ABSTRACT

Title of Thesis: Charcoal Catalyzed Ozone Decomposition of Organic Pollutants in Water

Kin Ho, Master of Science in Chemical Engineering, 1991

Thesis Directed by Dr. J. W. Bozzelli
Prof. of Chemical Engineering, Chemistry and Environmental Science

A laboratory study has been performed on the wastewater treatment (destruction of organic species in water) using a novel process called Integrated Adsorption-Oxidation (IAO) where activated carbon is being utilized as a catalyst-adsorbent, and ozone as oxidant. The results of ozonation alone on the pollutants in water are also reported to provide a comparison with the adsorption-oxidation scheme in semi-batch reactions. All experiments were conducted at room temperature in a semi-batch reactor using five (water soluble) representative chemicals as pollutants: Aniline, Acetamide, Pyridine, N,N-dimethyl formamide and O-cresol. We also studied two volatile compounds: Trichloroethylene and Chloroform. Phenol was studied in a continuous flow reactor.

Results indicate that this new integrated adsorption-oxidation technique provides substantially improved performance over either ozonation or adsorption operating as separate treatment processes. The presence of carbon appears to serve a catalytic effect, where the ozone and active

radical species produced in the reaction process now act to regenerate charcoal during the process. This changes a separation technology to a destruction technology.

A detailed analysis of the reaction process supplies important information for understanding the reaction mechanism, and in developing a kinetic model for the future.

Improvements in destruction rate constants for this combined adsorption/oxidation process compared to rate constants for reaction with ozone alone are:

Compound	Ratio
Aniline	1.21
Pyridine	1.13
N,N-dimethyl Formamide	1.59
O-cresol	1.17
Acetamide	1.68
Trichloroethylene	1.14
Chloroform	1.11

Ratio = k_{IAO} / $k_{ozone\ alone}$

CHARCOAL CATALYZED OZONE DECOMPOSITION OF ORGANIC POLLUTANTS IN WATER

BY

KIN HO

Thesis submitted to the Faculty of the School of
the New Jersey Institute of Technology in Partial
Fulfillment of the Requirements for the Degree of
Master of Science in Chemical Engineering
1991

APPROVAL SHEET

Title of Thesis: Charcoal Catalyzed Ozone Decomposition of Organic Pollutants in Water

Name of Candidate: Kin Ho

Master of Science in Chemical Engineering

1991

Thesis and Abstract Approved:

Joseph W. Bozzelli
Professor
Dept. of Chemical Engineering,
Chemistry and Environmental Science

Henry Shaw
Professor
Dept. of Chemical Engineering,
Chemistry and Environmental Science

Deran Hanesian
Professor
Dept. of Chemical Engineering,
Chemistry and Environmental Science

VITA

Name: Kin Ho

Permanent Address:
57 Qinglong Fang, Apt. 803 #
S. Xianlie Rd.
Canton
P.R.China

Degree and Date to be Conferred:
Master of Science in Chemical Engineering
1991

Collegiate Institutions Attended	Dates	Degree	Dates
South China University of Tech.	80-84	B.S.	July 84
New Jersey Institute of Tech.	89-91	M.S.	May 91

Major: Chemical Engineering

Position Held:
Assistant Engineer \ Engineer
Design Institute, Canton Chemical
Industry Corporation
Canton, P.R.China
1984-1988

ACKNOWLEDGEMENT

I would like to express my honest thanks to Professor J.W. Bozzelli, my advisor and my committee chairman, for presenting to me the challenges of ozonation experiments, and for his encouragement, guidance and instruction. Also, I would like to thank Prof. Shaw and Prof. Hanesian for serving on my committee, giving me the helpful comments.

I am grateful to the members of my research group. Most notably, I thank Qianping Peng, V. Desai, Qingrui Yu, Dustin Ho and Samuel Chern. Thanks to Yogesh and Bill, for the continual help they provided for implementation of my experiments.

Thanks to Riyard, Ph.D. of Stevens Institute of Technology, for his cooperation on the experiments of TCE, Chloroform and on the CSTR runs.

I thank my parents, who instilled in me long ago the discipline, desire and determination for this research work.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

INTRODUCTION

Groundwater and water in rivers, lakes and seas has become a victim of irresponsible industrialization. The growing quantities of pollution in waterways and water-sheds caused by industrial occupants has led to significant contamination in the environment. The need for producing "organic-free" water has become extremely important especially in the industrial nations. Continuous efforts are being made to develop methods of purifying water either by removing these pollutants or by converting them into harmless products.

The general accepted approach by federal, state and local water pollution abatement and control agencies has been to preserve the utility of existing water supplies by means of pollution abatement and water reclamation. The methods of controlling water pollution are well documented and include: I) precipitation, biological treatment, ultrafiltration, ion exchange; II) adsorption by charcoal; III) oxidation by varies oxidizing chemicals such as ozone, chlorine, hydrogen peroxide and IV) incineration.<43,44>

Adsorption is a physiochemical process which is based on the ability of certain solids to concentrate and accumulate dissolved pollutants from solution onto their surfaces. Activated carbon is an essential absorbent in the conventional adsorption process since it has a high affinity for organics. The effectiveness of activated carbon for removal of organic compounds from the liquid phase by adsorption is enhanced by its large surface area, a critical factor in the adsorption process. For the most part, activated carbon surfaces are nonpolar, making the adsorption of inorganics difficult and the adsorption of organics easily effected. <1,2>

Among numerous physical and chemical techniques for water purification, oxidation of trace organic impurities in water is an attractive method because of its low cost, high efficiency and simplicity. Moreover, the intermediate oxidation products formed are usually easily degraded, low molecular weight oxy-compounds. The reaction generally gives highly desirable end products such as carbon dioxide and water.

Ozone appears to be one of the promising alternatives for disinfection because of its virucidal characteristics. It has been known as a powerful oxidant, secondary only to fluorine among the commercially available oxidizing agents as shown in Table I-1 <3>. As such, ozonation has been demonstrated as an effective technique for eliminating organic pollutants in aqueous solution. This technique destroys the initial species and does not render any harmful residues in the effluent water after treatment. On the contrary ozone contributes to increase the highly favorable dissolved oxygen levels, and it makes further treatment unnecessary.

