ABSTRACT

Title of Thesis : Oxidation of N,N-Dimethylformamide and
N,N-Dimethylacetamide in a Photoreactor

Su-Jen Syu, Master of Science in Chemistry, 1988

Thesis Directed by : Dr. Ching-Rong Huang, Professor in
Department of Chemical Engineering,
Chemistry and Environmental Science.

Oxidation of N,N-dimethylformamide(DMF) and N,N-dimethylacetamide(DMA) was investigated in a 30 liter semi-batch reactor. Five reaction processes were studied by using UV alone, O_3 alone, O_2/UV, O_2/O_3/UV and H_2O_2/UV respectively. Mathematical models have been developed to interpret the reaction kinetics. Reaction rate constants and mass transfer coefficients were determined by using Rosenbrock Hillclimb optimization algorithm. The experimental data and the predicted results from the models were compared. The kinetic parameters obtained from the previous semi-batch modes were applied to the continuous stirred tank reactor (CSTR) system. Results of this work show that the laboratory scale investigation using semi-batch reactor has great potential to develop the kinetic parameters required for the large scale CSTR system for the degradation of several aqueous pollutants.

OXIDATION OF N,N-DIMETHYLFORMAMIDE AND

N,N-DIMETHYLACETAMIDE IN A PHOTOREACTOR

by

SU-JEN SYU

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial fulfillment of
the requirements for the degree of
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APPROVAL SHEET

Title of Thesis: Oxidation of N,N-Dimethylformamide and

N,N-Dimethylacetamide in a Photoreactor

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ACKNOWLEDGMENT

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CONTENTS

LIST OF TABLES

Table

LIST OF FIGURES

INTRODUCTION

Waste water from various industrial processes may contain traces of oxidation products (acids, phenols, ketones, aldehydes.....etc.). Since we are more concerned over the hazardous effects of these chemicals, these contaminants must be removed before effluents can be discharged into our living environment. Recent legislation, including the Safe Drinking Water Act, Resource Conservation and Recovery Act, and the Federal Water Pollution Control Act have been enacted to focus on the control and regulation of chemicals entering into air, water and soils (27).

The chlorination method used at waste water treatment plant has been found to yield materials which are toxic to aquatic lives and which also may pose a health hazard to humans (1,2). To avoid these effects, responsible industries endeavor to remove the toxic materials before effluent discharge. Many methods have been proposed and developed for this purpose. Because of the powerful oxidizing capability and competitively low cost, ozone has become one of the most promising oxidants for water and industrial wastes treatment in recent year.

The ozonation process has been used in the treatment of waste water to complete the oxidation of the organics in water, to reduce the residual color, and to disinfect. In general, the end product of the ozonation process is less

harmful and will not form additional toxic residues. However, ozone alone cannot completely oxidize a number of refractory organic compounds which may be found in industrial effluents. The simultaneous combination of ozone and ultraviolet radiation has been studied (3-7). It was found that the oxidation of organic micropollutants in water is significantly more effective with the O_3/UV combination than with ozone alone. It was suggested that ultraviolet light provides a energy source for the organic micropollutants and the ozone. Considerably more excited state species and free radicals may be produced than the process using just ozone alone.

Another promising oxidant is hydrogen peroxide. Hydrogen peroxide has a higher oxidation potential(2.8 volts) than that of ozone(2.07 volts). As with ozone, the hydrogen peroxide can not oxidize the organic molecules completely. The synergistic combination of ultraviolet irradiation and hydrogen peroxide is a part of the topic to be studied in this thesis.

The specific objective of this work is to present a laboratory scale investigation of the O_2/O_3/UV process for the destruction of several organic micropollutants in aqueous solutions. The O_2/UV and H_2O_2/UV reaction processes were also studied. The experimental data for each of these processes were compared with the corresponding predicted results from the kinetic models.

The reaction rates and the mass transfer parameters

2

can be calculated through the Rosenbrock Hillclimb regression procedure and the fourth order Runge-Kutta integration method (25). The theoretical steady-state outlet concentration for continuous stirred tank reactor (CSTR) was calculated by utilizing the reaction rates and the mass transfer parameters obtained from the $O_2/O_3/UV$ process under the semi-batch reaction mode.

The compound selected for this work were N,N-dimethylformamide(DMF) and N,N-dimethylacetamide(DMA). The concentration prepared for all experimental runs were around 100 ppm. Tap water contains residual chlorine, an oxidizing agent, was used in the preparation of solutions.

CHAPTER 1

A. Previous Study

1. UV Light Oxidation

The disinfectant properties of ultraviolet light have been known for many years (8). Ultraviolet radiation was used to remove organism and to destroy microorganisms.

Smith (9) reported the results of photodecomposition for removing the dodecyl benzene sulfonate (DBS) in water. He proposed the following simplified mechanism under two assumption: The first assumption is that the stationary-state hypothesis is valid. The second assumption is that the kinetic constants are independent of wave length.

$$DBS + hv \quad ------> \quad DBS^*$$
$$2DBS^* \quad ------> \quad 2DBS$$
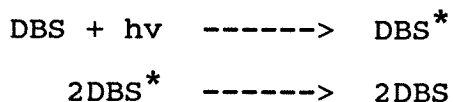
It was verified by Smith's experimental measurements that this reaction has the 1/2 power dependencies of the degradation rate on pollutant concentration and light intensity.

Ruzo and co-workers (10) proposed the mechanisms for the decomposition of halogenated aromatics. First, transition of electrons from the Pi ground state to an excited Pi state occurs. From this state, the carbon-hydrogen bond undergoes fission, and produce an aryl and a hydrogen radical. These radicals may then abstract hydrogen from the medium or dimerize.

Bulla and Edgerley (11) investigated the photochemical degradation of refractory organic compounds using UV radiation. They conducted an experimental study of the applicability of the photochemical decomposition process towards the treatment of the refractory organic compounds, aldrin, dieldrin, and endrin. These are all chlorinated hydrocarbons and pesticides. They described that a photochemical process utilizing ultraviolet radiation might prove effective in reducing pollution by these refractory compounds.

2. The decomposition mechanisms for ozone in aqueous solution:

A number of studies have been made of ozone decomposition in aqueous solutions. A series of reactions was proposed by Weiss (12) to explain the mechanism of ozone decomposition in aqueous solutions. Weiss proposed the first step reaction was:

$$O_3 + OH^- \longrightarrow O_2^- + HO_2.$$
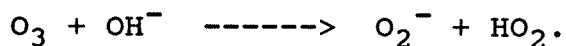
being followed by the chain reactions:

$$O_3 + HO_2. \longrightarrow 2O_2 + OH.$$
$$O_3 + OH. \longrightarrow O_2 + HO_2.$$
$$HO_2. + HO_2. \longrightarrow O_3 + H_2O$$
$$HO_2. + OH. \longrightarrow O_2 + H_2O$$
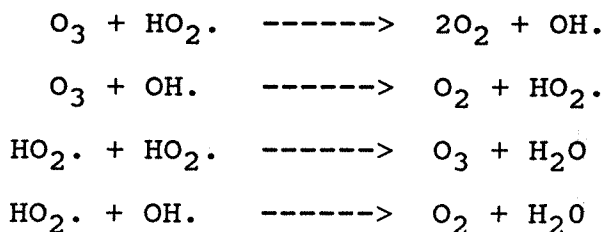
He concluded that at low values of $[OH^-]$, the

decomposition rate can be considered proportional to 3/2 power.

Alder and Hill (13), on the basis of their kinetic studies, suggested a first order reaction with respect to ozone concentration and proposed the following mechanism to correlate with their results:

$$O_3 + H_2O \longrightarrow HO_3^+ + OH^-$$
$$HO_3^+ + OH^- \longrightarrow 2HO_2.$$
$$O_3 + HO_2. \longrightarrow HO. + 2O_2$$
$$HO_2. + HO. \longrightarrow H_2O + O_2$$
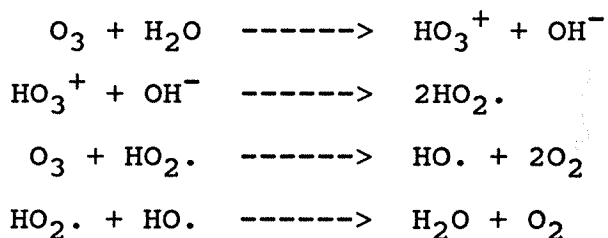
Based upon the review of the chemistry of ozone in water from the literature, Peleg (14) suggested the following mechanisms:

$$O_3 + H_2O \longrightarrow O_2 + 2OH.$$
$$O_3 + OH. \longrightarrow O_2 + HO_2.$$
$$O_3 + HO_2. \longrightarrow 2O_2 + OH.$$
$$OH. + OH. \longrightarrow H_2O_2$$
$$OH. + HO_2. \longrightarrow H_2O + O_2$$
$$OH. + OH^- \longrightarrow O^- + H_2O$$
$$O^- + O_2 \longrightarrow O_3^-$$
$$HO_2. + HO_2. \longrightarrow H_2O_2 + O_2$$
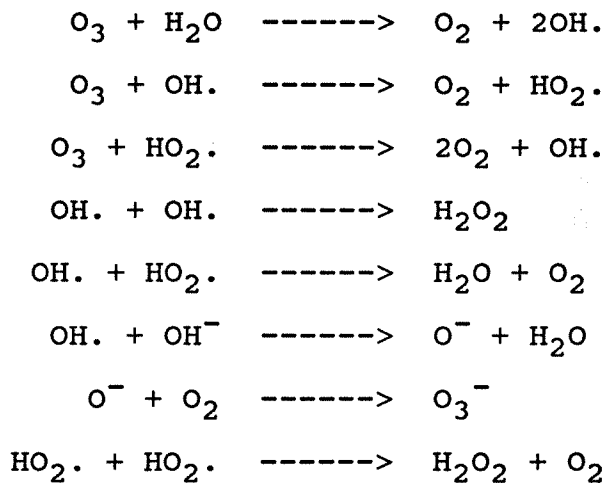
Hoigene and his co-workers have published many studies in recent years dealing with the kinetic of ozone oxidation of organic materials in aqueous solution. The more recent

work presented by Staehiln and Hoigne (15) in 1982 suggested the following two sets of the mechanism:

(1)

$$O_3 + OH^- ------> .O_2^- + HO_2.$$

$$HO_2. <======> H^+ + .O_2^-$$

$$O_3 + .O_2^- ------> .O_3^- + O_2$$

$$.O_3^- + H_2O ------> OH. + OH^- + O_2$$

(2)

$$O_3 + OH^- ------> HO_2^- + O_2$$

$$H_2O_2 <======> HO_2^- + H^+$$

$$O_3 + HO_2^- ------> OH. + .O_2^- + O_2$$

$$O_3 + .O_2^- ------> .O_3^- + O_2$$

$$O_3^- + H_2O ------> OH. + OH^- + O_2$$
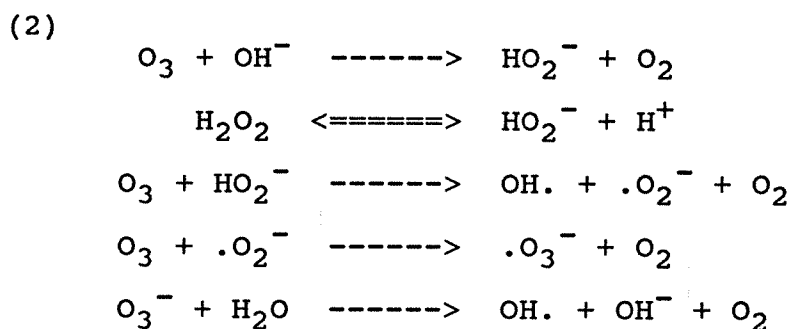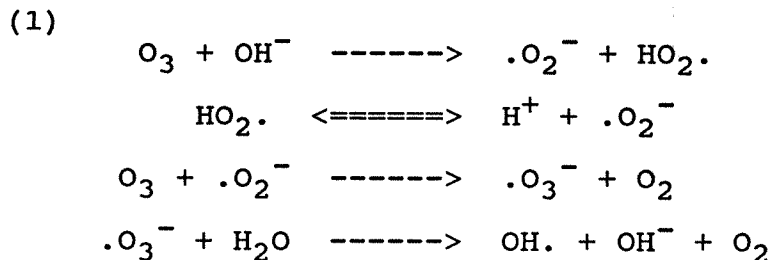
The overall reaction is same in either case:

$$2O_3 + H_2O ------> OH. + HO_2. + 2O_2$$
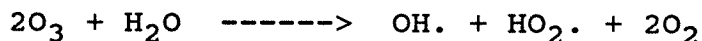
As can be observed, the proposed decomposition behavior of ozone in water do not agree with one another. It would appear that the hydroxyl radical is the most important intermediate in the decomposition of ozone in water. The hydroxyl radical has the higher oxidation potential (2.8 volts) than that of ozone (2.07 volts) (see Table 1). Consequently, one may conclude that the hydroxyl radical plays an important part in ozone reactions with organic compounds in water solution.

