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ABSTRACT

AN INVESTIGATION OF THE MECHANISM OF ADVANCED OXIDATION PROCESSES (AOP) INVOLVING FREE RADICALS AND CHARGED SPECIES

by
Yaw-Kuen Lin

Hydrogen peroxide is a key component in Advanced Oxidation Processes (AOP). Its decomposition at different pH conditions has been studied and some interesting results were observed. When the pH value of hydrogen peroxide solution is less than 9, its rate of decomposition is independent of pH. On the other hand, in the pH range of 9-12.6, its rate of decomposition increases as pH increases, and goes through a maximum value then suddenly decreases with respect to pH. A reaction kinetic model with three rate constants in the form of beta probability function was used to describe the experimental data of the decomposition of hydrogen peroxide at various pH values.

The decomposition of hydrogen peroxide at different pH conditions with UV radiation was also examined. The results showed that the higher the alkalinity, the higher the decomposition rate of hydrogen peroxide. A reaction kinetic model was proposed to describe the experimental data of the decomposition of hydrogen peroxide at various pH values under UV radiation.

The decomposition of phenol at different pH conditions in the presence of H_2O_2/UV was studied not only in order to verify the kinetic model of the decomposition of hydrogen peroxide under UV radiation but also to investigate the mechanism of the decomposition of phenol. The results showed that the higher the alkalinity, the lower the decomposition rate of phenol. These results were in good agreement with those of the decomposition of hydrogen peroxide under UV radiation. A mechanism for the decomposition of phenol at various pH conditions was proposed.

The effect of bicarbonate ion, a known scavenger of free radicals, on the decomposition of hydrogen peroxide with and without UV radiation has been investigated. The results showed that bicarbonate ion not only is a free radical scavenger but also causes an incremental increase in hydrogen peroxide decomposition. A reaction kinetic model was proposed to describe the experimental data of the decomposition of hydrogen peroxide at different bicarbonate ion concentrations.

The effect of bicarbonate ion on the decomposition of phenol in the presence of H_2O_2/UV was studied in order to verify all kinetic models proposed in this study.

AN INVESTIGATION OF THE MECHANISM OF ADVANCED OXIDATION PROCESSES (AOP) INVOLVING FREE RADICALS AND CHARGED SPECIES

by
Yaw-Kuen Lin

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AN INVESTIGATION OF THE MECHANISM OF ADVANCED OXIDATION PROCESSES (AOP) INVOLVING FREE RADICALS AND CHARGED SPECIES

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This dissertation is dedicated to
my parents, my wife and my beautiful daughter, Victoria.

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TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

Chapter **Page**

TABLE OF CONTENTS
(Continued)

Chapter **Page**

TABLE OF CONTENTS
(Continued)

Chapter **Page**

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES
(Continued)

Figure **Page**

CHAPTER 1

INTRODUCTION

Advanced Oxidation Processes (AOP), which utilize ultraviolet (UV) radiation with hydrogen peroxide (H_2O_2), are widely used for treatment of hazardous organics in groundwater and industrial wastewater [Glaze et al. (1988), Kawagnchi (1992), Lipczynska-Kochany (1993), Shu (1993), and Smith (1992)]. AOP involve the generation of the hydroxyl radical (OH•), a very active intermediate that generally has great oxidizing power.

Hydrogen Peroxide, which plays a key role in AOP, is a thermodynamically unstable compound. Many efforts have been made to clarify the base-induced decomposition of hydrogen peroxide [Abbot and Brown (1990), Duke and Hass (1961), Evans et al.(1985), Galbacs et al. (1983), Koubek et al. (1963), Oki et al. (1964), and Tanabe et al. (1965)]. Most researchers report that hydrogen peroxide decomposition rate exhibits a maximum in the pH range of 11-12. However, Oki et al. (1964) and Tanabe et al. (1965) revealed that the maximum decomposition rate occurred in the pH range of 13-13.5. Abbot and Brown (1990) report that the decomposition rate increases with the alkalinity. A maximum does not appear up to pH = 13.6.

A mechanism for decomposition of hydrogen peroxide was proposed by Duke and Hass in 1961 as follows:

$$H_2O_2 + OH^- \xleftrightarrow{K_{H_2O_2}} HO_2^- + H_2O$$

$$H_2O_2 + HO_2^- \xrightarrow{k_1} H_2O + OH^- + O_2$$

In the approach taken in our investigation, we proposed a mechanism composed of a series of simultaneous reactions involving charged species. The rate constants for these reactions and their unusual variation with respect to pH values were obtained. To our surprise, the variation follows the beta probability function. Thus, we expressed quantitatively the three rate constants as a function of pH by beta probability function.

Huang et al. (1994) found that the pH is one of the key factors in the presence of H_2O_2/UV for the treatment of textile wastewater. In order to increase the understanding of AOP, the kinetics of base-induced decomposition of hydrogen peroxide without UV radiation need to be confirmed. In this study, we reported experimental results at elevated pH and proposed an enhanced kinetic mechanism of base-induced decomposition of hydrogen peroxide.

The decomposition of hydrogen peroxide under UV radiation has been widely studied. Many investigators [Hochanadel (1962), Malaiyandi et al. (1980), Ogata et al. (1980), Shu (1993)] proposed similar mechanisms. These mechanisms can not be used to describe results at high pH conditions. It needs to be modified for these higher conditions.

Weir et al. (1987) studied the destruction of benzene by H_2O_2/UV process. They pointed out that at high pH levels, benzene decomposed more slowly. Shu (1993) reported that at high pH conditions, phenol decomposed more sluggishly when the H_2O_2/UV process was used. In order to explain this phenomena accurately, the pH dependence of the decomposition of hydrogen peroxide should be studied first.

Glaze et al. (1988) reported that in the groundwater, there is a significant amount of bicarbonate ion, which should trap OH radicals and interfere with the destruction of

target compounds such as trichloroethylene (TCE) and tetrachloroethylene (PCE). Bicarbonate ion is one kind of scavengers. In order to further understand these results, data on the effect of bicarbonate ions on the decomposition of hydrogen peroxide with and without UV radiation must be obtained.

1.1 Objective

The primary objective of this study is to investigate the mechanism of base-induced decomposition of hydrogen peroxide and the pH dependence of the rate of decomposition of hydrogen peroxide under UV radiation. Other objectives include studies of phenol decomposition induced by the H_2O_2/UV system to obtain a mechanism of decomposition of phenol and verify the mechanism in base-induced and UV-induced decomposition of hydrogen peroxide. In addition, the effect of bicarbonate ion as a scavenger of hydroxyl radical on decomposition of hydrogen peroxide and phenol in the H_2O_2/UV process and on decomposition of hydrogen peroxide without UV radiation will be studied. The rate constants will be determined from experimental data by using the Rosenbrock Hillclimb Optimization Algorithm with the LSODE solver.

1.2 Target Compound

Phenol is toxic if absorbed through the skin and may result in death, even if the exposed area is as small as that of a hand or forearm. Contact with skin also causes dangerous and painful burns (Kirk - Othmer 1982). Phenol can be found in wastewater from various industries such as dye manufacturing, epoxy resins, additives and aromatic chemical,

solvents, and aromatic chemical and pharmaceutical, etc. (Stryker et al. 1985). Its high toxicity and its presence in wastewater from a variety of industries makes phenol a suitable substance that serves as a model in studying the degradation of related compounds such as chlorophenol, chlorinated pesticides, phenoxyl herbicides, etc. (Shu 1993).

CHAPTER 2

LITERATURE REVIEW

As expected, much literature was searched for the fundamental study of hydrogen peroxide. They are divided into; (1) base-induced decomposition of hydrogen peroxide, (2) H_2O_2 decomposition using UV radiation, (3) oxidation of target compound in the presence of H_2O_2/UV, (4) effect of scavengers in the presence of H_2O_2/UV.

2.1 Advanced Oxidation Processes

Advanced Oxidation Processes (AOP) involve the generation of hydroxyl radical (OH.), a very active intermediate that generally has far greater oxidizing power than ozone (Glaze et al. 1987 a, b). Hydrogen peroxide is a key component in the presence of H_2O_2/UV, an example of an AOP. Physicochemical processes, one of AOP which are sometimes able to destroy biorefractory contaminants, are affected less by environmental and contaminant variables. The catalyzed decomposition of hydrogen peroxide by iron (II), commonly known as Fenton's reagent, produces the hydroxyl radical (OH•).

$$H_2O_2 + Fe^{2+} \rightarrow OH\bullet + OH^- + Fe^{3+}$$

Fenton's chemistry is well-documented in the chemistry literature and is now being used to treat aqueous industrial waste stream. The supporting research has measured industrial

waste treatment kinetics, mass balances, and toxicity reduction associated with the oxidation of chlorobenzenes and chlorophenols [Bowers et al. (1989), sedlak et al. (1991)]. The remediation of contaminated soils is the most recent application of Fenton's process chemistry [Watts et al. (1990, 1991, 1992), Tyre et al. (1991)].

2.2 Base-induced Decomposition of Hydrogen Peroxide

The study of base-induced decomposition of hydrogen peroxide has been the subject of many investigation (Schumb et al. 1955). Many efforts have been made to clarify the base-induced decomposition of hydrogen peroxide [Abbot and Brown (1990), Duke and Hass (1961), Evans et al. (1985), Galbacs et al. (1983), Koubek et al.(1963), Oki et al. (1964), and Tanabe et al. (1965)].

The specific reaction rate of hydrogen peroxide decomposition increases linearly with concentration of hydroxyl ion until pH level reaches 13.4, and above 14.0 linearly with the square of hydroxyl ion concentration. The pH range in which the N-shape variation of the rate has been observed is nearly independent of the reaction temperature (Oki et al. 1964). Most researchers reported that in most alkaline solutions a maximum in decomposition rate occurred in the pH range of 11-12. Oki et al. (1964) and Tanabe et al. (1965) revealed that the maximum occurred in the pH range of 13-13.5. Abbot and Brown (1990) reported that the more the alkalinity, the higher the decomposition rate and that no maximum appeared up to pH = 13.6.

The mechanism of hydrogen peroxide decomposition proposed by Duke and Hass (1961) is as follows:

$$H_2O_2 + OH^- \xleftrightarrow{K_{H_2O_2}} HO_2^- + H_2O$$

$$H_2O_2 + HO_2^- \xrightarrow{k_1} H_2O + OH^- + O_2$$

The dissociation constant of hydrogen peroxide is 1.78×10^{-12} (Evans and Uri 1949). Early work on the base-induced decomposition of hydrogen peroxide has been summarized by Schumb et al.(1955). Duke and Haas (1961) reported a kinetic study using highly purified reagents. They observed a rate equation of the type $v = k_2[H_2O_2][HO_2^-]$ with $k_2 = 7.4 \times 10^{-4}$ l/mole-sec at 35^0C; k_2 is equal to 2k where k is the conventional second-order rate constant at the pK_a of H_2O_2 (11.5 at 35^0C)(Evans and Uri 1949). A similar value for k_2 (7.0×10^{-4} l/mole-sec) was subsequently obtained by Goodman et al. (1962). These results were shown to be incorrect by Koubek et al. (1963). Using ethylenediaminetetra-acetate (EDTA) to complex catalytic impurities, and purified alkali, they observed an initial rate of decomposition of about one hundredth that reported by Duke and Haas and Goodman et al.. Koubek and co-researchers did not claim to have observed the spontaneous decomposition of hydrogen peroxide. However, Galbacs and Csanyi (1983), again using EDTA, reported a value of 3×10^{-6} l/mole-sec for the second-order rate constant k at 35^0C and pH of 11.6, which they believed to be the true rate of base-induced decomposition.

2.3 H_2O_2 Decomposed by UV Radiation

The H_2O_2/UV has been shown to generate hydroxyl radicals and other reactive species by photochemical reaction of UV radiation on hydrogen peroxide. Hochanadel (1962) and Ogata et al. (1980) proposed a similar mechanism.

$$H_2O_2 + h\nu \xrightarrow{k_{IH_2O_2}} 2\ OH\bullet$$

$$H_2O_2 + OH\bullet \xrightarrow{k_{10f}} HO_2\bullet + H_2O$$

$$H_2O_2 + HO_2\bullet \xrightarrow{k_{11f}} OH\bullet + H_2O + O_2$$

$$2\ OH\bullet \xrightarrow{k_{14}} H_2O_2$$

$$2\ HO_2\bullet \xrightarrow{k_{15}} H_2O_2 + O_2$$

Bielski et al. (1985) and Shu (1993) proposed the mechanism with rate constants which are in Table 2.1.

Table 2.1 The Mechanism and Rate Constants Used by Shu (1993)

Reactions	rate constants (l/mole-sec)	reference
$H_2O_2 + OH\bullet \xrightarrow{k_{10f}} HO_2\bullet + H_2O$	2.7×10^7	Christense et al.(1982)
$H_2O_2 + HO_2\bullet \xrightarrow{k_{11f}} OH\bullet + H_2O + O_2$	3.7	Koppenol et al. (1978)
$2\ OH\bullet \xrightarrow{k_{14}} H_2O_2$	4.0×10^9	Thomas et al. (1965)
$2\ HO_2\bullet \xrightarrow{k_{15}} H_2O_2 + O_2$	8.3×10^5	Beilski et al. (1978)
$OH\bullet + HO_2\bullet \xrightarrow{k_{16}} H_2O + O_2$	3.7×10^{10}	Burrows et al. (1981)

But this mechanism can only be applied when the pH is lower than 7. For alkaline conditions, this mechanism needs to be modified.

2.4 Oxidation of Target Compound in the Presence of H_2O_2/UV

The process of H_2O_2/UV has gained acceptance as a capable method to destroy toxic and hazardous organic compounds in water.

Weir et al. (1987) studied the destruction of benzene in the presence of H_2O_2/UV. They pointed out that at higher pH levels, benzene decomposed more slowly. They said that it is probable for hydrogen peroxide to decompose by itself to oxygen and water at base-induced condition that could not provide free radicals to oxidize benzene. Their study also showed that the effect of temperature on the decomposition was not significant.

Destruction of aromatic pollutants such as benzene, toluene, chlorobezene, phenol, chlorophenols, dimethyl phthalates, and diethyl phthalate by H_2O_2/UV process were studied by Sundstrom et al. (1989). They found that the higher hydrogen peroxide concentration to pollutants ratios, the higher decomposition rates could happen. The intermediates formed while the aromatic pollutants degraded and caused the solution brown color which increased the absorbance at 254 nm comprehensively. The reaction rates were obtained by the order of 2,4,6-trichlorophenol > toluene > phenol > 2,4-dichlorophenol > chlorobezene > 2-chlorophenol > diethyl phthalate > dimethyl phthalate. It apparently showed that most aromatic pollutants studied in this paper received high degradation rates for UV radiation alone. However, there were three compounds: phenol,

dimethyl phthalate, and diethyl phthalate could hardly decomposed by UV radiation alone. Nevertheless, they could be significantly improved by H_2O_2/UV process.

Prat et al. (1988) studied bleaching water treatment in the paper industry by the process of H_2O_2/UV. They also reported that the reaction rate decreased as pH increased.

Shu (1993) investigated the destruction of phenol in the process of H_2O_2/UV. He reported that the higher the alkalinity, the lower the decomposition rate of phenol. He did not discuss this phenomena further. He proposed a mechanism which applied for the condition of pH < 7.

Phenol + OH• → Catechol + Hydroquinone

Phenol + OH• → Ph• (Phenolic radical)

Catechol + Hydroquinone + OH• → Organic acid

Phenol + Ph• → Higher molecular

Phenol + HO_2• → Products

2.5 Scavenger Effect in the Presence of H_2O_2/UV

Glaze et al. (1988) reported that in some ground water there is significant amount of bicarbonate ion which might trap OH radicals and interfere with the destruction of target compounds. The OH radical is far more reactive with TCE than with the bicarbonate ion. However, the molarity of the bicarbonate ion is much greater than that of organic contaminants in some ground water. Glaze et al. (1989) pointed out that chloride is not a

significant scavenger of hydroxyl radicals except at very low pH values, suggesting that AOP may be useful for the treatment of concentrated brine solution.

CHAPTER 3

REACTION MECHANISM AND KINETIC MODELS

3.1 Outline

Advanced Oxidation Processes using hydrogen peroxide with UV radiation are widely used for treating some types of wastewater. Even though these processes have high efficiency in degrading water contaminants, their mechanisms are not well understood especially in alkaline solution. In this research, a series of experiments were conducted to determine the rate constants for a group of reactions. Then by computer simulation, kinetic model were studied. Some rate constants obtained from the literature are adopted in these kinetic models.

The reaction kinetic models used in this work were initially developed by Dr. C. R. Huang in 1983 and revised in 1984, 1988, 1990 and 1993. This study focused on the reaction mechanisms in alkaline conditions and in the presence of scavengers. In order to distinguish the effects of the different processes and solve for reaction rate constants for the degradation of the target compound, phenol, the following six experiments were conducted:

(1) Effect of pH on the decomposition of hydrogen peroxide without UV radiation

(2) Effect of pH on the decomposition of hydrogen peroxide with UV radiation

(3) Effect of pH on the decomposition of phenol in the presence of hydrogen peroxide with UV radiation

(4) Effect of bicarbonate on the decomposition of hydrogen peroxide without UV radiation

(5) Effect of bicarbonate on the decomposition of hydrogen peroxide with UV radiation

(6) Effect of bicarbonate ion on the decomposition of phenol in the presence of hydrogen peroxide with UV radiation.

The reaction kinetic models set up for each experiment are based on the following four assumptions:

1. The reactions in each mechanism are considered to be first order with respect to both reactants
2. Temperature effect is negligible
3. The reactants and intermediates which absorb UV radiation will be taken into account by a light intensity model by measuring absorbance at 254 nm
4. Complete mixing is achieved by bubbling.

3.2 Effect of pH on the Decomposition of Hydrogen Peroxide without UV Radiation

The mechanism for the decomposition of hydrogen peroxide in alkaline solutions proposed by Duke and Hass (1961) is as follows:

$$H_2O_2 + OH^- \xleftrightarrow{K_{H_2O_2}} HO_2^- + H_2O$$

$$H_2O_2 + HO_2^- \xrightarrow{k_1} H_2O + OH^- + O_2$$

However, this mechanism can not fit the experimental data. Thus, we proposed two more reaction steps (the formation of oxide ion, O^{2-}, and its backward reaction) which are:

$$OH^- + HO_2^- \xrightarrow{k_2} O^{2-} + H_2O_2$$

$$O^{2-} + H_2O_2 \xrightarrow{k_3} OH^- + HO_2^-$$

From this mechanism, the rate expression of the decomposition of H_2O_2 is determined as follows:

$$\frac{d[H_2O_2]}{dt} = -k_1[H_2O_2][HO_2^-] + k_2[OH^-][HO_2^-] - k_3[O^{2-}][H_2O_2]$$

$$\frac{d[OH^-]}{dt} = k_1[H_2O_2][HO_2^-] - k_2[OH^-][HO_2^-] + k_3[O^{2-}][H_2O_2]$$

$$\frac{d[O^{2-}]}{dt} = k_2[OH^-][HO_2^-] - k_3[O^{2-}][H_2O_2]$$

The concentration of HO_2^- can be expressed in terms of $[H_2O_2]$ and $[OH^-]$. The dissociation constant of hydrogen peroxide, K_{H2O2} has a value of 1.78×10^{-12} (Evans and Uri 1949).

$$K_{H_2O_2} = \frac{[HO_2^-][H_3O^+]}{[H_2O_2]} = \frac{[HO_2^-]k_w}{[H_2O_2][OH^-]}$$

$$[HO_2^-] = K_{H_2O_2}[H_2O_2][OH^-]/k_w = 1.78 \times 10^2 [H_2O_2][OH^-]$$

The rate expression for the decomposition of hydrogen peroxide becomes

$$\frac{d[H_2O_2]}{dt} = -k_1 \times 1.78 \times 10^2 [H_2O_2]^2 [OH^-] + k_2 \times 1.78 \times 10^2 [OH^-]^2 [H_2O_2] - k_3 [O^{2-}][H_2O_2]$$

$$\frac{d[OH^-]}{dt} = k_1 \times 1.78 \times 10^2 [H_2O_2]^2 [OH^-] - k_2 \times 1.78 \times 10^2 [OH^-]^2 [H_2O_2] + k_3 [O^{2-}][H_2O_2]$$

$$\frac{d[O^{2-}]}{dt} = k_2 \times 1.78 \times 10^2 [OH^-]^2 [H_2O_2] - k_3 [O^{2-}][H_2O_2]$$

Initial conditions for the experiment were:

$[H_2O_2]_0 = 4.73 \times 10^{-3}$ mole/l

$[OH^-]_0 =$ variable

$[O^{2-}]_0 = 0.$

The rate constants were determined from experimental data using the Rosenbrock Hillclimb Optimization Algorithm with the LSODE solver.

3.3 Effect of pH on the Decomposition of Hydrogen Peroxide with UV Radiation

Hydrogen peroxide plays a very important role in the process of H_2O_2/UV. Hydrogen peroxide could serve as a source of hydroxyl radicals in the aqueous solution under UV radiation. Shu (1993) proposed a mechanism for the decomposition of hydrogen peroxide with UV radiation as follows:

$$H_2O_2 + h\nu \xrightarrow{k_{1H_2O_2}} 2\ OH\bullet$$

$$H_2O_2 + OH\bullet \xrightarrow{k_{10f}} HO_2\bullet + H_2O$$

$$H_2O_2 + HO_2\bullet \xrightarrow{k_{11f}} OH\bullet + H_2O + O_2$$

$$2\ OH\bullet \xrightarrow{k_{14}} H_2O_2$$

$$2\ HO_2\bullet \xrightarrow{k_{13}} H_2O_2 + O_2$$

$$OH\bullet + HO_2\bullet \xrightarrow{k_{16}} H_2O + O_2$$

This mechanism can only apply in neutral solutions. For alkaline conditions, this mechanism needs to be modified.

For alkaline conditions, the following reaction must be included in the mechanism deveolped by Shu (1993):

$$OH\bullet + HO_2^- \xrightarrow{k_{17}} O_2^-\bullet + H_2O$$

$$HO_2\bullet \xleftrightarrow{k_{HO_2\bullet}} H^+ + O_2^-\bullet$$

$$HO_2\bullet + O_2^-\bullet \xrightarrow{k_{18}} HO_2^- + O_2$$

$$O_2^-\bullet + H_2O_2 \xrightarrow{k_{19}} HO_2^- + HO_2\bullet$$

The dissociation constant K_{HO2} is 1.6×10^{-5} reported by Bielski et al. in 1985. The rate constant k_{18} for the reaction of hydroperoxyl radical ($HO_2\bullet$) and superoxide ion radical ($O_2^-\bullet$), is 7.9×10^7 l/mole-sec, reported by Rabani et al. in 1969.

