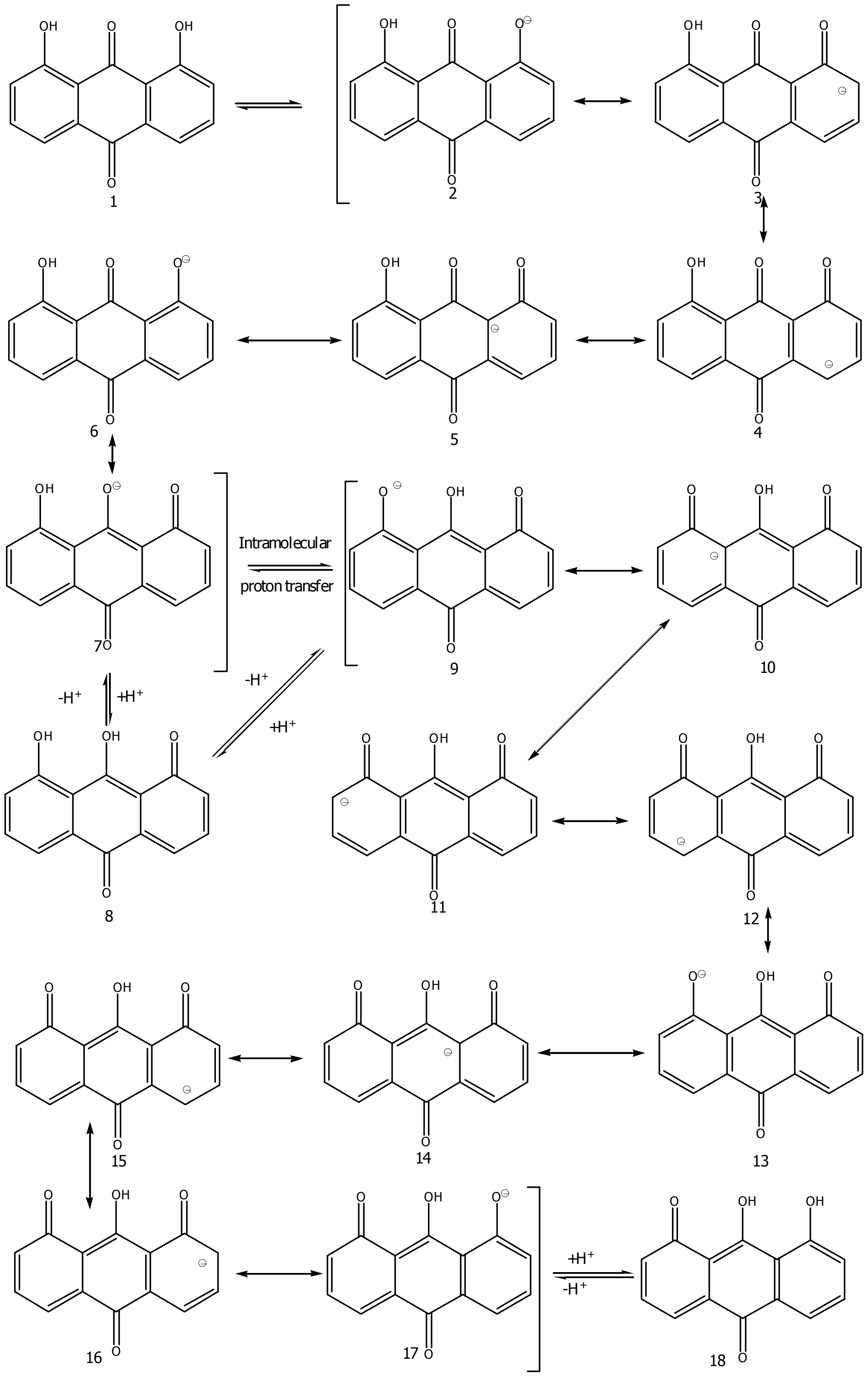

Figure 48 Acid dissociation of 1, 8-dihydroxyanthraquinone

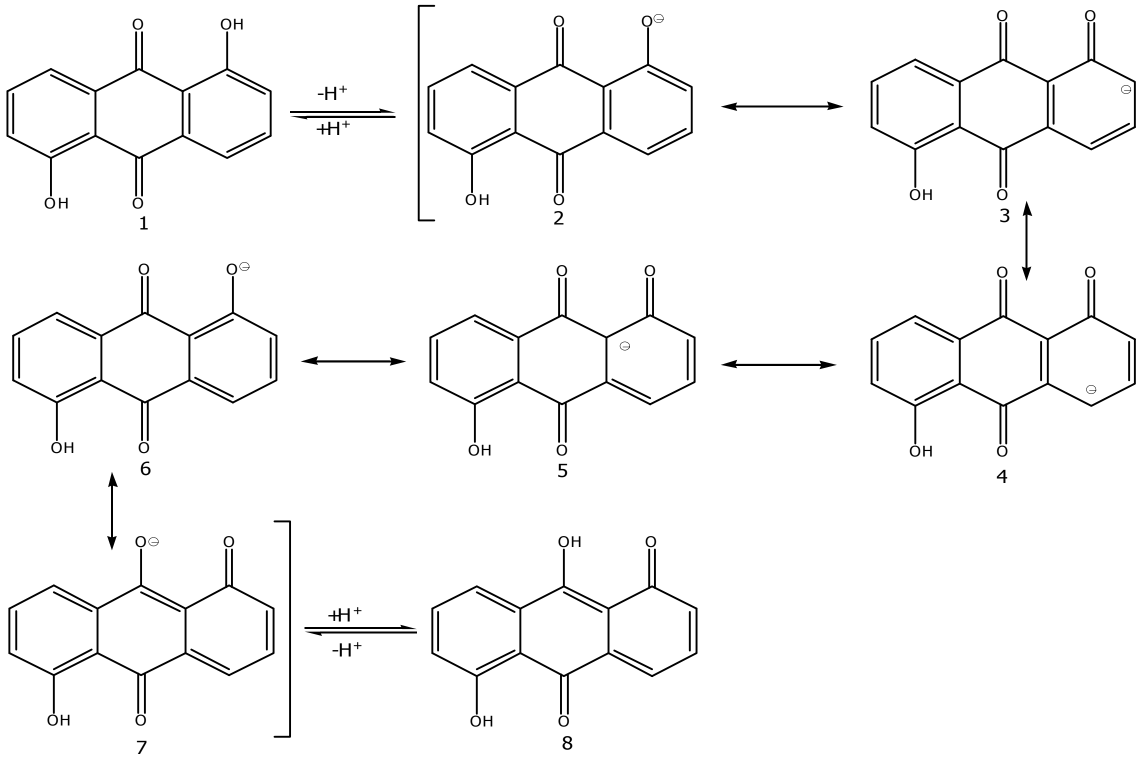

Figure 49 Acid dissociation of 1, 5-dihydroxyanthraquinone

Refer to Figure 46, when sodium hydroxide was added to the solution, it became immediately blue. It is due to the formation of an anion in the catalytic system. The band in the range 520 - 620 nm. are increased but it changes to the original colour very fast. Figure 52 is the absorbtion band of 1, 4 - dihydroxyanthraquinone in acid solution. The absorbtion band in the catalytic styrene epoxidation system is shown the like band in Figure 50. It can refer that the deprotonation of 1, 4 - dihydroxyanthraquinone is hard to occur in the catalytic system because the solution has high proton concentration that occurred from mCPBA. In addition from Figure 51, anionic are not stable. It can not give proton to the oxidant.

Refer to the Figure 53 - 55, the absorbtion bands of 1, 2 - dihydroxyanthraquinone in various condition are not change. This can be due to the fact that 1, 2 - dihydroxyanthraquinone is the poor proton donor.

In the case of 1, 8 - dihydroxyanthraquinone, the solution becomes red when it reacts with NaOH. It produces conjugated anion base (Figure 57). The absorbtion band in the range 450 - 650 nm. was increased but the solution change to the original colour in 20 minute. These indicates that anion are more stable than conjugated base of 1, 4 - dihydroxyanthraquinone and 1, 2 - dihydroxyanthraquinone. Refer to the Figure 56 and 58. The absorbtion bands were the like band. It shows that the anion changes to original structure by protonation.

From the Figure 60, the absorbtion band of 1, 5 - dihydroxyanthraquinone has low absorptin in the range 450 nm. and 650 nm. than 1, 8 - dihydroxyanthraquinone when NaOH was added to this solution. The red solution became to yellow in a few minutes. The anion were less stable than the case of 1, 8 - dihydroxyanthraquinone. In Figure 59, anion occurred in the system because the absorbtion band in the range 450 - 650 is increased. The anion did not occur when the acid was added to the solution Figure 61 is showed that 1, 5-dihydroxyanthraquinone is not reacting with acid.