3. The Kinetic of Ozone Decomposition

7

Although a number of studies have been made for ozone decomposition in aqueous solutions, the findings of these investigators are conflicting, especially concerning the order of reaction. Table 2 shows the range of variables covered by various investigators and their conclusions concerning the reaction order relative to ozone (16,28). It shows that the pH and temperature affect the rate and order of the decomposition of ozone in water.

In general, researchers have agreed that increasing the pH will increase the decomposition of ozone in aqueous solution.

Kuo and co-workers (17) applied the Arrhenius equation to correlate the experimental data.

$$k_r = b\exp(-E/RT)$$

The activation energy ,E, was calculated from the slope in the semi-log plot of k_r vs. 1/T and was found to be independent of pH value.

4. Ozone Reaction with Organic Compound

At ordinary temperatures ozone is a blue gas, but at the concentrations at which it is normally produced the color is not noticeable unless the gas is viewed through considerable depth. In water solution, ozone has an oxidizing potential of 2.07 volts at 20° C, making it capable of oxidizing most organic and inorganic species. Ozone gas is sparingly soluble in water. The solubility in

water is given in Table 12 (19). The mass transfer of ozone from the gas phase into the liquid phase has become a vitally important factor in the ozone waste water treatment process.

Yocum (21) proposed five generalized steps which occur in the reaction of ozone with organic species:

(1) Ozone diffusion through the gas film to the gas-liquid interface.

(2) Ozone transfer across the interface into the liquid film.

(3) Liquid reactant diffusion from bulk into liquid film.

(4) Ozone oxidation of the reactant.

(5) Continued reaction to new products or diffusion back into the bulk liquid phase.

B. Reaction Mechanism and Kinetic Model

The reaction mechanisms and kinetic models for the experimental conditions (UV alone, O_3 alone, O_2/UV, $O_2/O_3/UV$ and H_2O_2/UV) were first developed by Professor C.R. Huang in 1983. These models were revised in 1984 (22,23) and were applied by Sowa (24) in 1987. Results obtained by Sowa were within the theoretical range.

The kinetic models for those reactions were carried out under following assumptions. The first assumption is that the oxidation reaction of pollutant is a first order irreversible reaction. The second assumption is that the reaction intermediates will not reach steady state and its concentration is a function of residence time.

The rate of mass transfer of oxygen and ozone from the gas phase into the liquid phase can be described by the following equations:

$$\frac{dc_{O2}}{dt} = k_{LO2}a(c_{O2*} - c_{O2})$$

$$\frac{dc_{O3}}{dt} = k_{LO3}a(c_{O3*} - c_{O3})$$

These two mass transfer equations are valid for systems that consist of gas-liquid phases. The detailed reaction mechanism and kinetic model for each experimental conditions are presented as follows:

1. Reaction with UV light alone

10

The reaction is represented by the equation:

$$A + h\nu \quad \underset{k_3}{\overset{k_{IA}I}{\Longleftrightarrow}} \quad A^* \quad \overset{k_2}{\longrightarrow} \quad \text{Decomp. prod.}$$
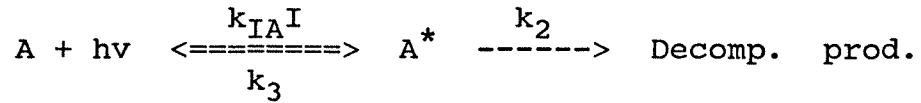
An overall mass balance for the reactants yields the following expression:

$$(1) \quad \frac{dC_A}{dt} = -k_{IA}IC_A + k_3C_A^*$$

$$(2) \quad \frac{dC_A^*}{dt} = -k_2C_A^* + k_{IA}IC_A - k_3C_A^*$$

These equations have been solved by applying Laplace Transform and the results are as follows.

$$\frac{C_A}{C_{A(0)}} = e^{-bt}[\cosh(at) + \frac{c}{a}\sinh(at)]$$

where :

$$a = [\frac{(k_2 + k_3 + k_{IA}I)^2}{4} - k_2k_{IA}I]^{1/2}$$

$$b = \frac{k_2 + k_3 + k_{IA}I}{2}$$

$$c = \frac{k_2 + k_3 - k_{IA}I}{2}$$

The value of $K_{IA}I$, K_2 and K_3 can be obtained by applying the initial reactant concentration and with the aid of Rosenbrock Hillclimb optimization algorithm.

2. Reaction with ozone alone

Ozone(O_3), hydroxyl radical(OH.) and hydroperoxide radical(HO_2.) are considered as oxidizing reagents of the pollutant in this reaction scheme.

The ozonator used in this study was guaranteed to produce no less than 2 wt% concentration in pure, clean and dry oxygen environment (5). Since oxygen accompanied the ozone produced by the ozonator, it is necessary to consider the presence of oxygen in the reaction mechanism.

The following equations show the mechanism in this experimental process:

$$O_3 + H_2O \underset{k_{7b}}{\overset{k_{7f}}{\rightleftharpoons}} O_2 + 2OH.$$

$$O_3 + OH. \underset{k_{8b}}{\overset{k_{8f}}{\rightleftharpoons}} O_2 + HO_2.$$

$$A + O_3 \xrightarrow{k_1} Decomp. \; prod.$$

$$A + OH. \xrightarrow{k_4} Decomp. \; prod.$$

$$A + HO_2. \xrightarrow{k_5} Decomp. \; prod.$$

$$O_{2l} \xrightarrow[\text{mass transfer}]{k_{LO2}a} O_{2g}$$

$$O_{3l} \xrightarrow[\text{mass transfer}]{k_{LO2}a} O_{3g}$$
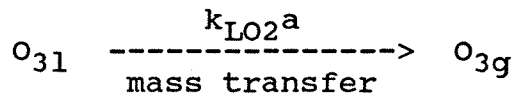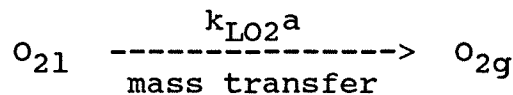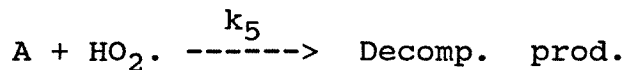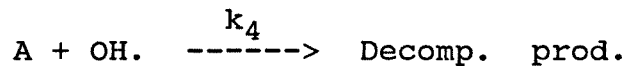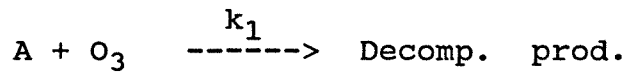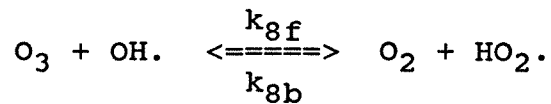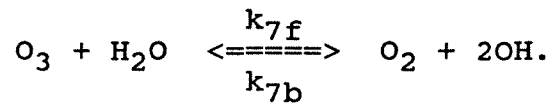
A mass balance for each reactant gives a set of differential equations:

12

$$(1) \quad \frac{dC_A}{dt} = -k_1 C_A C_{O3} - k_4 C_A C_{OH.} - k_5 C_A C_{HO2.}$$

$$(2) \quad \frac{dC_{O3}}{dt} = -k_1 C_A C_{O3} - k_{7f} C_{O3} + k_{7b} C_{O2} C_{OH.}^2$$
$$- k_{8f} C_{O3} C_{OH.} + k_{8b} C_{O2} C_{HO2.}$$
$$+ k_{LO3} a (C_{O3*} - C_{O3})$$

$$(3) \quad \frac{dC_{O2}}{dt} = k_{7f} C_{O3} - k_{7b} C_{O2} C_{OH.}^2 + k_{8f} C_{O3} C_{OH.}$$
$$- k_{8b} C_{O2} C_{HO2.} + k_{LO2} a (C_{O2*} - C_{O2})$$

$$(4) \quad \frac{dC_{OH.}}{dt} = -k_4 C_A C_{OH.} + 2k_{7f} C_{O3} - 2k_{7b} C_{O2} C_{OH.}^2$$
$$- k_{8f} C_{O3} C_{OH.} + k_{8b} C_{O2} C_{HO2.}$$

$$(5) \quad \frac{dC_{HO2.}}{dt} = -k_5 C_A C_{HO2.} + k_{8f} C_{O3} C_{OH.} - k_{8b} C_{O2} C_{HO2.}$$

The values of rate constants and mass transfer parameters, can be obtained by solving the differential equations with Rosenbrock Hillclimb regression procedure and the fourth order Runge-Kutta integration method on a computer. The initial values of Runge-Kutta method are the initial concentrations of the species and the solubility of oxygen in water.

3. Reaction with oxygen and UV light

Three species are considered to decompose the pollutant in this reaction process. They are activated oxygen (O_2^*), hydroxyl radical (OH.) and hydroperoxide radical ($HO_2.$).

The following equations represent the mechanism for O_2/UV reaction process.

$$O_2 + hv \xrightarrow{\quad k_{IO2}I \quad} O_2^*$$

$$O_2^* + H_2O \underset{k_{9b}}{\overset{k_{9f}}{\rightleftharpoons}} OH\cdot + HO_2\cdot$$

$$A + hv \underset{k_3}{\overset{k_{IA}I}{\rightleftharpoons}} A^* \xrightarrow{\quad k_2 \quad} \text{Decomp. prod.}$$

$$A + O_2^* \xrightarrow{\quad k_6 \quad} \text{Decomp. Prod.}$$

$$A + OH\cdot \xrightarrow{\quad k_4 \quad} \text{Decomp. prod.}$$

$$A + HO_2\cdot \xrightarrow{\quad k_5 \quad} \text{Decomp. prod.}$$

$$O_{2l} \xrightarrow[\text{mass transfer}]{\quad k_{LO2}a \quad} O_{2g}$$
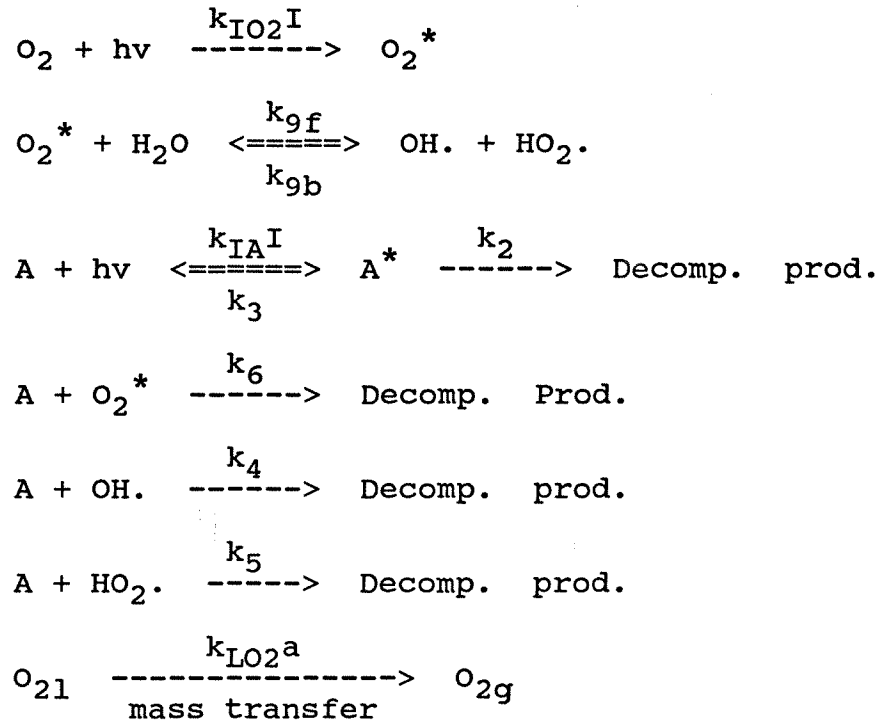
A mass balance for each reactant gives the following set of differential equations:

$$(1) \quad \frac{dC_A}{dt} = -k_6 C_A C_{O2*} - k_4 C_A C_{OH\cdot} - k_5 C_A C_{HO2\cdot} - k_{IA}I C_A + k_3 C_{A*}$$

$$(2) \quad \frac{dC_{A*}}{dt} = k_{IA}I C_A - k_3 C_{A*} - k_2 C_{A*}$$

$$(3) \quad \frac{dC_{O2}}{dt} = -k_{IO2}I C_{O2} + k_{LO2}a(C_{O2*} - C_{O2})$$

$$(4) \quad \frac{dC_{O2*}}{dt} = k_{IO2}I C_{O2} - k_{9f}C_{O2*} + k_{9b}C_{OH\cdot}C_{HO2\cdot} - k_6 C_A C_{O2*}$$

14

$$(5) \quad \frac{dC_{OH.}}{dt} = k_{9f}C_{O2*} - k_{9b}C_{OH.}C_{HO2.} - k_4C_AC_{OH.}$$

$$(6) \quad \frac{dC_{HO2.}}{dt} = k_{9f}C_{O2*} - k_{9b}C_{OH.}C_{HO2.} - k_5C_AC_{HO2.}$$

Again, the initial concentration of the species and the solubility of oxygen were used to solve the rate constants and the mass transfer coefficients. The rate constants, $K_{IA}I$, K_2 and K_3, which were obtained from the reaction with UV light alone were introduced into this reaction scheme. This is to simplify the expression in the optimization program and to achieve a better optimization result. The constants, K_4 and K_5, obtained from the reaction with O_3 alone were used as the initial input parameters in the Rosenbrock Hillclimb optimization program.