Aqueous phase ozone reaction chemistry is complex. Dissolved ozone primarily reacts along two major pathways: either directly with dissolved solutes or by spontaneous decomposition resulting in secondary oxidants.<31> Oxidation products found in water after application of ozone include decomposition products of ozone itself and oxidation products from the organic materials present. The former products consists of oxygen(O_2), the ozonide radical anion(O_3^-), superoxide ion(O_2^-), perhydroxyl radical(HO_2) and hydroxyl free radical(OH). In addition, hydrogen peroxide is produced in small quantities by decomposition of ozone in water, or as by-product of ozone oxidation of dissolved organic materials.<4,5>

Most of these above intermediates are highly reactive, particularly in water at ambient temperatures, and their rapid decomposition leads to oxygen or hydroxyl ion as final, stable decomposition products in aqueous solutions. The hydroxyl free radical is unusually reactive, having an oxidation potential greater than that of ozone itself (See Table I-1). Consequently, deliberate formation of hydroxyl free radical assists in oxidizing organic materials. <4,5>

Although ozone's high oxidation potential makes ozonation thermodynamically favorable, the reaction proceeds only if the kinetics are also favorable. Researchers have indicated that the direct reactions of ozone are highly selective and the ozonation of organic solutes often are kinetically limited.<6> In order to accelerate oxidation reactions, catalysts are sometimes added to ozone-organic reaction systems. It is expected that catalysts enhance decomposition of ozone into more highly reactive radical oxidants such as hydroxyl radical. Once initiated, chain branching reactions may show both ozone and the other oxy-radicals react more rapidly with organic solutes along alternative pathways.

Since the solid surface in our experiments design is responsible for catalytic activity, a large readily available surface of easily handled materials is desirable.<7> Activated carbon was chosen in our system as the catalyst to meet these requirements. Plus it has a highly porous surface area. Activated carbon additionally absorbs organics which will not easily be oxidized by ozone.<8> It also increases the concentration of organics available to react, thereby further accelerating the reaction rate.

The scope of this study is to collect kinetic data on activated charcoal catalyzed ozonation of organic contaminants in aqueous solution, evaluate destruction removal efficiencies based on adsorption thermodynamics/kinetics and oxidation reduction potentials. This data will enable us to establish an empirical model after this treatment scheme allowing for better engineering to size of commercial units.

The experiments we have performed have been designed to verify the existence of a catalytic effect for the destruction of several specific groups of target chemicals. The materials being selected and studied included: Aniline, Pyridine, Acetamide, N,N-dimethyl Formamide, Cresol, Phenol, and Trichloroethylene as well as chloroform. The last two are known as volatile organic compounds (VOC's).

Different types of experiments were used to gain insight into the catalysis of oxidation reactions by activated carbon. Experimental conditions were varied along with significance of oxidant levels, target pollutant levels and catalyst dosages. Two different reactor configurations were employed: a semi-batch reactor and a CSTR (continuous stirred tank reactor).

Table I-1

Oxidation Potential of Commercially Available Oxidizing Agents

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

PREVIOUS STUDIES

Ozonation technology has received a significant amount of attention for destruction and/or conversion of organic and inorganic compounds in aqueous phase during the past decade. <9-18> Most researchers have focused on the treatment of organics as the pollutants. A brief review of the related and important investigations is presented in the following pages.

Much is known of the organic oxidation of ozone in non-aqueous solvents, particularly with unsaturated compounds. Oehlschlaeger <18> has described the known reactions of ozone with organic compounds containing various functional groups. In general, unsaturated and substituted hydrocarbons react with ozone in a known manner. Substitutes which withdraw electrons from aromatic rings, such as halogen, nitro, carbonyl and carboxyl groups deactivate the ring toward ozone, thus slowing down the rate of ozone attack. On the other hand, electron-releasing Substitutes, such as alkyl, methoxyl and hydroxyl groups activate the ring toward ozone oxidation. This behavior of substituted groups on aromatics and other unsaturate is consistent with a free radical mechanism of ozone attack and subsequent reactions in the aqueous solution.<18>

Primary and secondary amines react readily with ozone to produce nitro and nitroxide compounds, plus other products in which the carbon chains have been attacked with overall reactions:

$R\text{-}NH_2 + O_3 \text{-----}> R\text{-}NO_2 + H_2O$

$2\ R_2NH + O_3 \text{-----}> 2\ R_2NO + H_2O$

The rate of ozone attack on methyl substituted benzenes increase as the number of methyl Substitutes increases. Gould and Webber<19> reported that phenol is attacked very readily by ozone, the aromatic ring being ruptured after 4 to 6 equivalents of ozone per equivalent weight of phenol originally present have been absorbed.

Rate constants and reaction mechanisms have been studied and proposed on the experimental data of ozone reactions. J.Hoigne and coworkers<20,21> developed different empirical methods to determine the rate constants in the range of 1E-2 to 1E-5 1/Mol-Sec, in which ozone reacted in presence of various concentrations of non-ionized compounds in water such as aliphatic alcohols, chlorosubstituted ethylenes and substituted benzenes. Rate constants of ozone with acidic and basic organic chemicals dissolved in water were then reported over a wide range of pH values. The second order rate constants increased with pH as the degree of deprotonation of the dissolved substances.

Giamalva et. al.<22> investigated reactions of ozone with carbon-hydrogen bond containing compounds in carbon tetrachloride solvent over 36-60 ^{o}C temperature range. The reaction mechanism involved prior complexation of ozone with oxygen atom or with hydrogen atom abstraction.

P. Gehhringer et. al.<23> reported that the decomposition rates of small amounts (100 ppb) of tri- and perchloroethylene in drinking water were considerably lower than rates of higher level TCE and PCE. He postulated the reason for this lower reaction rate is that predominance of primary attacking species became scavenged (lost to the system) by the solutes present mainly bicarbonate and nitrate ions. In the direct reaction of ozone with TCE, the TCE concentration decreased from 100 ppb to 70 ppb in an 80 sec time period. The combined action of gamma-radiation and ozone resulted in TCE reduction to 10 ppb in 45 seconds with the gamma-irritation dose of 12 Gy.

Eisenhauer <24> studied the ozonation of Phenol in water. One experiment showed the reduction in phenol concentration from 100 to 0 ppm in 30 minutes at ozone gas mixture flow rate of 0.5 L/Min and an ozone concentration of 23.5 Mg/L. Another experiment showed the reduction in phenol concentration from 200 to 50 ppm in 60 minutes at the same ozone flow rate but a simply reduced ozone concentration of 21 Mg/L.