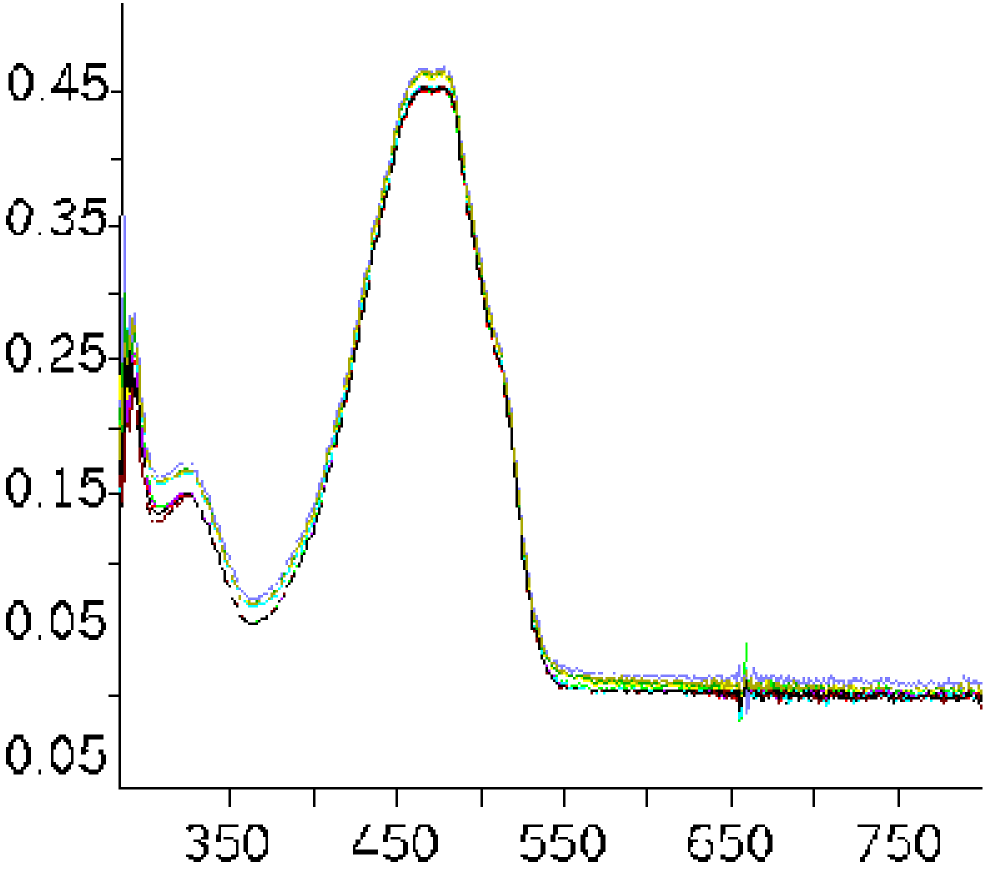

Figure 50 UV-spectrum of 1, 4-dihydroxyanthraquinone in catalytic system

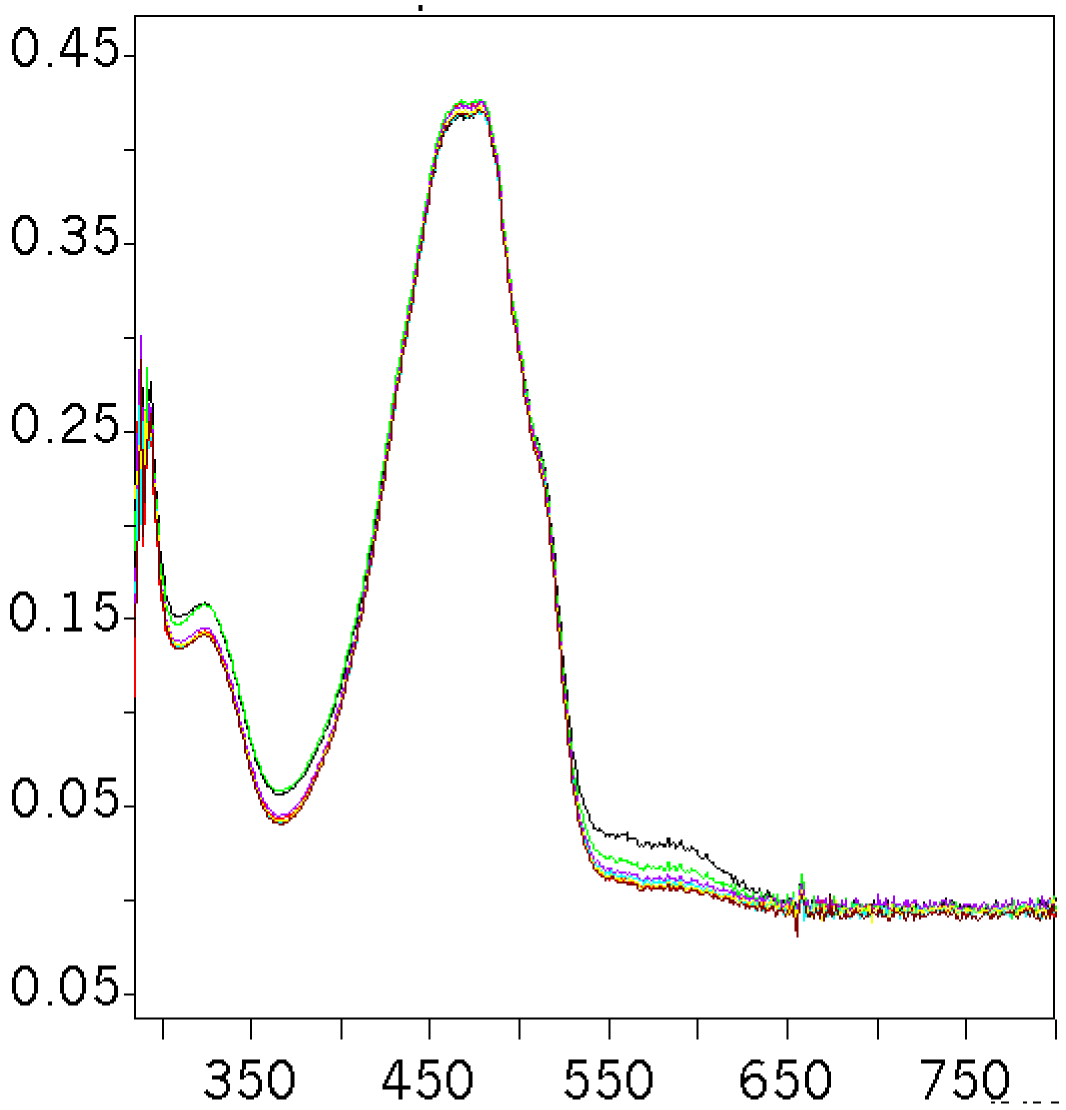

Figure 51 UV-spectrum of 1, 4- dihydroxyanthraquinone in catalytic system (Added 0.001 M NaOH 0.05 ml)

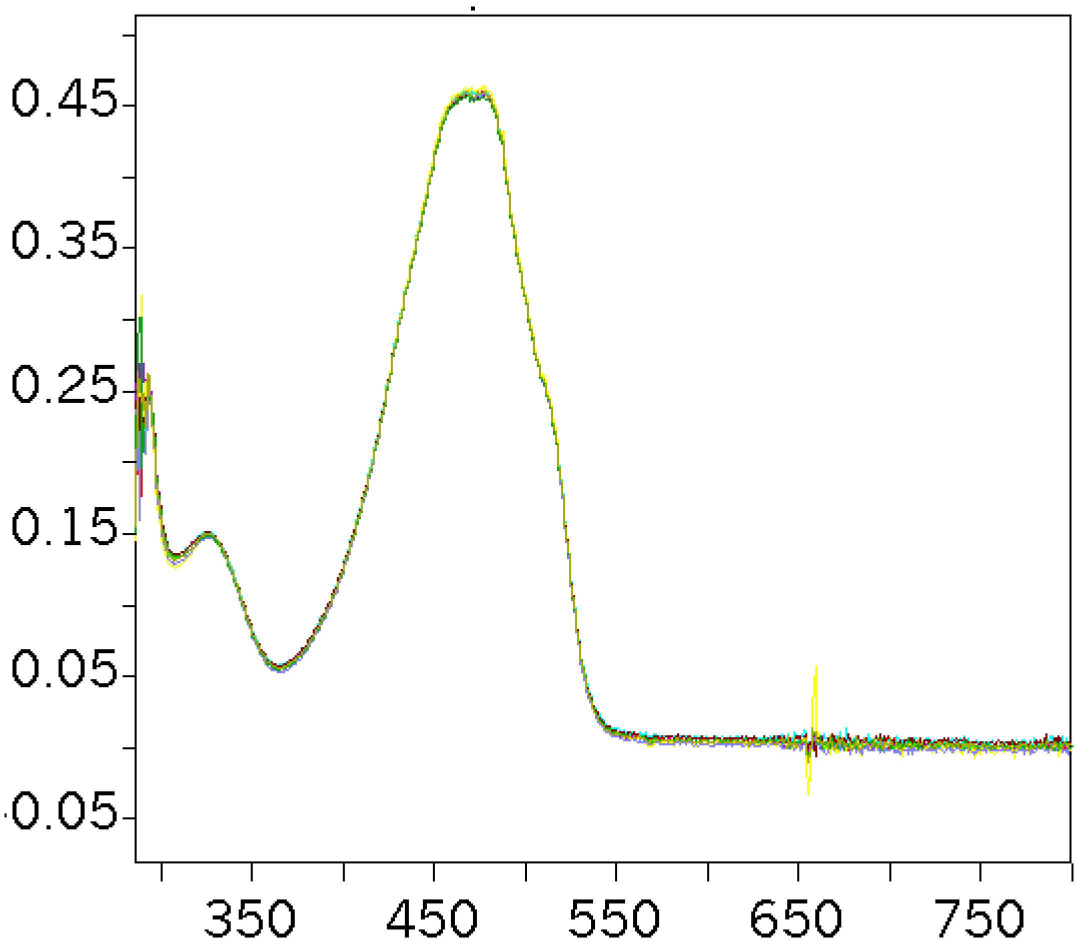

Figure 52 UV-spectrum of 1, 4- dihydroxyanthraquinone in catalytic system (Added 0.001 M HNO_3 0.05 ml)