4. Reaction with oxygen, ozone and UV light

As in the O_3 alone reaction scheme, the presence of oxygen in the system and its reaction must also be considered in the kinetics. The following are the five different ways by which the pollutant A can be decomposed:

(1) with UV light(hv)

(2) with ozone(O_3)

(3) with the activated oxygen(O_2^*)

(4) with the hydroxyl radical(OH.)

(5) with the hydroperoxide radical($HO_2.$)

15

The following mechanism represents the reaction process.

$$O_3 + H_2O + h\nu \xrightarrow{\quad k_{IO3}I \quad} O_2 + 2OH\cdot$$

$$O_3 + OH\cdot \underset{k_{8b}}{\overset{k_{8f}}{\Longleftrightarrow}} O_2 + HO_2\cdot$$

$$O_2 + h\nu \xrightarrow{\quad k_{IO2}I \quad} O_2{}^*$$

$$O_2{}^* + H_2O \underset{k_{9b}}{\overset{k_{9f}}{\Longleftrightarrow}} OH\cdot + HO_2\cdot$$

$$A + h\nu \underset{k_3}{\overset{k_{IA}I}{\Longleftrightarrow}} A^* \xrightarrow{\quad k_2 \quad} \text{Decomp. prod.}$$

$$A + O_3 \xrightarrow{\quad k_1 \quad} \text{Decomp. prod.}$$

$$A + O_2{}^* \xrightarrow{\quad k_6 \quad} \text{Decomp. prod.}$$

$$A + OH\cdot \xrightarrow{\quad k_4 \quad} \text{Decomp. prod.}$$

$$A + HO_2\cdot \xrightarrow{\quad k_5 \quad} \text{Decomp. prod.}$$

$$O_{2l} \xrightarrow[\text{mass transfer}]{k_{LO2}a} O_{2g}$$

$$O_{3l} \xrightarrow[\text{mass transfer}]{k_{LO3}a} O_{3g}$$
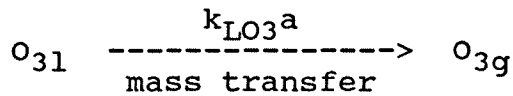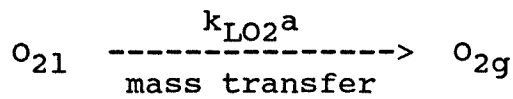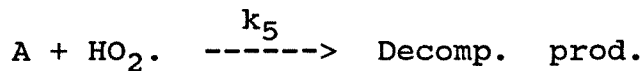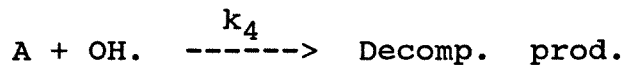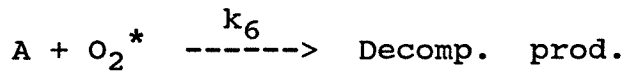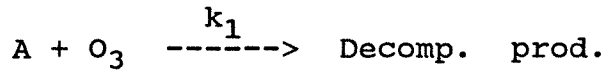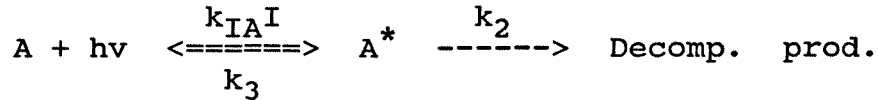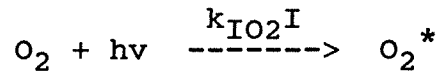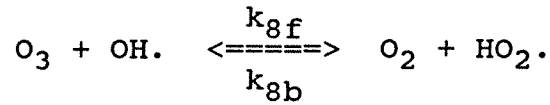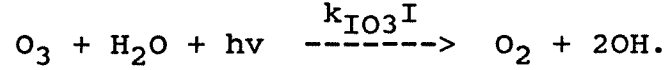
The mass balance developed for each reactant yields the following set of differential equations:

$$(1) \quad \frac{dC_A}{dt} = -k_{IA}IC_A + k_3C_{A^*} - k_1C_AC_{O3} - k_6C_AC_{O2^*} \\ - k_4C_AC_{OH\cdot} - k_5C_AC_{HO2\cdot}$$

16

$$(2) \quad \frac{dC_{A*}}{dt} = k_{IA}IC_A - k_3C_{A*} - k_2C_{A*}$$

$$(3) \quad \frac{dC_{O3}}{dt} = -k_{IO3}IC_{O3} - k_{8f}C_{O3}C_{OH.} + k_{8b}C_{O2}C_{HO2.} \\ - k_1C_AC_{O3} + k_{LO3}a(C_{O3*} - C_{O3})$$

$$(4) \quad \frac{dC_{O2}}{dt} = k_{IO3}IC_{O3} + k_{8f}C_{O3}C_{OH.} - k_{8b}C_{O2}C_{HO2.} \\ - k_{IO2}IC_{O2} + k_{LO2}a(C_{O2*} - C_{O2})$$

$$(5) \quad \frac{dC_{O2*}}{dt} = k_{IO2}IC_{O2} - k_{9f}C_{O2*} + k_{9b}C_{OH.}C_{HO2.} \\ - k_6C_AC_{O2*}$$

$$(6) \quad \frac{dC_{OH.}}{dt} = 2k_{IO3}IC_{O3} - k_{8f}C_{O3}C_{OH.} + k_{8b}C_{O2}C_{HO2.} \\ + k_{9f}C_{O2*} - k_{9b}C_{OH.}C_{HO2.} - k_4C_AC_{OH.}$$

$$(7) \quad \frac{dC_{HO2.}}{dt} = k_{8f}C_{O3}C_{OH.} - k_{8b}C_{O2}C_{HO2.} + k_{9f}C_{O2*} \\ - k_{9b}C_{OH.}C_{HO2.} - k_5C_AC_{HO2.}$$
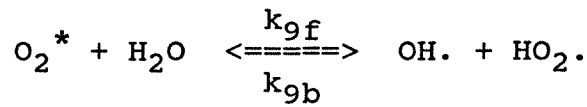
As before, the initial concentration of the species and the solubility of oxygen in water were used to solve the equation for the rate constants and mass transfer coefficients.

Similarly, the $K_{IA}I$, K_2 and K_3 values obtained from the UV alone reaction scheme were used to simplify the kinetic model expression. The values of K_{8f}, K_{8b}, K_1, K_4, K_5, $K_{LO3}a$, $C_{O3}*$, $K_{LO2}a$, and $C_{O2}*$ obtained from the ozone alone reaction scheme and the values of $K_{IO2}I$, K_{9f}, K_{9b}, and K_6 obtained from the oxygen with UV light reaction schemes were used as the initial input values in the Rosenbrock

17

Hillclimb regression program.

5. Reaction with hydrogen peroxide and UV light

There are four different ways to decompose the pollutant A in this reaction process:

(1) with UV light(hv)

(2) with hydrogen peroxide(H_2O_2)

(3) with hydroxyl radical (OH.)

(4) with hydroperoxide radical(HO_2.)

In these species, the hydroxyl radical(OH.) has the highest oxidation potential(2.8 volts). The following mechanism suggests that the photolysis of hydrogen peroxide (H_2O_2) produces hydroxyl radical(OH.).

$$H_2O_2 + hv \quad \xrightarrow{k_{IH2O2}I} \quad 2OH.$$

$$H_2O_2 + OH. \quad \underset{k_{10b}}{\overset{k_{10f}}{\rightleftharpoons}} \quad HO_2. + H_2O$$

$$O_3 + OH. \quad \underset{k_{8b}}{\overset{k_{8f}}{\rightleftharpoons}} \quad O_2 + HO_2.$$

$$A + hv \quad \underset{k_3}{\overset{k_{IA}I}{\rightleftharpoons}} \quad A^* \quad \xrightarrow{k_2} \quad Decomp. \ prod.$$

$$A + O_3 \quad \xrightarrow{k_1} \quad Decomp. \ prod.$$

$$A + H_2O_2 \quad \xrightarrow{k_{11}} \quad Decomp. \ prod.$$

$$A + OH. \quad \xrightarrow{k_4} \quad Decomp. \ prod.$$

$$A + HO_2 \cdot \xrightarrow{\quad k_5 \quad} \text{Decomp. prod.}$$
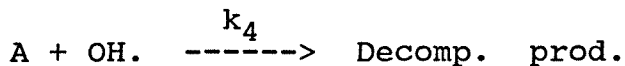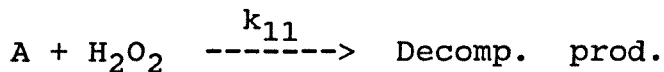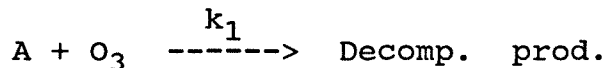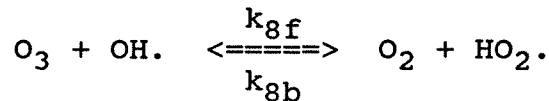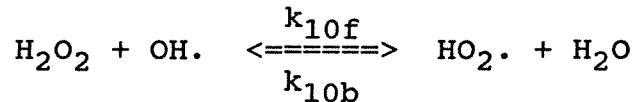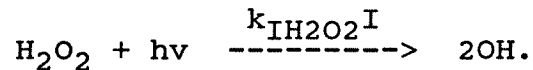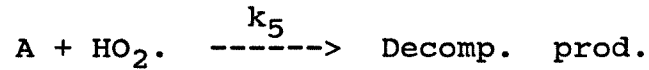
The mass balance for each reactant in this system gives a set of differential equations as follows:

(1)
$$\frac{dc_A}{dt} = -k_1 c_A c_{O3} - k_{11} c_A c_{H2O2} - k_4 c_A c_{OH \cdot} - k_5 c_A c_{HO2 \cdot} - k_{IA} I c_A$$

(2)
$$\frac{dc_{A*}}{dt} = k_{IA} I c_A - k_2 c_{A*} - k_3 c_{A*}$$

(3)
$$\frac{dc_{H2O2}}{dt} = -k_{IH2O2} I c_{H2O2} - k_{10f} c_{H2O2} c_{OH \cdot} + k_{10b} c_{HO2 \cdot} - k_{11} c_A c_{H2O2}$$

(4)
$$\frac{dc_{O3}}{dt} = -k_1 c_A c_{O3} - k_{8f} c_{O3} c_{OH \cdot} + k_{8b} c_{O2} c_{HO2 \cdot}$$

(5)
$$\frac{dc_{O2}}{dt} = k_{8f} c_{O3} c_{OH \cdot} - k_{8b} c_{O2} c_{HO2 \cdot}$$

(6)
$$\frac{dc_{OH \cdot}}{dt} = 2 k_{IH2O2} I c_{H2O2} - k_{10f} c_{H2O2} c_{OH \cdot} + k_{10b} c_{HO2 \cdot} - k_{8f} c_{O3} c_{OH \cdot} + k_{8b} c_{O2} c_{HO2 \cdot} - k_4 c_A c_{OH \cdot}$$

(7)
$$\frac{dc_{HO2 \cdot}}{dt} = k_{10f} c_{H2O2} c_{OH \cdot} - k_{10b} c_{HO2 \cdot} + k_{8f} c_{O3} c_{OH \cdot} - k_{8b} c_{O2} c_{HO2 \cdot} - k_5 c_A c_{HO2 \cdot}$$

As done previously, the initial reactant concentration and the rate constants($K_{IA}I$, K_2 and K_3) obtained from the UV alone reaction process were used to solve the above

19

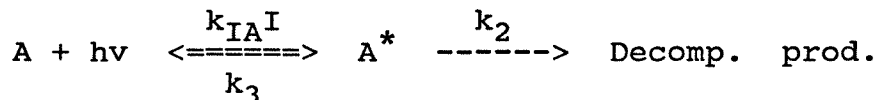equations. The rate constants(K_1, K_4, and K_5) obtained from the ozone alone reaction process were used as the initial input value in the Rosenbrock Hillclimb regression program. The values of rate constants ($K_{IH2O2}I$, K_{10f}, K_{10b}, and K_{11}) were found by trial and error method starting with 0.1.