From equilibrium,

$$[O_2^-\bullet]=1.6 \times 10^{-5}\,[HO_2\bullet]\,/[H^+] = 1.6 \times 10^{9}[HO_2\bullet][OH^-]$$

The rate expression is as follows:

$$\frac{d[H_2O_2]}{dt} = -k_1 \times 1.78\times 10^2 [H_2O_2]^2[OH^-] + k_2 \times 1.78\times 10^2 [OH^-]^2[H_2O_2] - k_3[O^{2-}][H_2O_2]$$
$$-k_{IH_2O_2} I[H_2O_2] - k_{10f}[H_2O_2][OH\bullet] - k_{11f}[H_2O_2][HO_2\bullet] + k_{14}[OH\bullet]^2 + k_{15}[HO_2\bullet]^2$$
$$-k_{19}[O_2^-\bullet][H_2O_2]$$

$$\frac{d[OH^-]}{dt} = k_1 \times 1.78\times 10^2 [H_2O_2]^2[OH^-] - k_2 \times 1.78\times 10^2 [OH^-]^2[H_2O_2] + k_3[O^{2-}][H_2O_2]$$

$$\frac{d[O^{2-}]}{dt} = k_2 \times 1.78\times 10^2 [OH^-]^2[H_2O_2] - k_3[O^{2-}][H_2O_2]$$

$$\frac{d[OH\bullet]}{dt} = 2k_{IH_2O_2} I[H_2O_2] - k_{10f}[H_2O_2][OH\bullet] + k_{11f}[H_2O_2][HO_2\bullet]$$
$$-2k_{14}[OH\bullet]^2 - k_{16}[OH\bullet][HO_2\bullet] - k_{17}[OH\bullet][HO_2^-]$$

$$\frac{d[HO_2\bullet]}{dt} = k_{10f}[H_2O_2][OH\bullet] - k_{11f}[H_2O_2][HO_2\bullet] - k_{15}[HO_2\bullet]^2$$
$$-k_{16}[OH\bullet][HO_2\bullet] - k_{18}[HO_2\bullet][O_2^-\bullet] + k_{19}[O_2^-\bullet][H_2O_2]$$

Initial conditions:

$[OH\bullet]_0=0$

$[HO_2\bullet]_0=0$

The rate constant k_{17} and k_{19} are optimized in order to give the best fit to the experimental data.

3.4 Effect of pH on the Decomposition of Phenol under UV Radiation alone and the Presence of Hydrogen Peroxide with UV Radiation

Phenol is one of the most common compounds used in the fundamental study of the mechanism of the decomposition of the phenol group in the presence of H_2O_2/UV. It is partially ionized at a pH value of 9 (Kirk-Othmer 1982). The phenolate not only absorbs UV radiation (Lipczynska-Kochany 1993) but also reacts with hydroxyl radical (Buxton et al. 1988). The objective of this experiment is to determine the mechanism of decomposition of phenol and to verify the mechanisms of hydrogen peroxide decomposition with and without UV radiation as discussed in sections 3.2 and 3.3.

3.4.1 Effect of pH on the Decomposition of Phenol under UV Radiation alone

The dissociation constant of phenol is 1.78×10^{-10} (Kirk-Othmer 1982). The mechanism of decomposition of phenol under UV radiation alone is proposed as follows:

$$\text{phenol} + H_2O \xleftrightarrow{K_{phenol}} \text{phenolate anion} + H_3O^+$$

$$\text{Phenol} + h\nu \xrightarrow{k_{lph}I} \text{products}$$

$$\text{Phenolate anion} + h\nu \xrightarrow{k_{lpha}I} \text{products}$$

The rate constants $k_{lph}I$ and $k_{lpha}I$ can be obtained by fitting experimental data taken at pH values between 7 and 11.

3.4.2 Effect of pH on the Decomposition of Phenol in the Presence of Hydrogen Peroxide with UV Radiation

The intermediate products of phenol decomposition under the presence of H_2O_2/UV in neutral conditions which have been reported are catechol, hydroquinone, and phenolic radical. In neutral conditions, the concentration of phenolate can be neglected. Thus, the following mechanism is proposed:

$$\text{Phenol} + h\nu \xrightarrow{k_{Ph}I} \text{products}$$

$$\text{Phenol} + OH\bullet \xrightarrow{k_{20}} \text{Catechol}$$

$$\text{Phenol} + OH\bullet \xrightarrow{k_{21}} \text{Hydroquinone}$$

$$\text{Phenol} + OH\bullet \xrightarrow{k_{22}} Ph\bullet\text{(Phenolic radical)}$$

$$\text{Catechol} + OH\bullet \xrightarrow{k_{23}} \text{Products(Organic acid)}$$

$$\text{Hydroquinone} + OH\bullet \xrightarrow{k_{24}} \text{Products(Organic acid)}$$

$$\text{Phenol} + Ph\bullet \xrightarrow{k_{25}} \text{Higher molecular}$$

$$\text{Phenol} + HO_2\bullet \xrightarrow{k_{26}} \text{Products}$$

The reaction rate for each species is as follows:

$$\frac{d[H_2O_2]}{dt} = -k_1 \times 1.78\times10^2 [H_2O_2]^2[OH^-] + k_2 \times 1.78\times10^2 [OH^-]^2[H_2O_2]$$
$$-k_3[O^{2-}][H_2O_2] - k_{IH_2O_2} I[H_2O_2] - k_{10f}[H_2O_2][OH\bullet] - k_{11f}[H_2O_2][HO_2\bullet]$$
$$+k_{14}[OH\bullet]^2 + k_{15}[HO_2\bullet]^2 - k_{19}[O_2^-\bullet][H_2O_2]$$

$$\frac{d[OH^-]}{dt} = k_1 \times 1.78\times10^2 [H_2O_2]^2[OH^-] - k_2 \times 1.78\times10^2 [OH^-]^2[H_2O_2]$$
$$+k_3[O^{2-}][H_2O_2]$$

$$\frac{d[O^{2-}]}{dt} = k_2 \times 1.78\times10^2 [OH^-]^2[H_2O_2] - k_3[O^{2-}][H_2O_2]$$

$$\frac{d[OH\bullet]}{dt} = 2k_{IH_2O_2} I[H_2O_2] - k_{10f}[H_2O_2][OH\bullet] + k_{11f}[H_2O_2][HO_2\bullet]$$
$$-2k_{14}[OH\bullet]^2 - k_{16}[OH\bullet][HO_2\bullet] - k_{17}[OH\bullet][HO_2^-] - k_{20}[ph][OH\bullet]$$
$$-k_{21}[ph][OH\bullet] - k_{22}[ph][OH\bullet] - k_{23}[Ca][OH\bullet] - k_{24}[HQ][OH\bullet]$$
$$-k_{27}[pha][OH\bullet]$$

$$\frac{d[HO_2\bullet]}{dt} = k_{10f}[H_2O_2][OH\bullet] - k_{11f}[H_2O_2][HO_2\bullet] - k_{15}[HO_2\bullet]^2$$
$$-k_{16}[OH\bullet][HO_2\bullet] - k_{18}[HO_2\bullet][O_2^-\bullet] + k_{19}[O_2^-\bullet][H_2O_2] - k_{27}[ph][HO_2\bullet]$$

$$\frac{d[ph]}{dt} = -k_{Iph} I[ph] - k_{20}[ph][OH\bullet] - k_{21}[ph][OH\bullet] - k_{22}[ph][OH\bullet] - k_{25}[ph][ph\bullet]$$
$$-k_{27}[ph][HO_2\bullet]$$

$$\frac{d[Ca]}{dt} = k_{20}[ph][OH\bullet] - k_{23}[Ca][OH\bullet]$$

$$\frac{d[HQ]}{dt} = k_{21}[ph][OH\bullet] - k_{24}[HQ][OH\bullet]$$

$$\frac{d[ph\bullet]}{dt} = k_{22}[ph][OH\bullet] - k_{25}[ph][ph\bullet]$$

$$\frac{d[pha]}{dt} = -k_{Ipha}I[pha] - k_{27}[pha][OH\bullet]$$

where: [ph] = [phenol], [Ca] = [Catechol], [HQ] = [Hydroquinone], [ph•] = [phenolic radical], [pha] = [phenolate anion]

Initial conditions: t = 0, [ph] = $[ph]_0$, [Ca] = 0, [HQ] = 0, [ph•] = 0, [pha] = $[pha]_0$

The rate constants for the above reactions can be obtained by fitting the experimental data of the concentration of phenol, hydroquinone, and catechol with respect to time during the process of H_2O_2/UV.

In the alkaline condition, phenolate anion will dominate. It will react with hydroxyl radical. Thus, the following reaction needs to be considered.

Phenolate anion + OH• $\xrightarrow{k_{27}}$ products

The rate constant of phenolate anion reacting with hydroxyl radical can be obtained by fitting experimental data and applying the rate constants obtained for neutral condition.

3.5 Effect of Bicarbonate on the Decomposition of Hydrogen Peroxide without UV Radiation

Bicarbonate ion might trap OH radicals and interfere with the destruction of the target compound (Glaze et al. 1988). It was also observed that the bicarbonate ion can also decompose hydrogen peroxide without UV radiation and it may interfere with the destruction of the target compound. The following mechanism is proposed for the decomposition of hydrogen peroxide in the presence of bicarbonate ion:

$$HCO_3^- + H_2O \xleftrightarrow{K_{HCO_3^-}} H_3O^+ + CO_3^{=}$$

$$H_2O_2 + HCO_3^- \xrightarrow{k_{HCO_3^-}} HO_2^- + H_2O + CO_2$$

$$H_2O_2 + CO_3^{=} \xrightarrow{k_{CO_3^=}} HO_2^- + HCO_3^-$$

Using $K_{HCO3^-} = 5.62 \times 10^{-11}$, the concentration of $CO_3^{=}$ can be computed as:

$$[CO_3^{=}] = \frac{K_{HCO_3^-}[HCO3^-]}{[H_3O^+]}$$

$$= \frac{K_{HCO_3^-}}{K_w}[HCO3^-][OH^-]$$

$$= 5.62 \times 10^3 [HCO3^-][OH^-]$$

The reaction rate for each species are as follows:

$$\frac{d[H_2O_2]}{dt} = -k_1 \times 1.78 \times 10^2 [H_2O_2]^2 [OH^-] + k_2 \times 1.78 \times 10^2 [OH^-]^2 [H_2O_2] - k_3 [O^{2-}][H_2O_2]$$
$$-k_{HCO_3^-}[H_2O_2][HCO_3^-] - k_{CO_3^=}[H_2O_2][CO_3^=]$$

$$\frac{d[OH^-]}{dt} = k_1 \times 1.78 \times 10^2 [H_2O_2]^2 [OH^-] - k_2 \times 1.78 \times 10^2 [OH^-]^2 [H_2O_2] + k_3 [O^{2-}][H_2O_2]$$

$$\frac{d[O^{2-}]}{dt} = k_2 \times 1.78 \times 10^2 [OH^-]^2 [H_2O_2] - k_3 [O^{2-}][H_2O_2]$$

$$\frac{d[HCO_3^-]}{dt} = -k_{HCO_3^-}[H_2O_2][HCO_3^-] + k_{CO_3^=}[H_2O_2][CO_3^=]$$

$$\frac{d[CO_3^=]}{dt} = -k_{CO_3^=}[H_2O_2][CO_3^=]$$

Initial condition: t = 0, $[H_2O_2] = [H_2O_2]_0$

The rate constants k_{HCO3-} and $k_{CO3=}$ can be obtained by fitting experimental results.

3.6 Effect of Bicarbonate on the Decomposition of Hydrogen Peroxide with UV Radiation

The objective of this experiment is to find out the rate constant of the reaction of bicarbonate ion and carbonate ion with hydroxyl radical. From the literature, the mechanism for the reaction of bicarbonate ion and carbonate ion with hydroxyl radical is shown below:

$$HCO_3^- + OH\bullet \xrightarrow{k_{30}} CO_3\bullet^- + H_2O$$

$$CO_3^{=} + OH\bullet \xrightarrow{k_{31}} CO_3\bullet^- + OH^-$$

$$CO_3\bullet^- + H_2O_2 \xrightarrow{k_{32}} HO_2\bullet + HCO_3^-$$

The reaction rate for each species are as follows:

$$\frac{d[H_2O_2]}{dt} = -k_1 \times 1.78\times10^2 [H_2O_2]^2[OH^-] + k_2 \times 1.78\times10^2 [OH^-]^2[H_2O_2] - k_3[O^{2-}][H_2O_2]$$
$$-k_{IH_2O_2} I[H_2O_2] - k_{10f}[H_2O_2][OH\bullet] - k_{11f}[H_2O_2][HO_2\bullet] + k_{14}[OH\bullet]^2 + k_{15}[HO_2\bullet]^2$$
$$-k_{19}[O_2^-\bullet][H_2O_2] - k_{HCO3-}[HCO_3^-][H_2O_2] - k_{CO3=}[CO_3^{=}][H_2O_2] - k_{32}[CO_3^-\bullet][H_2O_2]$$

$$\frac{d[OH^-]}{dt} = k_1 \times 1.78\times10^2 [H_2O_2]^2[OH^-] - k_2 \times 1.78\times10^2 [OH^-]^2[H_2O_2] + k_3[O^{2-}][H_2O_2]$$
$$+k_{31}[CO_3^{=}][OH\bullet]$$

$$\frac{d[O^{2-}]}{dt} = k_2 \times 1.78\times10^2 [OH^-]^2[H_2O_2] - k_3[O^{2-}][H_2O_2]$$

$$\frac{d[HCO_3^-]}{dt} = -k_{HCO_3^-}[H_2O_2][HCO_3^-] + k_{CO_3^=}[H_2O_2][CO_3^=] + k_{32}[H_2O_2][CO_3^-\bullet]$$
$$-k_{30}[HCO_3^-][OH\bullet]$$

$$\frac{d[CO_3^=]}{dt} = -k_{CO_3^=}[H_2O_2][CO_3^=] - k_{31}[CO_3^=][OH\bullet]$$

$$\frac{d[CO_3^-\bullet]}{dt} = k_{30}[HCO_3^-][OH\bullet] + k_{31}[CO_3^=][OH\bullet] - k_{32}[H_2O_2][CO_3^-\bullet]$$

$$\frac{d[OH\bullet]}{dt} = 2k_{IH_2O_2}I[H_2O_2] - k_{10f}[H_2O_2][OH\bullet] + k_{11f}[H_2O_2][HO_2\bullet]$$
$$-2k_{14}[OH\bullet]^2 - k_{16}[OH\bullet][HO_2\bullet] - k_{17}[OH\bullet][HO_2^-]$$
$$-k_{30}[HCO_3^-][OH\bullet] - k_{31}[CO_3^=][OH\bullet]$$

$$\frac{d[HO_2\bullet]}{dt} = k_{10f}[H_2O_2][OH\bullet] - k_{11f}[H_2O_2][HO_2\bullet] - k_{15}[HO_2\bullet]^2$$
$$-k_{16}[OH\bullet][HO_2\bullet] - k_{18}[HO_2\bullet][O_2^-\bullet] + k_{19}[O_2^-\bullet][H_2O_2]$$
$$+k_{32}[H_2O_2][CO_3^-\bullet]$$

Initial conditions: $[H_2O_2] = [H_2O_2]_0$, $[HCO_3^-] = [HCO_3^-]_0$, $[CO_3^=] = [CO_3^=]_0$, $[CO_3^-\bullet] = 0$, $[OH\bullet] = 0$, $[HO_2\bullet] = 0$

The rate constant k_{32} is 8.0×10^5 l/mole-sec (Behar et al. 1970). The rate constants k_{30} and k_{31} can be obtained by fitting the experimental data.

3.7 Effect of Bicarbonate Ion on the Decomposition of Phenol in the Presence of Hydrogen Peroxide with UV Radiation

The objective of this experiment is to determine the effect of bicarbonate ion on the decomposition of phenol in the process of H_2O_2/UV. Bicarbonate ion should trap hydroxyl radical and stabilize phenol in AOP. All the reactions which appeared in previous sections should be considered in this process and the reaction of carbonate ion radical ($CO_3\bullet^-$) and phenol was also considered.

$$\text{Phenol} + CO_3\bullet^- \xrightarrow{k_{28}} \text{Products}$$

The reaction rate for each species is as follows:

$$\frac{d[H_2O_2]}{dt} = -k_1 \times 1.78\times 10^2 [H_2O_2]^2[OH^-] + k_2 \times 1.78\times 10^2 [OH^-]^2[H_2O_2] - k_3[O^{2-}][H_2O_2]$$
$$-k_{IH_2O_2} I[H_2O_2] - k_{10f}[H_2O_2][OH\bullet] - k_{11f}[H_2O_2][HO_2\bullet] + k_{14}[OH\bullet]^2 + k_{15}[HO_2\bullet]^2$$
$$-k_{19}[O_2^-\bullet][H_2O_2] - k_{HCO3-}[HCO_3^-][H_2O_2] - k_{CO3=}[CO_3^=][H_2O_2] - k_{32}[CO_3^-\bullet][H_2O_2]$$

$$\frac{d[OH^-]}{dt} = k_1 \times 1.78\times 10^2 [H_2O_2]^2[OH^-] - k_2 \times 1.78\times 10^2 [OH^-]^2[H_2O_2] + k_3[O^{2-}][H_2O_2]$$
$$-k_{31}[CO_3^=][OH\bullet]$$

$$\frac{d[O^{2-}]}{dt} = k_2 \times 1.78\times 10^2 [OH^-]^2[H_2O_2] - k_3[O^{2-}][H_2O_2]$$

$$\frac{d[HCO_3^-]}{dt} = -k_{HCO_3^-}[H_2O_2][HCO_3^-] + k_{CO_3^=}[H_2O_2][CO_3^=] + k_{32}[H_2O_2][CO_3^-\bullet]$$
$$-k_{30}[HCO_3^-][OH\bullet]$$

$$\frac{d[CO_3^=]}{dt} = -k_{CO_3^=}[H_2O_2][CO_3^=] - k_{31}[CO_3^=][OH\bullet]$$

$$\frac{d[CO_3^-\bullet]}{dt} = k_{30}[HCO_3^-][OH\bullet] + k_{31}[CO_3^=][OH\bullet] - k_{32}[H_2O_2][CO_3^-\bullet] - k_{28}[ph][CO_3^-\bullet]$$

$$\frac{d[OH\bullet]}{dt} = 2k_{IH_2O_2}I[H_2O_2] - k_{10f}[H_2O_2][OH\bullet] + k_{11f}[H_2O_2][HO_2\bullet]$$
$$-2k_{14}[OH\bullet]^2 - k_{16}[OH\bullet][HO_2\bullet] - k_{17}[OH\bullet][HO_2^-] - k_{20}[ph][OH\bullet]$$
$$-k_{21}[ph][OH\bullet] - k_{22}[ph][OH\bullet] - k_{23}[Ca][OH\bullet] - k_{24}[HQ][OH\bullet]$$
$$-k_{27}[pha][OH\bullet] - k_{30}[HCO_3^-][OH\bullet] - k_{31}[CO_3^=][OH\bullet]$$

$$\frac{d[HO_2\bullet]}{dt} = k_{10f}[H_2O_2][OH\bullet] - k_{11f}[H_2O_2][HO_2\bullet] - k_{15}[HO_2\bullet]^2$$
$$-k_{16}[OH\bullet][HO_2\bullet] - k_{18}[HO_2\bullet][O_2^-\bullet] + k_{19}[O_2^-\bullet][H_2O_2] - k_{27}[ph][HO_2\bullet]$$
$$+k_{32}[CO_3^-\bullet][H_2O_2]$$

$$\frac{d[ph]}{dt} = -k_{Iph}I[ph] - k_{20}[ph][OH\bullet] - k_{21}[ph][OH\bullet] - k_{22}[ph][OH\bullet] - k_{25}[ph][ph\bullet]$$
$$-k_{27}[ph][HO_2\bullet] - k_{28}[ph][CO_3\bullet^-]$$

$$\frac{d[Ca]}{dt} = k_{20}[ph][OH\bullet] - k_{23}[Ca][OH\bullet]$$

$$\frac{d[HQ]}{dt} = k_{21}[ph][OH\bullet] - k_{24}[HQ][OH\bullet]$$

$$\frac{d[ph\bullet]}{dt} = k_{22}[ph][OH\bullet] - k_{25}[ph][ph\bullet]$$

$$\frac{d[pha]}{dt} = -k_{Ipha}I[pha] - k_{27}[pha][OH\bullet]$$

The rate constant k_{28} can be obtained by fitting the experimental data.

CHAPTER 4

EXPERIMENTS AND EQUIPMENT

4.1 Materials and Chemicals

Hydrogen peroxide, Cobaltous sulfate heptahydrate ($CoSO_4.7H_2O$) and sodium hexametaphosphate were obtained from Fluka Chemika. The phenol used was from Sigma Chemical Co., with 0.15 % H_3PO_4 as inhibitor. Sodium bicarbonate and sodium carbonate were from Aldrich Chemical Co.

4.2 Analytical Methods

4.2.1 Analysis of the Concentration of Hydrogen Peroxide

The method of analysis of hydrogen peroxide concentration as proposed by Masschelien et al. (1977) was used in this study. It is described as follows:

1. An 80-ml sample solution was placed in a 100 ml volumetric flask, 1 ml of the Co^{++} reagent (19 g $CoSO_4.7H_2O$ in 1 liter distilled water) and 1 ml of the sodium hexametaphosphate solution (10g/l) was added, then it was made up to 100 ml with saturated bicarbonate solution.
2. The absorbance was measured at 260 nm by comparing the solution with a blank reagent solution.
3. A calibration curve was made from standard hydrogen peroxide solutions in different concentrations.

4.2.2 Analysis of the Concentration of Phenol, Catechol, and Hydroquinone

The concentration of phenol, catechol, and hydroquinone was analyzed by High Performance Liquid Chromatogragh (HPLC). The stationary phase was Nova-Pak 3.9 mm x 150 mm C_{18} column. The mobile phase was 35 % of 1% acetic acid in methanol and 65 % of 1 % acetic acid in water.

4.3 Experimental Equipment

4.3.1 Photochemical Reactor

The experiments were conducted in a photochemical reactor, Model RPR-100 which was made by New England Photochemical Co.. There were 16 high pressure mercury Arc UV lamps (wavelength 254 nm, 35 watts/lamp) arranged on the inner wall of the reactor which gave a total power of 560 watts. The reactor consisted of a vertical cylindrical quartz vessel (ID = 40 mm, Height = 320 mm) with an air sparger for stirring. The experimental setup is shown in Figure 4.1.

4.3.2 Spectrophotometer

A Varian DMS 200 UV-Vis spectrophotometer was used to measure the concentration of hydrogen peroxide at 260 nm.