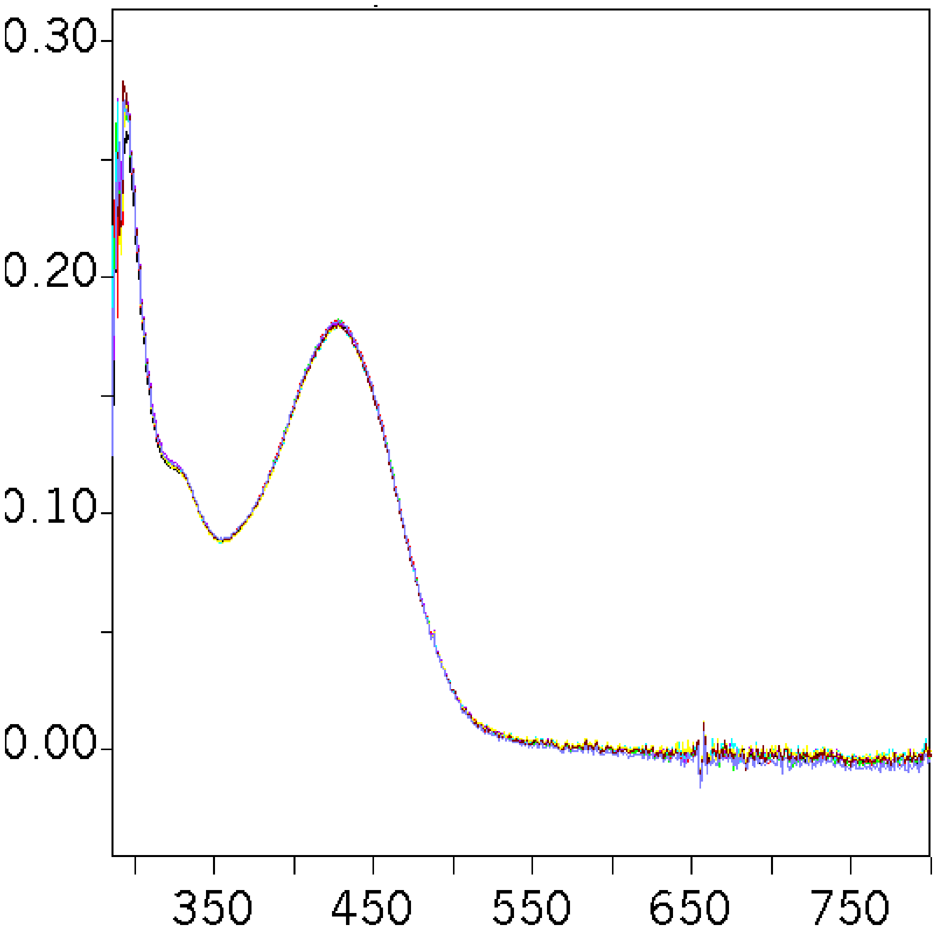

Figure 53 UV-spectrum of 1, 2- dihydroxyanthraquinone in catalytic system

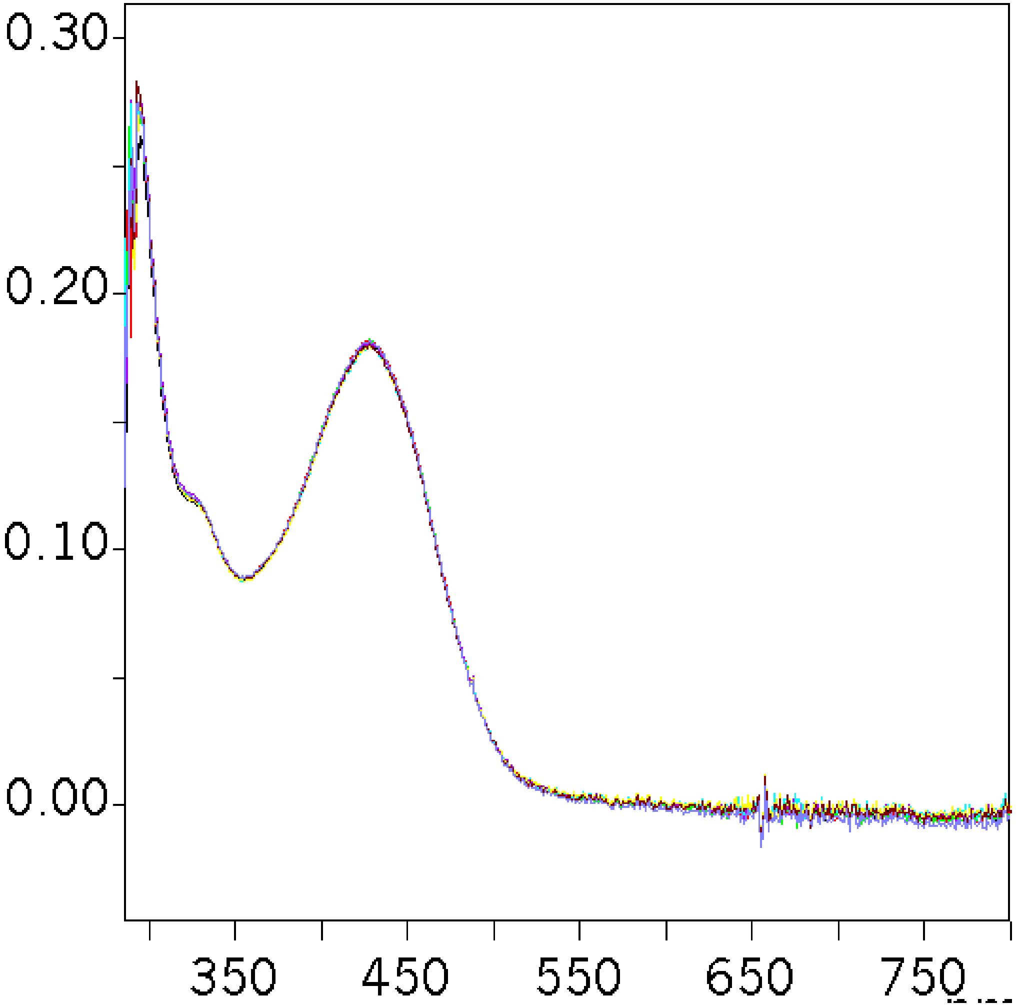

Figure 54 UV-spectrum of 1, 2- dihydroxyanthraquinone in catalytic system (Added 0.001 M NaOH 0.05 ml)

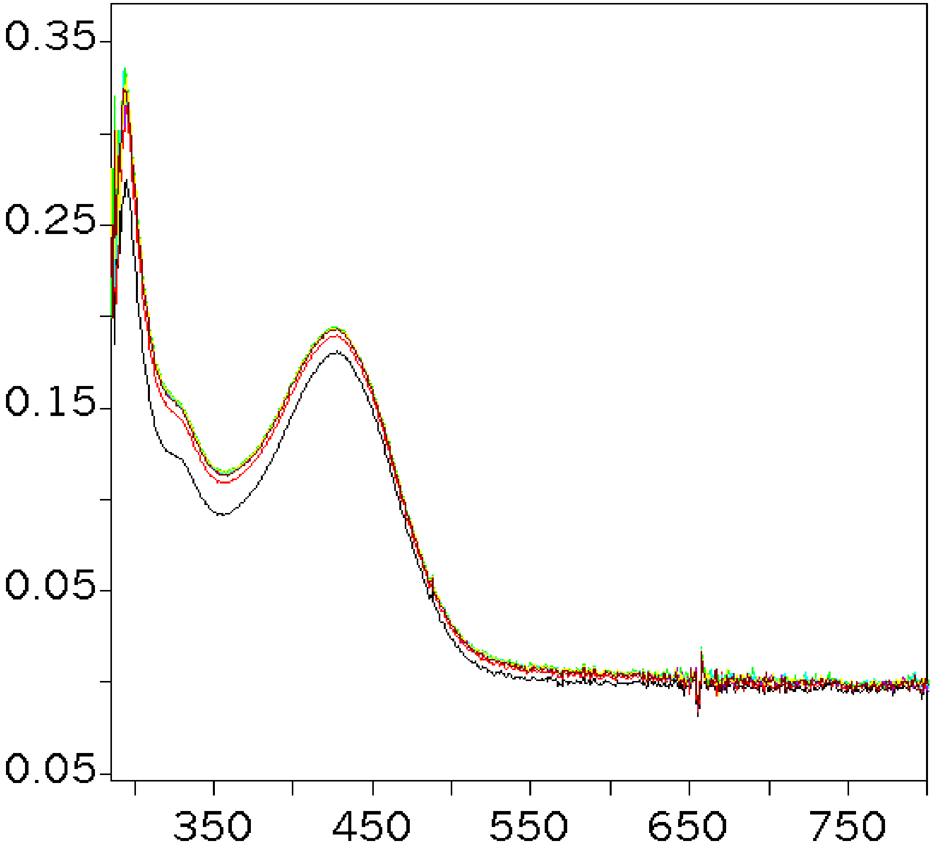

Figure 55 UV-spectrum of 1, 2-dihydroxyanthraquinone in catalytic system (Added 0.001 M HNO_3 0.05 ml)