6. CSTR study under the $O_2/O_3/UV$ system

The reaction rate and mass transfer coefficient obtained from the $O_2/O_3/UV$ reaction process were used to model the data of the continuous flow system under the same reaction schemes. The mass balance for pollutant A under CSTR system becomes:

Accumulation of A = Input - Output - Disappearance

by reaction

$$\frac{dC_A}{dt} = \frac{Q}{V}C_{A0} - \frac{Q}{V}C_A - r_A$$

where

$$r_A = -k_{IA}IC_A + k_3C_{A*} - k_1C_AC_{O3} - k_6C_AC_{O2*}$$
$$- k_4C_AC_{OH.} - k_5C_AC_{HO2}.$$

Then, the mass balance for the reaction component becomes:

$$(1) \quad \frac{dC_A}{dt} = \frac{Q}{V}C_{A0} - \frac{Q}{V}C_A - r_A$$

$$(2) \quad \frac{dC_{A*}}{dt} = k_{IA}IC_A - k_3C_{A*} - k_2C_{A*}$$

20

$$(3) \quad \frac{dC_{O3}}{dt} = -k_{IO3}IC_{O3} - k_{8f}C_{O3}C_{OH.} + k_{8b}C_{O2}C_{HO2.}$$
$$- k_1 C_A C_{O3} + k_{LO3}a(C_{O3*} - C_{O3})$$

$$(4) \quad \frac{dC_{O2}}{dt} = k_{IO3}IC_{O3} + k_{8f}C_{O3}C_{OH.} - k_{8b}C_{O2}C_{HO2.}$$
$$- k_{IO2}IC_{O2} + k_{LO2}a(C_{O2*} - C_{O2})$$

$$(5) \quad \frac{dC_{O2*}}{dt} = k_{IO2}IC_{O2} - k_{9f}C_{O2*} + k_{9b}C_{OH.}C_{HO2.}$$
$$- k_6 C_A C_{O2*}$$

$$(6) \quad \frac{dC_{OH.}}{dt} = 2k_{IO3}IC_{O3} - k_{8f}C_{O3}C_{OH.} + k_{8b}C_{O2}C_{HO2.}$$
$$+ k_{9f}C_{O2*} - k_{9b}C_{OH.}C_{HO2.} - k_4 C_A C_{OH.}$$

$$(7) \quad \frac{dC_{HO2.}}{dt} = k_{8f}C_{O3}C_{OH.} - k_{8b}C_{O2}C_{HO2.} + k_{9f}C_{O2*}$$
$$- k_{9b}C_{OH.}C_{HO2.} - k_5 C_A C_{HO2.}$$

The equations from (2) to (7) are the same as those of the $O_2/O_3/UV$ mechanism.

The equations above were used to solve the concentration of pollutant A in the exit stream by the fourth order Runge-Kutta method. The data obtained by this kinetic model was also compared with the experimental data.

CHAPTER 2

A. Apparatus Details

1. Reactor

The vertical cylindrical reactor was designed to operate as a batch, semi-batch and continuous reactor. The schematic diagram of the reactor is shown in Figure 1. The reactor was made of acrylic plastic. The holdup volume of the reactor is approximately 35 liter. The overall height of the reactor is 5.5 inches with different diameters. The bottom portion of the reactor has 5 inches outside diameter and 1 inch in height. The outside diameter of the upper portion of the reactor is 7.5 inches. The reason for different diameters is to keep the reactor volume within a limit of ten gallons and at the same time, to allow sufficient space to house the ultraviolet light source in the upper section of the reactor. The wall thickness of the reactor is 0.25 inch.

The reactor has nine sample ports along the cylinder axis. These sample ports are equally spaced about 6 inches apart along the upper section of the reactor.

Agitation in the reactor was provided by a bubbling gas flow. The gas (ozone or nitrogen) was introduced from the bottom of the reactor through a four head dispenser of medium porosity. Exhaust gases were vented from the top of the reactor to the laboratory hood.

Liquid feed enters the reactor through a centrifugal

pump. The liquid feed inlet is at the top and the outlet is at the bottom of the reactor; however, this can be interchanged.

2. Ozonator

The ozonator used was the Model-816 ozone generator purchased from Welsbach Ozone System Corporation, Philadelphia, PA. The ozone generator produced a minimum of 16 gm of ozone per hour. The ozone generator is water cooled and is the corona discharge type. It can be fed with dry commercial grade air or oxygen. 99.6% grade oxygen was used for all experiments that required ozone.

3. Ultraviolet Light Source

The UV lamp was supplied by Canrad-Hanovia, Inc.. It is an immersion type high pressure mercury vapor lamp with an arc length of 25 inches and has a power rating of 5 kw. The lamp is encased in two concentric wells called immersion wells. Annular space between the UV lamp and wall is 1.75 inches wide.

The immersion wells are made of quartz glass. The inner well, which houses the mercury lamp, is connected to a nitrogen gas line. Commercial grade nitrogen gas was used here. The purpose is to provide an inert atmosphere around the lamp in order to prevent external vapors and fumes coming in contact with the lamp, thus avoiding an explosion hazard.

The outer well is used to circulate cooling water. It is connected to the laboratory water supply. The water removes most of the radiated infrared energy and removes all of the convection heat energy produced by the lamp. A thermocouple is used to monitor the temperature of the cooling water at the outlet.

A stabilized ballast supplies power to the lamp. The UV lamp can be operated at three power settings: 125, 200, and 300 W/inch. All of the experiments were conducted at the 200 W/inch power level.

4. Gas Chromatograph

A Hewlett-Packard model 5730A gas chromatograph was used for all pollutant concentration analysis. The GC is fitted with a flame ionization detector(FID) and is connected with a Hewlett-Packard Model 3380A integrator.

Two capillary columns were used in this study. Both target pollutants(DMF and DMA) can be analyzed by them. They are the Chrompack WCOT fused silica column(cat# 7763) and the Alltech column(cat# 995110). The liquid phase of the Chrompack WCOT column was CP wax 57CB. It was 26 meters in length, with a film thickness of 1.2 um. The inside diameter was 0.32 mm, and the outside diameter was 0.45 mm. The liquid phase of the Alltech was Superox(or Carbowax), and it was 10 meters in length, with a film thickness of 1.2 um. The inside diameter was 0.53 mm.

Zero grade hydrogen gas was used for FID detector and

prepurified grade (99.998%) nitrogen gas served as a carrier gas in this study. The GC was operated under the following condition for all of the analysis in this work:

N_2 pressure = 50 psig   column temperature = 140°C

Air pressure = 40 psig   detector temperature = 300°C

H_2 pressure = 40 psig   injection port temperature = 250°C

Under the operating condition above, the retention time was 1.45 minutes for DMF and 1.84 minutes for DMA when the Chrompack WCOT column was used. For the Alltech column, the retention time for DMF was 1.30 minutes and for DMA, 1.75 minutes.

B. Experimental Procedure

1. Preparation for Running an Experiment

The reactor was cleaned several times using tap water to eliminate the residue if any. The concentrated form of solution for each pollutant (DMF,DMA) was prepared using distilled water in a 4 liter flask with cover. It was mixed by a magnetic mixer. 100 ppm of pollutant solution was prepared by diluting the concentrated solution with tap water in the feed tank. 40 liter of 100 ppm of pollutant solution were prepared for the batch and semi-batch reaction. The starting reactant concentration are summarized in Table 3. It was mixed for at least five minutes before pumping into the reactor. A stainless steel centrifugal pump and Tygon tubing were used to pump the feed solution into the reactor. The first few liters of the feed were discarded from the reactor as a purge of the pump and transfer lines.

2. Collection of the Sample

The samples were collected at frequent intervals during the experimental trials. The central sample port was used exclusively at this study. The location of the sample ports are indicated on the reactor diagram, Figure 1. Each sample jar was rinsed twice with solution from the reactor prior to collection of the sample to eliminate the collection of the dead volume in the sample port. Each sample size was approximately 20 ml. All the samples were subjected to analysis immediately after collection in order

to avoid any possible decomposition. Each sample was analyzed at least three times to ensure reproducible results.

3. Analysis of Samples

The gas chromatograph was optimized overnight at the operating condition mentioned in the previous section. To ensure result consistency, it is necessary to change the septum and preheat septum at least 24 hours. The capillary column was conditioned at the operating temperature with nitrogen flow overnight before ran experiments.

To determine the pollutant concentration, it is necessary to prepare a set of target pollutant solutions with known concentration. These concentration values are 1, 16, 50, 100, 150, and 200 ppm. These samples were analyzed on the GC several times. They were used to make the calibration curve which was plotted as standard concentration versus the area under the peak. The concentration of the sample collected from the reactor was thus calculated using the calibration curve. The volume of the sample injected into the GC was held constant at 1.0 ul. A concrete effort was made to maintain operating condition of GC by keeping syringe type and injection technique as constant as possible during the analysis work.

4. Reaction with UV Alone

This is a batch experiment. The 100 ppm of target

solution was pumped into the reactor until the 30 liter level was achieved. Then, nitrogen gas was bubbled into the reactor through the ozone generator to maintain a constant flow. The pressure was maintained at 9-10 psig for a flow rate of about 4.7 liter/min. At this time, an initial sample was collected. The ultraviolet light source was then activated. Before using the UV lamp, cooling water and nitrogen was introduced to protect the UV lamp. The lamp was plugged in and initially set to 125 W/inch. Approximately 30 seconds later the power level was adjusted to 200 W/inch. At this moment, the timing of the experiment was started.

5. Reaction with Ozone Alone

This is a semi-batch experiment. The reactor filling and sample collection are identical to those described in the previous section.

In this experimental process, oxygen gas was introduced into the ozonator. The ozonator was used to initiate ozone gas. The ozone gas was exhausted to the ambient air until the noticeable ozone had achieved. Then, the ozone flow was bubbled from the bottom of the reactor, and the timing of the experiment was started. Ozone flow was adjusted to 9-10 psig for a flow rate of about 4.7 liter/min.

6. Reaction with Oxygen and UV Light

This is a semi-batch experiment. The reactor filling, UV lamp operation and the sample collection procedure are

the same as those described in the UV alone experiment. The ozonator was used in the same way to monitor the oxygen flow rate in this process. Once again, the oxygen flow was adjusted to 9-10 psig (flow rate = 4.7 liter/min). In this treatment process, oxygen was bubbled into the reactor which is simultaneously irradiated with UV light (200 W/inch). At this time, the timing of this experiment was started.

7. Reaction with Oxygen, Ozone and UV Light

This is a semi-batch experiment. The reactor filling, UV lamp operation and the sample collection are identical to those described in the reaction with UV alone experiment. The ozonator was operated in the same way as those described in the reaction with ozone alone experiment. In this experiment, ozone flow was bubbled into the reactor while the power level of the UV lamp was adjusted to 200 W/inch. Then, the timing of this experiment was started.

8. Reaction with Hydrogen Peroxide and UV Light

This is a batch experiment. Before running this experiment, a smaller scaled reaction was done to test whether the hydrogen peroxide can react with the target pollutant. About 100 ppm of target pollutant solution was prepared in the 4 liter beaker. It was mixed by the magnetic mixer. Before adding the H_2O_2 into the beaker the first sample was collected. An excess amount of H_2O_2 (35 wt% in water) was then added to the beaker and the timing of

this experiment begun. The samples were collected from the beaker at frequent intervals and were analyzed by gas chromatograph to determine the concentration of the target pollutant. This experimental trial took 3 hours and showed that the target pollutants (Both DMF and DMA) did not react with the H_2O_2.

Some species, e.g. nitrobenzene, can easily react with H_2O_2 without UV light. The DMF and DMA, however, did not react with H_2O_2 without UV light. A stoichiometric excess of H_2O_2 (35 wt% in water) was added to the blending tank to make sure that there were enough amounts of H_2O_2 to react with both pollutants and intermediates produced. The H_2O_2 solution mixed with 40 liter of target solution for 5 minutes. The reactor was filled as described previously. Nitrogen gas was bubbled into the reactor for mixing, and an initial sample was collected. The ultraviolet lamp was warmed up for 30 seconds with power at the 125 W/inch level. Then, the power was switched to 200 W/inch and started the timing of this experiment. For the DMF case, 42.6 ml of hydrogen peroxide solution was added to the feeding tank. For DMA, 47 ml was required. These qualities were calculated based on the stoichiometric equation for complete reaction of 40 liter of 100 ppm target pollutant solution. The reaction rate and the mass transfer parameters for each compound are summarized in Tables 4 and 6.