4.3.3 High Performance Liquid Chromatogragh (HPLC)

A Waters 600E system controller, a Waters 715 Ultra Wisp sample processor and a Waters 994 programmable photodiode array detector all coupled with a Chromatography

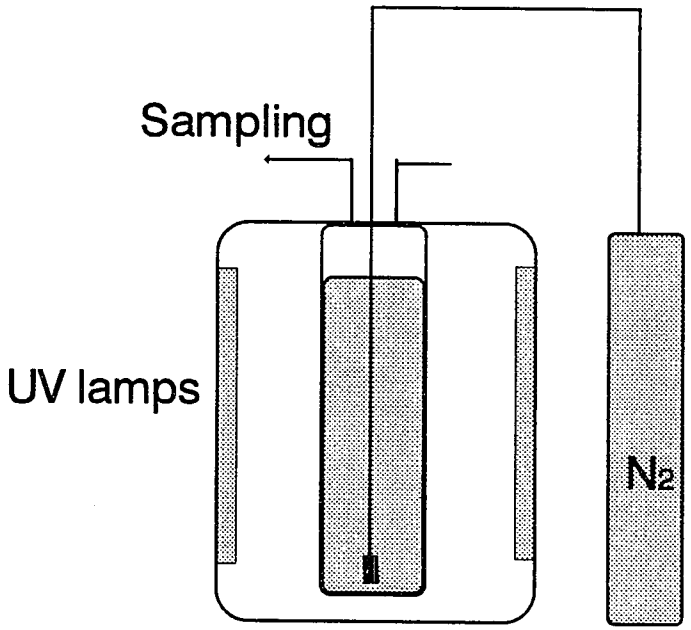

Figure 4.1 Batch experimental setup

server data acquiring system was used to determine the concentration of phenol and its intermediates. The stationary phase was Nova-Pak 3.9 mm x 150 mm C_{18} column. The mobile phase was 35 % of 1% acetic acid in methanol and 65 % of 1 % acetic acid in water.

4.3.4 Sample Collection

A 1-ml sample was collected to determine the concentration of hydrogen peroxide. A 0.5-ml sample was collected for analysis of the concentration of phenol.

4.4 Experiments

4.4.1 Standard Calibration Curve

Hydrogen peroxide solutions were prepared in 1.0 to 20 ppm to develop the calibration curve for the spectrophotometer. The phenol, catechol, and hydroquinone were prepared in 1.0 to 19 ppm for HPLC. By plotting the absorbance or HPLC peak area versus the concentration of compounds, the calibration curve was obtained. The retention time of phenol, catechol, and hydroquinone in analysis of HPLC is shown in Figure 4.2.

4.4.2 The Absorbance of Phenol and Its Intermediates

Phenol and its intermediate has strong absorbance at 254 nm. Therefore, it must be considered in the modeling. As a result, the sample must be collected and analyzed by spectrophotometer at 254 nm.

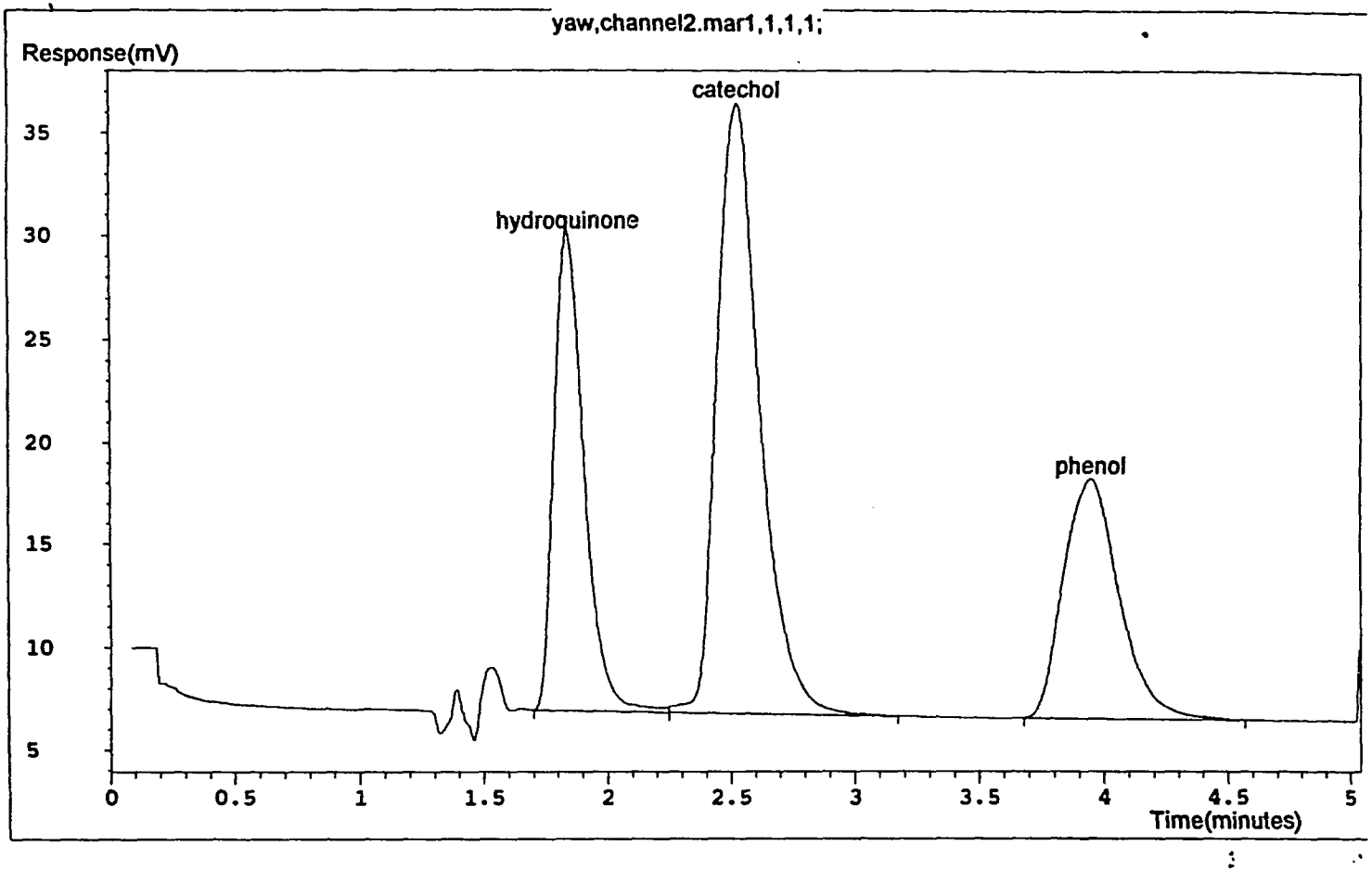

Figure 4.2 The Retention Time of Phenol, Catechol, and Hydroquinone in the Analysis of HPLC

4.4.3 Kinetic Model Study of Base-induced Decomposition of Hydrogen Peroxide

A series of hydrogen peroxide decomposition reactions were performed at different pH conditions. Reaction models were run to determine which set of input parameters would provide results consistent with the experimental data. The rate constants were determined using the Rosenbrock Hillclimb Optimization Algorithm with the LSODE solver.

The pH of the reaction solution was determined at the beginning and at the end of each reaction. The pH change did not exceed 0.1 unit. The temperature was at 22 ± 0.1^0C.

4.4.4 Kinetic Model Study of the Decomposition of Hydrogen Peroxide under UV Radiation in Different pH Conditions

A series of hydrogen peroxide decomposition reactions with UV radiation was performed at pH values of 3.08, 6.94, 9.61, 10.89, 11.50. The fundamental reaction rate constants for pH < 7 were obtained from the literature. These rate constants were applied at pH = 6.94 to confirm the kinetic model and to determine the rate constant, $k_{H2O2}I$, by fitting the experimental data. The rate constants of the important reactions at higher pH conditions can be obtained by fitting the experimental data obtained at pH = 10.80. The resulting rate constants were used at pH = 11.50 to confirm the kinetic mechanism proposed.

4.4.5 Kinetic Model Study of Oxidation of Phenol with UV Radiation alone at Different pH Conditions

Phenol is partially ionized at pH = 9 and becomes a phenolate anion. Three experiments at conditions of pH = 6.45, 9.35, 10.80 were conducted. The effects of absorbance of reactants and intermediates were considered in this model. The rate constant $k_{Iph}I$ was

obtained by fitting experimental data taken at pH = 6.45. The rate constant $k_{lpha}I$ was determined by fitting experimental data obtained at pH = 10.80. These rate constants were verified by comparing the prediction of the model to experimental data at pH = 9.35.

4.4.6 Kinetic Model Study of Effect of Bicarbonate on the Decomposition of Hydrogen Peroxide

In order to find the relationship between the decomposition of hydrogen peroxide and the dosage of bicarbonate, the ratio of bicarbonate to hydrogen peroxide was 2, 10 and 100 in three experimental runs, respectively. The rate constants k_{HCO3^-} and $k_{CO3=}$ could be obtained by same procedure.

4.4.7 Kinetic Model Study of the Effect of Bicarbonate As a Scavenger of OH. Radical

Different dosages of bicarbonate were used in experimental runs. When the ratio HCO_3^-/H_2O_2 = 100 was reached, the effect of bicarbonate on the kinetics was significant. The rate constants k_{30} and k_{31} were obtained by same procedure as section 4.4.5.

4.4.8 Bicarbonate Interfere with the Destruction of Phenol in the Presence of H_2O_2/UV

Bicarbonate can trap free radical and can interfere with the destruction of target compound. To investigate this phenomenon, two different dosages of bicarbonate were added to the reaction system of phenol-H_2O_2/UV. The model prediction using the previous rate constants was compared to experimental data.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Effect of pH on the Decomposition of Hydrogen Peroxide

The effect of the hydroxyl ion (OH^-) on the decomposition of hydrogen peroxide was determined using the proposed mechanism as follows:

$$H_2O_2 + OH^- \xleftrightarrow{K_{H_2O_2}} HO_2^- + H_2O$$

$$H_2O_2 + HO_2^- \xrightarrow{k_1} H_2O + OH^- + O_2$$

$$OH^- + HO_2^- \xrightarrow{k_2} O^{2-} + H_2O_2$$

$$O^{2-} + H_2O_2 \xrightarrow{k_3} OH^- + HO_2^-$$

Figure 5.1 shows the normalized concentration (Ca/Ca_0) of decomposed hydrogen peroxide versus reaction time in the pH range of 11.46 to 12.58. The points are experimental data, and the lines are model predicted concentration values. The concentration of decomposed hydrogen peroxide predicted by proposed the mechanism are in excellent agreement with the experimental data. By using numerical methods of parameter estimation at different pH conditions individually, we got k_1, k_2, k_3 at different pH values. When the pH is lower than 11.2, the three rate constants gradually approach a constant value of $k_1 = 9.17 \times 10^{-3}$ l/mole-sec, $k_2 = 2.5 \times 10^{-3}$ l/mole-sec, $k_3 = 1.67 \times 10^{-1}$ l/mole-sec. The theoretical predicted curves based on these three constants and experimental data were plotted in Figure 5.2. Points represent the experimental data, while lines show the model prediction. The concentration of decomposed hydrogen

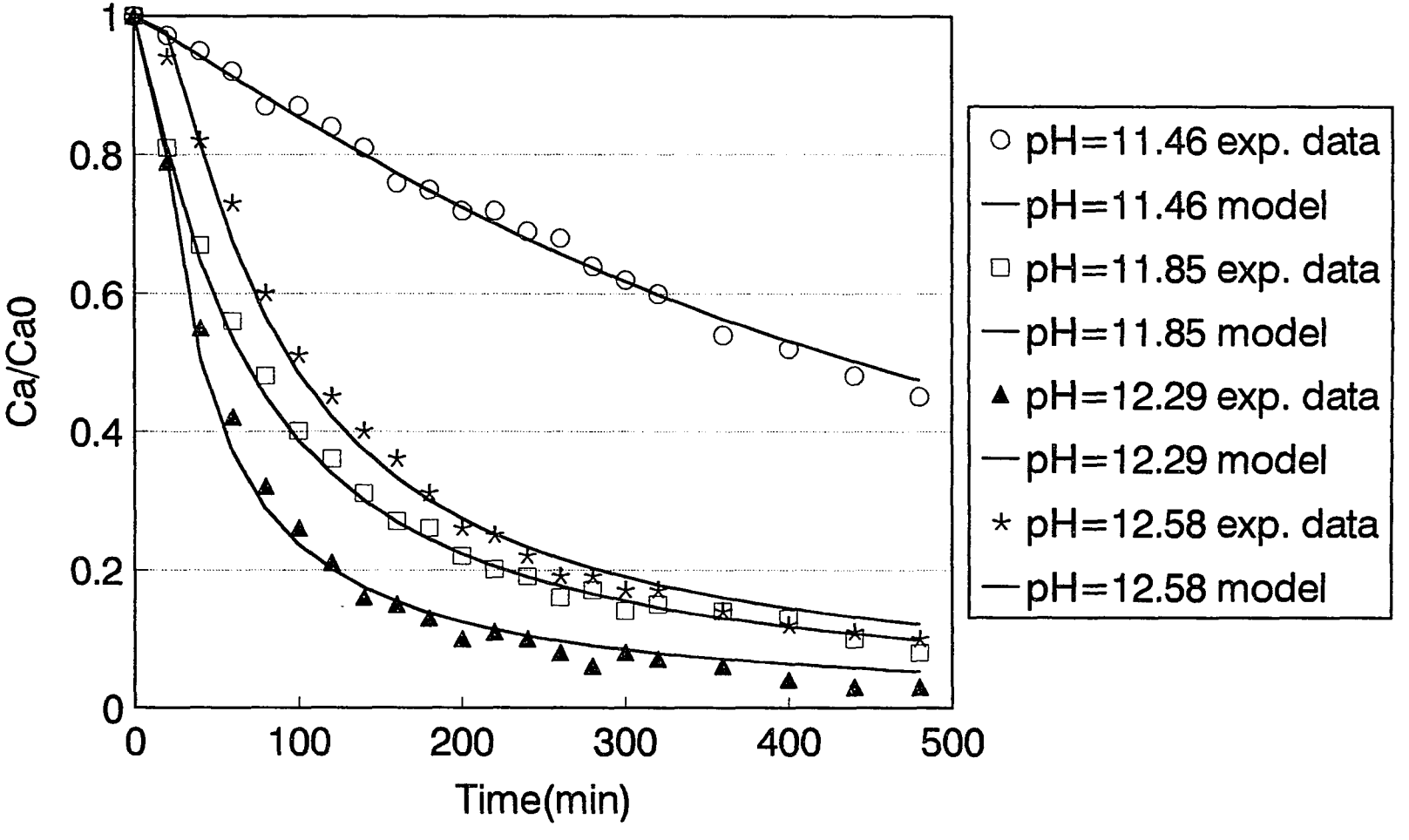

Figure 5.1 The Decomposition of Hydogen Peroxide Under Different pH Conditions (I)
Initial H2O2 conc.(Ca0)=4.73x10-3 mole/l , Ca=concentration of hydrogen peroxide at any time

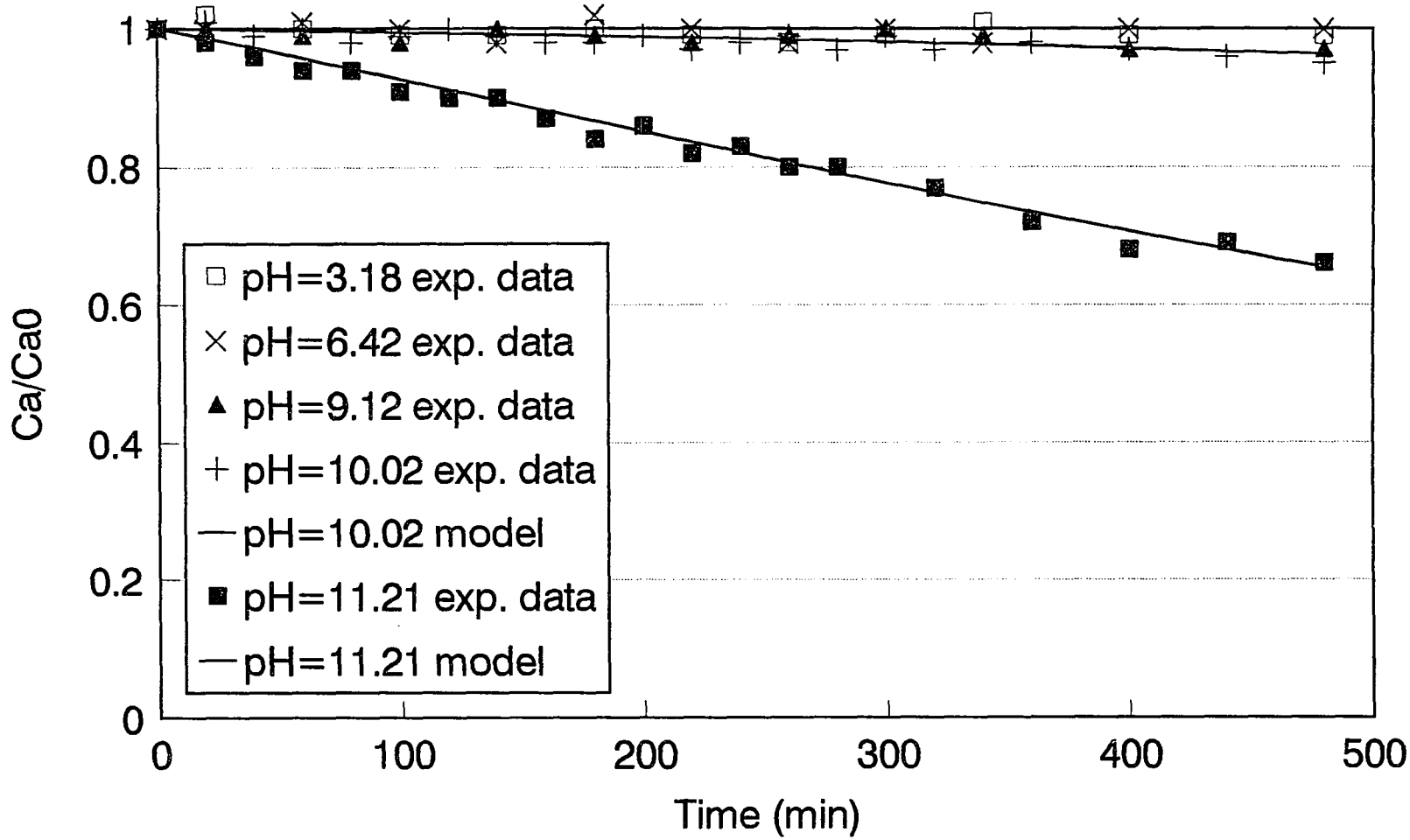

Figure 5.2 The Decomposition of Hydrogen Peroxide Under Different pH Conditions (II)
Initial H2O2 conc.(Ca0)=4.73x10-3 mole/l , Ca=concentration of hydrogen peroxide at any time

peroxide predicted by the proposed mechanism are in excellent agreement with the experimental data. Less than 1 % of the original hydrogen peroxide is decomposed after 9 hours of reaction time at pH values below 9. The rate constants are summarized in Table 5.1. These results show that as the pH value increases, the rate of decomposition of hydrogen peroxide as indicated by k_1 also increases. This increase continues until a maximum is reached at a pH value of 12.29.

Table 5.1. Summary of Rate Constants k_1, k_2 and k_3 of Decomposition of Hydrogen Peroxide under Different pH Conditions

pH	k_1, l/mole-sec	k_2, l/mole-sec	k_3, l/mole-sec
<11.2	9.17×10^{-3}	2.50×10^{-3}	1.67×10^{-1}
11.46	1.08×10^{-2}	4.88×10^{-3}	3.52×10^{-1}
11.85	3.87×10^{-2}	1.50×10^{-2}	7.97×10^{-1}
12.29	5.00×10^{-2}	5.48×10^{-2}	9.40×10^{-1}
12.58	9.97×10^{-3}	1.67×10^{-3}	1.43×10^{-1}

The observation of a maximum rate was in agreement with results published by Oki et al. (1964) and Duke and Hass (1961). However, the reported pH values at which the decomposition of hydrogen peroxide is at a maximum appear to vary. Our results indicated that the maximum is at a pH of 12.29, as compared to Oki et al. where the pH is 13.4 and Duke and Hass where the pH is 11.5. The deviation of results by different investigators may be caused by the additives in hydrogen peroxide by different suppliers.

It is interesting to note that the two charged species reaction showed that both rate constant k_2 and k_3 also reaches a maximum value at the same pH value of 12.29. These two reactions were added to our proposed mechanism which gave a much better representation of our experimental data.

In our study, the rate constants k_1, k_2 and k_3, for the decomposition of hydrogen peroxide under different pH conditions followed the beta probability function with parameters $\alpha > 0$, $\beta > 0$ (Larson, 1967):

$$f(0) = 0$$

$$f(x) = \frac{\Gamma(\alpha+\beta)}{\Gamma(\alpha)\Gamma(\beta)} x^{\alpha-1}(1-x)^{\beta-1} \qquad 0 < x < 1$$

After the shifting of the base line, the beta probability function becomes the following:

$$k_i = k_{i0} \qquad \text{pH} < 11.2$$

$$k_i = k_{i0} + a_i \frac{\Gamma(\alpha_i+\beta_i)}{\Gamma(\alpha_i)\Gamma(\beta_i)} x^{\alpha_i-1}(1-x)^{\beta_i-1} \qquad 11.2 \le \text{pH} \le 12.7$$

$$\text{where} \quad x = \frac{pH - 11.2}{1.5}$$

i=1,2,3

Figures 5.3, 5.4, and 5.5 shows the variation of the rate constants k_1, k_2 and k_3 with respect to pH. It can be seen that the curves are slightly skewed to the right. By numerical method of parameter estimation, the parameters k_{i0}, a_i, α_i and β_i were obtained and the results are tabulated in Table 5.2.

From parameters listed in Table 5.2, we could predict the rate constants of the decomposition of hydrogen peroxide in the pH range from 3 to 12.70 using the beta probability function.