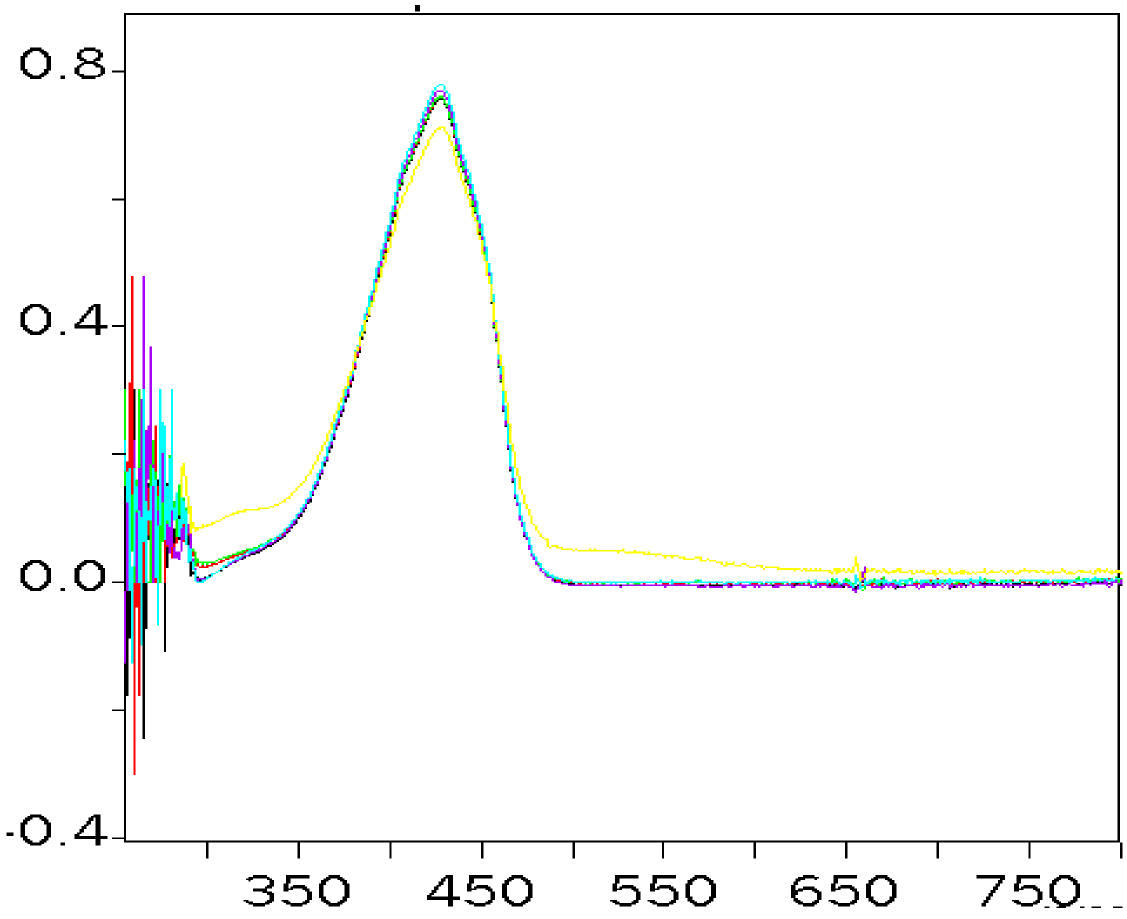

Figure 56 UV-spectrum of 1, 8-dihydroxyanthraquinone in catalysis system

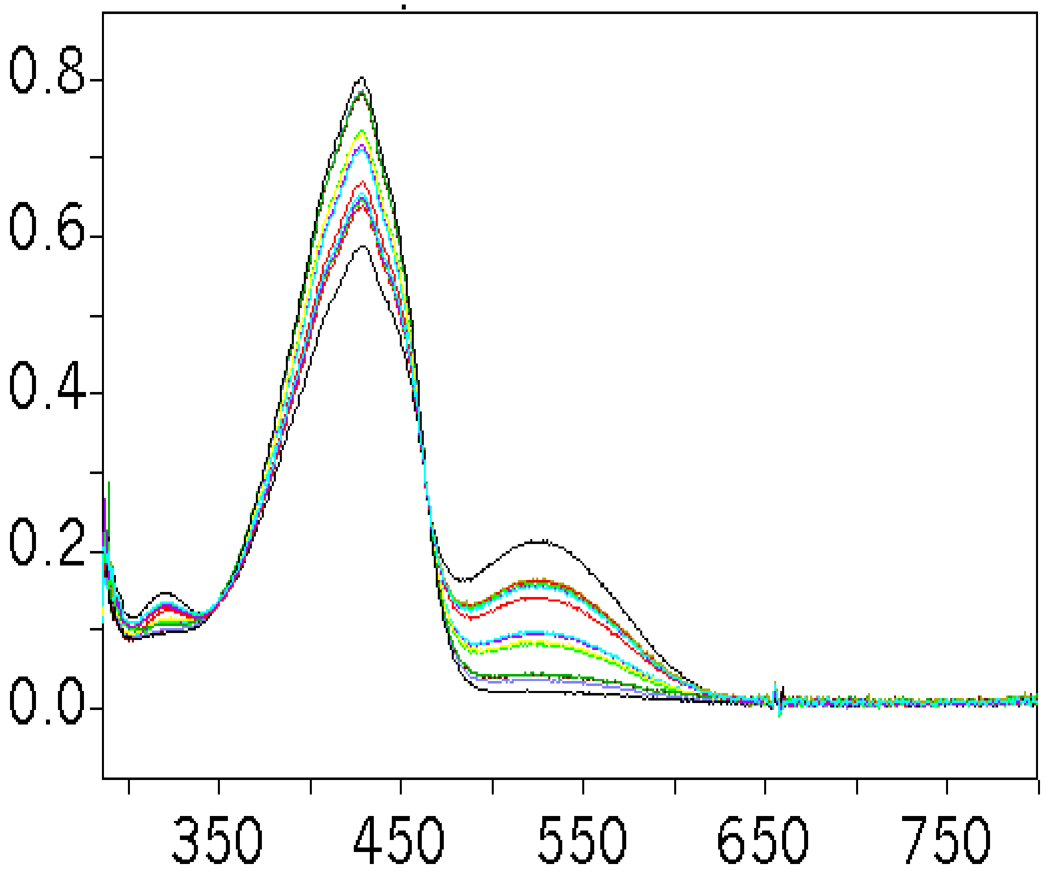

Figure 57 UV-spectrum of 1, 8- dihydroxyanthraquinone in catalytic system (Added 0.001 M NaOH 0.05 ml)

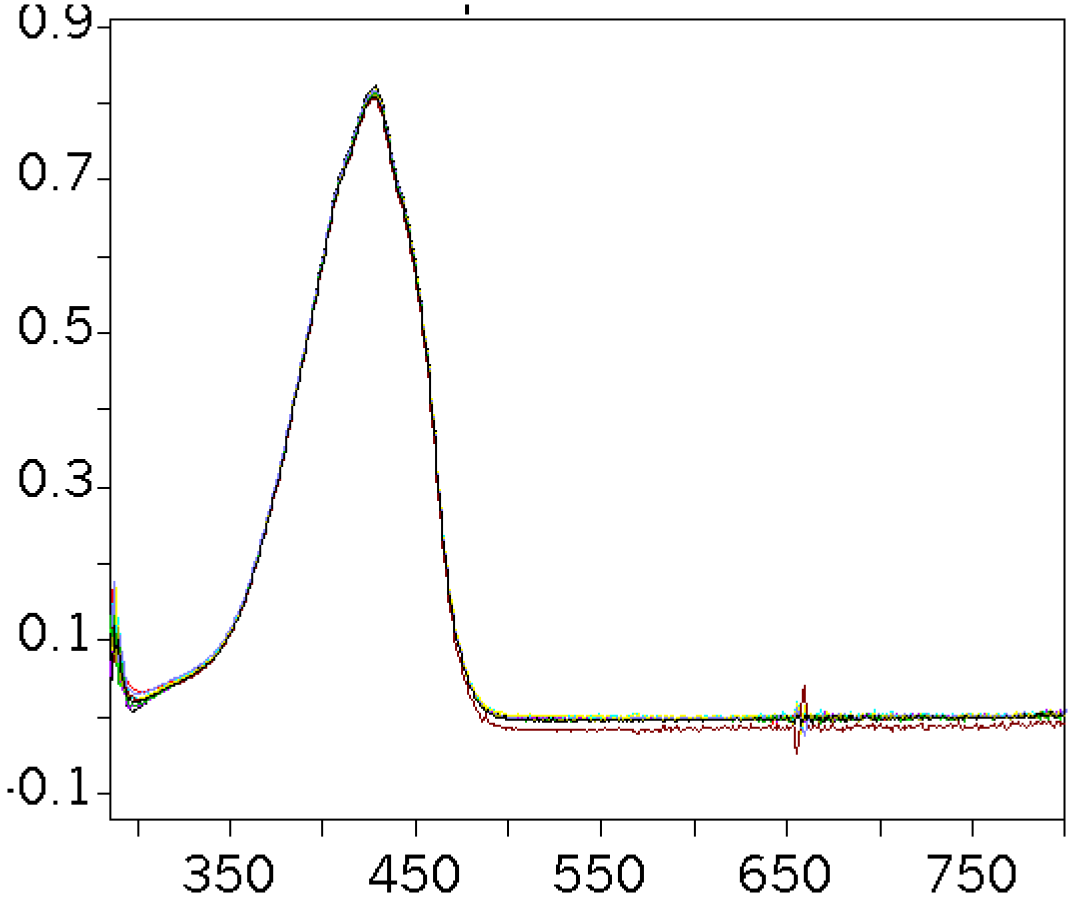

Figure 58 UV-spectrum of 1, 8-dihydroxyanthraquinone in catalysis system (Added 0.001 M HNO_3 0.05 ml)