9. CSTR Experiments

A series of four continuous experiments were run for each of the two compounds. These two solutions are fed at different rates and positioned in either the top or bottom of the reactor. The $O_2/O_3/UV$ experimental condition was used in each case. The flow meter used in this work was calibrated and the two flow rates chosen are 4.5 liter/min and 2.75 liter/min. 80 liter of 100 ppm target pollutant solution was prepared in the feeding tank for the CSTR experimental trial. Prior to each CSTR experiment, the reactor was filled with tap water. Before starting the experiment, samples were collected from the reactor and the feeding tank. The feed, ozone flow and UV light must be turned on simultaneously. Feed flow was monitored by using a flowmeter in the feed. The procedures for samples collection and analysis are the same as described previously.

The experimental run was terminated when the feed solution was exhausted.

CHAPTER 3

A. Experimental Results

The degradation of DMF and DMA by using UV light, Ozone, O_2/UV, $O_2/O_3/UV$, and H_2O_2/UV have been studied in a photoreactor. Experimental results of residence time vs. conversion are summarized in Table 10. The process using ozone alone is the slowest reaction and does not reach completion in 5 hrs. System processed by H_2O_2/UV is the fastest step and achieves completion within 10 minutes.

Figures 2-11 present the disappearance curves for DMF and DMA for each process. Points represent experimental data in each figure, while the smooth curve was generated from the kinetic model described in previous chapter. It appears to be in good agreement with the experimental and theoretical results for most cases. The sum of squared differences between the experimental and predicted values is in the order of 10^{-2} to 10^{-4}, except for the UV alone process.

Outlines of the reaction rate constants and mass transfer parameters from the kinetic model are given in Tables 4-7. The results are discussed below.

1. Reactions with UV Light

Figures 2-3 describe the fall off behavior of the reactions with UV alone. It is obviously a moderate reaction, with greater than 99% substrate disappearance achieved for both DMF and DMA within 90 minutes.

A comparison of the curve fitting of the experimental data versus mathematical model revealed that an improvement in the mechanism is desired for UV alone system.

Nitrogen gas was bubbled through the solution to impart the desired mixing effect in this system. Since the N-N bond is very stable, it was assumed that nitrogen gas did not undergo decomposition with UV light.

2. Reactions with Ozone Alone

The results of O_3 alone degradation is shown in Figures 4-5. It is a slow reaction and does not complete even after 5 hrs residence time. This could be the results of "retarding" or "stabilizing" of ozone by the solutes, DMF and DMA.

The solution's pH value will affect the ozonation rate. The pH value of this study was fixed around 7. The lifetime of ozone in water thus depends upon solutes which yield radical types of intermediates, which additionally catalyze the decomposition of ozone, and upon solutes which scavenge the hydroxyl free radicals (18). Such scavengers (e.g. bicarbonate ions and aliphatic alcohols) quench the chain reactions and thus "stabilize" the ozone.

Owing the facts of slow reaction of DMF and DMA with O_3, these two solutes could be of such scavengers. DMA and DMF react with ozone primarily through the O_3 mechanism from predicted results of the proposed kinetic model. This agrees well with the characters of slow ozonation of DMF and DMA.

Ozonation in the presence of UV radiation and/or H_2O_2 causes organic oxidations to proceed at significantly increased rates. This effect also matches well with this study as shown in Table 10.

3. Reactions with O_2/UV

The reaction with oxygen and UV light is illustrated in Figures 6-7. An extended period of time was required to obtain 99% conversion. This finding is in agreement with the relatively slow O_2/UV reactions suggested in previous work.

In the O_2/UV case, reaction occurs mainly through the UV, OH. radical, and HO_2. radical mechanism. Since relatively little study of this reaction has been performed, these results are supposed to be reasonable.

4. Reactions with O_2/O_3/UV

The combined effect of O_2/O_3/UV degradation is demonstrated in Figures 8-9. Basically completed destruction occurred after 90 and 82 minutes for DMF and DMA respectively. This process is more effective than ozone process. This finding agrees well with the previous work (20).

As would be expected, reaction in the O_2/O_3/UV system is complex. It came out that the O_3, HO_2. radical, and UV mechanism are dominant from the calculation of the mathematical model. Some question about the role of the hydroxyl radical in this reaction scheme remains. This may

be explained by the limited knowledge of the mechanisms of organic decomposition by $O_2/O_3/UV$ process.

5. Reactions with H_2O_2/UV

As discussed from the ozone alone system, the photooxidization by H_2O_2/UV is significantly faster than ozone alone process. A complete reaction was observed within 10 minutes as shown in Figures 10-11. The curve predicted by the mathematical model is also very smooth as seen in these figures.

The synergistic combination of UV irradiation and the oxidization agent, H_2O_2 is the fastest approach to degrade DMF and DMA among the methods studied here. The reactions with HO_2. radical, H_2O_2, and UV mechanism were found to be most important for this system.

Hydrogen peroxide is known to be photosensitive. The degradation rate of DMF and DMA with H_2O_2 is affected by the energy of the incident light. There was no reaction with the addition of H_2O_2 until the solution was exposed to UV light.

6. $O_2/O_3/UV$ process operated with simulated CSTR mode

Figures 12-27 depict the results of continuous flow (CSTR) experiments for each compound. Only the reaction with $O_2/O_3/UV$ was studied in this manner.

Two flow rates: 2.75 and 4.5 liter/min were studied for each compound. Two flow patterns were investigated: feed solution introduced at the top of the reactor, or at the

bottom, with exit from the opposite end.

Each figure presents one set of experimental data, shown as points, and one set of theoretical curves obtained by applying the semi-batch rate constants and mass transfer parameters developed in the $O_2/O_3/UV$ system.

Table 11 summarizes the results of this work, in terms of predicted vs. experimentally determined steady state exit concentrations. It appears that sensibly good approach was obtained for the top enter-bottom exit case at the flow rate of 4.5 liter/min. Differences between the predicted and experimental data are less than 4.1 %. This fact could partially due to the improved mixing in the reactor when operated in this mode. Feed solution falling into the reactor increased the level of agitation somewhat. Also, the higher the flow is, the more the mixing could be.
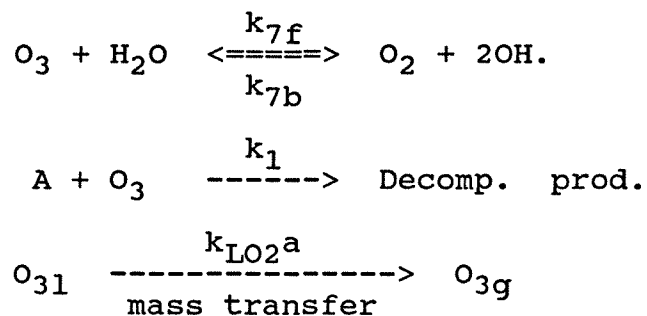
Application of the parameters developed in the semi-batch reactor using the $O_2/O_3/UV$ system to the continuous case has given reasonably good match when CSTR behavior was assumed. This finding, points the way to the usefulness in developing laboratory scale semi-batch parameters for eventually large scale continuous flow.

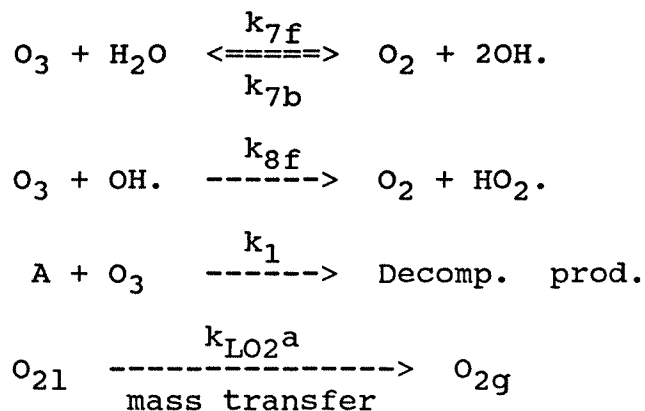## B. Simplification of the Reaction Mechanism

Analysis of the results from the optimization program showed that some terms introduced little contribution to the kinetic model. These terms were the product of the rate constant with its associated concentration. This fact suggested that these terms could be eliminated from the model. The simplified reaction mechanisms for each target pollutant (DMF and DMA) under the different reaction process are represented as follow:
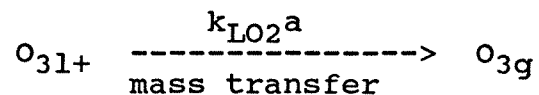
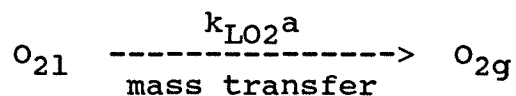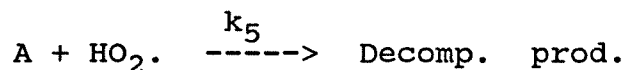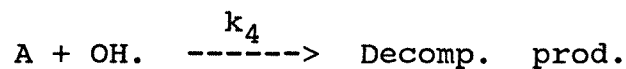### 1. The Simplified Mechanism for Reaction with Ozone Alone
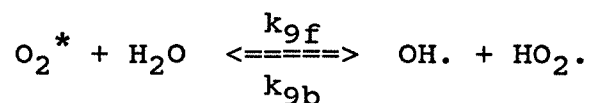
(a) for DMF:

$$O_3 + H_2O \quad \underset{k_{7b}}{\overset{k_{7f}}{<====>}} \quad O_2 + 2OH.$$

$$A + O_3 \quad \xrightarrow{k_1} \quad Decomp. \quad prod.$$

$$O_{31} \quad \underset{mass\ transfer}{\xrightarrow{k_{LO2}a}} \quad O_{3g}$$

(b) for DMA:

$$O_3 + H_2O \quad \underset{k_{7b}}{\overset{k_{7f}}{<====>}} \quad O_2 + 2OH.$$

$$O_3 + OH. \quad \xrightarrow{k_{8f}} \quad O_2 + HO_2.$$

$$A + O_3 \quad \xrightarrow{k_1} \quad Decomp. \quad prod.$$

$$O_{21} \quad \underset{mass\ transfer}{\xrightarrow{k_{LO2}a}} \quad O_{2g}$$

37

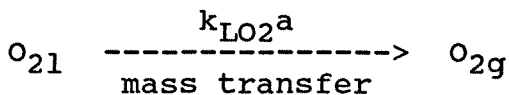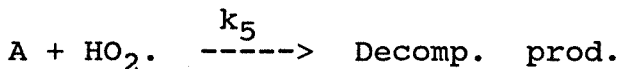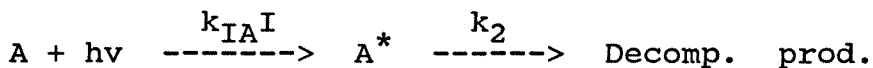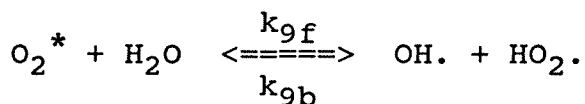$$O_{3l+} \quad \xrightarrow[\text{mass transfer}]{k_{LO2}a} \quad O_{3g}$$

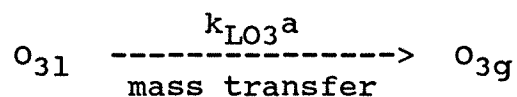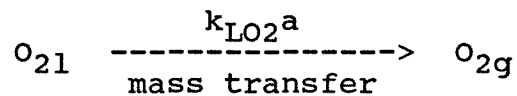## 2. the Simplified Mechanism for O_2/UV Reaction

(a) for DMF:

$$O_2 + h\nu \quad \xrightarrow{k_{IO2}I} \quad O_2{}^*$$

$$O_2{}^* + H_2O \quad \underset{k_{9b}}{\overset{k_{9f}}{\rightleftharpoons}} \quad OH. + HO_2.$$

$$A + h\nu \quad \xrightarrow{k_{IA}I} \quad A^* \quad \xrightarrow{k_2} \quad \text{Decomp. prod.}$$

$$A + OH. \quad \xrightarrow{k_4} \quad \text{Decomp. prod.}$$

$$A + HO_2. \quad \xrightarrow{k_5} \quad \text{Decomp. prod.}$$

$$O_{2l} \quad \xrightarrow[\text{mass transfer}]{k_{LO2}a} \quad O_{2g}$$

(b) for DMA:

$$O_2 + h\nu \quad \xrightarrow{k_{IO2}I} \quad O_2{}^*$$

$$O_2{}^* + H_2O \quad \underset{k_{9b}}{\overset{k_{9f}}{\rightleftharpoons}} \quad OH. + HO_2.$$

$$A + h\nu \quad \xrightarrow{k_{IA}I} \quad A^* \quad \xrightarrow{k_2} \quad \text{Decomp. prod.}$$

$$A + HO_2. \quad \xrightarrow{k_5} \quad \text{Decomp. prod.}$$

$$O_{2l} \quad \xrightarrow[\text{mass transfer}]{k_{LO2}a} \quad O_{2g}$$
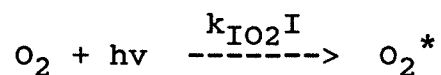
3. the Simplified Mechanism for O_2/O_3/UV Reaction