Table 5.2 The Parameters k_{i0}, a_i, α_i and β_i from the Parameter Estimation of Beta Probability Function

i	k_{i0}	a_i	α_i	β_i
1	9.17×10^{-3}	4.00×10^{-2}	4.88	3.37
2	2.50×10^{-3}	1.83×10^{-1}	8.78	4.62
3	1.67×10^{-1}	1.073	4.21	3.19

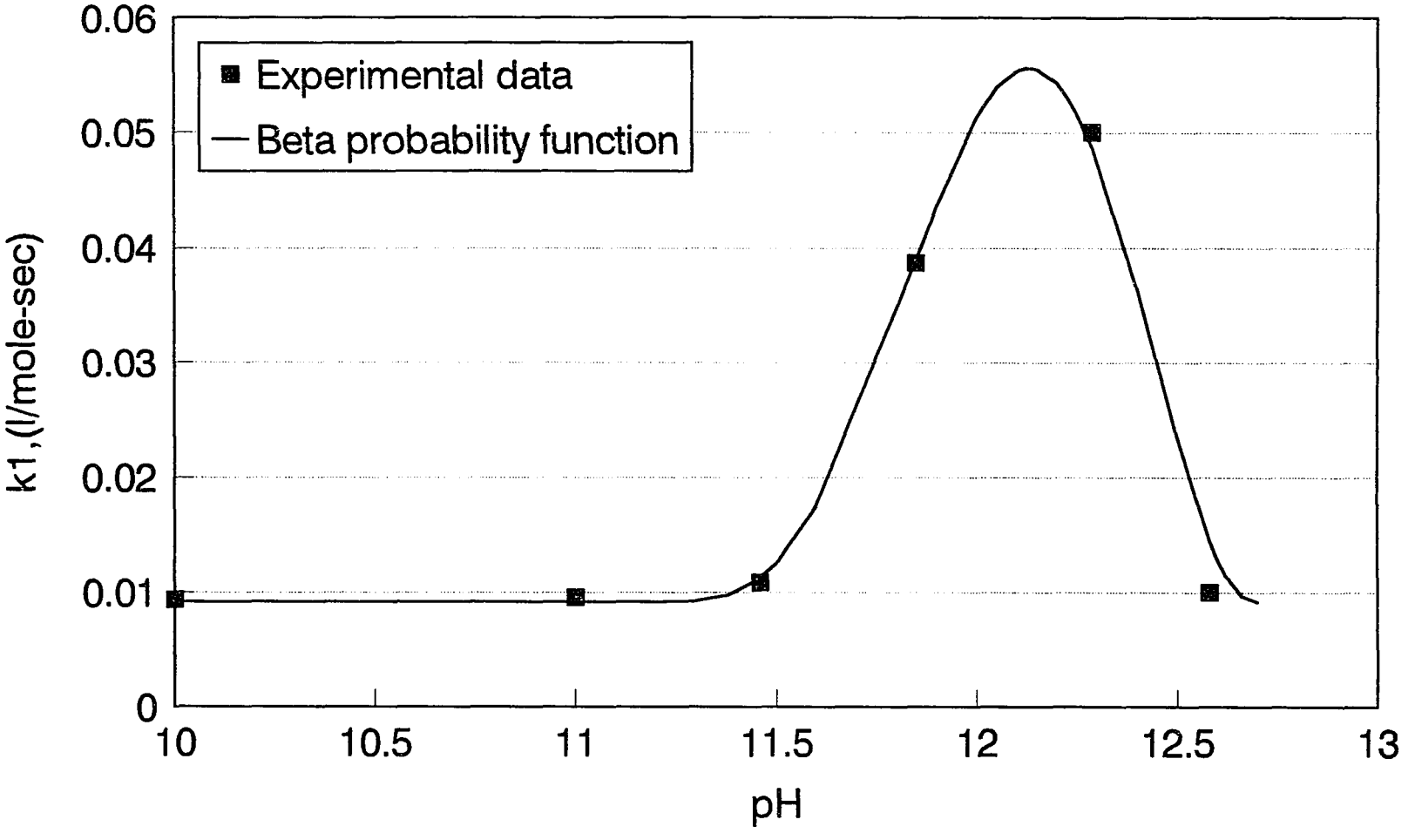

Figure 5.3 Rate Constant, k1 of Decomposition of Hydrogen Peroxide Under Different pH Conditions
Initial H2O2 conc.=4.73x10-3 mole/l

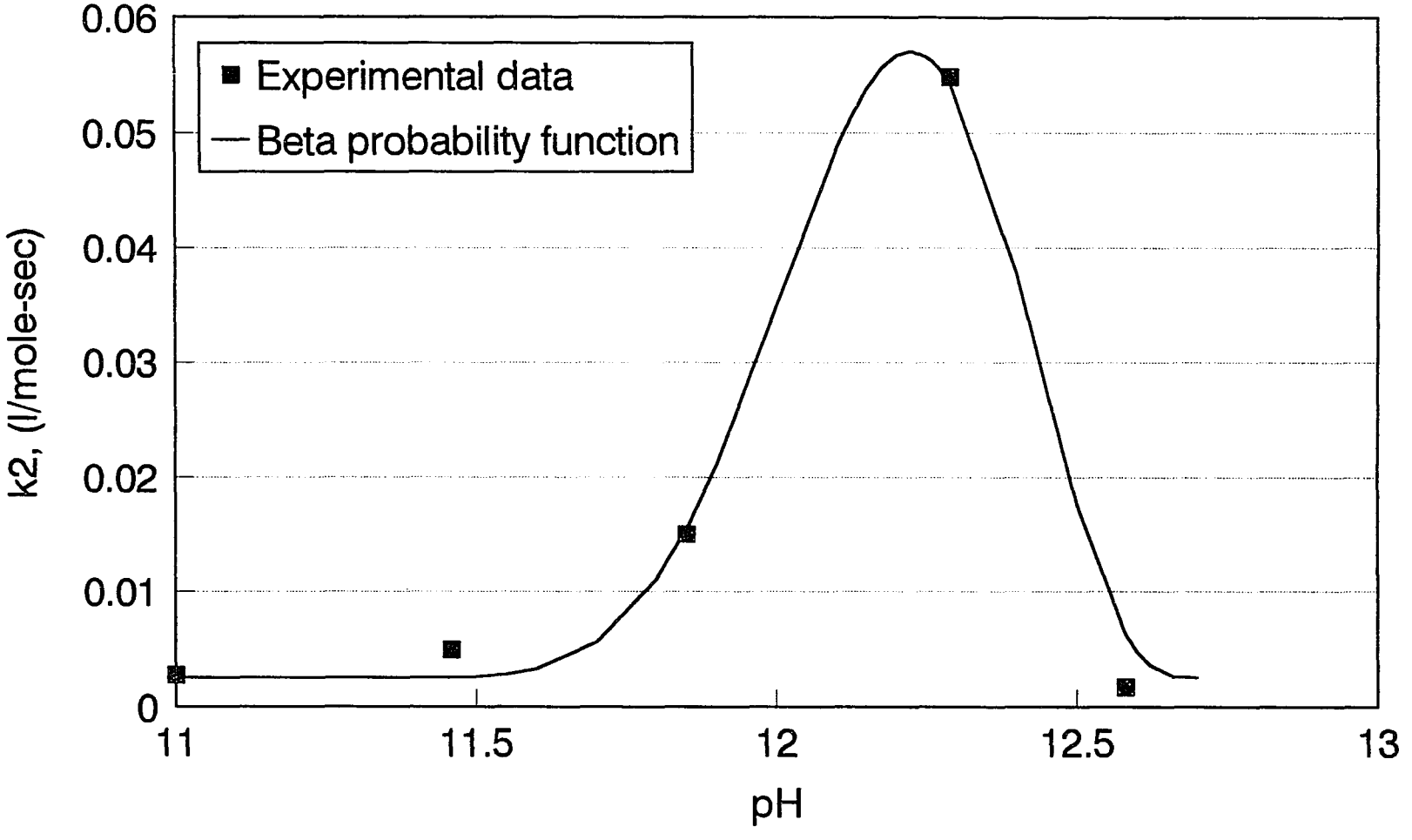

Figure 5.4 Rate Constant, k2 of Decomposition of Hydrogen Peroxide Under Different pH Conditions

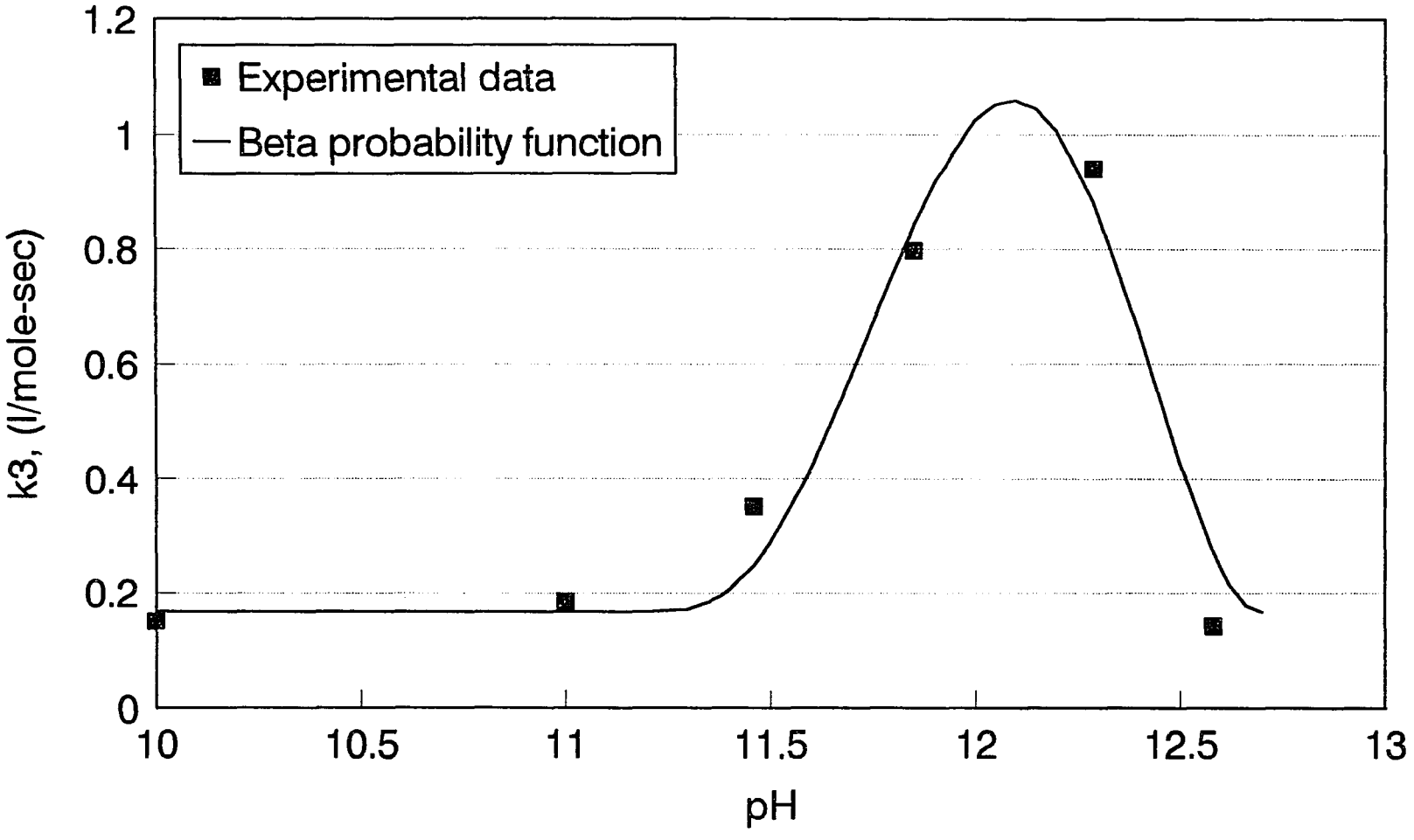

Figure 5.5 Rate constant, k3 of Decomposition of Hydrogen Peroxide Under Different pH Conditions

5.2 Effect of pH on the Decomposition of Hydrogen Peroxide under UV Radiation

The decomposition of H_2O_2 under UV radiation is fundamental in understanding the AOP reaction mechanisms. From previous study of Shu (1993), the photodecomposition rate constants of hydrogen peroxide were approached by considering five reactions (as shown in Table 5.3). The results gave a good fitting of experimental data. However, this mechanism can only be applied in the pH range of 3-9. In alkaline conditions, this mechanism should be modified.

Figure 5.6 shows the normalized concentration (Ca/Ca_0) of decomposed hydrogen peroxide versus reaction time in the pH range of 3 to 11.5 under UV radiation. The results showed that the higher the alkalinity, the higher the decomposition rate of hydrogen peroxide. Since the mechanism reported by Shu (1993) can not be applied in this condition, four additional reactions were picked from the literature. Table 5.3 showed the reactions used in this study compared to the previous work of Shu (1993).The products of reactions k_{17} and k_{19} have been modified because there is no significant pH variation during the reaction. The results gave a good fitting of experimental data. The rate constants k_{17} and k_{19} were obtained from computer modeling and are shown in Table 5.3. The comparison of these two constants obtained from this study with those reported by other authors is shown in Table 5.4. It should be noted that rate constant k_{17} obtained from this study is very close to the one reported by Christensen et al. in 1982, but the products between these two reactions are different as shown in Table 5.4. Besides, rate constant k_{19} obtained from this study is three times that of the one reported by Ferradini et

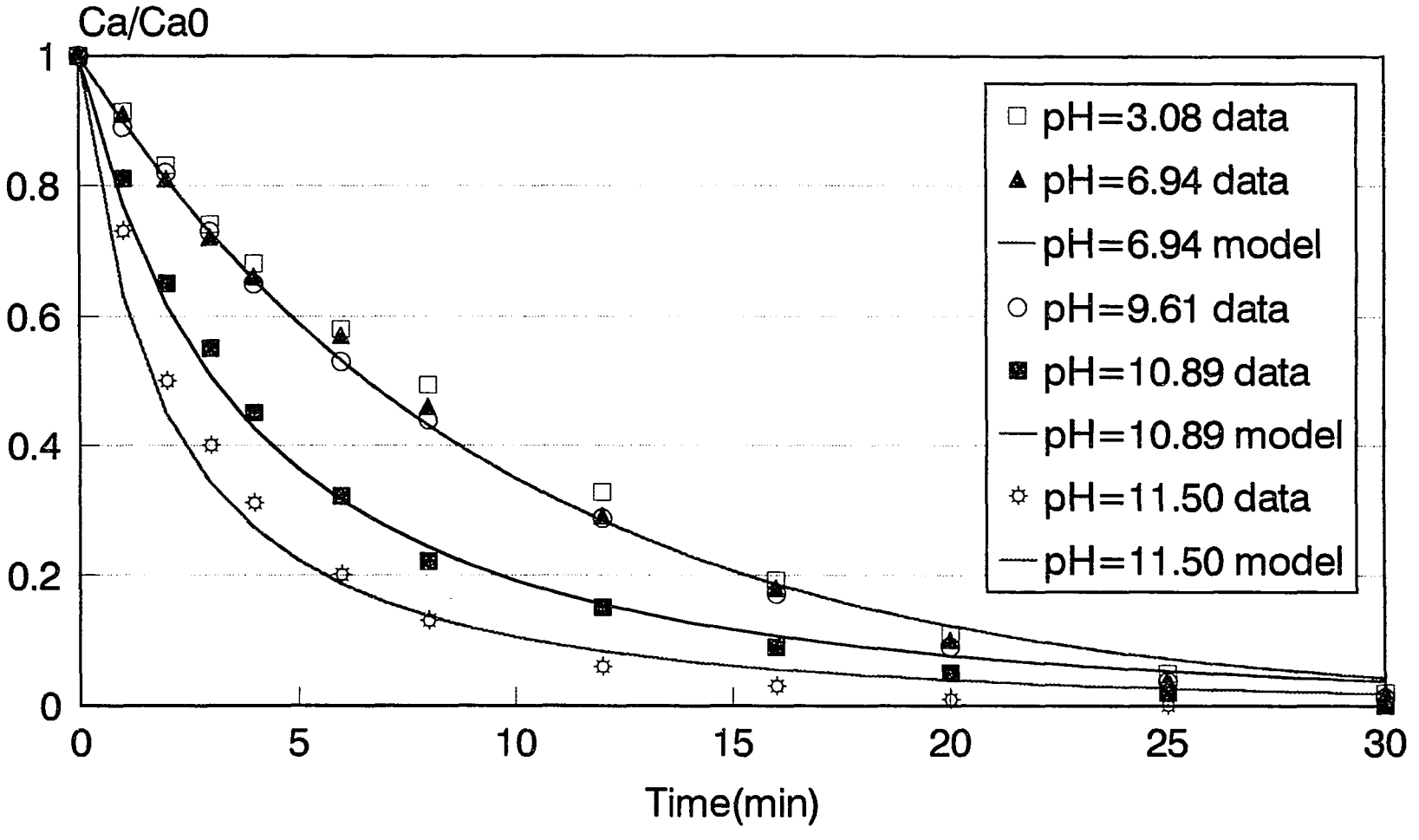

Figure 5.6 Decomposition of Hydrogen Peroxide under Different pH with UV

Initial H2O2 conc. =4.73 x 10-3 mole/l, UV light intensity= 280 Watts

al. in 1978. Again, the products between these two reactions are different as shown in Table 5.4.

Table 5.3 The Reactions Used in This Study Compared to the Previous Work of Shu (1993)

Reactions	Rate constants	this study	Previous work
$H_2O_2 + h\nu \xrightarrow{k_{IH_2O_2}} 2\ OH\bullet$	$k_{IH2O2}I=5.8\times10^{-4}$	X	X
$H_2O_2 + OH\bullet \xrightarrow{k_{10f}} HO_2\bullet + H_2O$	$k_{10f}= 2.7 \times 10^{7}$	X	X
$H_2O_2 + HO_2\bullet \xrightarrow{k_{11f}} OH\bullet + H_2O + O_2$	$k_{11f}= 3.7$	X	X
$2\ OH\bullet \xrightarrow{k_{14}} H_2O_2$	$k_{14} = 4.0 \times 10^{9}$	X	X
$2\ HO_2\bullet \xrightarrow{k_{15}} H_2O_2 + O_2$	$k_{15} = 8.3 \times 10^{5}$	X	X
$OH\bullet + HO_2\bullet \xrightarrow{k_{16}} H_2O + O_2$	$k_{16} = 3.7 \times 10^{10}$	X	X
$OH\bullet + HO_2^- \xrightarrow{k_{17}} O_2^-\bullet + H_2O$	$k_{17}= 7.4 \times 10^{9}$(1)	X	not considered
$HO_2\bullet \xleftrightarrow{k_{HO_2\bullet}} H^+ + O_2^-\bullet$	pK= 4.8 (2)	X	not considered
$HO_2\bullet + O_2^-\bullet \xrightarrow{k_{18}} HO_2^- + O_2$	$k_{18}=7.9 \times 10^{7}$ (3)	X	not considered
$O_2^-\bullet + H_2O_2 \xrightarrow{k_{19}} HO_2^- + HO_2\bullet$	$k_{19}= 6.61$ (1)	X	not considered

(1) Obtained from computer simulation in this study.
(2) Reported by Bielski et al. in 1985
(3) Reported by Rabani et al. in 1969

Table 5.4 Comparison of k_{17} and k_{19} Obtained from this Study and from other Authors

Reactions	Rate constants	Source
$OH\bullet + HO_2^- \xrightarrow{k_{17}} O_2^-\bullet + H_2O$	7.4×10^9	this study
$OH\bullet + HO_2^- \xrightarrow{k_{17}} OH^- + HO2\bullet$	7.5×10^9	Christensen et al.(1982)
$O_2^-\bullet + H_2O_2 \xrightarrow{k_{19}} HO_2^- + HO_2\bullet$	6.61	this study
$O_2^-\bullet + H_2O_2 \xrightarrow{k_{19}} OH^- + OH\bullet + O_2$	2.25	Ferradini et al.(1978)

From computer modeling, at higher alkalinity the $k_{19}[O_2^-\bullet][H_2O_2]$ term becomes more important for the decomposition of hydrogen peroxide. Figure 5.7 shows the concentration of OH radical during the decomposition of H_2O_2 by UV radiation at different pH conditions. This data is obtained from computer simulation. The result shows that the concentration of OH radical at pH = 10.89 is one order less than that at pH = 6.94. At higher alkalinity there is a significant amount of HO_2^- ion, which should trap OH radicals and interfere with the destruction of target compounds. This was proven by the experiment where the decomposition of the target compound was monitored in the presence of H_2O_2/UV. This result will be discussed later in section 5.4.

Figure 5.8 shows the decomposition of H_2O_2 under different light intensities at pH = 6.94. The results gave a good fitting to the experimental data. The rate constants were taken from computer simulation as shown in Table 5.5. Figure 5.9 shows the rate constant

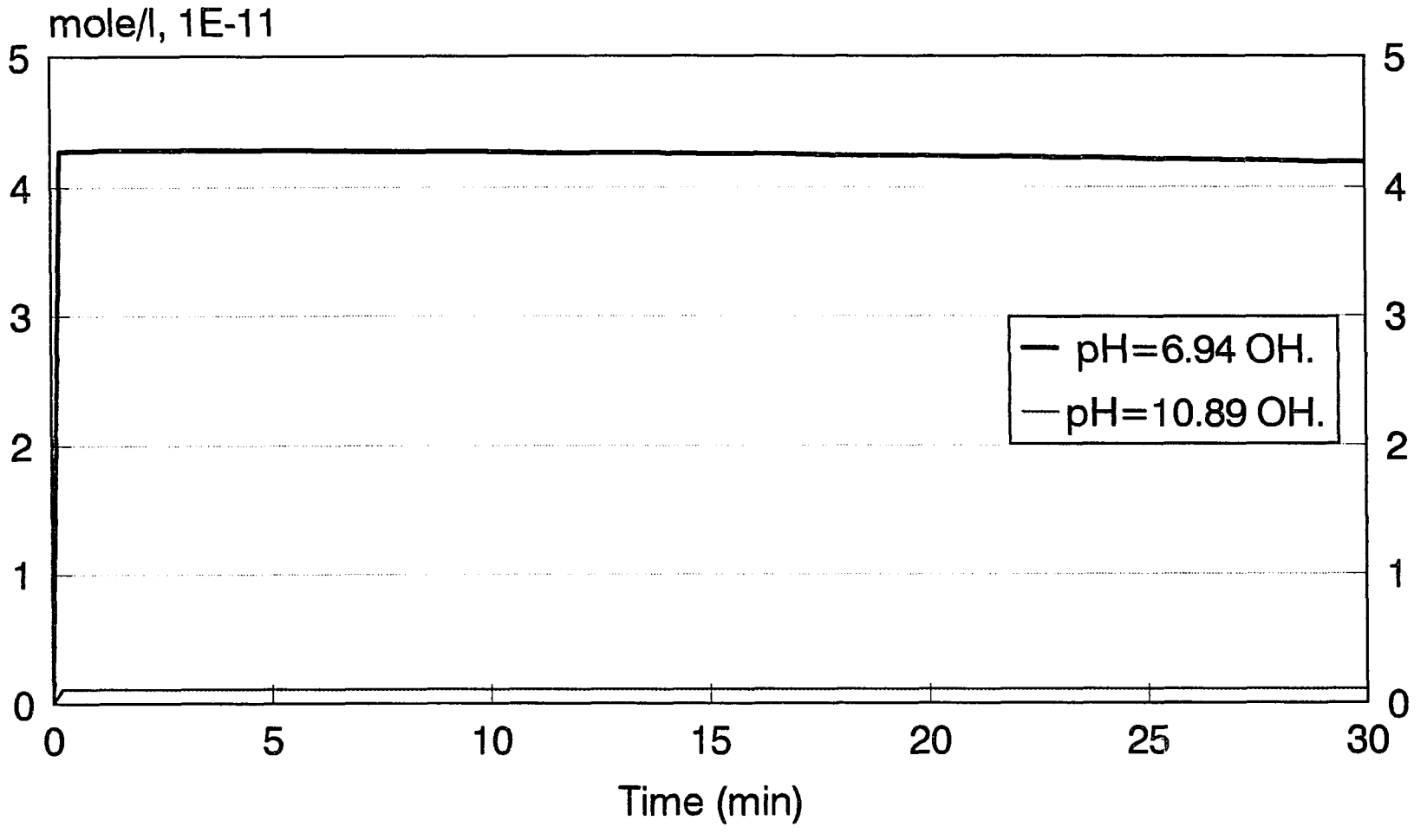

Figure 5.7 The Concentration of OH Radical During the Decomposition of Hydrogen Peroxide by UV Radiation
Light intensity= 280 Watt, initial H2O2 conc.= 4.73 x 10-3 mole/l