Oxidation reactions initiated by ozone in water are generally rather complex. Two types of ozonation reactions have typically been proposed. These include: (a) direct reactions of ozone with the organic compound and (b) free radical reactions where the radical species such as hydroxyl free radical intermediate are generated via reaction of the ozone. It is important to understand the mechanism of decomposition of ozone in aqueous solution and further develop a system model with ozone and organic compound.<25>

Early in 1935 Weiss<26> depicted ozone decomposition could be catalyzed by the hydroxyl ion. The first step reaction initiated with: ^Hrxn (Kcal/Mol)

$O_3 + OH^-$ ------> $O_2^- + HO_2$	-7.9

being followed by the chain reactions:

$O_3 + HO_2$ ------> $2\ O_2 + OH$	-38.6
$O_3 + OH$ ------> $O_2 + HO_2$	-34.1
$2\ HO_2$ ------> $O_3 + H_2O$	-30.7
$HO_2 + OH$ ------> $O_2 + H_2O$	-81.29

Alder and Hill <27>, on the basis of their kinetic studies, suggested a first order reaction with respect to ozone concentration and proposed the following mechanism to correlate their results:

$O_3 + H_2O$ ------> $HO_3^+ + OH^-$	-3.65
$HO_3^+ + OH^-$ ------> $2\ HO_2$	33.98
$O_3 + HO_2$ ------> $HO + 2\ O_2$	-38.62
$HO_2 + OH$ ------> $H_2O + O_2$	-70.78

A more completed and perhaps more accurate reaction mechanism has been discussed through reviewing the chemistry of ozone in water by Preleg<28>:

$O_3 + H_2O$ ------> $O_2 + 2\ OH$	32.16
$O_3 + OH$ ------> $O_2 + HO_2$	-40.09
$O_3 + HO_2$ ------> $2\ O_2 + OH$	-38.62
$OH + OH$ ------> H_2O_2	-30.49
$OH + HO_2$ ------> $H_2O + O_2$	-70.78

$OH + OH^- \text{------>} O^- + H_2O$

$O^- + O_2 \text{------>} O_3^-$

$HO_2 + HO_2 \text{------>} H_2O_2 + O_2$ -29.02

Hoigne and co-workers[19,29,30,31] have published many studies in recent years dealing with the kinetics of ozone oxidations of organic materials in aqueous solution. More complicated chain mechanisms have been discussed and predicted derived from Weiss model. The elementary reactions other than the one mentioned above were as follows:

$O_2^- + O_3 \text{------>} O_3^- + O_2$ 0

$O_{3-} + H^+ \text{<=====>} HO_3$ -17

$HO_3 \text{------>} OH + O_2$ -18.12

Investigators generally agreed that decomposition of ozone in an aqueous solution produced hydroxyl ions and that OH was the most important intermediate in the system since hydroxyl radical has the higher oxidation potential, 2.8 volts, than that of ozone (2.07 volts).

It has long been known that ozone could be utilized as pretreatment to both carbon adsorption and biological treatment [32,33,34,35]. Several research studied combination of ozonation plus subsequent treatment with GAC (Granular Activated Carbon) adsorption have been completed where GAC adsorption was preceded by ozone treatment.

J.DeWaters and F.Digiano[35] recently reported that ozonation was found to encourage biofilm growth and biodegradant of Natural Organic Matter (NOM) while biofilm organisms grown on ozonated NOM easily degraded trace concentrations of phenol.

In a pilot study by Glaze and Wallace<33>, unozonated and ozonated waters were fed to GAC columns in two different runs. Preozonation before GAC Adsorption did not show a dramatic effect on trihalomethane precursors.

It is noticed that ozone oxidation of organic compounds prior to GAC adsorption adds oxygen to the original organic material, thereby increasing its polarity. In turn, this can be expected to lower its adsorptivity onto GAC. That is to say, increased polarity did lower adsorptivity when ozonation was conducted before GAC adsorption treatment. <25,42>

One additional treatment concept: combination of ozonation and adsorption suggested application of both technologies simultaneously. Two reports have been found upon the color removal from peat water, and in munitions wastewater treatment. G. McKay and G. McAleavey <2> investigated the simultaneous ozonation and carbon adsorption process in a three phase fluidized bed column (42 mm diameter and 1.25 m long). They observed that in adsorption only experiment, 30% color removal was obtained after one hour. Ozonation alone decolorized the water by 15%. However, in the combined adsorption/ozonation, contact column values of around 55% color removal were obtained. This indicates that a synergistic effect is occurring because the combined treatment produced 10% higher conversion than the sum of the individual treatments.

K. Jain and A. Bryer <48> studied the feasibility of munitions wastewater treatment by combined adsorption-oxidation. Three munitions chemicals: TNT, RDX and HMX were used in the continuous flow experiments with initial concentrations of 20-40, 20 and 4 ppm respectively. Experiments were conducted in a identical Plexiglass columns (30 in. long x 1-1/8 in. I.D..). 6 grams of carbon were placed in 3 layers. Gas flow rate was held at 285-330 cc/min, and liquid flow rate was 39-41 ml/min. Their results demonstrated the potential for increasing the adsorption-oxidation effect 2, 1.6 and 2 times for TNT, HMX and RDX respectively when steady state was approached. Pure solutions of RDX (50 Mg/L) and HMX (5 Mg/L) showed virtually a complete absence of reactivity with ozone alone and only marginal adsorption-oxidation effect over the 400 minutes.

EXPERIMENTAL METHOD

Laboratory reactors which are commonly used to determine reaction rate constants and mass transfer in liquid-gas phase reaction are of two general types:

(a) semi-batch reactors with gas continuously inlet into the reactor which is already filled with liquid;

(b) continuous flow reactor with both gas and liquid continuously inlet into reactor.

Continuous flow reactors are generally the most dependable and data from them is simple to obtain. However, they are time-consuming and expensive because it is necessary to wait until the system reaches steady-state for the purpose of sample taking.<7>

A semi-batch reactor offers advantages of convenience and savings in time when numerous runs are desired. <7,36> A wide variety of conditions and feed stocks can be treated with slight modifications to the equipment.

A. Experimental Apparatus and Instrumentation:

A corona discharge ozone gas source and a separatory funnel shaped reactor, at room temperature, was used in this semi-batch study with respect to liquid. A block diagram of the reaction system is shown in Figure III-1.