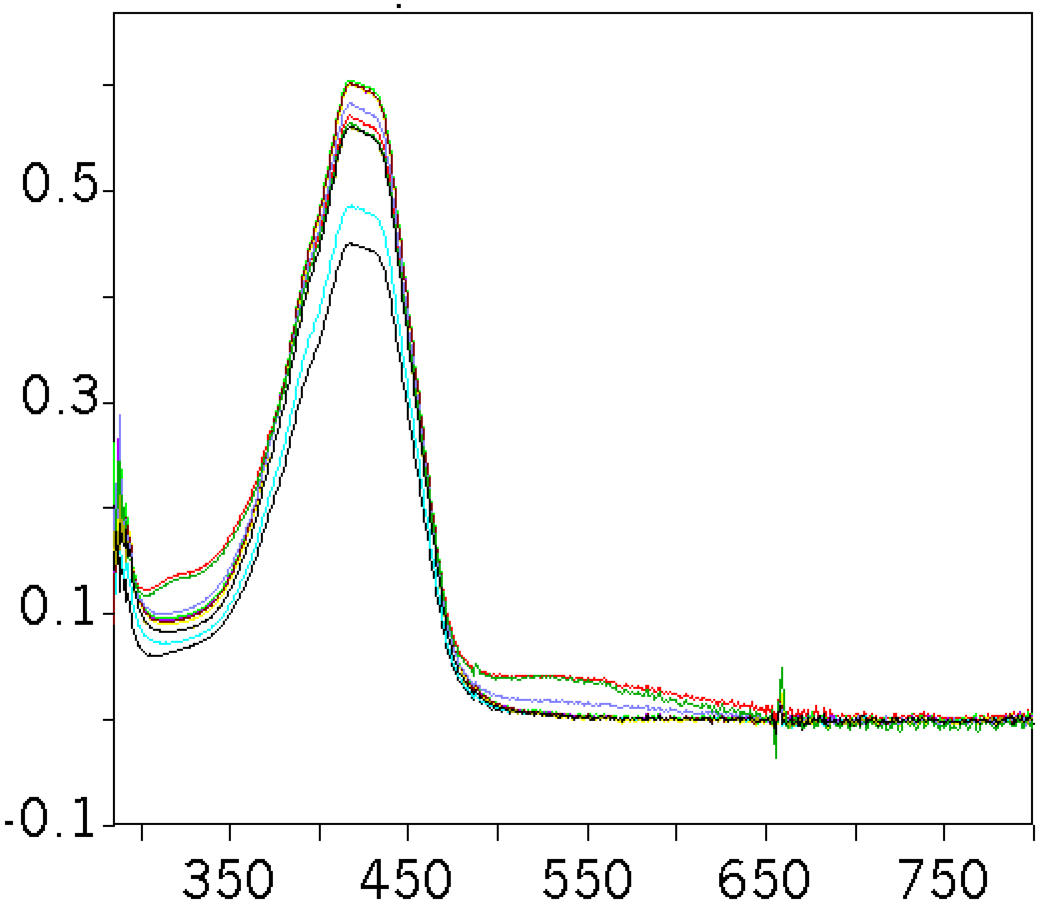

Figure 59 UV-spectrum of 1, 5-dihydroxyanthraquinone in catalysis system

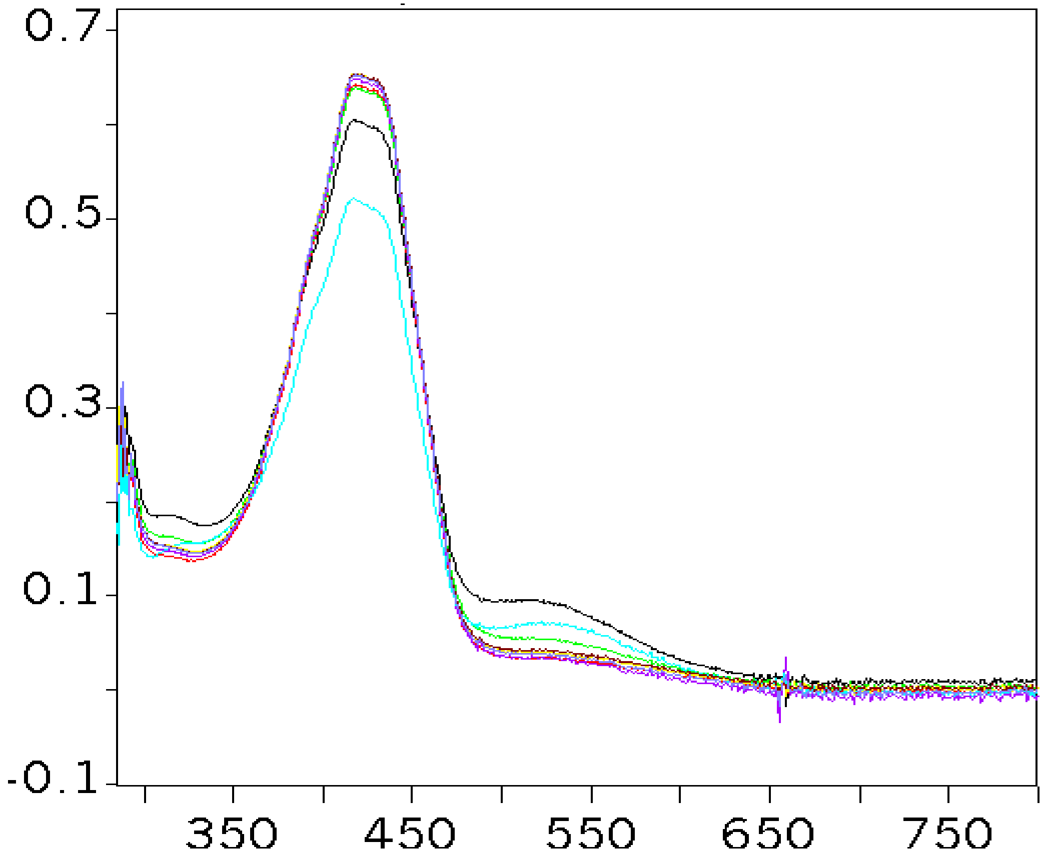

Figure 60 UV–spectrum of 1, 5– dihydroxyanthraquinone in catalytic system (Added 0.001 M NaOH 0.05 ml)

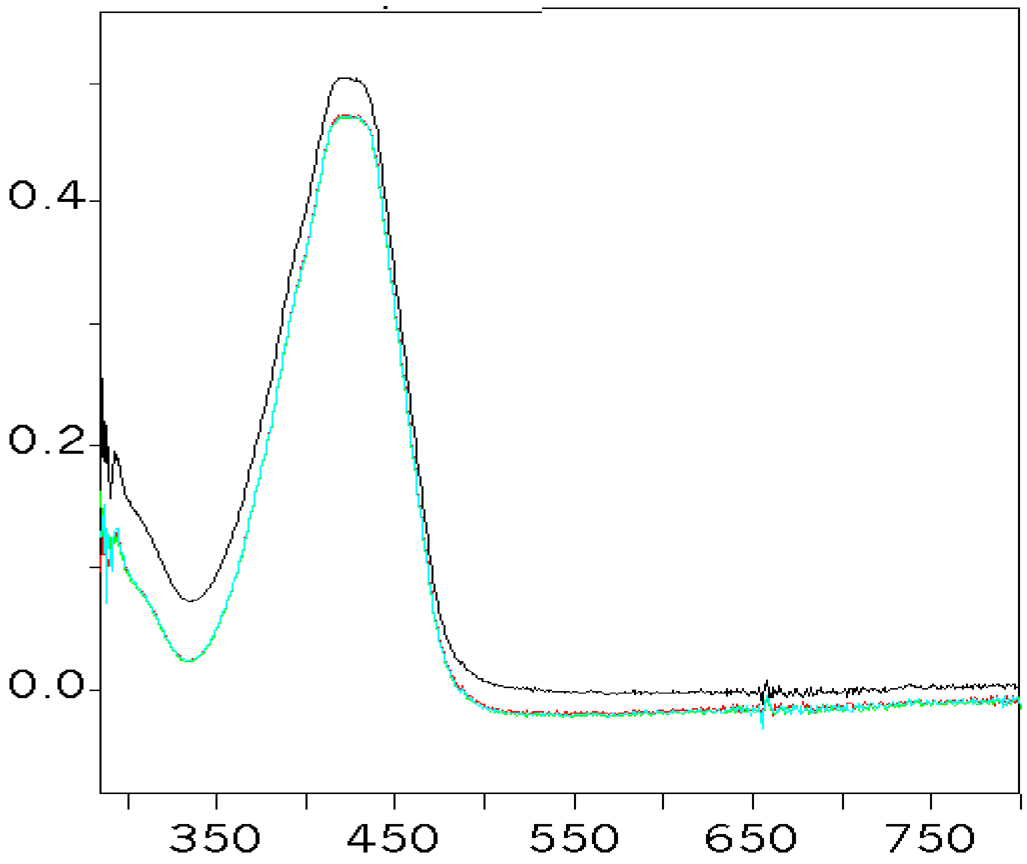

Figure 61 UV-spectrum of 1, 5-dihydroxyanthraquinone in catalysis system (Added 0.001 M HNO_3 0.05 ml)

3.2.2 Concentration effect of silver nitrate, 1, 2-dihydroxyanthraquinon, 1, 8- dihydroxyanthraquinone on styrene epoxidation rate

3.2.2.1 Concentration effect of 1, 2 - dihydroxyanthraquinone and 1, 8- dihydroxyanthraquinone

Catalytic efficiency of styrene epoxidation by mCPBA depends upon how the reaction rate varies with the concentration of catalyst. Plots of increasing styrene oxide versus time when used various concentration of catalyst are shown in Figure 62 - 63. Plot of the rate vesus the concentrations of catalyst are shown in Figure 64-65.

Refer to the Figure 62 - 65, 1, 8-dihydroxyanthraquinone gave the highest epoxidation rate when the 0.0047 g of this quinone is used as catalyst. The rate is 6×10^{-5} molar /minute. The rate does not change when much than 0.08 g is used. It was expected that the protons were decreased by carbonyl of excess 1, 8 - dihydroxyanthraquinone. 1, 2-dihydroxyanthraquinone has low epoxidation rate. The rate is 3×10^{-5} molar/minute. Although the epoxidation rate at 1 minute of 0.001047 g and 0.00160 g of this quinone were higher than the low concentration, the rate decreases when the reaction time increases. It can indicate that 1, 2 - dihydroxyanthraquinone has low efficiency styrene epoxidation than 1, 8 - dihydroxyanthraquinone.

3.2.2.2 Reaction rate of styrene epoxidation study that used 1, 2-DHAQ, 1, 8-DHAQ and silver nitrate as catalyst

Refer to Figure 60-71, the styrene epoxidation rate was decreased when the concentration of silver nitrate was increased. It can refer that Ag^+ inhibited styrene epoxidation. This is supported by IR spectra as shown in the Figure66-67. This is the mixed of styrene and silver nitrate spectra that compared with the styrene spectra in Figure 67. It has the strong absorb peak at 1400 cm^{-1} in C=C aromatic region. It shows that Ag^+ induce with electron of benzene ring, making the electron defective alkene that it has low efficiency for epoxidation by mCPBA.

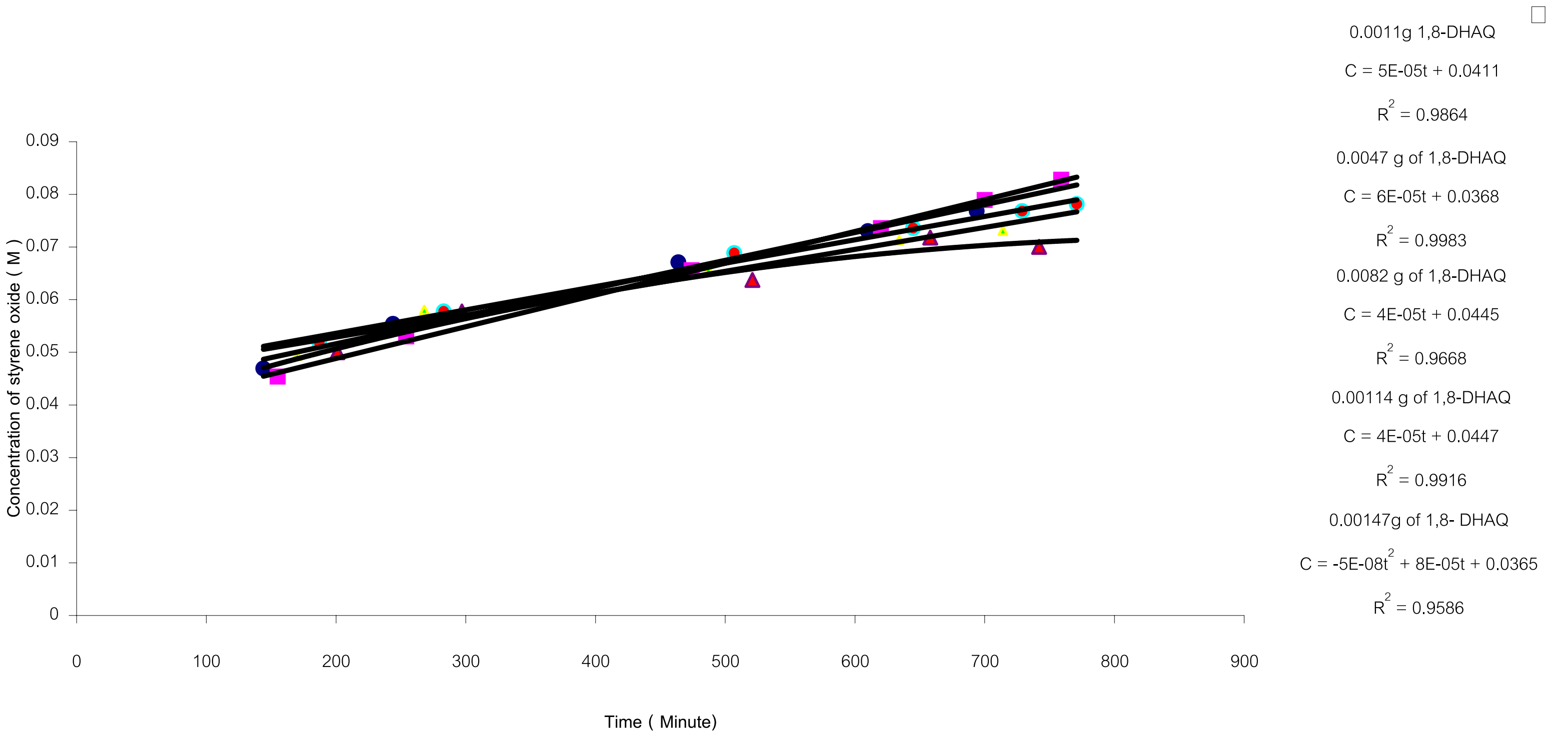

Figure 62 Styrene epoxidation catalysis by various concentration of 1, 8-dihydroxyanthraquinone