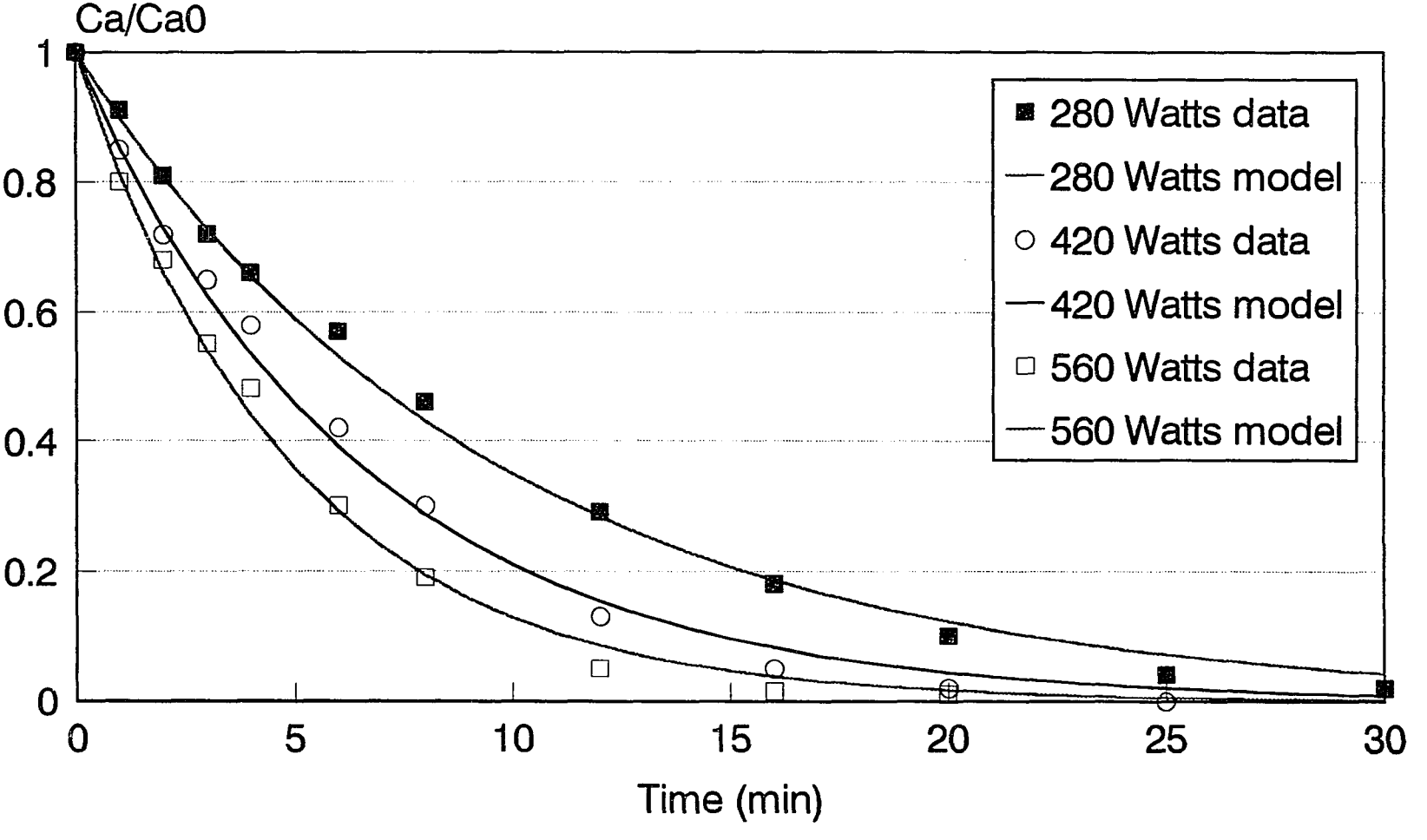

Figure 5.8 The Decomposition of Hydrogen Peroxide by Different UV Light Intensities

Initial H2O2 conc. = 4.73 x 10-3 mole/l, pH=6.94

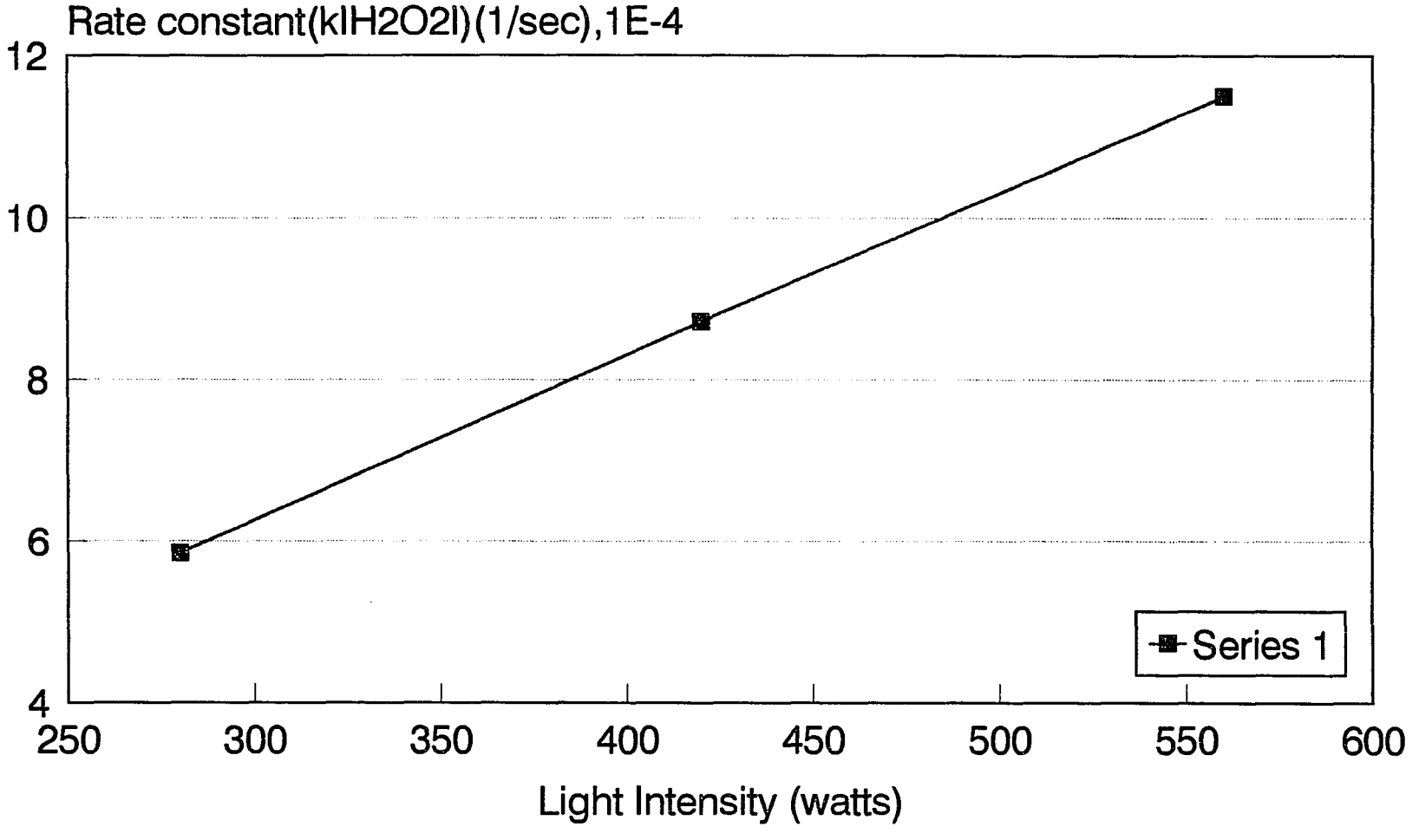

Figure 5.9 Rate Constant of Hydrogen Peroxide Decomposition Versus Light Intensity
pH=6.94

of hydrogen peroxide decomposition versus light intensity. The results demonstrated the almost linear relationship between $k_{IH2O2}I$ and light intensities.

Table 5.5 Rate Constant $k_{IH2O2}I$ Varied with Light Intensities

Light intensity	rate constant ($k_{IH2O2}I$)(l/sec)
280 Watt	5.85×10^{-4}
420 Watt	8.71×10^{-4}
560 Watt	1.15×10^{-3}

5.3 Effect of pH on the Decomposition of Phenol under UV Radiation alone

Phenol can be decomposed by direct photolysis. It is already partially ionized at pH = 9.0 and becomes a phenolate anion (pKa = 9.75, Kirk-Othmer 1982). The phenolate anion absorbs more of the light emitted by a Xe lamp than the phenol molecules (Lipczynska-Kochany 1993). The rate of decomposition of the phenolate anion by direct photolysis is different from the rate of decomposition of phenol by direct photolysis. Three pH conditions pH = 6.45, 9.35 and 10.80 were studied. The color of solution becomes brown during the reaction. Thus, the transmittance of solution must be considered in the modeling because the penetration of UV light in the reactor plays an important role for the destruction of organics in AOP system.

Figure 5.10 shows the transmittance of phenol solution with respect to time under different pH conditions during direct photolysis. Results have shown that in the beginning

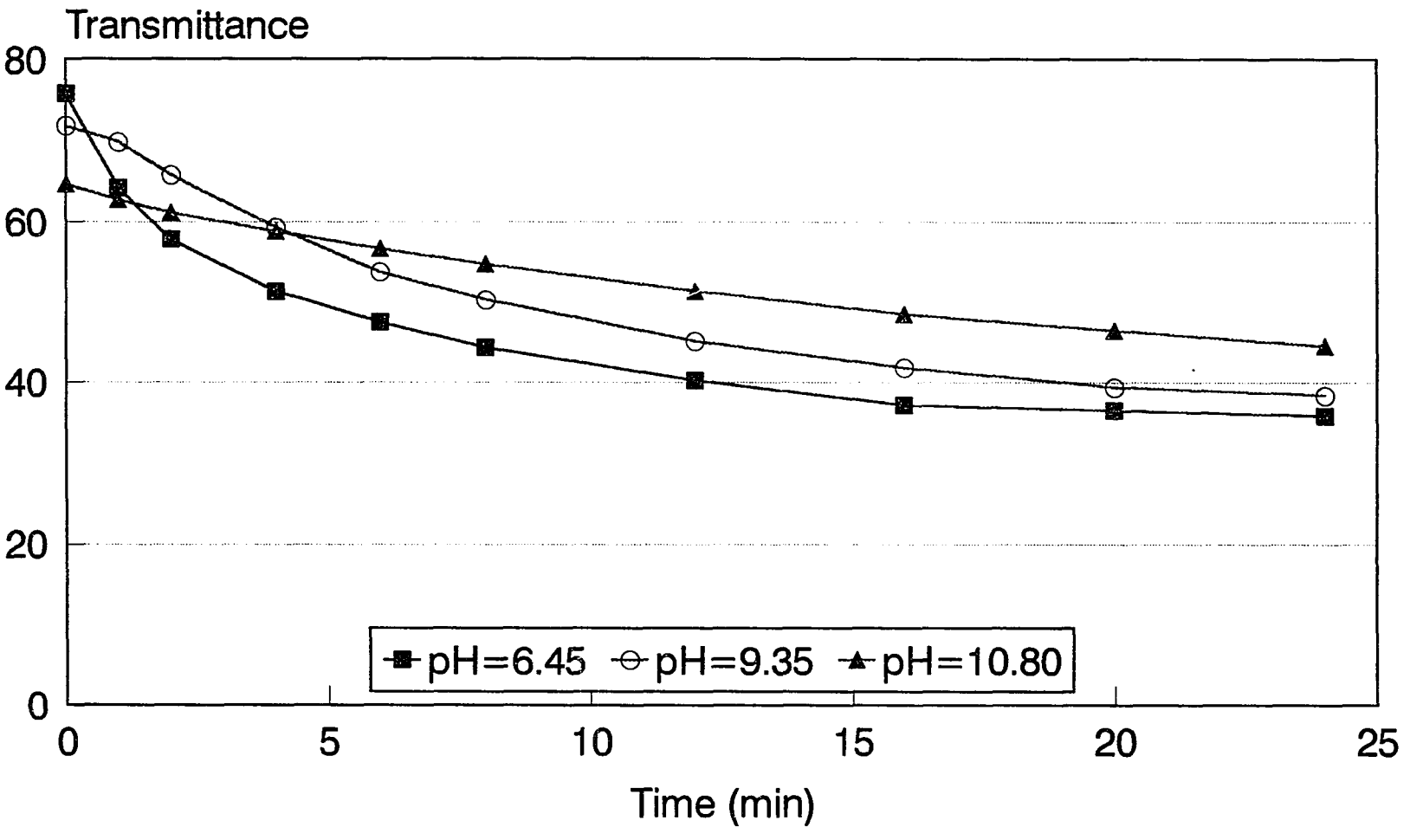

Figure 5.10 Transmittance Variation During Destruction of Phenol by UV Radiation under Different pH Conditions
Initial phenol conc.(Cphenol0)=16.73 ppm, light intensity=280 watts

of the reaction the phenolate anion absorbs more of the light emitted by the UV lamp than phenol molecules. However, the products of phenol absorb more light than those of the phenolate anion. It should be noted that at pH = 10.80 under this condition almost all of the phenol became phenolate anion. Therefore, in the photolysis process, the effect of absorbance of products must be considered when modeling is conducted. In HPLC analysis, it is hard to separate the phenol and phenolate anion because they have similar properties. Fortunately the initial concentration of phenol and phenolate anion can be known at different conditions by the dissociation constant of phenol.

Figure 5.11 shows the concentration of phenol plus phenolate anion with respect to time under different pH conditions. The points are experiment data, and the lines denote the predicted model. The photodecompositon rate constants $k_{Iph}I$ and $k_{Ipha}I$ were solved by computer simulation at pH = 6.45 and pH = 10.80, respectively. The rate constants are summarized in Table 5.6. The results in Table 5.6 shows that $k_{Ipha}I$ is smaller than $k_{Iph}I$. This means that the phenolate anion is more difficult to decompose by direct photolysis than phenol.

The reaction curve for pH = 9.31 is predicted by applying these two rate constants. The prediction of the model is in good agreement with the experimental data.

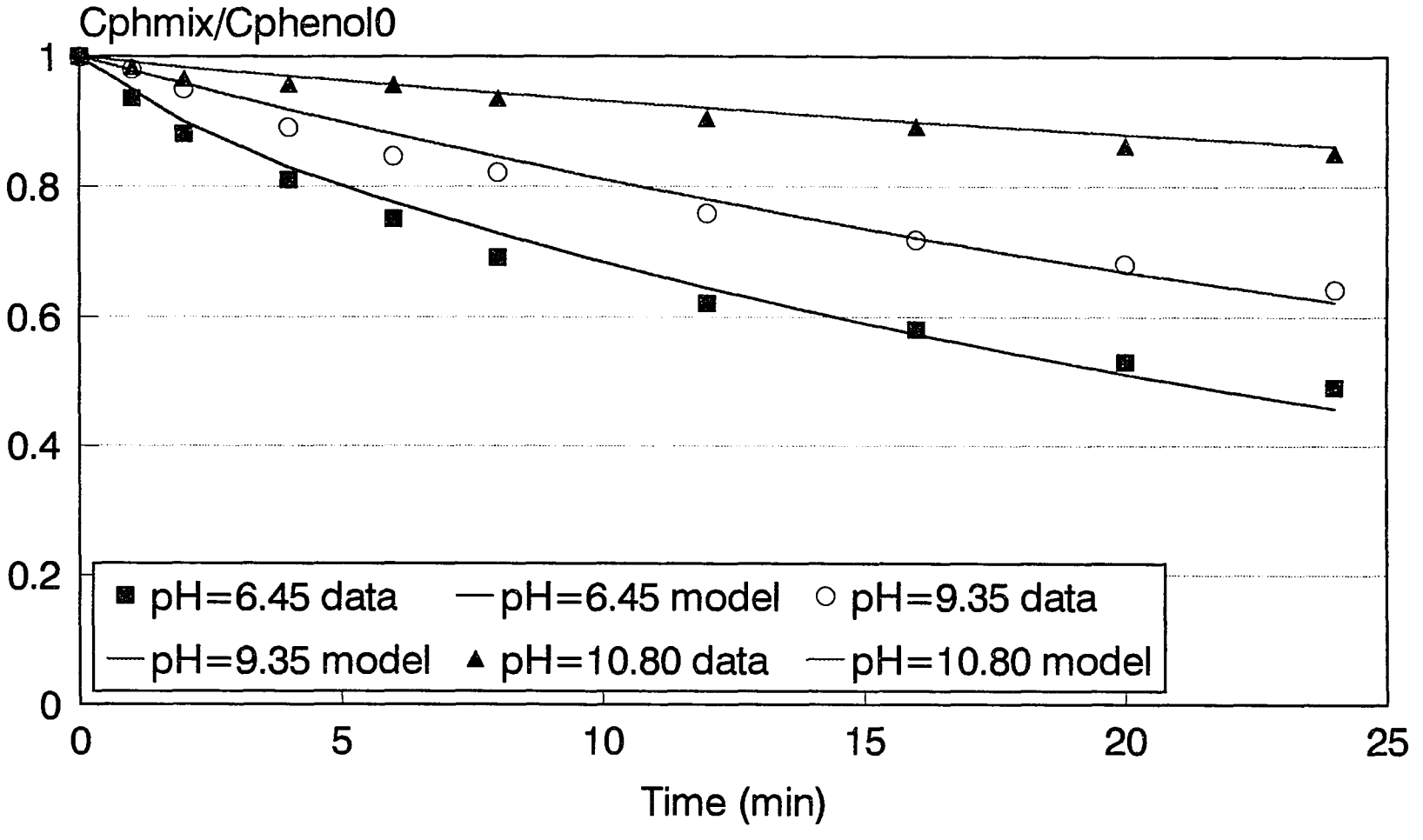

Figure 5.11 Destruction of Phenol by UV Radiation alone under Different pH Conditions
Initial phenol conc.(Cphenol0)=16.73 ppm, Cphmix=Cphenol+Cphenolate,
light intensity=280 watts

Table 5.6 The Photodecomposition Rate Constants of Phenol and Phenolate and Dissociation Constant of Phenol

Reactions	rate constant (l/sec)
phenol + $H_2O \xleftrightarrow{K_{phenol}}$ phenolate anion + H^+	1.78×10^{-10} (*)
Phenol + hν $\xrightarrow{k_{lphI}}$ products	7.67×10^{-4}
Phenolate anion + hν $\xrightarrow{k_{lpha I}}$ products	9.07×10^{-5}

(*) Obtained from Kirt-Othmer 1982

5.4 Effect of pH on the Decomposition of Phenol in the Presence of H_2O_2/UV

In this study, the effect of direct photolysis and the absorbance of products was considered. It is known that both phenol and the phenolate anion react with hydroxyl radicals and have comparable rate constants (Buxton et al. 1988). Three pH conditions pH = 6.49, 9.31 and 10.76 were used in this experiment. From HPLC analysis the intermediates, catechol and hydroquinone, were detected. The phenolic radical exists during the reaction as suggested by the literature [Leuven (1972), Matthews et al.(1965)].

Figure 5.12 shows the transmittance of phenol solution with respect to time under different pH conditions in the presence of H_2O_2/UV. Initially, the transmittance of a solution with a pH =10.76 is less than that of a solution with a pH = 6.49. However, as reaction time increases, transmittance of the solution with a pH =10.76 significantly increased compared with transmittance of the solution with a pH = 6.49. These results were considered in the following modeling.

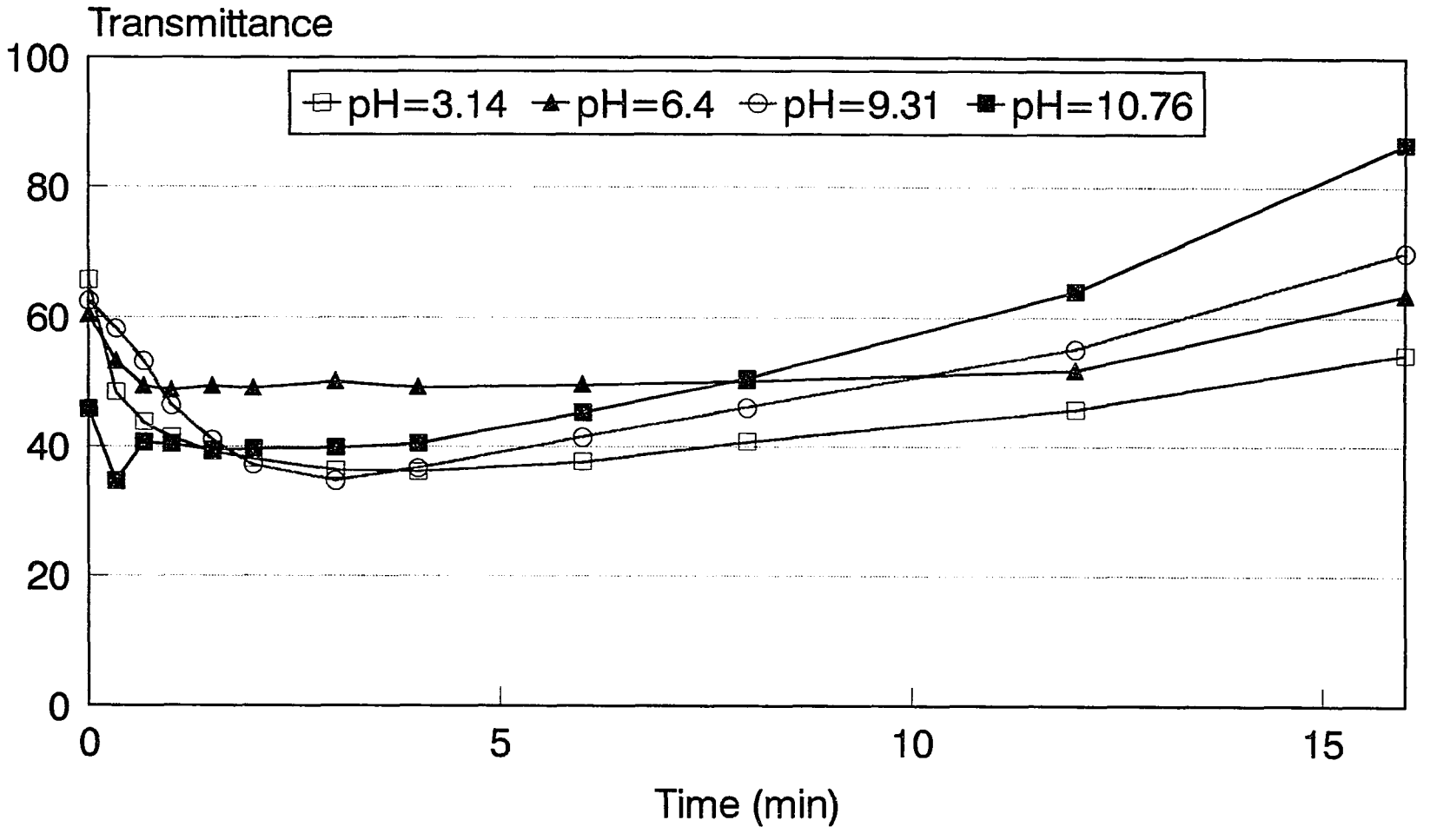

Figure 5.12 Transmittance Variation During Destruction of Phenol in the Presence H2O2/UV under Different Conditions
Light intensity = 280 watts

Figure 5.13 shows the variation of the concentration of phenol and its intermediates, catechol, hydroquinone, and phenolic radical, with respect to time at pH = 6.49 in the presence of H_2O_2/UV. The points are the experimental data and the lines are predicted model. In this condition the phenolate anion can be neglected. There is very good agreement between the experimental data and the kinetic model prediction for phenol, catechol, and hydroquinone concentration. However, the reaction curve for the phenolic radical was constructed solely using computer simulation since phenolic radical can not be detected experimentally. The rate constants obtained from computer simulation are summarized in Table 5.7.