1. Reactor

The reactor was a modified separatory funnel with sample port at the bottom along the vertical axis. The liquid hold-up volume of the reactor was 400 milliliters. An inlet gas tube, 8 mm O.D. glass, was submerged down to bottom of the reactor with fritted cylinder, 12 mm diameter, fused onto the lower end. Complete mixing was achieved by dispersing gas through this coarse porosity sparger. Excess ozone exited through the top of the reactor to KI traps and finally exhausted via a vent line.

To avoid contamination to the ozone gas, glass and Teflon tubing instead of plastic were used in the system. Stainless steel tubing was also installed for portions of the gas generation system in contact with ozone since it is not significantly corroded by ozone.

2. Ozone generator

Ozone was produced by passing either dry commercial grade air or pure oxygen through a model T-23 ozone generator purchased from Welshbach Corporation, Philadelphia, PA. The generator is a water cooled, corona discharge type. The ozone-oxygen mixture could be varied between 0 to 8% ozone output, with a flow range of 0.015 to 0.16 S.C.F.M. gas effluent. Operating voltage for all experiments except VOC compounds (TCE and Chloroform), and Phenol runs were set at 90 volts on the discharge power supply, while gas flow rate was kept at 0.03 S.C.F.M. (1.06 L/min) at room temperature. These settings consistently showed excess ozone in the KI traps. Operation of the ozone generator is straightforward and required no maintenance during the period of use as long as water cooling was always turned on. Feed gas to ozonator was pure oxygen only in this study.

3. Gas Chromatograph

Samples collected from reactor were analyzed by a Perkin-Elmer 910 Gas Chromatograph equipped with a Flame Ionization Detector (FID). The GC used hydrogen as its flame source. 30 ml/min hydrogen, with excess air at 300 ml/min flow, was ignited to provide the flame. The flame oxidizes or pyrolyzes organic compounds into ionic intermediates. The charged species were attracted by bias voltage and captured by a collector, an ion current resulted, which was recorded.<37>

Carrier gas nitrogen, 30 ml/min, flowed through the analytical separation column and detector to carry the vaporized sample from injection port. A soap-film (bubble meter) was used to calibrate gas flows in our system because of its simplicity and independence to the type of gas used. The high flow rates were measured with a wet test meter, 1 liter per revolution (American Meter Corporation, Phila, PA).

A packed column, 2 meters in length, 1/8" O.D. stainless was used isothermally to achieve the necessary reactant and product separation. Columns were packed and chosen according to the adsorption characterization of target compounds. Details are summarized in Table III-1. Output of the FID was measured by a Hewlett Packard 3396A integrator coupled with a Sargent Welch model XKR chart recorder.

4. KI Traps

KI traps were used for capturing and measuring the excess ozone from the reactor. The KI trap was a 500-ML gas washing bottle with a sintered-glass dispersion tube at the lower end to deliver excess ozone to potassium iodide solution. Two gas washing bottles containing Potassium Iodide solution were located downstream of the reactor in series to determine the quantity of excess ozone in the off-gas.

KI solution was prepared by dissolving 20 grams potassium iodide in 1 liter fresh boiled and then cooled distilled water. This was stored at least one day in a refrigerator prior to use.

5. Spectrophotometer

A Spectronic 20 Spectrophotometer was used for most measurements of the aqueous ozone at wavelength 600 nm. Special cuvette holders allowed thermostating (room temperature). Cuvette path-lengths was 1 cm. The cuvette had to be left in positions in the instrument during filling and flushing, when residual ozone was determined by the indigo method. This will be further discussed later in section B.

6. PH Meter

PH values of target solution were monitored by a 6071 microcomputer based bench pH meter from Jenco Electronics, Ltd.

B. Experimental Procedures:

Organic target compounds were of reagent grade and used without further purification. All solutions were prepared from distilled water. 400 ml of target solution was used to initialize the reaction. Initial concentrations of the target compounds and their reaction time are given in Table III-2. Solutions were buffered at pH 7 with diluted sodium hydroxide and phosphate buffer solutions. Operating conditions are listed in Table III-3.

Determination of ozone solubility has been fully discussed in <38> and will not be included in this work.

1. Experiment:

Before each experimental run, ozone-oxygen mixture was diverted to bypass the reactor into a vertical cylinder which contained 200 ml KI solution for a measured period of time. The reaction was then immediately started as gas stream was shifted back to feed the reactor. 3 grams of granular activated carbon were added at the same time in the carbon plus ozone reaction runs. For volatile compounds, 0.01 gram of powdered activated carbon (PAC) was employed. Different dosages of PAC (0.01 gram and 0.05 gram) were used in the experiments when phenol was the reagent. The reactions were initiated with 400 ml buffered target solution. The system was operated at room temperature and atmospheric pressure. 4 ml samples were collected from the sampling port at appropriate time intervals and a total of 10 samples were taken during an average period of reaction.

2-3 drops of 10% Sodium Thiosulfate solution were immediately added to sampling vial prior to sampling for the sake of quenching the reaction. This eliminated any possibility of continued reaction and decomposed the remaining peroxides. Experiments with the same initial concentration were repeated twice, using the same time scales, to insure reproducibility.

2. Sample Analysis

All of the samples were subjected to analysis as soon as collected, especially samples for aqueous ozone measurement, in order to avoid any possible decay with time.

Concentrations of target compound were measured by gas chromatograph. A standard calibration curve was obtained for each compound before the samples were analyzed. Parameters of calibration curve for the standard solutions are listed in Table III-4. Typical calibration standard curves are presented in Figures III-(2-5).

3. Iodometric Method of Determination Gas Ozone

During the experiment time, the following reaction was occurred in the KI trap when the off-gas contained ozone from reactor passed through KI solution (impinger solution):<41>

$$O_3 + 2\ KI + H_2O \dashrightarrow O_2 + 2\ KOH + I_2 \qquad (1)$$

Once the experimental run had been conducted, 1-10 ml of KI solution taken from the KI trap was transferred to a beaker and diluted to 100 ml, its pH reduced to below 2.0 with 1 N sulfuric acid. This dark yellow solution was then titrated with 0.005 M sodium thiosulfate ($Na_2S_2O_3$) titrate until the yellow color is almost discharged. The I_2 reacted immediately with sodium thiosulfate according to the Equation (2):

$$I_2 + 2\ Na_2S_2O_3 \dashrightarrow 2\ NaI + 2\ NaS_2O_3 \qquad (2)$$

this reaction continued until all the sodium thiosulfate (standard) was used up. The iodine was then free to react with starch to produce a blue color:

$$I_2 + \text{Starch} \Longleftrightarrow \text{Blue complex}$$

1 ml of starch indicator, prepared from the clear supernate of soluble starch suspension in water over night, was added to the light yellow solution, and a blue color appeared. Carefully titrated again with sodium thiosulfate titrate until the end point at which the blue just disappeared. Blank tests must be done to correct sample titration results. The titration procedure is further described in reference <39>.