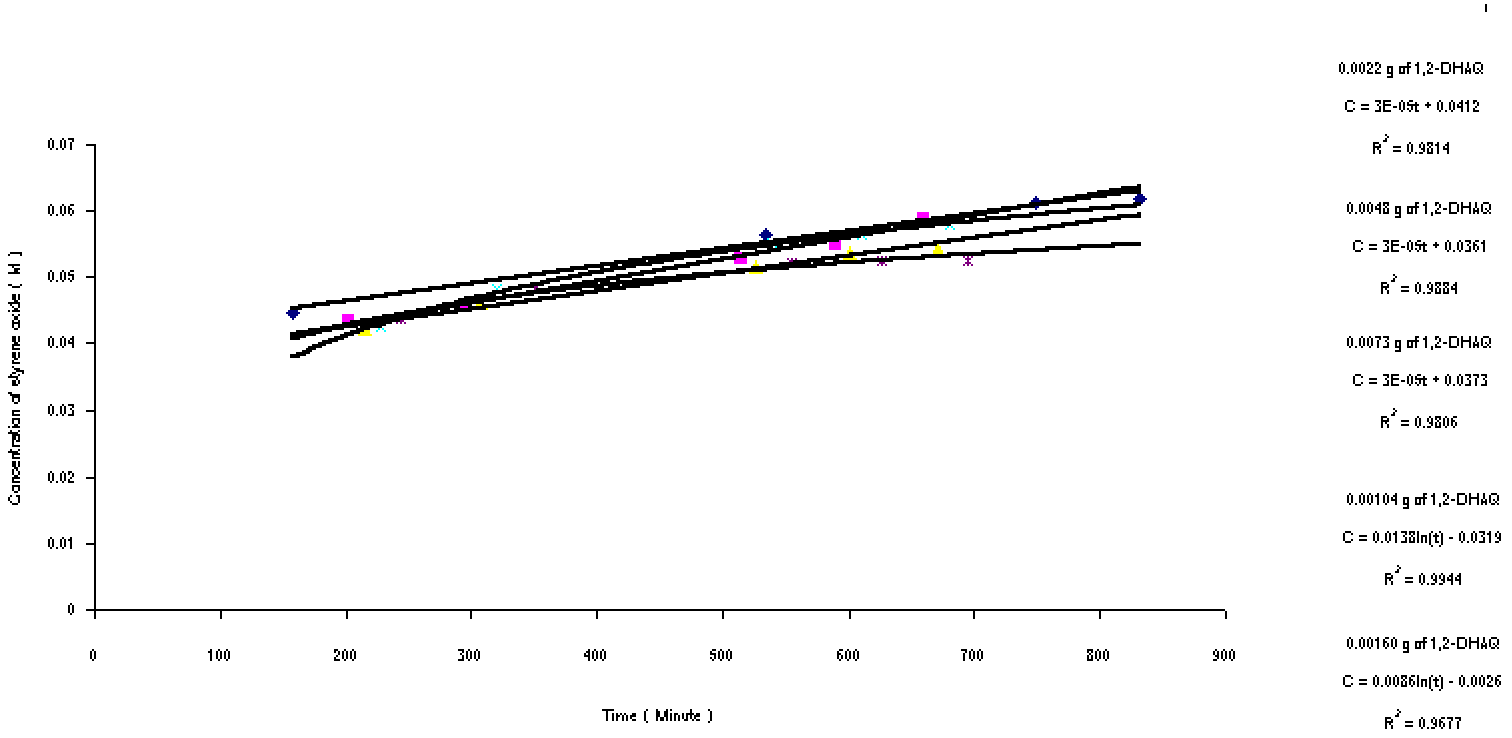

Figure 63 Styrene epoxidation catalysis by various concentration of 1, 2-dihydroxyanthraquinone

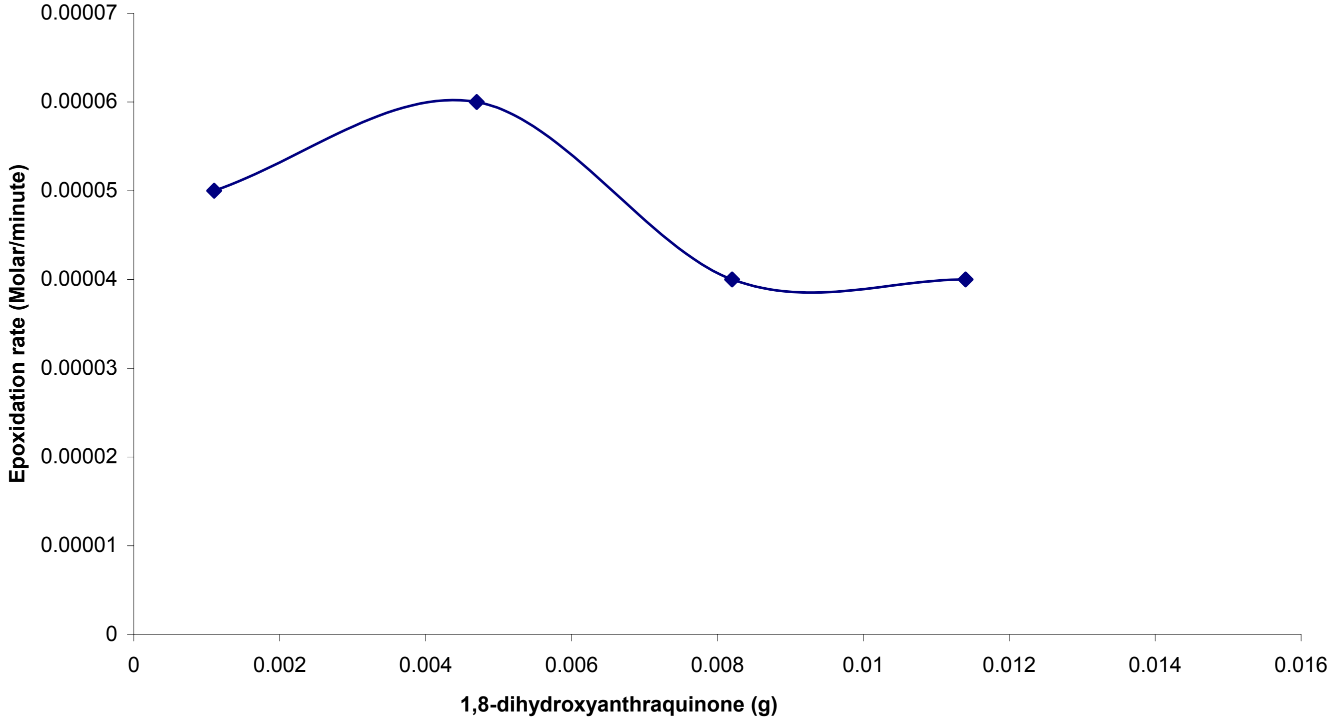

Figure 64 Plot of styrene epoxidation rate versus concentration of 1, 8-dihydroxyanthraquinone

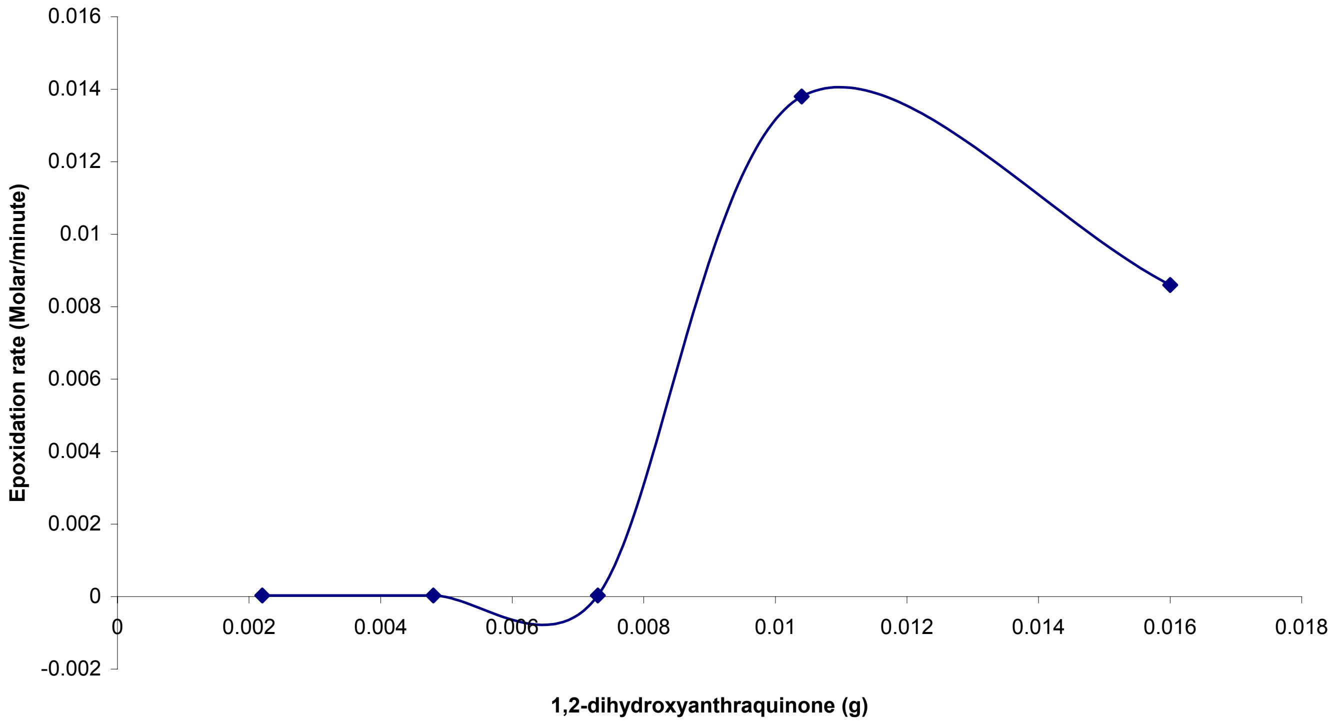

Figure 65 Plot of styrene epoxidation rate versus concentration of 1, 2-dihydroxyanthraquinone