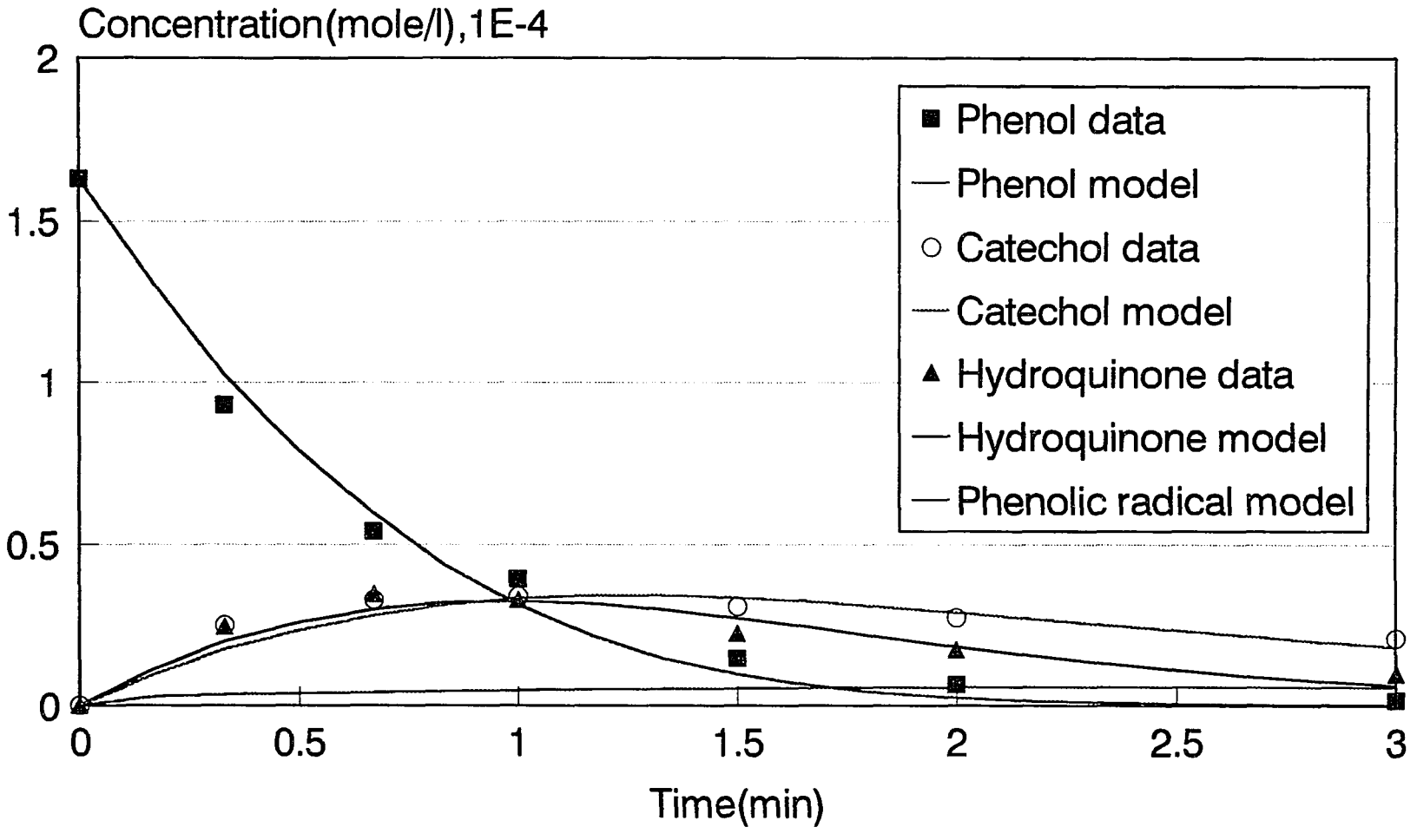

Figure 5. 13 Destruction of Phenol in the Presence of H2O2/UV at pH=6.49
With Intermediate of Catechol, Hydroquinone and Phenolic Radical
Initial pH=6.49, Initial H2O2 conc.=4.73 x 10-3 mole/l, light intensity = 280 watts

Table 5.7 The Reactions Considered in the Decomposition of Phenol in the Presence of H_2O_2/UV and Rate Constants

Reactions	Rate constants(l/mole-sec)
Phenol + hν $\xrightarrow{k_{iph}I}$ products	7.67×10^{-4}
Phenol + OH• $\xrightarrow{k_{20}}$ Catechol	6.44×10^{8}
Phenol + OH• $\xrightarrow{k_{21}}$ Hydroquinone	7.98×10^{8}
Phenol + OH• $\xrightarrow{k_{22}}$ Ph•(Phenolic radical)	3.50×10^{8}
Catechol + OH• $\xrightarrow{k_{23}}$ Products (Organic acid)	3.45×10^{9}
Hydroquinone+OH• $\xrightarrow{k_{24}}$ Products (Organic acid)	8.14×10^{8}
Phenol + Ph• $\xrightarrow{k_{25}}$ Higher molecular products	9.55×10^{2}
Phenol + HO_2• $\xrightarrow{k_{26}}$ Products	8.02×10^{4}
Phenol + CO_3•$^-$ $\xrightarrow{k_{28}}$ Products (#)	6.12×10^{5}
Phenolate anion + hν $\xrightarrow{k_{iphaI}}$ Products (*)	9.07×10^{-5}
Phenolate anion + OH• $\xrightarrow{k_{27}}$ Products (*)	3.86×10^{9}

(#) when bicarbonate is present.
(*) these two reactions became significant at higher pH conditions

Figure 5.14 shows the pH variation during decomposition of phenol at pH = 6.49 in the presence of H_2O_2/UV. The points are the experimental data, and the line is the predicted model. The result shows that pH value decreased with respect to reaction time. Although the trend were the same, the model did not quite predict the experimental data.

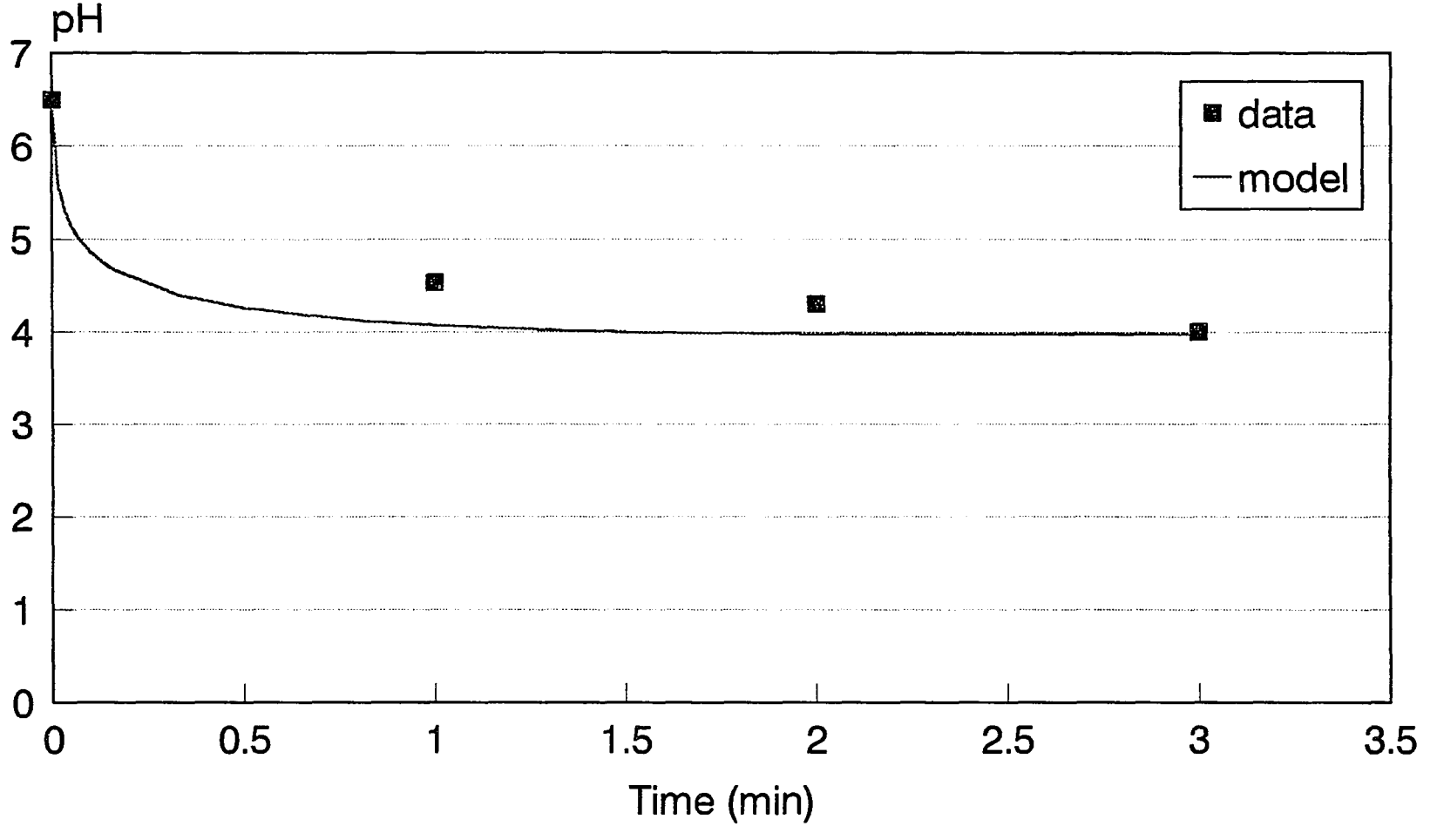

Figure 5. 14 pH Variation During the Destruction of Phenol in the Presence of H2O2/UV
light intensity = 280 watts

At pH = 10.76, 91% of phenol is ionized and becomes phenolate anion. Figure 5.15 showed the concentration of phenol plus phenolate ion with respect to time in the presence of H_2O_2/UV at pH = 10.76. The points are the experimental data, and the lines are the predicted model. Applying the rate constants from k_{20} to k_{26} for pH = 6.49, the rate constant k_{27} was obtained from computer simulation using experimental data at pH = 10.76. From the model, we get the predicted concentration curve of phenol and phenolate anion individually. By combining these two curves, the predicted concentration of phenol plus phenolate anion can be obtained. The model prediction gave a good agreement with the experimental data.

Figure 5.16 shows compares the experimental data to the model. In one caes phenol and phenolate anion is considered. In the other case, only phenol is taken into account. It indicated the predictions based on the inclusion of the formation of the phenolate anion were found to be in closer agreement with experimental data than those based on phenol only.

At pH = 9.31, 27% of phenol is ionized and becomes phenolate anion. Figure 5.17 shows the concentration of phenol plus phenolate anion versus time in the presence of H_2O_2/UV at pH = 9.31. The points are the experimental data and the lines are predicted model. The prediction curves of phenol only, phenolate anion only and phenol plus phenolate were obtained by applying the rate constants in Table 5.7.

Figure 5.18 shows the concentration of phenol plus phenolate anion at different pH conditions in the presence of H_2O_2/UV with respect to time. One can see that the higher

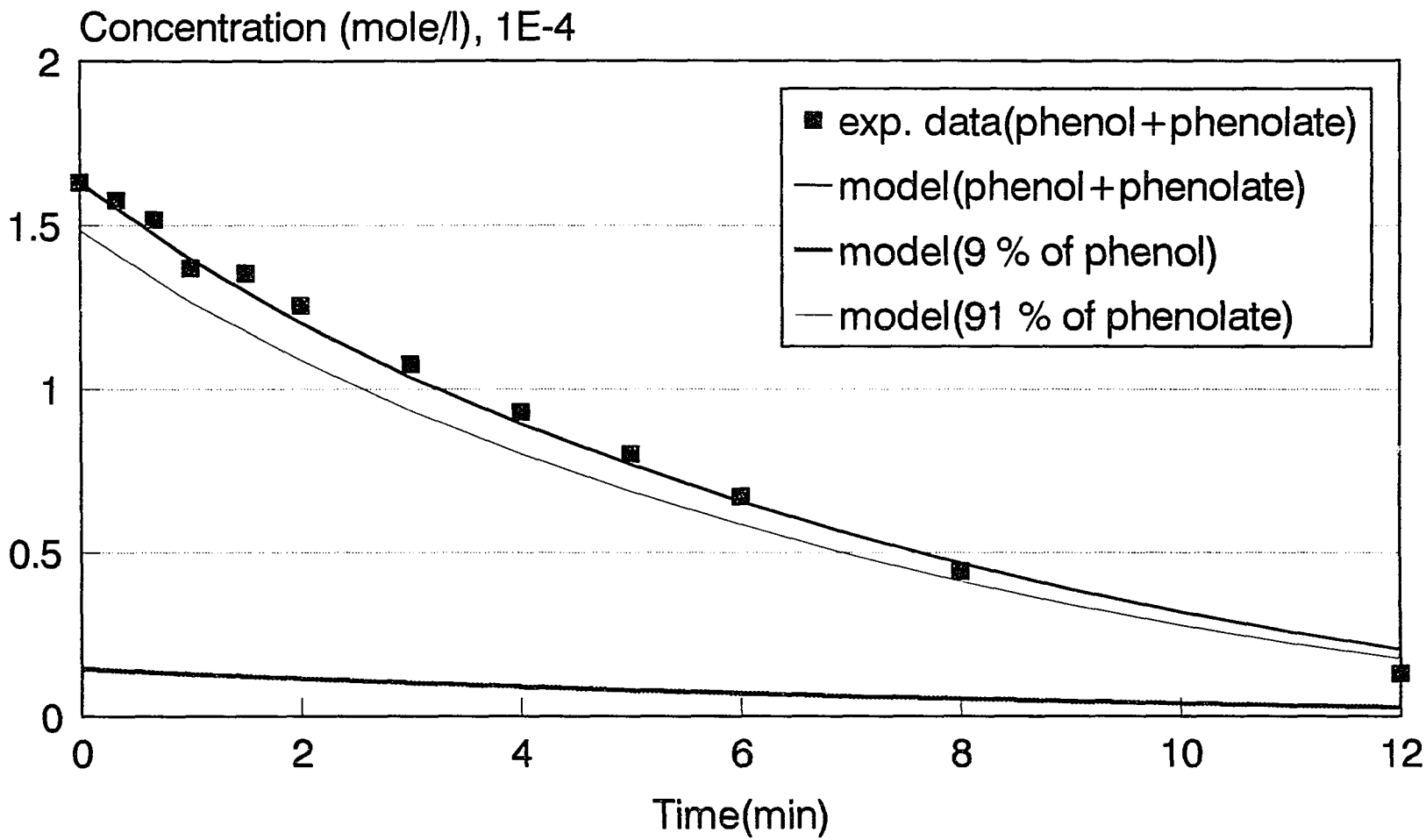

Figure 5.15 Destruction of Phenol and Phenolate Anion in the Presence of H2O2/UV at pH=10.76
Initial phenol conc.(pH=6.5)=1.63E-04 mole/l, initial H2O2 conc.=4.73E-3 mole/l,
light intensity=280 watts

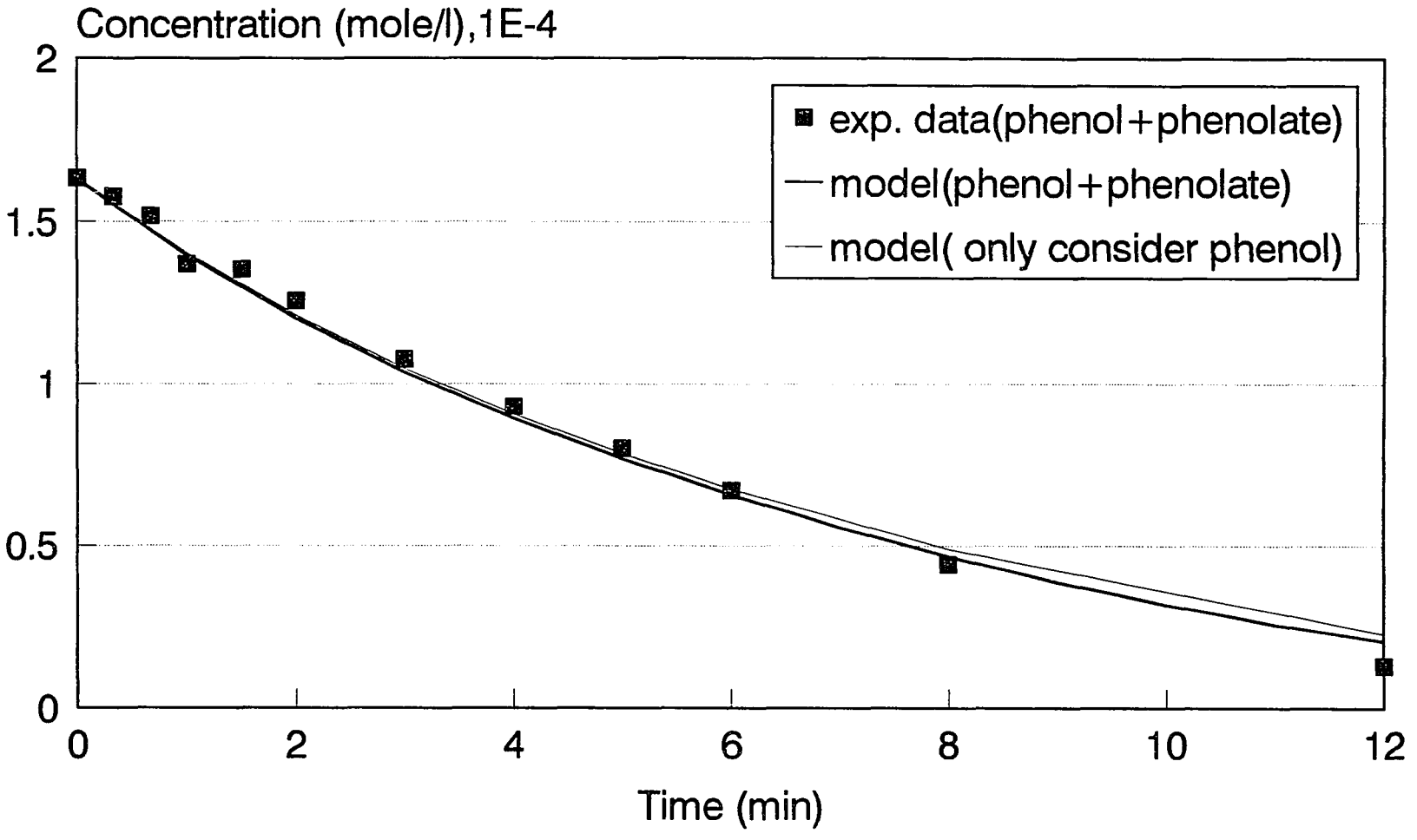

Figure 5.16 Comparison of the Accuracy of the Predictions of the Formation of Phenolate Anion and Only Considering Phenol in the presence of H2O2/UV at pH=10.76
Initial phenol conc.(pH=6.5)=1.63E-04 mole/l, initial H2O2 conc.=4.73E-3 mole/l, light intensity=280 watts

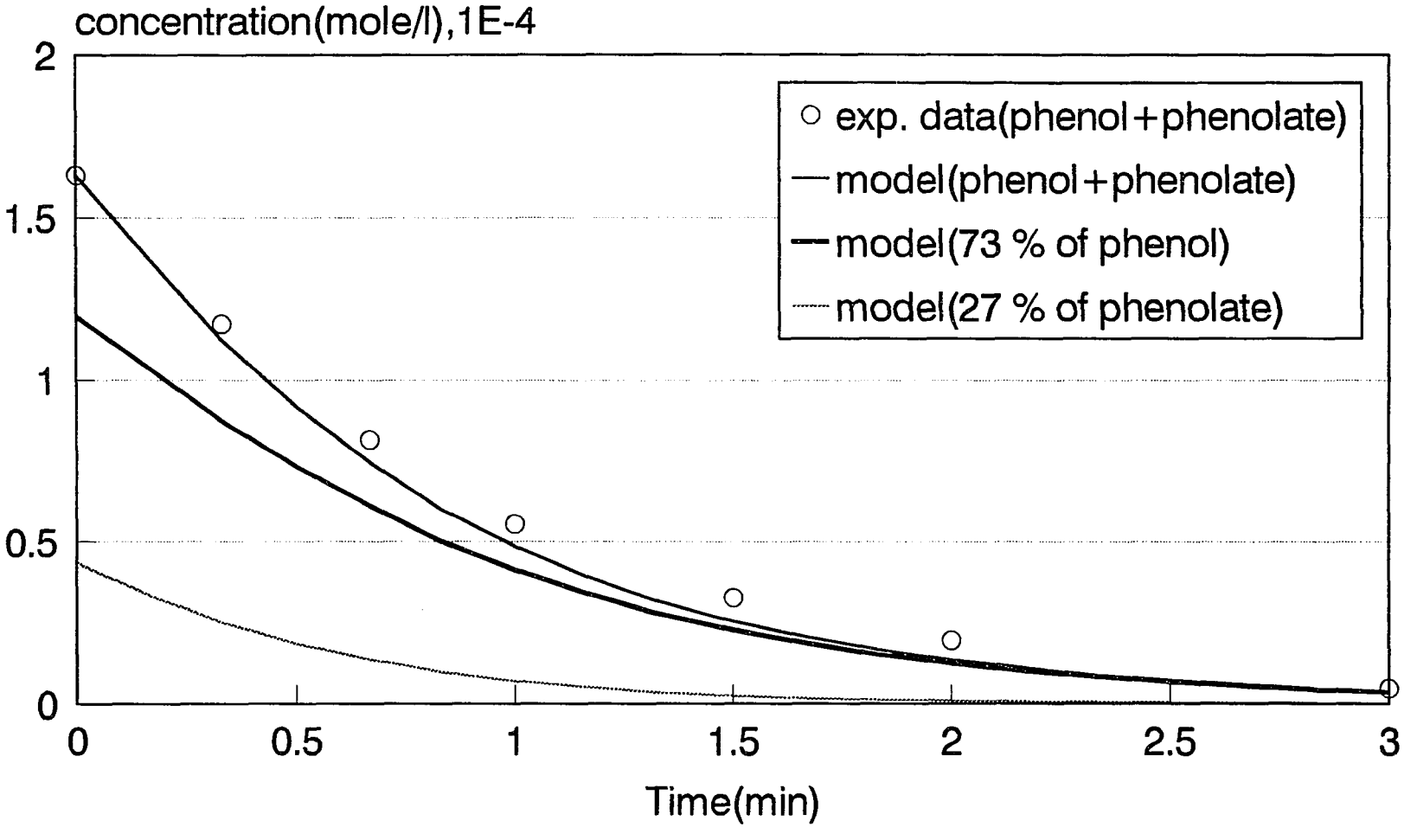

Figure 5.17 Destruction of Phenol and Phenolate Anion in the Presence of H2O2/UV at pH = 9.31
initial phenol conc.(pH=6.5)=1.63E-04 mole/l, initial H2O2 conc.=4.73E-3 mole/l,
light intensity=280 watts