The concentration of ozone is calculated by the following equation based on the mass balance from Equations (1) and (2):

$$\text{Mg/L } O_3 = \frac{M_{O3} * 1{,}000 * N * (A-B)}{2 * \text{ML Sample}} \qquad (3)$$

where: A = ML $Na_2S_2O_3$ of titration for sample

B = ML $Na_2S_2O_3$ of titration for blank

N = Normality of sodium thiosulphate

M_{O3} = Molecular weight of ozone (48 Mol/L)

then Equation (3) can be rearranged as:

$$Mg/L\ O_3 = \frac{24,000 * N * (A-B)}{ML\ Sample} \qquad (4)$$

4. Indigo Reagent for Determination of Aqueous Ozone

A solution of Indigo Reagent was prepared by dissolving 0.6 g/l (1 mM) potassium indigo trisulfonate in 20 mM phosphoric acid. PH 2 buffer came from 28 grams $NaH_2PO_4 \cdot 2H_2O$ and 35 grams H_3PO_4 (85%) dissolved in 1 L distilled water.

100 ml volumetric flasks were used for all sample, blank and background ozone analysis. To each 100 ml flask, 1 ml of indigo reagent and 10 ml of 0.5 M phosphate buffer reagent for pH 2 were added to all except the blank flask without indigo reagent. A 1 ml sample (filtered for removing the carbon particles in the sample when combined ozone-carbon experiments were conducted so as to provide necessary visibility) was transferred immediately to the flask and diluted to 100 ml. The 1 cm I.D. cuvette was then filled with this solution, the cuvette was then placed into the spectrometer for analysis. At least two readings for the same cuvette were taken to show the reproducibility.

The absorbance of the residual indigo present in the sample solutions was measured at 600 nm in the cuvette. Absorbance change at 600 nm is 2.0E+4 L/mol/cm of added ozone for all concentrations tested.<38> Original aqueous ozone was then calculated. Reference <38> gives further details of the ozone (aqueous) analysis.

C. Continuous Stirred Tank Reactor Runs

Continuous Stirred Tank Reactor (CSTR) experiments were laboratory-scale runs to provide the essential data needed for developing scale-up methods and to investigate the feasibility for destroying pollutants in water by integrated adsorption with ozone plus charcoal in continuous flow reactions.

The continuous flow ozonation system was fabricated differently than the reactor apparatus utilized in the semi-batch runs. It is shown in Figure III-6. The compound being studied in CSTR runs was only phenol, with 1000 ppm initial concentration from a stored reservoir.

1. CSTR System Design:

The reactor was a modified cylinder with hold-up volume 495 ml. Two fluid streams: target solution and ozonated water were separately introduced through glass tubes at the bottom of the reactor. In combined ozone-carbon reaction experiments, a third stream of carbon slurry was cocurrently fed to the reactor. A magnetic Teflon stirrer was used to continuously agitate and mix the liquid in the reactor. Mixing liquid overflowed from the top of the cylinder and samples were taken from this outlet.

Phenol solution and carbon slurry were stored in separate 1 gallon plastic reservoirs respectively. A

Masterflex No.7014 pump delivered the phenol solution from the storage tank to reactor. The carbon slurry tank was mounted above the reactor, thereby carbon slurry could flow through an adjustable valve to the reactor by gravity. The slurry was continuously stirred by a magnetic stirrer to prevent carbon particles from settling.

Ozone was supplied from the same ozonator as the one in semi-batch runs. Ozone-oxygen mixture was bubbled to a 400-milliliters glass mixer where ozone dissolved to the point of saturation in water. Tap water was controlled by a Calcuflow No.3 flowmeter and introduced into the reactor countercurrent to the incoming gas. A magnetic stirrer (Teflon stirrer bar) was needed to achieve a complete-mixed state. An activated carbon prefilter was installed upstream of the flowmeter to remove chlorine in water. The glass mixer was located over the reactor and output through overflow was then fed to the reactor by gravity. Samples of ozonated water for dissolved ozone concentration were taken through a by-pass stopcock located at the outlet of the mixer. All the settings and the flow paths are shown in Figure III-6.

2. CSTR Experiment:

Each fluid in the three reservoirs was kept well mixed with the magnetic stirrers. Tap water was added to the mixer at the flow rate required for each experiment. The flow range was 8 to 33.8 Ml/Min. Turned on ozonator, ozone-oxygen mixture was then bubbled in the glass mixer countercurrently with the tap water. When ozonated water started overflowing (at 400 ml) from the mixer to the reactor, both the pump and the adjust valve were turned on to the mark required for the individual run (see also Table III-5 for detail). Flow rate parameters for each stream in each run are listed in Table III-5. These streams began to fill the reactor to start the reaction. All the flow rates for each stream were held constant during the reaction period.

The hold-up residence time in reactor is: $t = V / Q$, where V is hold-up volume of reactor, Q is total liquid flow rate (flow of target solution plus ozonated water plus carbon slurry) of the system. Generally, the time when outlet (overflow at 400 milliliters) started from the reactor was called residence time in this system. Mean residence time was a constant value in each run (as per design in a CSTR) because the only variable Q in above equation was constant for each individual experimental run. A list of residence times for the different CSTR runs is shown in Table III-6. Residence time reflects the average reaction time of the operating system, it is a useful variable for the process design.

If the output concentration did not change with time, measurement after about three residence times, steady-state was assumed. Two samples were then collected from the system output. The volume of each sample was 4 ml at 2 min intervals to ensure the steady-state status. The reaction terminated by shutting off tap water, pump and valve.

Samples for target concentration, gaseous and aqueous ozone concentration were analyzed in the same way as mentioned in semi-batch runs (previous section).

Initial mixing concentration of phenol could be obtained from the following equation:

$$\text{Cphen (ppm)} = \frac{\text{Co} * \text{Qphen}}{\text{Qtot}}$$

where Co: concentration of phenol in its reservoir (1000 ppm initial concentration)

Qphen: flow rate of phenol into the reactor (ml/min)

Qtot: total flow rate fed to the reactor (ml/min) (see Table III-5 for detail)

Ozone concentration in the mixing fluid in the reactor was determined by using the indigo analysis method as described in the section B of this chapter.