(a) for DMF:

$$O_3 + H_2O + h\nu \xrightarrow{\ k_{IO3}I\ } O_2 + 2OH\cdot$$

$$O_2 + h\nu \xrightarrow{\ k_{IO2}I\ } O_2{}^*$$

$$O_2{}^* + H_2O \xrightarrow{\ k_{9f}\ } OH\cdot + HO_2\cdot$$

$$A + h\nu \xrightarrow{\ k_{IA}I\ } A^* \xrightarrow{\ k_2\ } Decomp.\ prod.$$

$$A + O_3 \xrightarrow{\ k_1\ } Decomp.\ prod.$$

$$A + HO_2\cdot \xrightarrow{\ k_5\ } Decomp.\ prod.$$

$$O_{2l} \xrightarrow[\text{mass transfer}]{\ k_{LO2}a\ } O_{2g}$$

$$O_{3l} \xrightarrow[\text{mass transfer}]{\ k_{LO3}a\ } O_{3g}$$

(b) for DMA:

$$O_3 + H_2O + h\nu \xrightarrow{\ k_{IO3}I\ } O_2 + 2OH\cdot$$

$$O_3 + OH\cdot \underset{k_{8b}}{\overset{k_{8f}}{\rightleftharpoons}} O_2 + HO_2\cdot$$

$$O_2 + h\nu \xrightarrow{\ k_{IO2}I\ } O_2{}^*$$

$$A + h\nu \xrightarrow{\ k_{IA}I\ } A^* \xrightarrow{\ k_2\ } Decomp.\ prod.$$

$$A + O_3 \xrightarrow{\ k_1\ } Decomp.\ prod.$$

$$A + OH\cdot \xrightarrow{\ k_4\ } Decomp.\ prod.$$

$$A + HO_2 \cdot \xrightarrow{k_5} Decomp. \ prod.$$

$$O_{2l} \xrightarrow[\text{mass transfer}]{k_{LO2}a} O_{2g}$$

$$O_{3l} \xrightarrow[\text{mass transfer}]{k_{LO3}a} O_{3g}$$
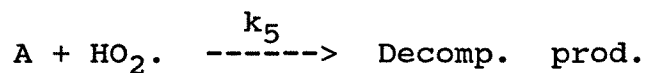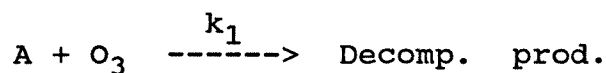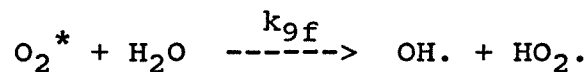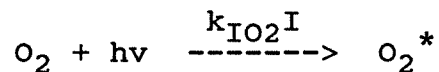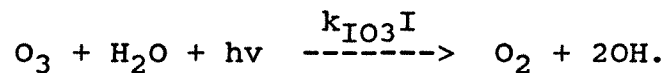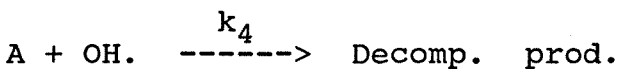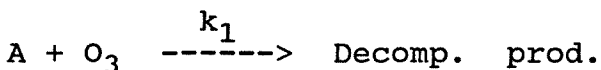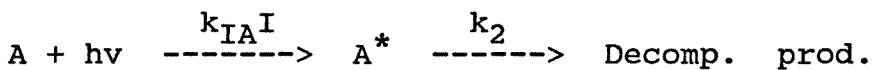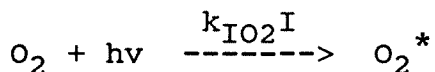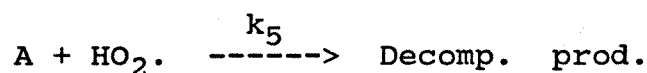
4. the Simplified Mechanism for H_2O_2/UV Reaction

(a) for DMF:

$$H_2O_2 + hv \xrightarrow{k_{IH2O2}I} 2OH \cdot$$

$$H_2O_2 + OH \cdot \underset{k_{10b}}{\overset{k_{10f}}{\rightleftharpoons}} HO_2 \cdot + H_2O$$
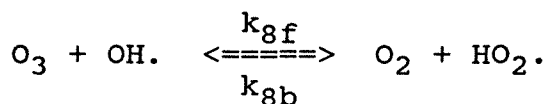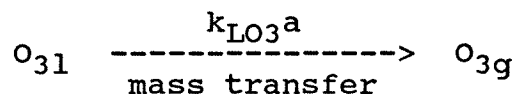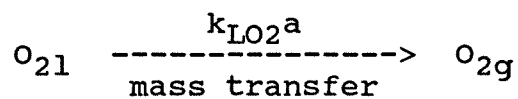
$$O_3 + OH \cdot \xrightarrow{k_{8f}} O_2 + HO_2 \cdot$$

$$A + hv \xrightarrow{k_{IA}I} A^* \xrightarrow{k_2} Decomp. \ prod.$$

$$A + O_3 \xrightarrow{k_1} Decomp. \ prod.$$

$$A + OH \cdot \xrightarrow{k_4} Decomp. \ prod.$$

$$A + HO_2 \cdot \xrightarrow{k_5} Decomp. \ prod.$$

(b) For DMA:

$$H_2O_2 + hv \xrightarrow{k_{IH2O2}I} 2OH \cdot$$

$$H_2O_2 + OH \cdot \underset{k_{10b}}{\overset{k_{10f}}{\rightleftharpoons}} HO_2 \cdot + H_2O$$

$$O_3 + OH \cdot \underset{k_{8b}}{\overset{k_{8f}}{\rightleftharpoons}} O_2 + HO_2 \cdot$$

$$A + h\nu \xrightarrow{\ k_{IA}I\ } A^* \xrightarrow{\ k_2\ } \text{Decomp. prod.}$$

$$A + HO_2 \cdot \xrightarrow{\ k_5\ } \text{Decomp. prod.}$$
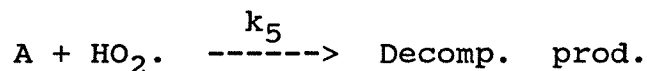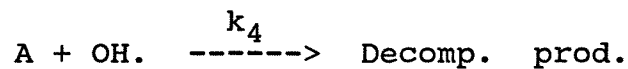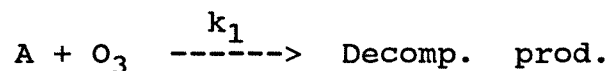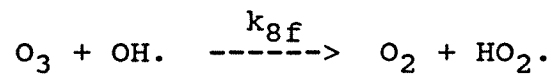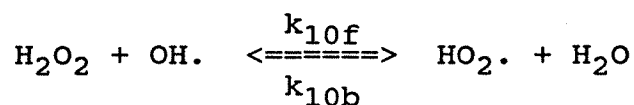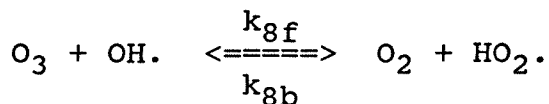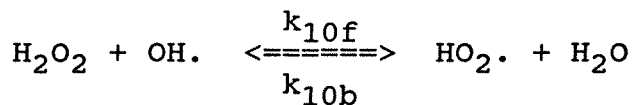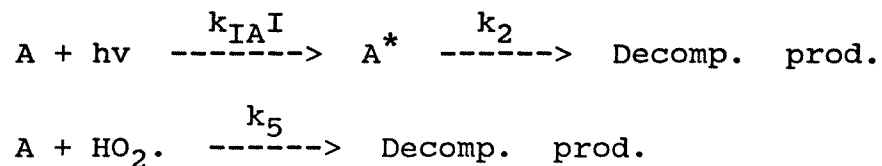
The mass balance for the simplified mechanism can also be developed. The Rosenbrock Hillclimb regression procedure and the fourth order Runge-Kutta integration method were used again to get a new set of reaction rates and mass transfer parameters. The results were summarized in Tables 5 and 7.

A comparison of the curve fitting of the experimental data between the proposed kinetic models and the simplified models revealed only a little improvement in data fitting.

C. Conclusions:

(1) Aqueous solutions of DMF and DMA can be degraded significantly by the UV, O_2/UV, O_2/O_3/UV, and H_2O_2/UV processes.

(2) DMA reacts faster than DMF in every case studied.

(3) H_2O_2/UV is the most rapid process for both compounds.

(4) The order of degradation rates can be generalized as: slowest O_3 < UV < O_2/O_3/UV < O_2/UV < H_2O_2/UV fastest.

(5) The reaction mechanisms proposed are suitable for the elucidation of the behavior of these systems. This is evinced by the good agreement obtained between experimental and theoretical results.

(6) The investigation using semi-batch reactor has great potential to develop the kinetic parameters required for the CSTR system.

D. Recommendations:

(1) A pH probe should be provided in future reactor installations. The pH value will significantly affect the oxidation potential of the oxidizing agent used.

(2) The mass transfer coefficient and the saturation concentration of ozone and oxygen should be determined in aqueous solution.

(3) A gas seizer installed on top outlet of the reactor could help to destroy solute bubbles and prevent flooding of the solution.

(4) To get a good match with the CSTR assumption should be determined a minimum feeding flow rate.

(5) The intensity of UV light should be monitored to study the energy effect on the reaction.

APPENDIX I

TABLES

Table 1

Comparison, Oxidation potential of

Ozone and its Photolysis Species

Species	Oxidation Potential volts	Relative* Oxidation Power
Fluorine, F_2	3.06	2.25
Hydroxyl Radical, OH.	2.80	2.05
Atomic Oxygen, O	2.42	1.78
Ozone, O_3	2.07	1.52
Hydrogen Peroxide, H_2O_2	1.77	1.30
Perhydroxyl Radical, HO_2.	1.70	1.25
Hypochlorous Acid, HOCl	1.49	1.10
Chlorine, Cl_2	1.36	1.00

* Based on Cl_2 as a reference

Table 2

Summary of Research on Kinetics of Ozone Decomposition (16,28)

Reference	pH Range	Temp. °C Range	RXN. Rate w/res. Ozone
Weiss (1935)	2-8	0	3/2
Alder/Hill (1935)	1-2.8	0-27	1
Stumm (1954)	7.6-10.4	1.2-19.8	1
Kilpatrick,et al(1956)	0-6.8	25	3/2
Raukas,et al (1962)	5.4-8.5	5-25	3/2
Hewes/Davison (1971)	2-4	30-60	2
Hewes/Davison (1971)	6	10-50	3/2-2
Hewes/Davison (1971)	8	10-20	1
Czapski (1968)	10-13	25	1
Rogozhkin (1970)	9.6-11.9	25	1
Shambaugh,et al (1976)	9	20	1
Rizzuti,et al (1976)	8.5-13.5	18-27	1
Sullivan/Roth (1979)	0.5-10.0	3.5-60	1
Li (1977)	2.1-10.2	25	3/2
Teramoto/Imamura (1979)	acidic	25	1-2
	basic	25	1

Table 3

Starting Reactant Concentrations

Rxn. Scheme	D M F		D M A	
UV	1.8205	(mg-mol/l)	1.5966	(mg-mol/l)
Ozone	1.6959		1.1011	
O_2/UV	1.4160		1.4437	
O_3/UV	1.5164		1.3920	
H_2O_2/UV	1.7849		1.3172	

CSTR Expt.				
2.75 l/min top	1.1562		0.9057	
4.5 l/min top	1.3397		0.9184	
2.75 l/min bot.	1.1781		0.8138	
4.5 l/min bot.	1.4712		0.8839	