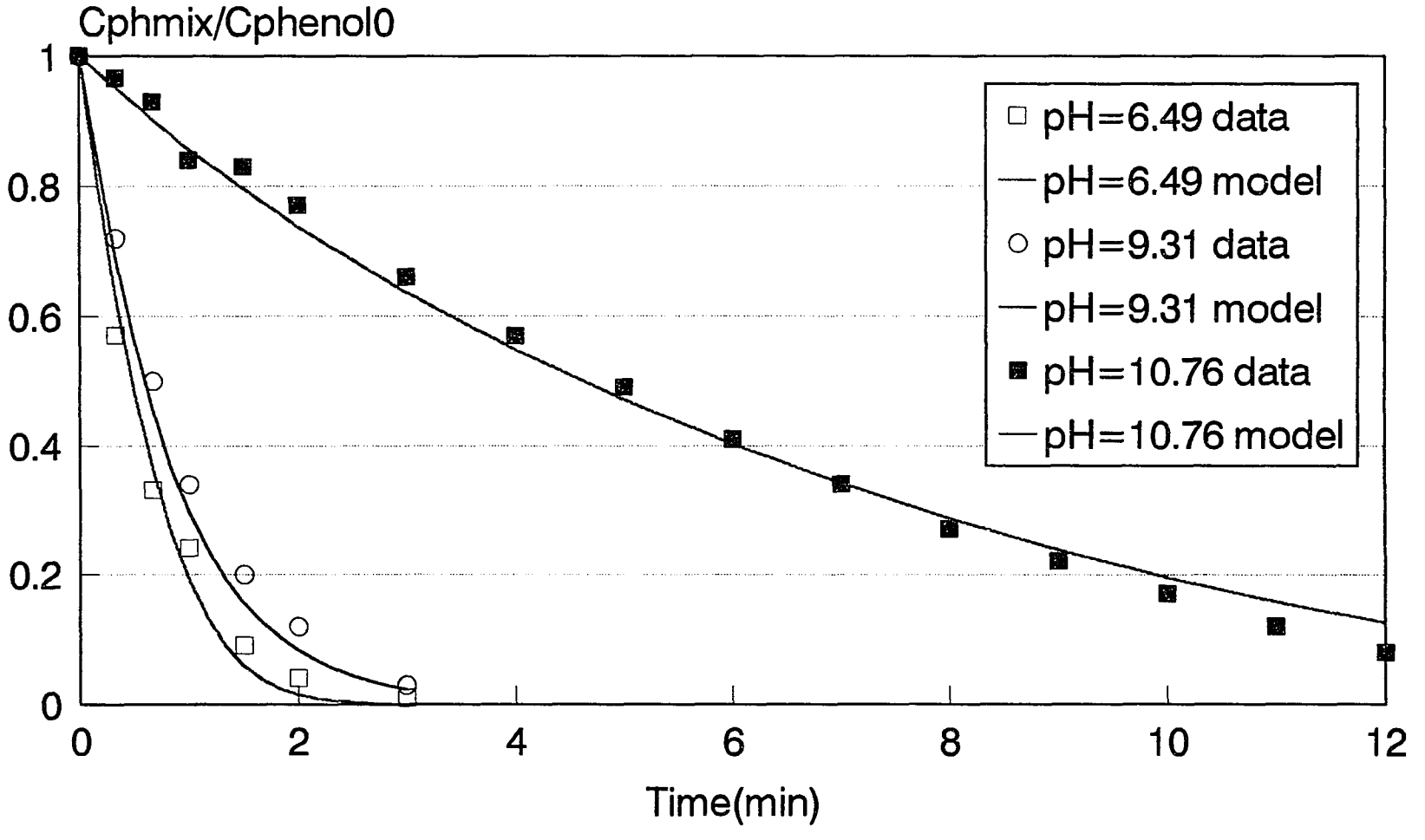

Figure 5.18 Destruction of Phenol and Phenolate Anion in the Presence of H2O2/UV under Different pH Conditions
Cphmix=Cphenol+Cphenolate, Cphenol0=initial conc. of phenol at pH=6.49=1.63e-04mole/l,
Light intensity=280 Watt, initial H2O2 conc. 4.73 x 10-3 mole/l

fact that at higher pH conditions, hydroperoxyl ion (HO_2^-) traps more hydroxyl radical and interferes with the decomposition of phenol and phenolate anion.

Comparison of rate constants of phenol and phenolate obtained from this study along with that obtained from other authors were summarized in Table 5.8.

Table 5.8 Summary of Rate Constants (1/mole-sec) of Phenol and Phenolate Obtained from this Study and that Obtained by other Authors

Reactions	Rate constant of this study	Rate constants of Other authors
Phenol + OH• → Catechol + Hydroquinone	1.44×10^9 (1)	6.2×10^9 (2)
Phenolate anion + OH•→ Products	3.86×10^9	9.2×10^9 (2)

(1) = $k_{20} + k_{21}$ in Table 5.6
(2)Reported by Matthews et al. in 1965.

Figure 5.19 shows the concentration of OH radical during destruction of phenol in different pH conditions in the presence of H_2O_2/UV. The data was obtained from computer simulation at three pH conditions. The results had good agreement with the results of the decomposition of hydrogen peroxide by UV radiation in Figure 5.7. The more the alkalinity, the lower the concentration of OH radical. But in this case, the time for the concentration of OH radical reaching steady state was more than three minutes at pH = 6.49. The one in Figure 5.7 reached steady state in seconds.

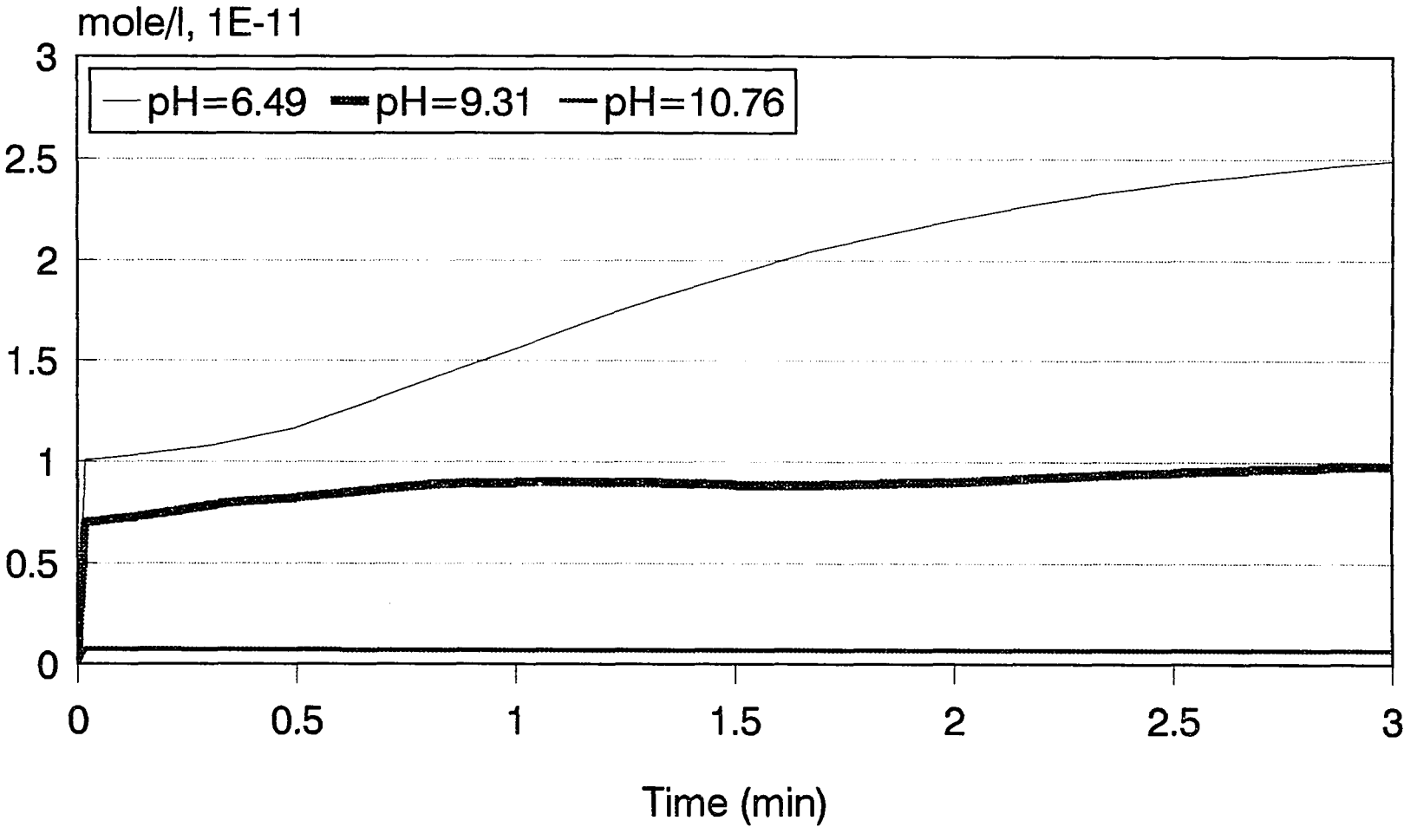

Figure 5.19 The Concentration of OH Radical During Destruction of Phenol in the Presence of H2O2/UV under Different pH Conditions

light intensity = 280 watts

5.5 Effect of Bicarbonate Ion on the Decomposition of Hydrogen Peroxide without UV Radiation

Bicarbonate ion might trap OH radicals and interfere with the destruction of target compound (Glaze et al. 1988). Results from this study also showed that bicarbonate ion can also decompose hydrogen peroxide without UV radiation and may interfere with the destruction of the target compound. The following proposed mechanism is a modified version of the mechanism described in section 5.1. As can been seen, there are three new reactions added. It is as follows:

$$H_2O_2 + OH^- \xleftrightarrow{K_{H_2O_2}} HO_2^- + H_2O$$

$$H_2O_2 + HO_2^- \xrightarrow{k_1} H_2O + OH^- + O_2$$

$$OH^- + HO_2^- \xrightarrow{k_2} O^{2-} + H_2O_2$$

$$O^{2-} + H_2O_2 \xrightarrow{k_3} OH^- + HO_2^-$$

$$HCO_3^- + H_2O \xleftrightarrow{K_{HCO_3^-}} H_3O^+ + CO_3^{=}$$

$$H_2O_2 + HCO_3^- \xrightarrow{k_{HCO_3^-}} HO_2^- + H_2O + CO_2$$

$$H_2O_2 + CO_3^{=} \xrightarrow{k_{CO_3^=}} HO_2^- + HCO_3^-$$

Sodium bicarbonate was used as a source of bicarbonate ion. Figure 5.20 shows the normalized concentration (Ca/Ca_0) of decomposed hydrogen peroxide versus reaction time with bicarbonate and carbonate ion in the absence of UV radiation. The results showed that the higher the bicarbonate ion concentration, the higher the rate of decomposition of hydrogen peroxide. With a reaction time of 100 minutes, the normalized concentration of decomposed hydrogen peroxide was 0.95 and 0.60 for the experiments where the ratio of bicarbonate ion to hydrogen peroxide was 10 and 100,

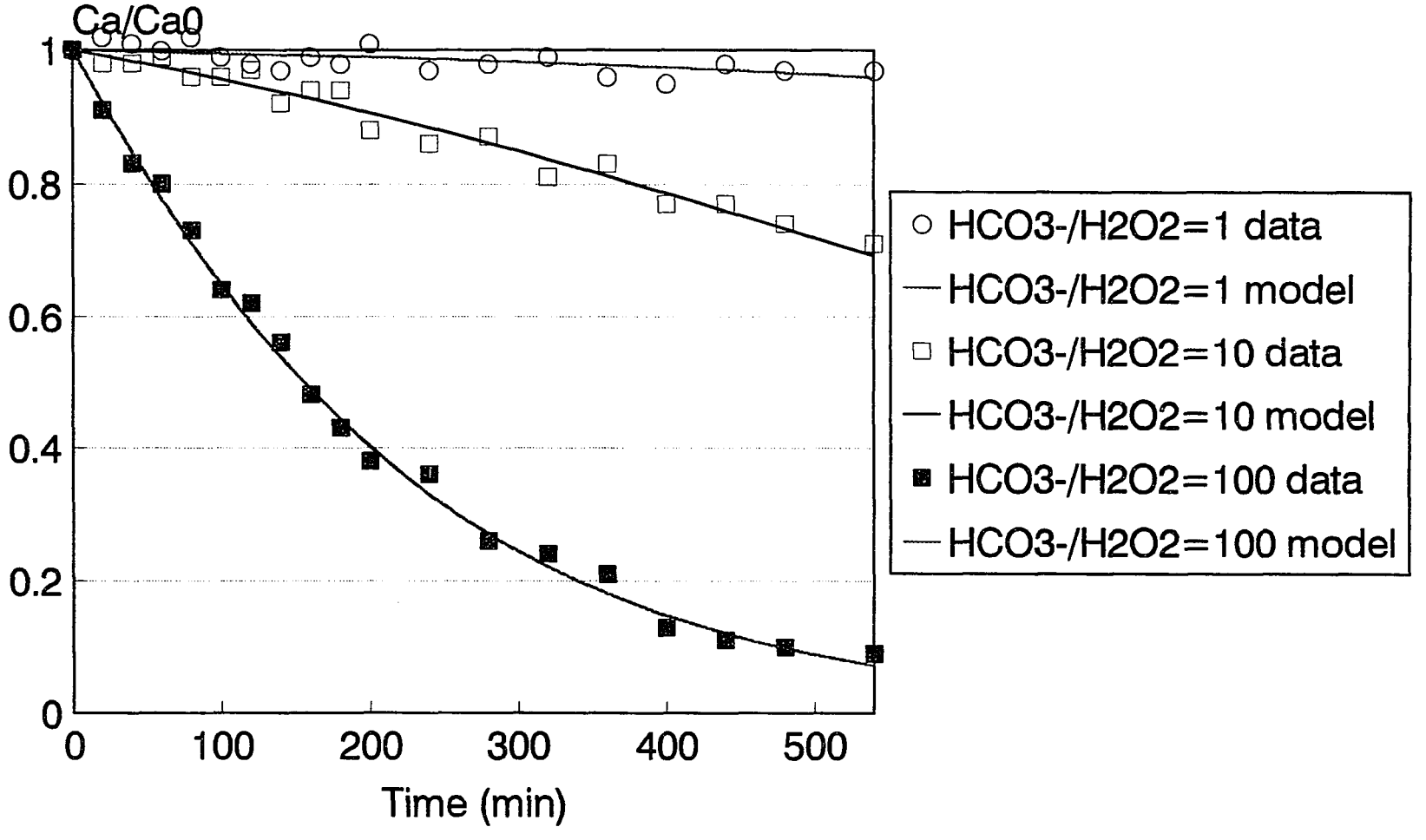

Figure 5.20 Decomposition of Hydrogen Peroxide under Different Concentration of Bicarbonate
Sodium bicarbonate as a source of bicarbonate ion, Initial H2O2 conc.(Ca0)=4.73 x10-3 mole/l,
Ca=concentration of hydrogen peroxide at any time pH1=8.60, pH10=8.35, pH100=8.47

respectively. The rate constants which were obtained by parameter estimation was summarized in Table 5.9. It should be noted that rate constant, $k_{CO3=}$, is three orders of magnitude larger than that of k_{HCO3-}. This result will be confirmed in section 5.5. The results gave a good fitting of the experimental data.

Table 5.9 Summary of Rate Constants k_{HCO3-} and $k_{CO3=}$ Obtained from Parameter Estimation

Reactions	Rate constant (l/mole-sec)
$H_2O_2 + HCO_3^- \xrightarrow{k_{HCO_3^-}} HO_2^- + H_2O + CO_2$	9.0×10^{-6}
$H_2O_2 + CO_3^= \xrightarrow{k_{CO_3^=}} HO_2^- + HCO_3^-$	1.10×10^{-2}

The experiment described above was repeated using sodium carbonate as a source of carbonate ion in place of sodium bicarbonate. Figure 5.21 shows the normalized concentration (Ca/Ca_0) of decomposed hydrogen peroxide versus time in the presence of carbonate and bicarbonate ion. However, this reaction takes place in the absence of UV radiation. The points are the experimental data, and the lines are the predicted model. The results showed that the higher the carbonate ion concentration, the higher the rate of decomposition of hydrogen peroxide. It was observed that for a given reaction time of 100 minutes, the normalized concentration of decomposed hydrogen peroxide was found to be 0.45 and 0.05 for a given ratio of bicarbonate ion to hydrogen peroxide of 3 and 10, respectively. There was very good agreement between the experimental data and the predicted model using the rate constants which were obtained from previous experiments.

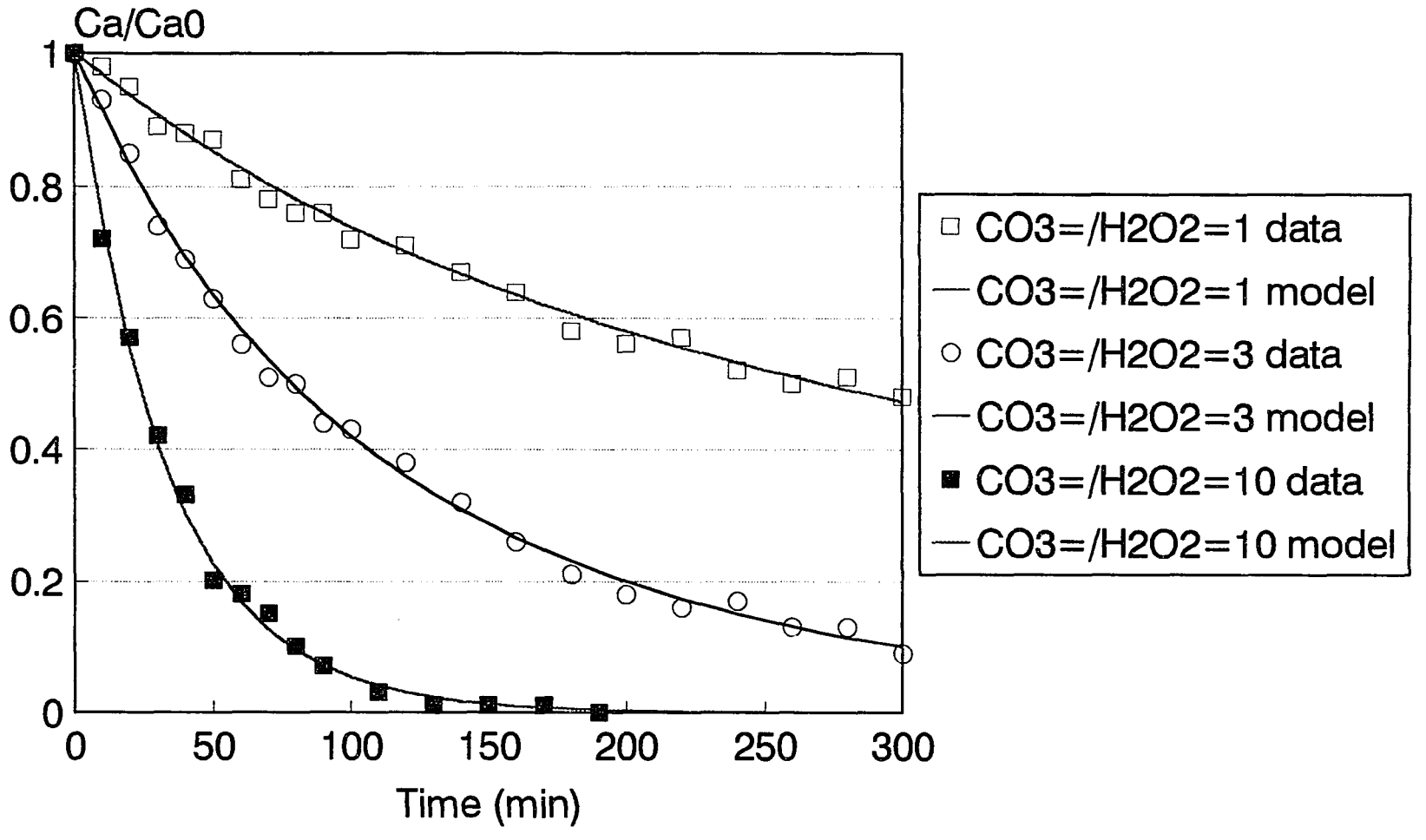

Figure 5.21 Decomposition of Hydrogen Peroxide under Different Concentration of Carbonate Sodium carbonate as a source of carbonate ion, initial H2O2 conc.= 4.73 x 10-3 mole/l, pH1=10.84, pH3=11.06, pH10=11.38

Comparing the experimental result of Figure 5.20 to that of Figure 5.21, one can see that the decomposition rate of hydrogen peroxide by carbonate is faster than that of hydrogen peroxide by bicarbonate.