To measure mixed carbon concentration, 100-150 ml of the effluent sample from reactor was taken and then filtered (a filtering flask using vacuum to draw it through was utilized). The filtered residue was placed in the hood for drying over night. The mixing carbon concentration in the reactor is then given by:

$$\text{Cc (ppm)} = \frac{\text{filtered residue (Mg)}}{\text{filtrate (L)}}$$

Table III-1

Packed Columns with Operating Conditions

Chromatographic Columns

Column Description Stationary Phase on Packing	Target Compound	Column Temp. (°C)	Retention Time (min)
4% Carbowax 20M + 0.8% KOH	Pyridine	180	2.4
on Graphpac-GB, 60/80	Aniline	200	3.2
1% Alltech AT-1400 on	O-Cresol	110	1.6
Chromosorb W-HP, 100/120	Phenol	120	1.7
Chromosorb 101	Dimethyl Formamide	200	4.4
	Trichloroethylene	170	3.1
	Acetamide	180	4.0
	Chloroform	150	3.6
5% SP2100 on	Aniline	100	1.2
Supelcoport, 80/100	Acetamide	70	1.1

Parameters of Column: Length -- 6 feet

Diameter -- 1/8" O.D. x 2.1 mm I.D.

Stainless Steel

Table III-2

Initial Concentrations for Semi-batch Runs

Target Compound	Molecular Weight	Concentration ppm	Concentration Mol/L	Reaction Time (min)
Aniline $C_6H_5NH_2$	93.12	1000 500	0.01074 5.369E-3	10
Acetamide CH_3CONH_2	59.07	2000 1500	0.03386 0.02539	60
Pyridine C_5H_5N	79.10	2000 1000	0.02528 0.01264	15
N,N-Dimethyl Formamide $HCON(CH_3)_2$	73.06	2000 1000	0.02736 0.01368	30
O-cresol $CH_3C_6H_4OH$	108.14	2000 1000	0.01849 9.247E-3	30
Trichloro-ethylene $CHClCCl_2$	131.37	500	3.806E-3	12
Chloroform $CHCl_3$	119.36	500	4.189E-3	12
Phenol C_6H_5OH	94.05	1000	0.01063	14

Table III-3

List of Conditions for Semi-batch Runs

Volume of Reactor = 400 Ml

Compound	Reaction Time (Min.)	Sampling Interval (Min.)	Flow Rate of O3 (L/Min)	Dosage of GAC or PAC * (Grams)
Aniline	10	1	1.06	3.0
Acetamide	60	6	1.06	3.0
Pyridine	15	1.5	1.06	3.0
N,N-dimethyl Formamide	30	3	1.06	3.0
O-cresol	30	3	1.06	3.0
Trichloro-ethylene	12	2	1.06	0.01 *
Chloroform	12	2	1.06	0.01 *
Phenol	14	2	0.60 0.60	0.01 * 0.05 *

Table III-4

STANDARD CURVES

CONCENTRATION vs. PEAK AREA

Compound	Linear Regression Fitting * Pa = A + B * C	Correlation Coefficient r
Aniline	-1.636E04 + 1.879E03 * C	0.9968
Acetamide	-5.650E04 + 3.058E02 * C	0.9797
Pyridine	3.352E04 + 7.713E02 * C	0.9942
N,N-Dimethyl formamide	4.920E04 + 6.487E02 * C	0.9956
O-Cresol	-8.937E03 + 5.060E02 * C	0.9985
Chloroform	-1.212E04 + 6.079E02 * C	0.9963
Trichloro-ethylene	-3.366E04 + 7.982E02 * C	0.9982
Phenol	1.580E03 + 6.185E02 * C	0.9998

Pa: Peak Area from 3396A Integrator with the conditions of GC: Attenuation -- 32

Amplifier range -- 100

C : Concentration of Standard (ppm)

* Concentration of unknown determined from:

$$C = \frac{Pa - A}{B}$$

See standard curves in Figures III-(2-5)

Table III-5

Stream Flow Rates in CSTR Runs

V (hold-up) = 495 ml (Ml/Min)

see Table IV-5 for concentrations

No.	Description	Phenol	Carbon	O_3 in Water or O_2 in H_2O* or water**	Total
1.	O_3 90 Volts	60	--	20	80
2.	O_3 90 Volts	40	--	22	62
3.	O_3 110 Volts	20	--	20.6	40.6
4.	O_3 + Carbon 90 Volts	8.8	18	9.2	36
5.	O_3 + Carbon 110 Volts	8.8	18	8	34.8
6.	O_3 + Carbon 90 Volts	29.6	17.6	33.8	81
7.	O_3 + Carbon 110 Volts	29.6	18	26.4	74
8.	Carbon	8.8	18	13.2 **	40
9.	Carbon	8.8	18	19.2 **	46
10.	Carbon + O_2	60	19.6	20 *	99.6

Table III-6

Residence Time in CSTR Runs

V (hold-up) = 495 ml

See Table IV-5 for concentrations

Case No.	Description	Total flow Rate Q (Ml/min)	t = V / Q (Min)
1.	O_3 90 Volts	80	6.2
2.	O_3 90 Volts	62	8.0
3.	O_3 110 Volts	40.6	12.2
4.	O_3 + Carbon 90 Volts	36	13.8
5.	O_3 + Carbon 110 Volts	34.8	14.2
6.	O_3 + Carbon 90 Volts	81	6.1
7.	O_3 + Carbon 110 Volts	74	6.7
8.	Carbon	40	10.8
9.	Carbon	46	5.0
10.	Carbon + O_2	99.6	12.4