Table 4

Reaction Rate and Mass Transfer Parameters for DMF

Param.	UV	O_3	O_2/UV	O_2/O_3/UV	H_2O_2/UV
k_{IA}^I	3.373E-2				
k_2	1.273				
k_3	7.763E-5				
k_1		2.746E-2		0.1741	0.5255
k_4		4.665E-7	0.1054	9.094E-5	8.984E-4
k_5		7.391E-4	7.106E-2	1.591	2.600
k_{7f}		7.961E-4			
k_{7b}		0.5356			
k_{8f}		1.117E-3		7.102E-4	5.176E-6
k_{8b}		0.4398		0.1936	0.1701
$k_{LO3}a$		0.2392		0.3882	
c_{O3*}		9.168E-2		0.1540	
$k_{LO2}a$		8.874E-5	4.193E-3	3.221E-4	
c_{O2*}		0.1213	0.1856	0.1838	
k_6			1.107E-6	1.705E-7	
k_{IO2}^I			0.3578	7.377E-3	
k_{9f}			3.332E-4	5.759E-4	
k_{9b}			2.596E-2	1.475E-2	
k_{IO3}^I				4.723E-3	
k_{11}					3.106E-6
k_{H2O2}^I					3.353E-2
k_{10f}					2.853E-2
k_{10b}					2.866E-4

Table 5

Reaction Rate and Mass Transfer Parameters calculated from the Simplified Mechanism for DMF

Param.	UV	O_3	O_2/UV	$O_2/O_3/UV$	H_2O_2/UV
k_{IA}^I					
k_2					
k_3					
k_1		2.842E-2		0.1689	0.6441
k_4			0.1054		2.285E-3
k_5			7.105E-2	1.589	2.113
k_{7f}	3.191E-3				
k_{7b}	0.8657				
k_{8f}					
k_{8b}					0.2011
$k_{LO3}a$		0.2336		0.3984	
c_{O3*}		9.048E-2		0.1566	
$k_{LO2}a$			4.189E-3	3.317E-4	
c_{O2*}	0.9172		0.1856	0.1984	
k_6					
k_{IO2}^I			0.3578	9.857E-3	
k_{9f}			3.332E-4	8.072E-4	
k_{9b}			1.105E-2		
k_{IO3}^I				2.619E-2	
k_{11}					
k_{H2O2}^I					3.886E-2
k_{10f}					2.960E-2
k_{10b}					1.997E-3

Table 6

Reaction Rate and Mass Transfer Parameters for DMA

Param.	UV	O_3	O_2/UV	O_2/O_3/UV	H_2O_2/UV
k_{IA}^I	2.358E-2				
k_2	1.401				
k_3	1.001E-3				
k_1		7.056E-2		0.2020	8.073E-3
k_4		8.767E-4	2.244E-4	9.999E-3	5.343E-5
k_5		0.1558	2.602	2.844	1.730
k_{7f}		9.999E-4			
k_{7b}		0.5993			
k_{8f}		3.634E-3		3.823E-2	3.808E-2
k_{8b}		0.1678		4.254E-2	0.3917
k_{LO3}^a		0.3308		0.3171	
c_{O3*}		0.1196		0.1985	
k_{LO2}^a		5.887E-4	0.1588	0.2044	
c_{O2*}		0.1856	0.1341	0.6794	
k_6			1.091E-6	8.318E-8	
k_{IO2}^I			1.6E-4	8.474E-3	
k_{9f}			1.302E-2	0.2023	
k_{9b}			0.7541	0.5388	
k_{IO3}^I				1.017E-2	
k_{11}					1.050E-3
k_{H2O2}^I					2.403E-2
k_{10f}					2.73
k_{10b}					1.196E-3

Table 7

Reaction Rate and Mass Transfer Parameters calculated from the Simplified Mechanism for DMA

Param.	UV	O_3	O_2/UV	$O_2/O_3/UV$	H_2O_2/UV
k_{IA}^I					
k_2					
k_3					
k_1		7.061E-2		0.1867	
k_4				8.755E-3	
k_5			2.602	2.825	1.722
k_{7f}		2.529E-4			
k_{7b}		0.6200			
k_{8f}		2.124E-3		3.482E-2	4.946E-2
k_{8b}				5.720E-2	0.1919
$k_{LO3}a$		0.3333		0.3536	
c_{O3*}		0.1195		0.1958	
$k_{LO2}a$		9.284E-3	8.708E-2	0.2176	
c_{O2*}		0.2025	0.1000	0.7296	
k_6					
k_{IO2}^I			5.187E-4	7.593E-3	
k_{9f}			1.302E-2	0.1848	
k_{9b}			0.8537	9.593E-2	
k_{IO3}^I				1.838E-3	
k_{11}					1.038E-2
k_{H2O2}^I					2.87E-2
k_{10f}					2.241E-2
k_{10b}					3.605E-3

Table 8

Key to Symbols in the Kinetic Model

$K_{IA}I$, $K_{IO2}I$, $K_{IO3}I$...Combined kinetic rate constants for photodecomposition

$k_2, k_3, k_4, k_5, k_6, k_{11}, k_7, k_8, k_9, k_{10}$...Kinetic rate constants

c_A, c_{O2}, etc....Concentration of each species

$K_{LO2}a$, $K_{LO3}a$...Mass transfer coefficients

c_{O2}, c_{O3}...Gas concentrations in liquid at saturation

c_{O2}, c_{O3}...Gas concentrations in the liquid phase

Q...Solution flow rate in CSTR model

Table 9

Unit for Rate Constants and Mass Transfer Parameters

$k_{IA}I$, $k_{IO2}I$, $k_{IO3}I$, k_{IH2O2}: $(W/L)^{-1}$ $(min)^{-1}$

k_2, k_3, k_{7f}, k_{9f}, k_{10b}: $(min)^{-1}$

$k_1, k_4, k_5, k_6, k_{7b}, k_{8f}, k_{8b}, k_{9b}, k_{10f}, k_1$: $(mg\text{-}mol/l)^{-1}$ $(min)^{-1}$

$k_{LO3}a$, $k_{LO2}a$: $(min)^{-1}$

c_{O2*}, c_{O3*}: $(mg\text{-}mol/l)$

Table 10

Summary of Residence Time and Conversion

(1) DMF:

Process	Residence Time (min)	Conversion %
UV alone	90	99.7
O_3 alone	340	50.1
O_2/UV	140	99.0
$O_2/O_3/UV$	90	99.4
H_2O_2/UV	8.85	99.3

(1) DMA:

Process	Residence Time (min)	Conversion %
UV alone	82	100
O_3 alone	310	89.9
O_2/UV	100	100
$O_2/O_3/UV$	90	100
H_2O_2/UV	6	100

Table 11

Steady State Concentrations in CSTR model

Flow (l/min)	D M F (C_A/C_{A0})			D M A (C_A/C_{A0})		
Top Enter	Exp	Pred	%Diff	Exp	Pred	%Diff
2.75	.5104	.6571	28.74	.4578	.5663	23.70
4.5	.7654	.7728	1.32	.7352	.7057	4.01
Bottom Enter						
2.75	.4711	.6656	41.29	.4029	.5696	41.38
4.5	.5793	.7730	33.44	.5792	.7042	21.58

Table 12

Solubility of Pure Ozone in Water (19)

Temperature, $^\circ$C	Bunsen coefficient, r	Henry's law coefficient, $H*10^{-4}$
0	0.49	3.95
5	0.44	3.55
10	0.375	3.0
20	0.285	2.29
30	0.20	1.61
40	0.145	1.17
50	0.105	0.85
60	0.08	0.64

$$r = \frac{\text{concentration of } O_3 \text{ in the liquid}}{\text{concentration of } O_3 \text{ in the gas, reduced to NTP}}$$
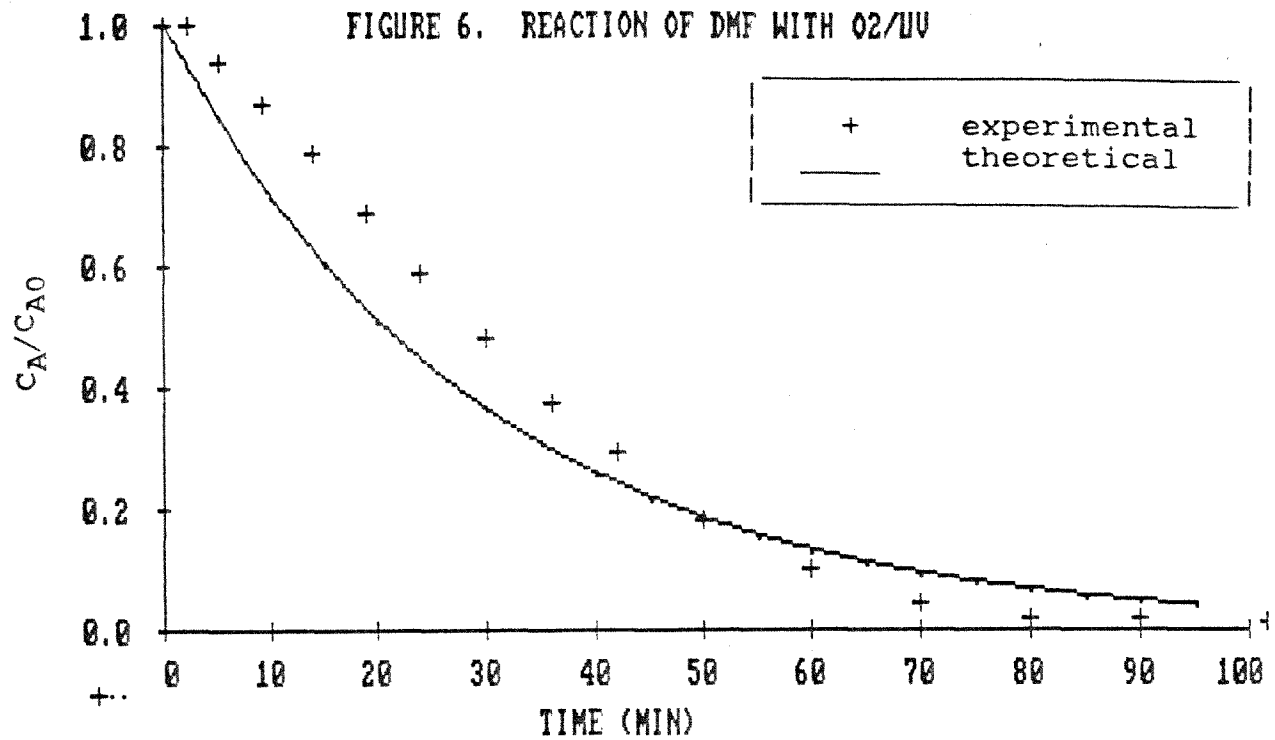
APPENDIX II

FIGURES

FIGURE 1. REACTOR APPARATUS

Vent to hood

Cooling water

N_2 enter

Cooling water exit

Feed solution inlet

UV lamp

N_2 well

Cold water well

Sample ports

Gas enter (O_3 or O_2)

Treated water exit

FIGURE 2. REACTION OF DMF WITH UV ALONE

+ experimental
theoretical

FIGURE 3. REACTION OF DMA WITH UV ALONE

+ experimental
theoretical

59

FIGURE 4. REACTION OF DMF WITH O3 ALONE

FIGURE 5. REACTION OF DMA WITH O3 ALONE

FIGURE 6. REACTION OF DMF WITH O2/UV

experimental +
theoretical ——

FIGURE 7. REACTION OF DMA WITH O2/UV

experimental +
theoretical ——

61

FIGURE 8.   REACTION OF DMF WITH O2/O3/UV

FIGURE 9.   REACTION OF DMA WITH O2/O3/UV

62

FIGURE 10. REACTION OF DMF WITH H2O2/UV

FIGURE 11. REACTION OF DMA WITH H2O2/UV

FIGURE 12. CSTR FOR DMF (4.5 LITER/MIN)

+ TOP ENTER (experimental)
___ TOP ENTER (theoretical)

FIGURE 13. CSTR FOR DMF (4.5 LITER/MIN)

+ BOTTOM ENTER (experimental)
___ BOTTOM ENTER (theoretical)

FIGURE 14. CSTR FOR DMF(2.75 LITER/MIN)

FIGURE 15. CSTR FOR DMF(2.75 LITER/MIN)

FIGURE 16. CSTR FOR DMF (TOP ENTER)

+ 4.5 l/min (experimental)
_____ 4.5 l/min (theoretical)

FIGURE 17. CSTR FOR DMF (TOP ENTER)

+ 2.75 l/min (experimental)
_____ 2.75 l/min (theoretical)

66

FIGURE 18. CSTR FOR DMF (BOTTOM ENTER)

+   4.5 l/min (experimental)
____ 4.5 l/min (theoretical)

FIGURE 19. CSTR FOR DMF (BOTTOM ENTER)

+   2.75 l/min (experimental)
____ 2.75 l/min (theoretical)

FIGURE 20. CSTR FOR DMA (4.5 LITER/MIN)

FIGURE 21. CSTR FOR DMA (4.5 LITER/MIN)

68

FIGURE 22.   CSTR FOR DMA(2.75 LITER/MIN)

FIGURE 23.   CSTR FOR DMA(2.75 LITER/MIN)