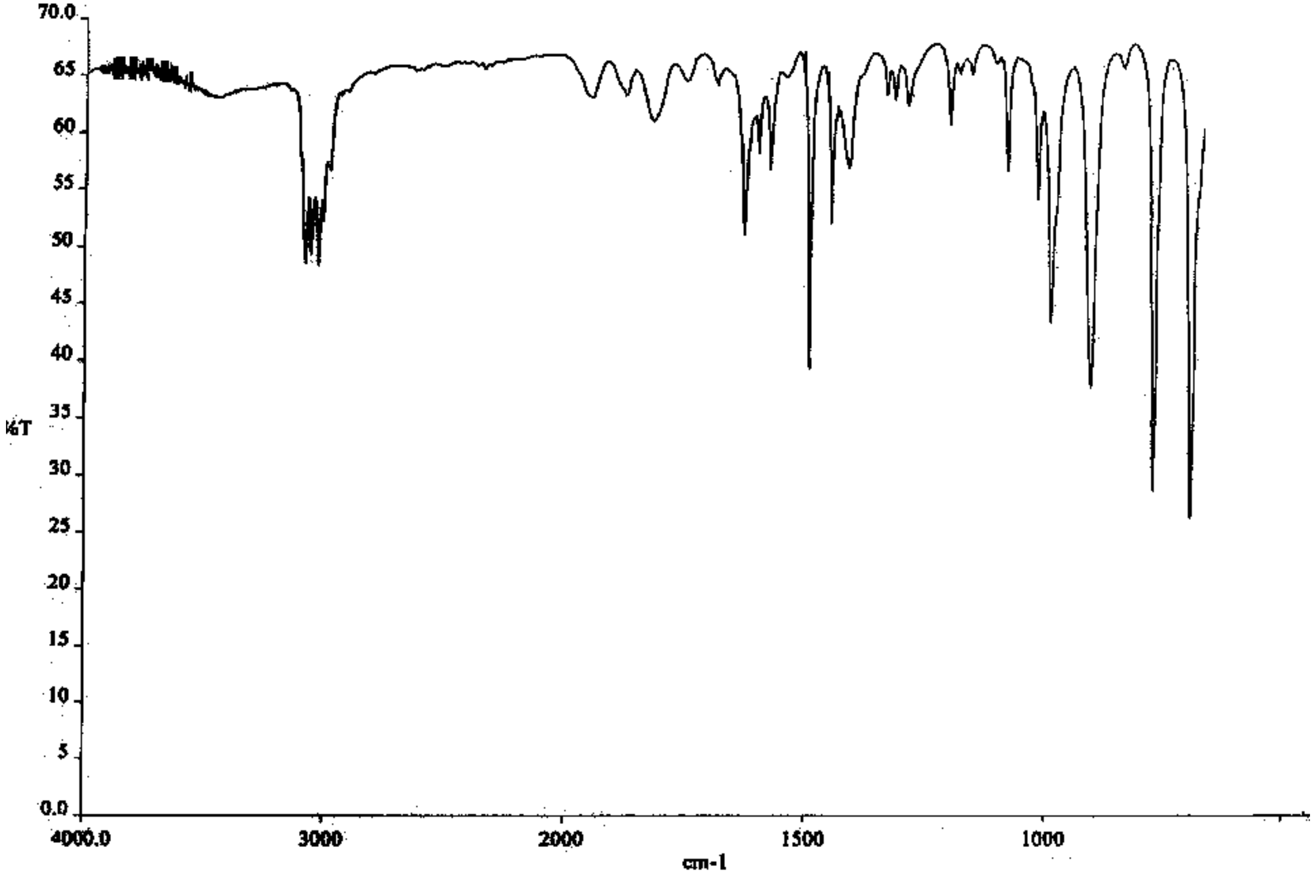

Figure 66 The infrared spectra of styrene

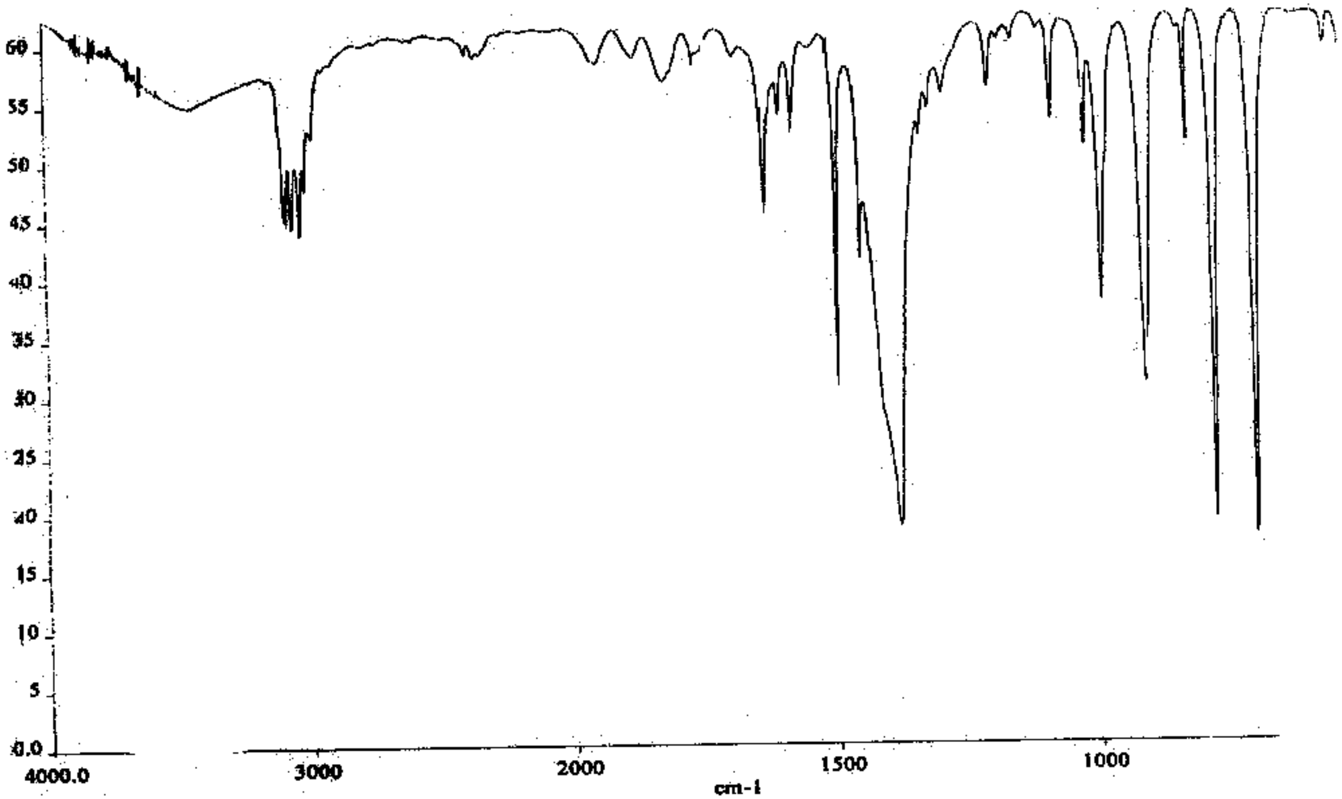

Figure 67 The infrared spectra of the mixed styrene and silver nitrate

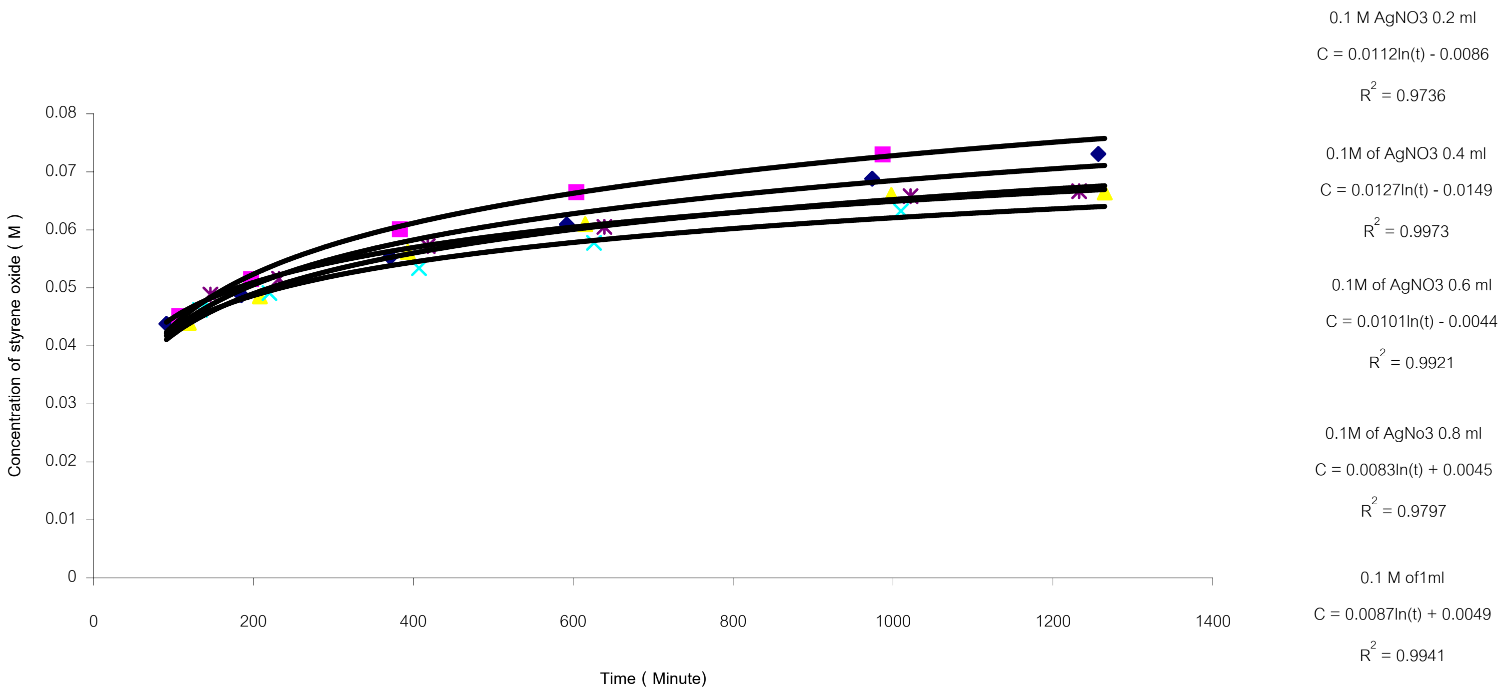

Figure 68 Styrene epoxidation catalysis by various concentrations of silver nitrate and 0.0022 g of 1, 8-dihydroxyanthraquinone