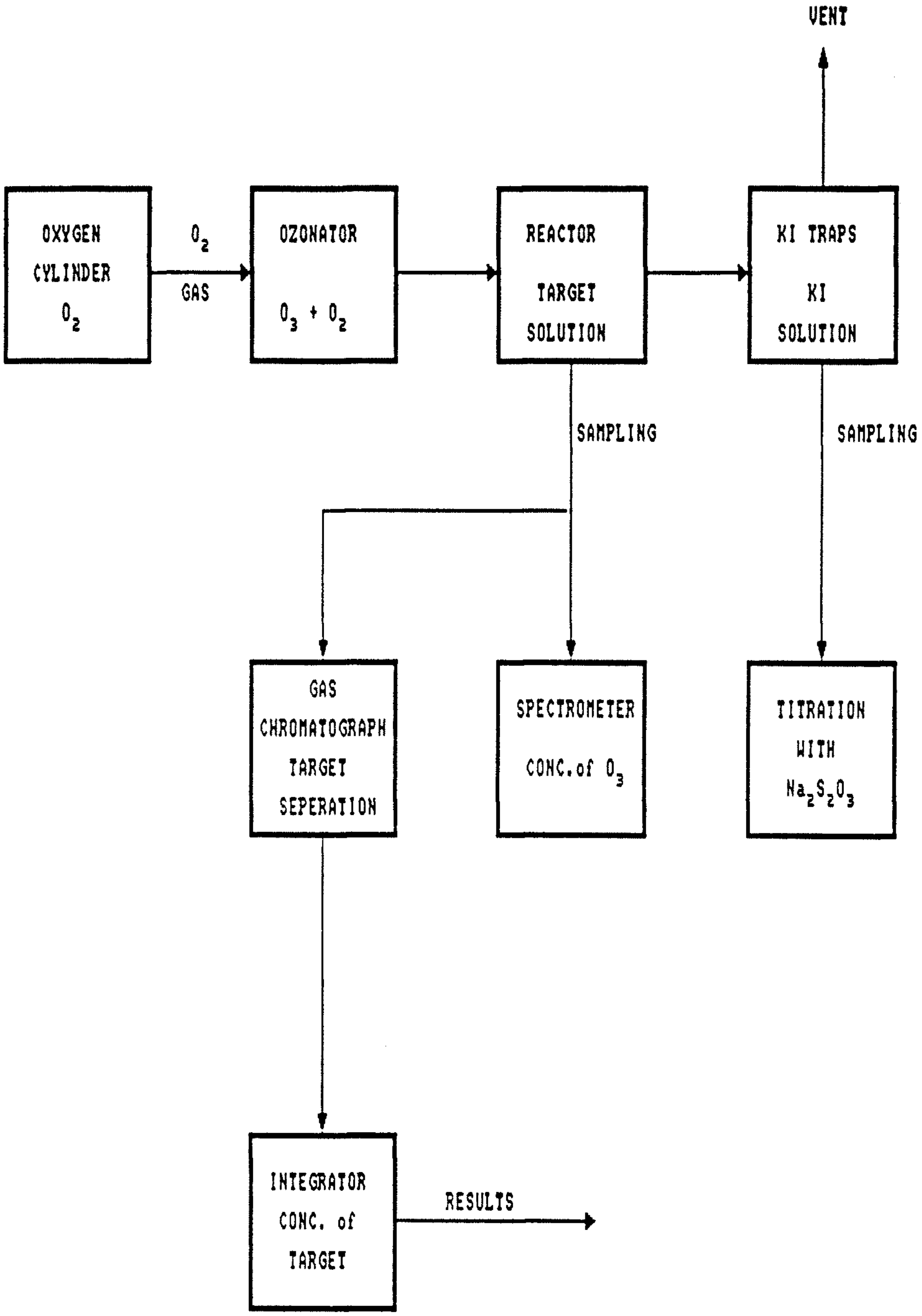


Figure III-1. Block Diagram of Semi-batch System

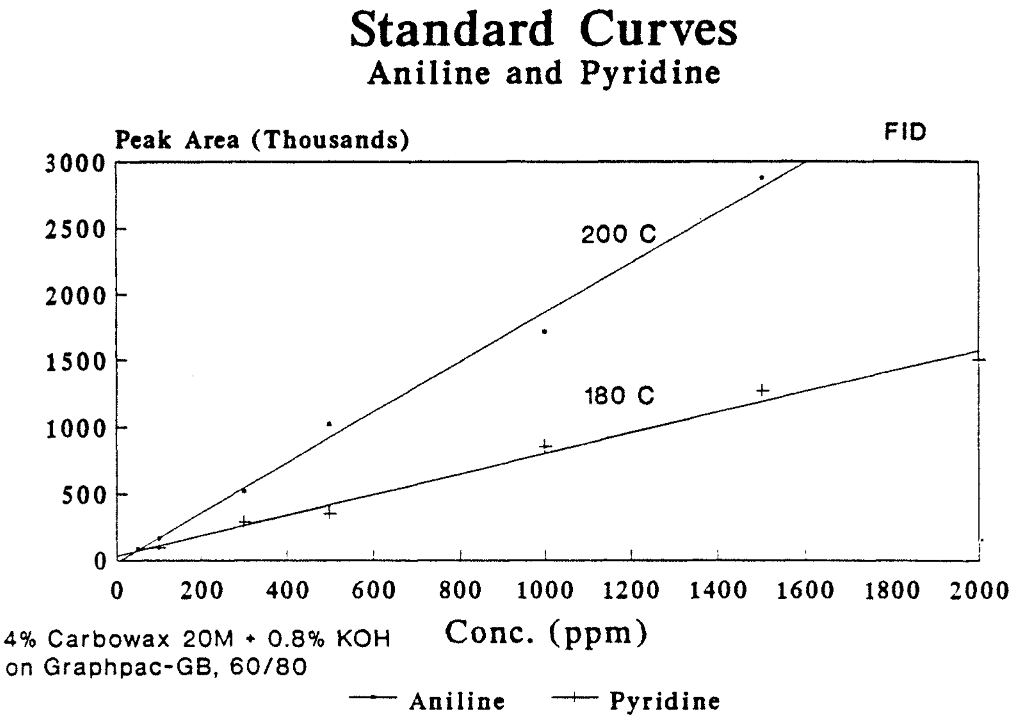


Figure III-2 Standard Curves for Aniline and Pyridine

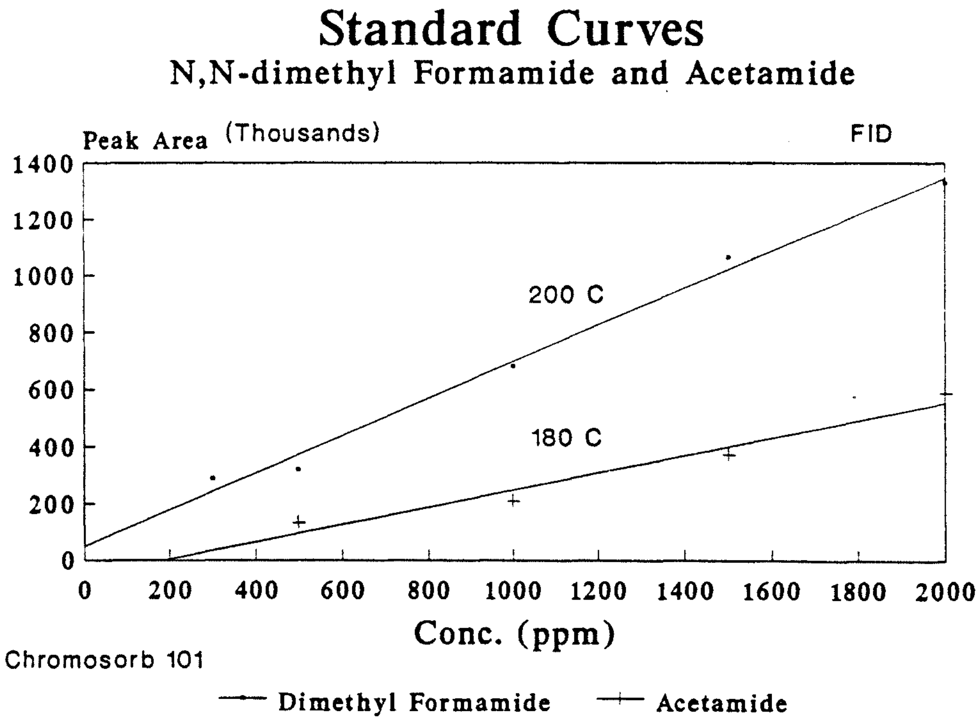