FIGURE 24.   CSTR FOR DMA (TOP ENTER)

+   4.5 l/min (experimental)
_____   4.5 l/min (theoretical)

FIGURE 25.   CSTR FOR DMA (TOP ENTER)

+   2.75 l/min (experimental)
_____   2.75 l/min (theoretical)

70

FIGURE 26. CSTR FOR DMA (BOTTOM ENTER)

4.5 l/min (experimental)
4.5 l/min (theoretical)

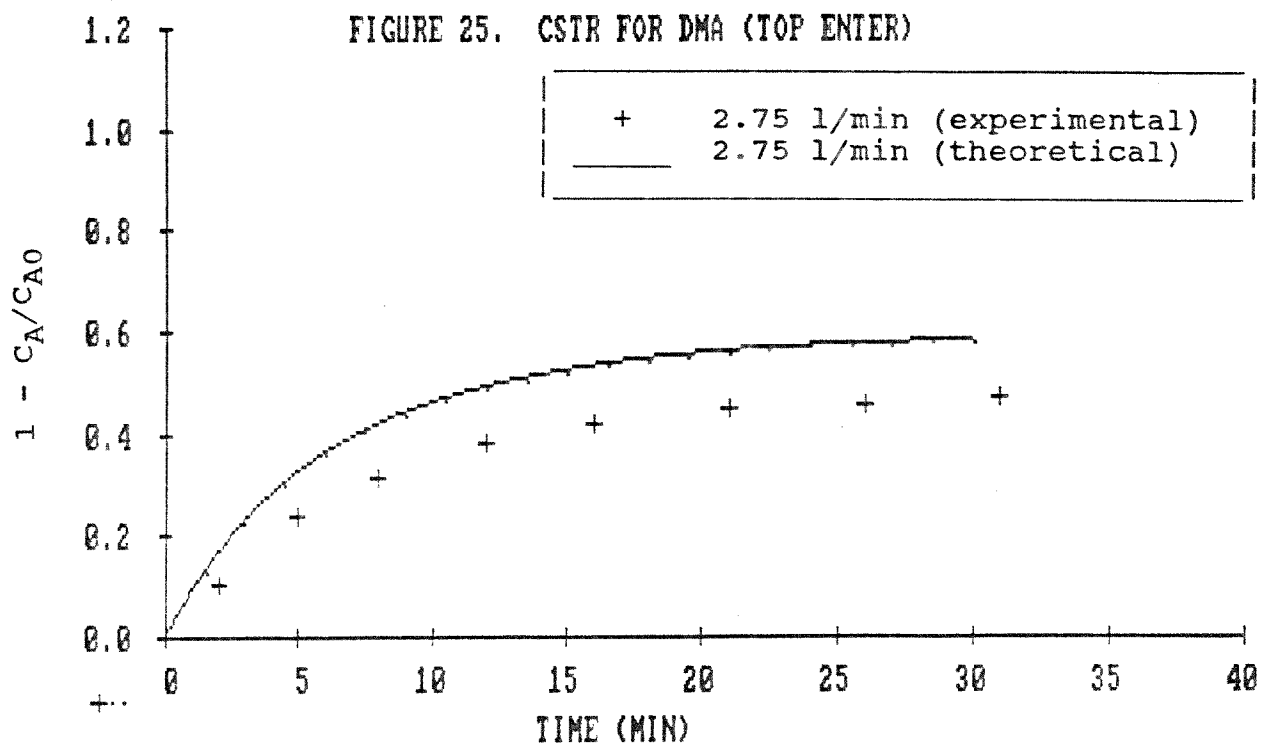FIGURE 27. CSTR FOR DMA (BOTTOM ENTER)

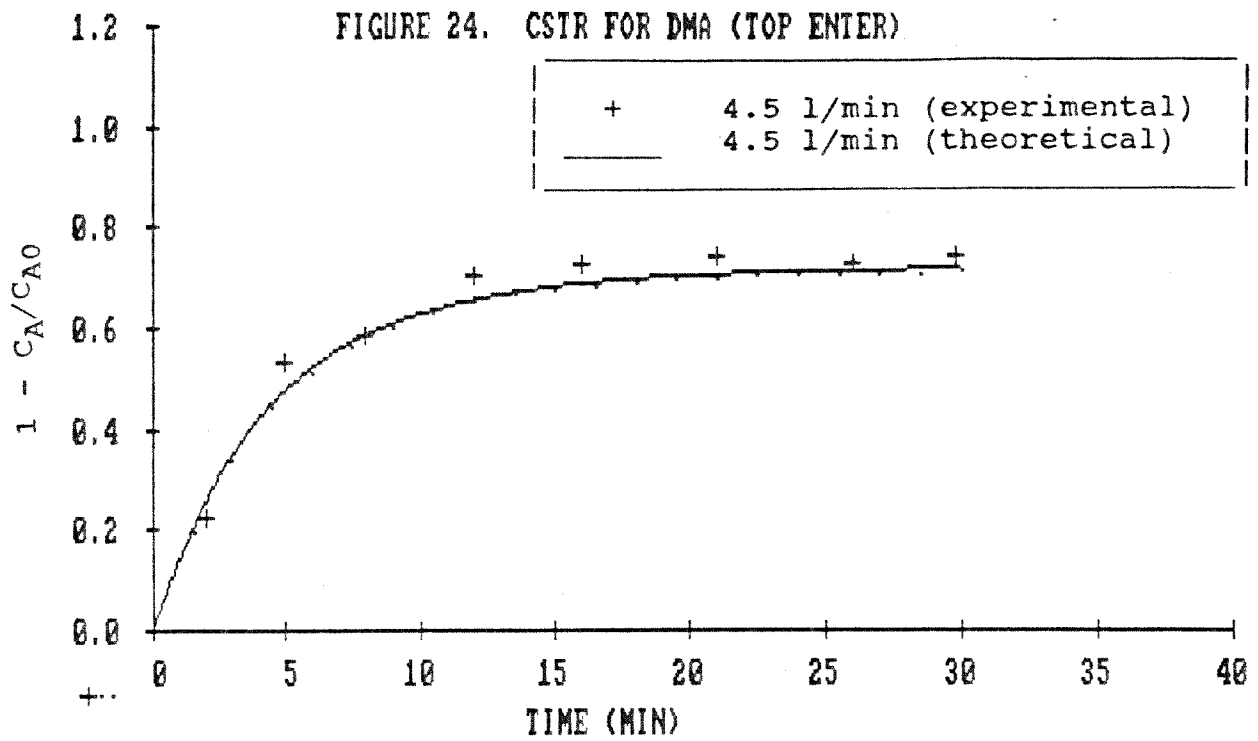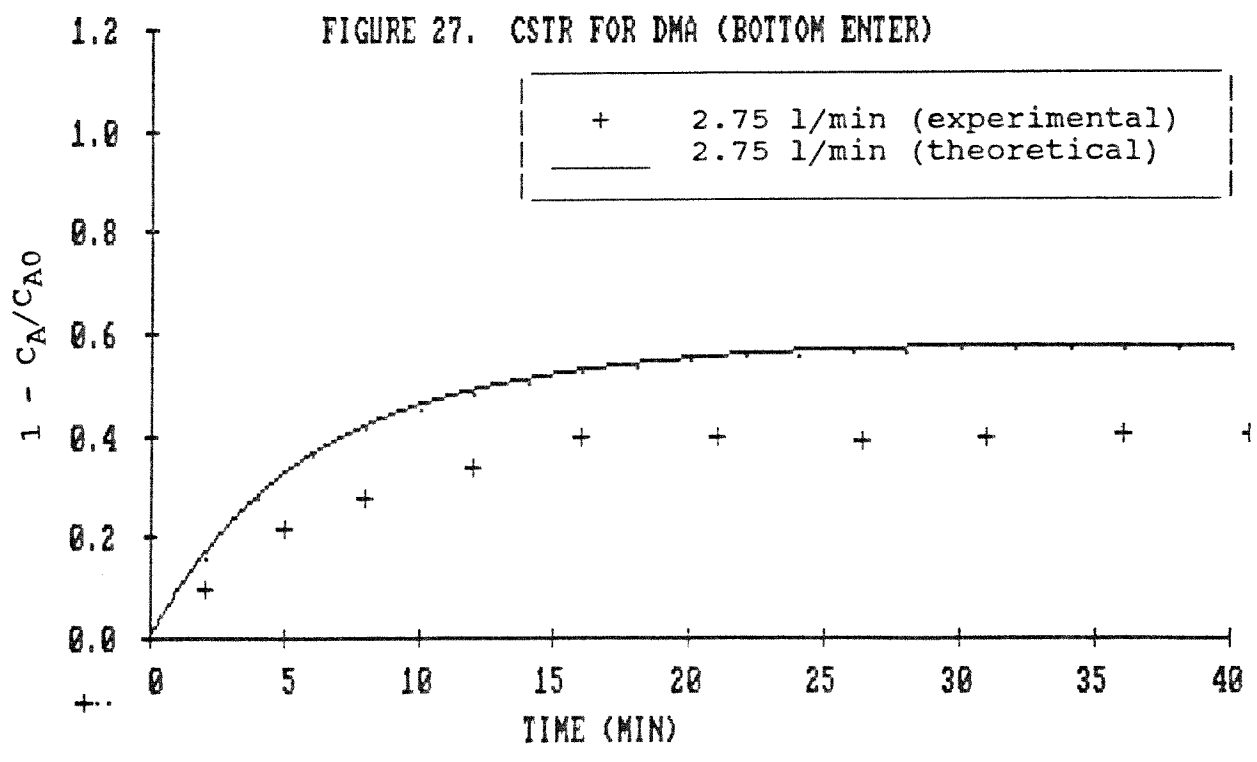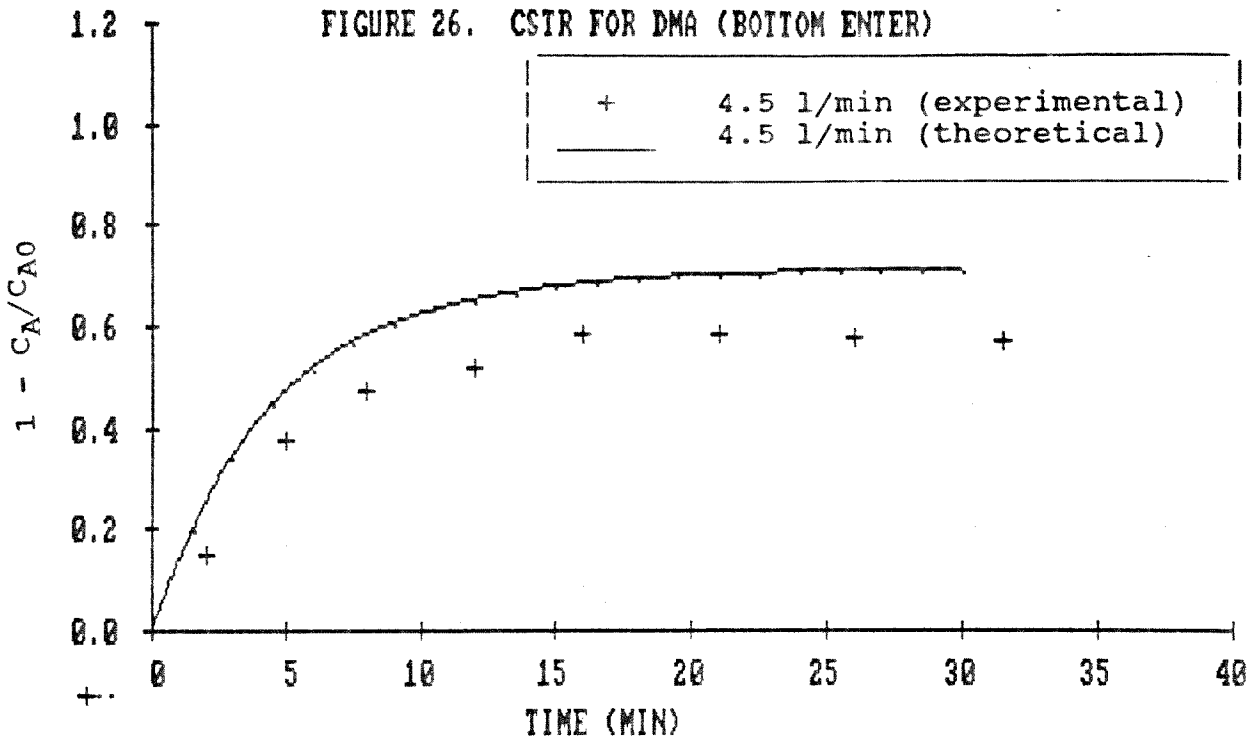2.75 l/min (experimental)
2.75 l/min (theoretical)

71

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