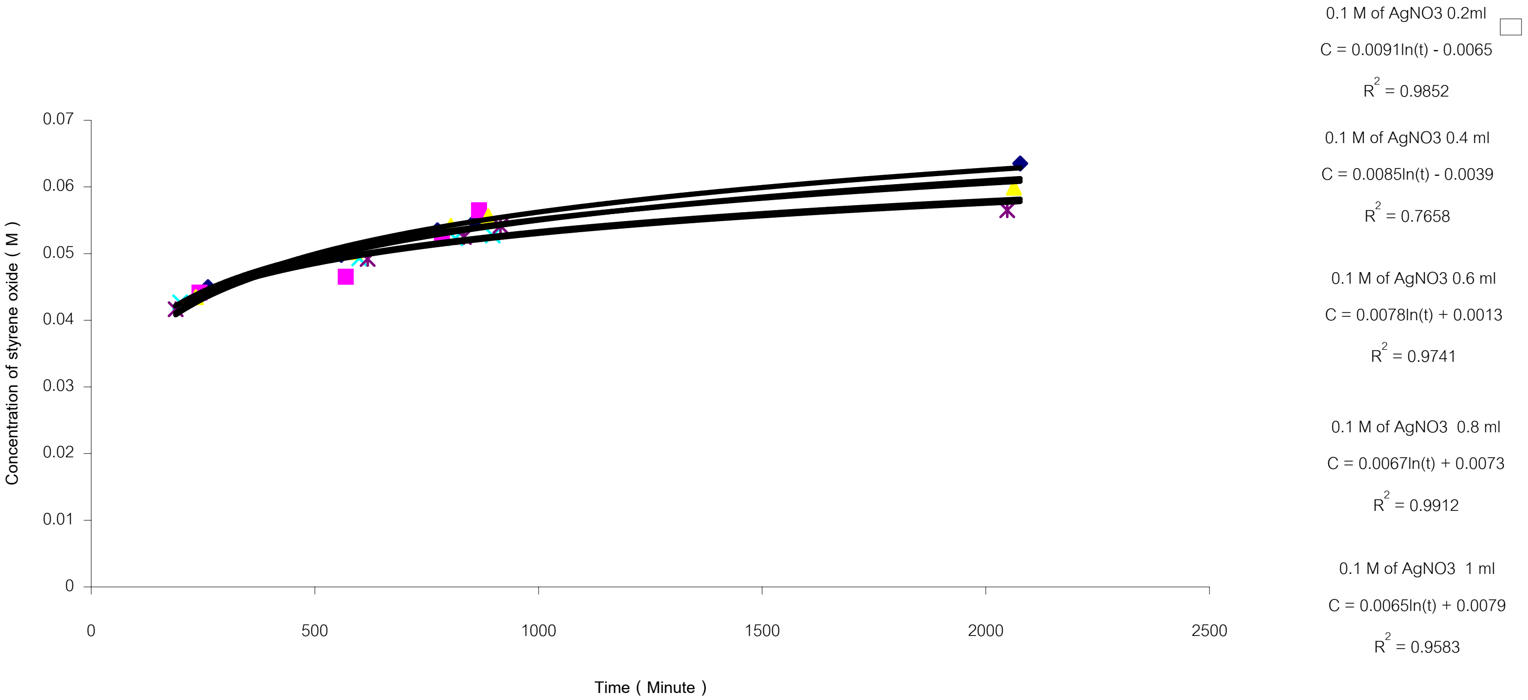

Figure 69 Styrene epoxidation catalysis by various concentrations of silver nitrate and 0.0022 g of 1, 2-dihydroxyanthraquinone

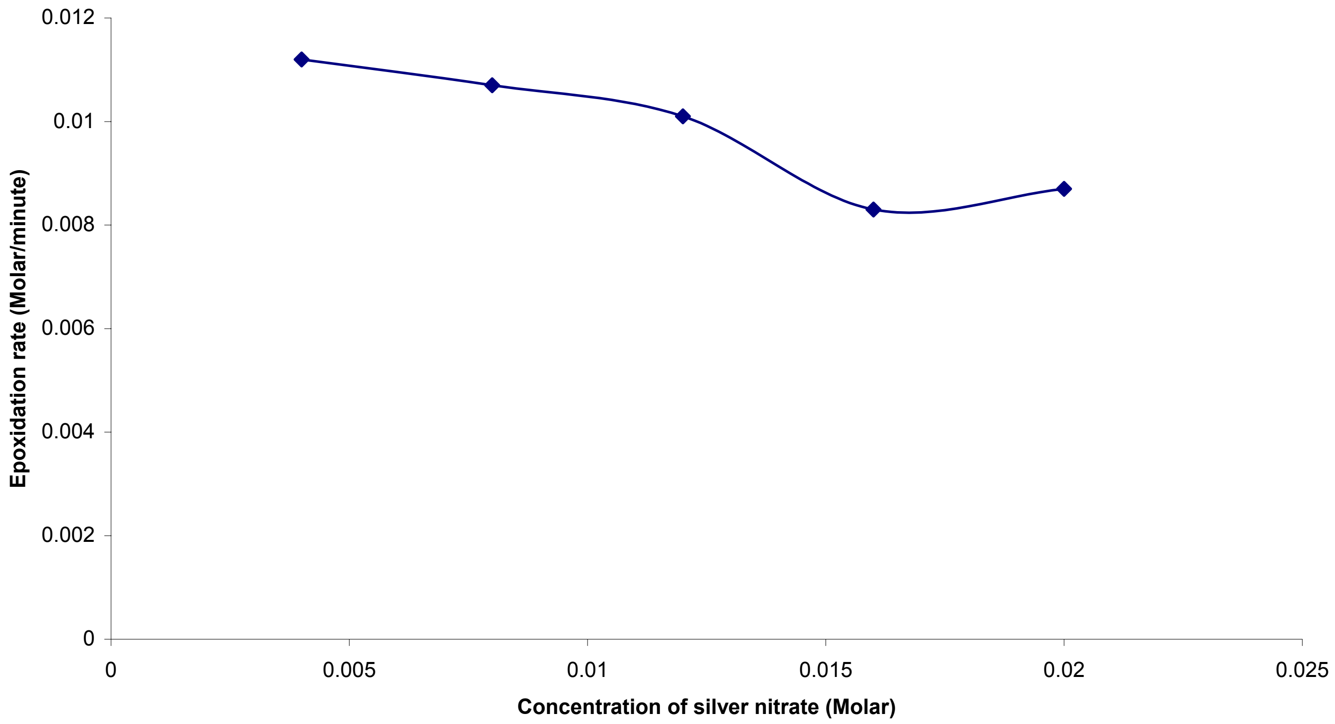

Figure 70 Plot of styrene epoxidation rate that used 0.0022 g of 1, 8-dihydroxyanthraquinone versus various concentration of silver nitrate

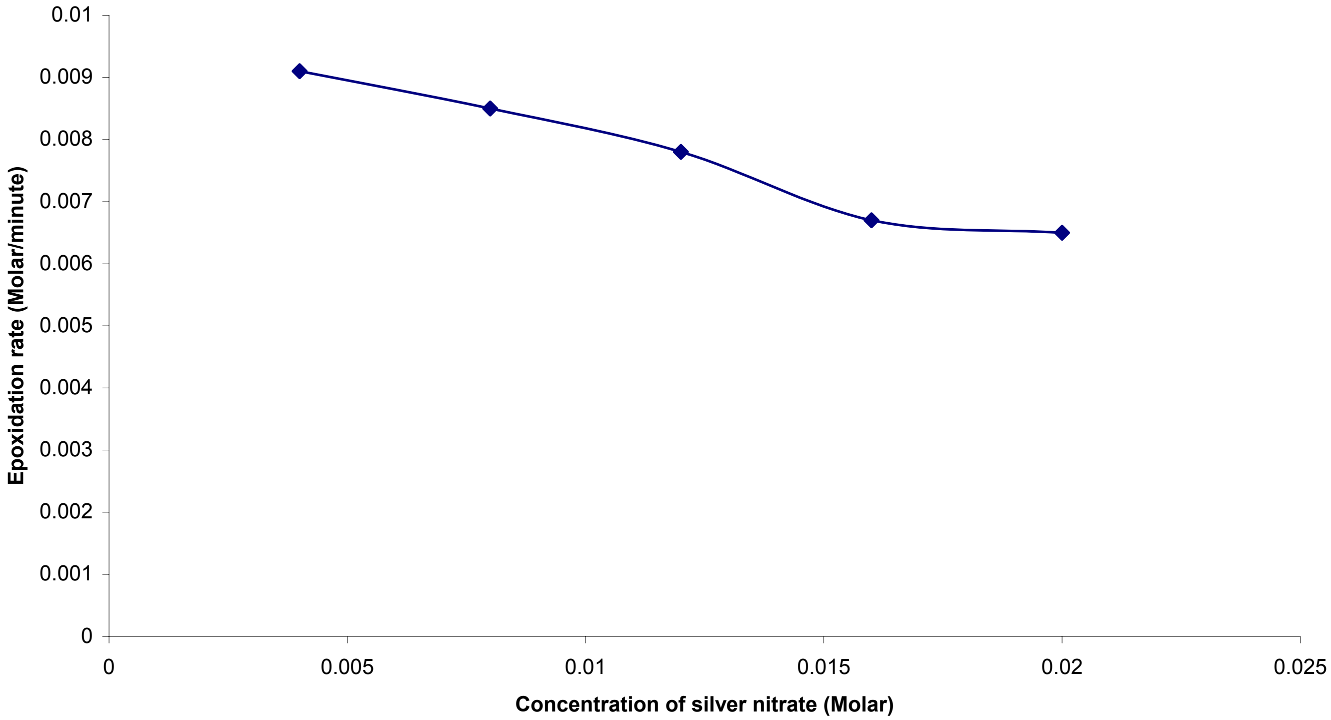

Figure 71 Plot of styrene epoxidation rate that used 0.0022 g of 1, 2-dihydroxyanthraquinone versus various concentration of silver nitrate