5.6 Effect of Bicarbonate Ion on the Decomposition of Hydrogen Peroxide with UV

From the literature, the mechanism for the reaction of bicarbonate ion and carbonate ion with hydroxyl radical is shown below:

$$H_2O_2 + h\nu \xrightarrow{k_{H_2O_2}} 2\,OH\bullet$$

$$HCO_3^- + OH\bullet \xrightarrow{k_{30}} CO_3\bullet^- + H_2O$$

$$CO_3^{=} + OH\bullet \xrightarrow{k_{31}} CO_3\bullet^- + OH^-$$

$$CO_3\bullet^- + H_2O_2 \xrightarrow{k_{32}} HO_2\bullet + HCO_3^-$$

Figure 5.22 shows the normalized concentration (Ca/Ca_0) of decomposed hydrogen peroxide versus time in the presence of bicarbonate ion and UV radiation. The results showed that when the ratio of the concentration of bicarbonate to hydrogen peroxide was 1 or 10, the effect of bicarbonate on the decomposition of hydrogen peroxide was not significant. The effect became significant when the ratio was 100. The rate constants k_{30} and k_{31} which were determined using computer modeling, are summarized in Table 5.10. It should be noted that rate constant k_{30} obtained from this study was twice that of the constant reported by Buxton et al. in 1969. Similarily, the rate

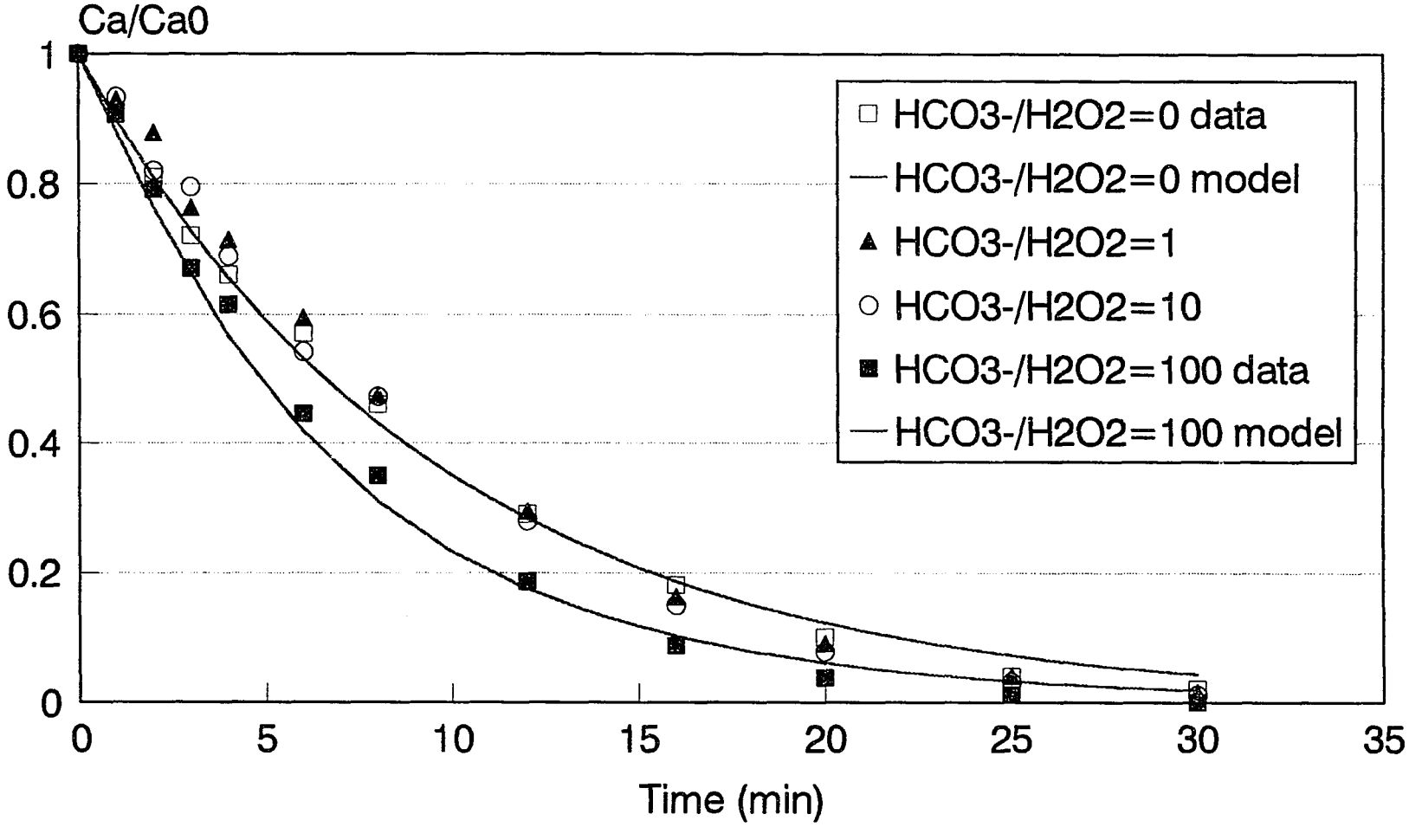

Figure 5.22 Decomposition of Hydrogen Peroxide with UV Radiation under Different Concentration of Bicarbonate

Initial H2O2 conc.(Ca0)=4.73 x 10-3 mole/l, Ca=concentration of hydrogen peroxide at any time,
UV light intensity=280 Watts, pH0=6.94, pH1=8.47, pH10=8.60, pH100=8.30

constant k_{31} obtained from this study was three times that of the one reported by Shali et al. in 1969.

Table 5.10 Comparison of Rate Constants (l/mole-sec) Obtained from this Study and from other Authors

Reactions	Rate constants of this study	Rate constants of previous studies
$HCO_3^- + OH\bullet \xrightarrow{k_{30}} CO_3\bullet^- + H_2O$	1.48×10^8	7.9×10^7 (Buxton et al. 1969)
$CO_3^{=} + OH\bullet \xrightarrow{k_{31}} CO_3\bullet^- + OH^-$	1.68×10^9	4.7×10^8 (Shali et al. 1969)
$CO_3\bullet^- + H_2O_2 \xrightarrow{k_{32}} HO_2\bullet + HCO_3^-$	8.5×10^5 (Behar et al. 1970)	8.5×10^5 (Behar et al. 1970)

5.7 Effect of Bicarbonate Ion on the Decomposition of Phenol in the Presence of H_2O_2/UV

To model this experiment, the rate constant obtained from previous experiments were applied and the reaction of carbonate ion radical ($CO_3\bullet^-$) and phenol was also considered.

$$\text{Phenol} + CO_3\bullet^- \xrightarrow{k_{28}} \text{Products}$$

Figure 5.23 shows the variation of the normalized concentration (Ca/Ca_0) of reacted phenol versus reaction time. These results were obtained from experiments under the following conditions: (1) in the presence of bicarbonate ion and H_2O_2/UV and (2) in the presence of H_2O_2/UV alone. It can be seen that the concentration of phenol is

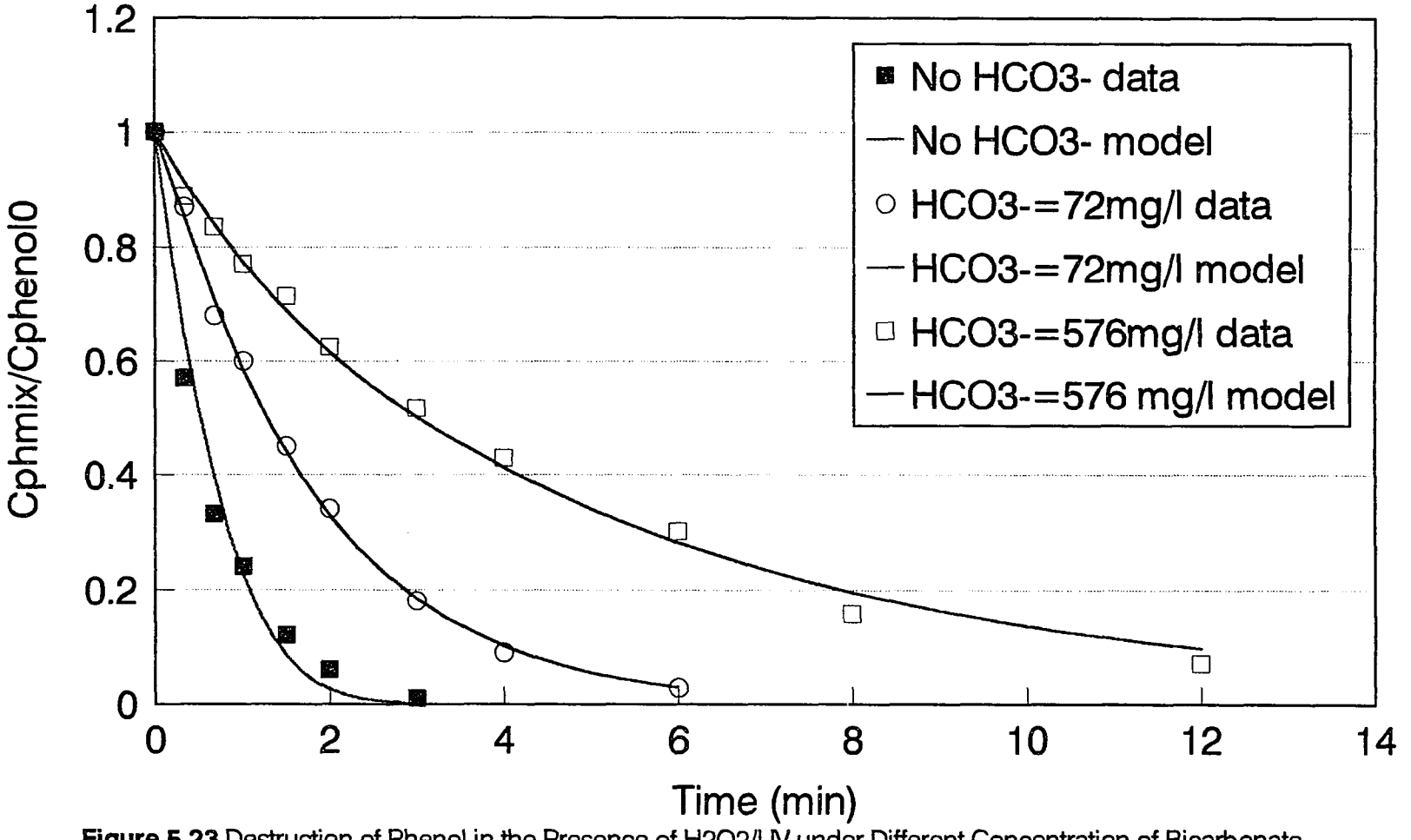

Figure 5.23 Destruction of Phenol in the Presence of H2O2/UV under Different Concentration of Bicarbonate

Sodium biacrbonate as a source of bicarbonate, Light intensity=280 Watt, Cphmix=Cphenol+Cphenolate, Cphenol0=1.63E-4 mole/l(15.3ppm), initial H2O2 conc. 4.73 x 10-3 mole/l, pH=6.49(No HCO3-), pH=8.30(HCO3-=72mg/l), pH=9.5(HCO3-=576 mg/l)

stabilized in the presence of bicarbonate ion. The higher the concentration of bicarbonate, the lower the decomposition rate of phenol. Bicarbonate is known as a strong hydroxyl radical scavenger (Glaze et al. 1988) and its presence in water reduces or even inhibits the reaction of these radicals on the organics. The model prediction using the rate constants which were obtained from previous experiments had good agreement with experimental data at different dosages of bicarbonate ion. The rate constant, k_{28}, was 6.12×10^5 l/mole-sec obtained from computer simulation.

Figure 5.24 shows comparison of the accuracy of the prediction of considering the reaction of carbonate ion radical ($CO_3\bullet^-$) and phenol and not considering the reaction. The results showed that the prediction of considering the reaction of carbonate ion radical ($CO_3\bullet^-$) is more accurate than that of not considering the reaction.

Figure 5.25 shows the effect of bicarbonate on the concentration of OH radical during the destruction of phenol in the presence of H_2O_2/UV. Results from the computer simulation demonstrated the relationship between bicarbonate concentration and OH radical--- the higher the concentration of bicarbonate, the lower the concentration of OH radical. This experiment proved that bicarbonate ions trap OH radicals.

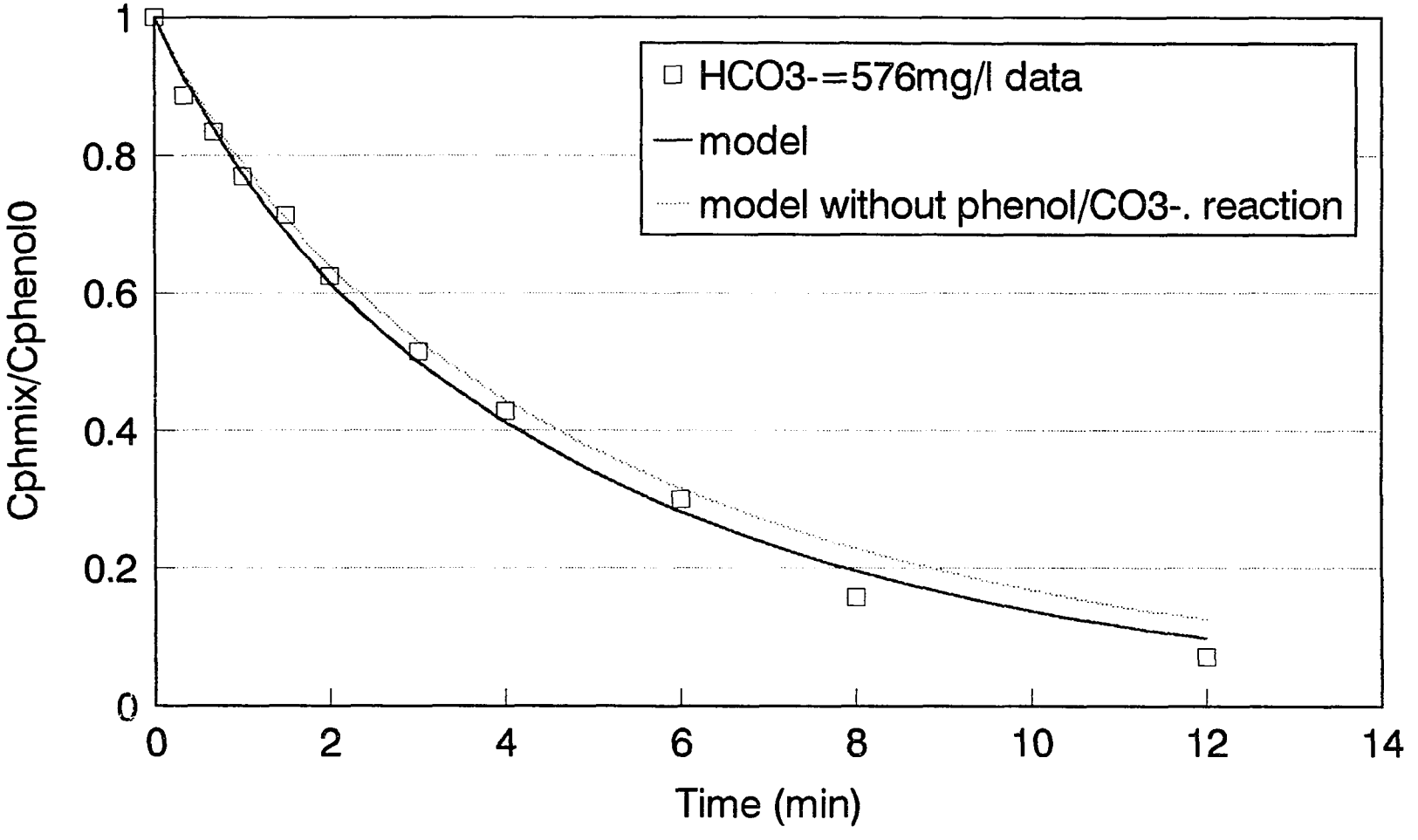

Figure 5.24 Comparison of the Reaction of Carbonate Ion Radical and Phenol and without Considering the Reaction

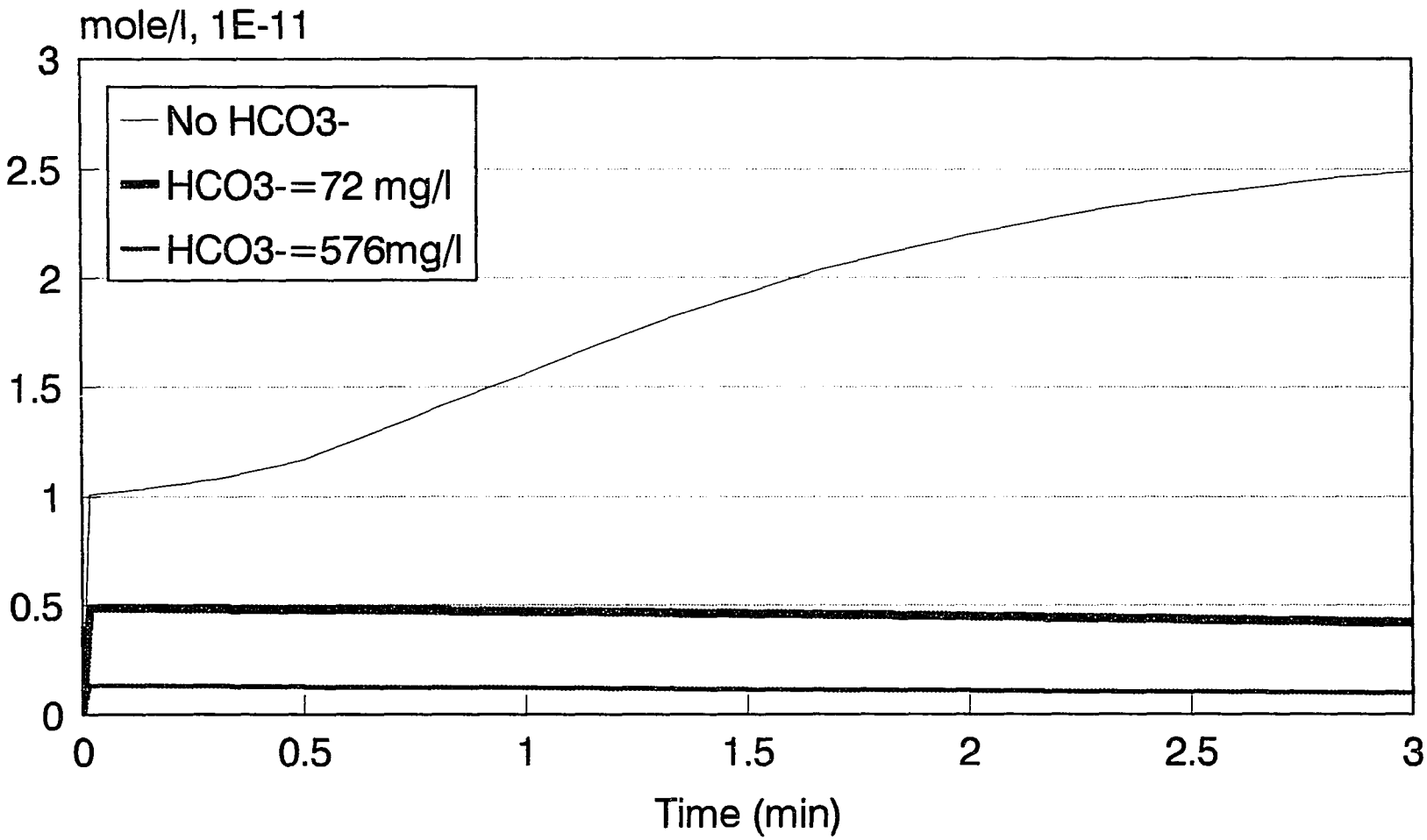

Figure 5.25 The Concentration of OH Radical During Destruction of Phenol in the Presence of H2O2/UV under Different Concentration of Bicarbonate

Initial H2O2 conc. 4.73 x 10-3 mole/l, pH=6.49(No HCO3-), pH=8.30(HCO3-=72mg/l), pH=9.5(HCO3-=576 mg/l), light intensity = 280 watts

5.8 Discussion

5.8.1 Base-induced Decomposition of Hydrogen Peroxide

The maximum rate of decomposition of hydrogen peroxide occurred at a pH value of 12. This result is consistent with results obtained by other researchers. Even though the rate of base-induced decomposition of hydrogen peroxide is much less than that of UV-induced decomposition of hydrogen peroxide, the first should not be ignored for the following reasons:

- The effect of base-induced decomposition becomes significant for long term storage of hydrogen peroxide.
- In the application of Fenton's reagent for soil remediation, this effect should be considered.
- To model the system of H_2O_2/UV, the effect of base-induced decomposition must be taken into account, especially at high pH conditions.

The beta probability function can fit three rate constants at different pH conditions. The rate constants at different pH conditions can be predicted by beta probability function.. This is fundamental information which should be used and incorporated into the AOP studies for the treatment of hazardous organics in wastewater.

5.8.2 UV-induced Decomposition of Hydrogen Peroxide under Different pH Conditions

The more the alkalinity, the higher the rate of decomposition of hydrogen peroxide. Computer simulation shows that the more the alkalinity, the lower the concentration of hydroxyl radical (OH•), since more hydroperoxyl ion (HO_2^-) traps hydroxyl radical at higher pH conditions.

The rate constants obtained from computer simulation in this part could be applied in Fenton's reagent reaction, since the reaction also involves hydroxyl radical. At higher pH conditions, hydroperoxyl ion trap hydroxyl radical. This is the reason why the condition of Fenton's reagent reaction must be kept at lower pH conditions.

5.8.3 Effect of pH on the Decomposition of Phenol in the Presence of H_2O_2/UV

The dissociation of phenol at higher pH conditions must be considered in the mechanism. Phenol and phenolate anion can not be separated by HPLC, but initial concentration of phenol and phenolate anion can be evaluated from the dissociation constant. The absorbance of the products of the phenol reaction is very significant and it needs to be applied in the modeling.

In the mechanism of phenol-H_2O_2/UV, the reaction between catechol or hydroquinone and hydroperoxyl radical (HO_2•) was not considered. The rate of reaction of phenol and hydroperoxyl radical is two orders of magnitude lower than the rate of phenol and hydroxyl radical. Also, the concentration of catechol and hydroquinone is lesser than that of phenol. Thus, the term k[catechol][HO_2•] and k[hydroquinone][HO_2•] can be neglected.

The more the alkalinity, the lower the rate of decomposition of phenol. This result is consistent with the result of the UV-induced decomposition of hydrogen peroxide. The hydroperoxyl ion traps hydroxyl radical and interferes with the decomposition of phenol. Taking into consideration the formation of phenolate anion improves the accuracy of the model prediction. From computer simulation, we can see the formation curve of hydroxyl radical with respect to time. From this, we can determine how quickly the concentration reaches steady state -- something that can not be measured experimentally.

At pH = 10.76 when phenolate anion is in the presence of H_2O_2/UV, neither catechol nor hydroquinone was detected by the HPLC. This means that no catechol and hydroquinone was formed in destruction of phenolate higher pH conditions in the process of H_2O_2/UV. This is the reason why catechol and hydroquinone were not considered as intermediates of the phenolate anion in the mechanism.

5.8.4 Effect of Bicarbonate Ion

The bicarbonate ion not only scavenges free radicals but also allows hydrogen peroxide to directly decompose. The effect of carbonate on the decomposition of hydrogen peroxide is larger than that of bicarbonate.

Experimental results show that the effect of bicarbonate ion on the decomposition of phenol in the presence of H_2O_2/UV is significant. Bicarbonate ion can trap hydroxyl radical and stabilize phenol. In some groundwater and soil contaminants, there is a significant amount of bicarbonate ion. Thus, this effect must be seriously considered, especially in soil remediation by Fenton's reagent.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

From the experimental studies and kinetic modeling the following conclusions can be made:

1. A mechanism of the base-induced decomposition of hydrogen peroxide was proposed. We found that all three rate constants from the mechanism go through a maximum value at pH = 12.29. The plot of rate constants versus pH followed the beta probability function.
2. Hydroperoxyl ion and bicarbonate ion can trap hydroxyl radical and interfere with the decomposition of phenol.
3. The kinetic models proposed in the study showed excellent agreement with the experimental data.
4. The rate constants obtained from computer simulation may prove very useful for scale-up to a commercial wastewater treatment.
5. The consideration of the formation of phenolate anion into the model improved the accuracy of the prediction.
6. The formation of hydroxyl radical with respect to time can be obtained by computer simulation.
7. Bicarbonate ion not only scavenges free radical but also allows hydrogen peroxide to directly decompose.

6.2 Recommendations

To fully understand the mechanisms suggested in this study, future studies should involve the following:

1. The mechanism should be applied in Fenton's reagent reaction to test its feasibility.
2. The technique of separation of phenol and phenolate anion should be studied.
3. Measuring the concentration of intermediate products may improve the kinetic model. The color of phenol degradation products is brown. The source of the color should be identified.

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