Figure III-3 Standard Curves for Dime-formamide & Acetamide

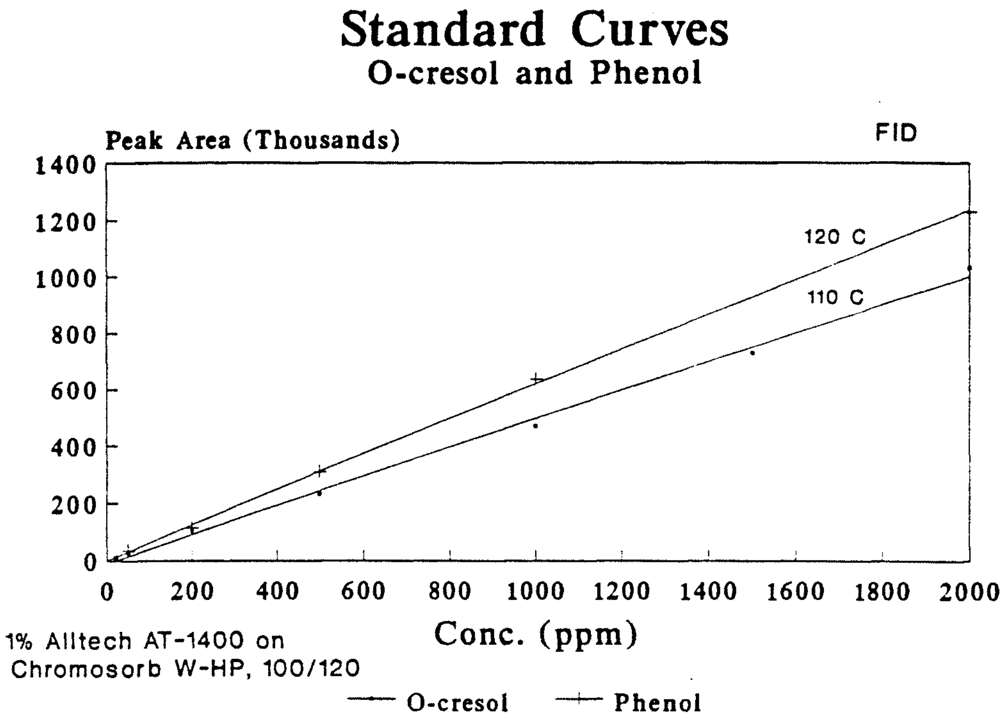


Figure III-4 Standard Curves for O-cresol and Phenol

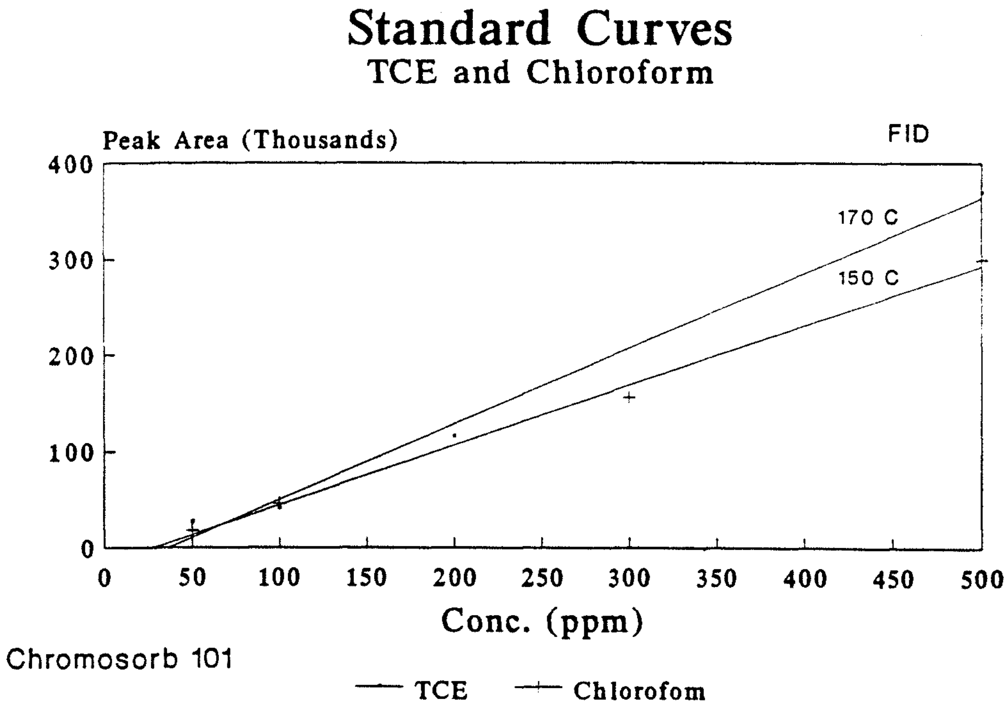
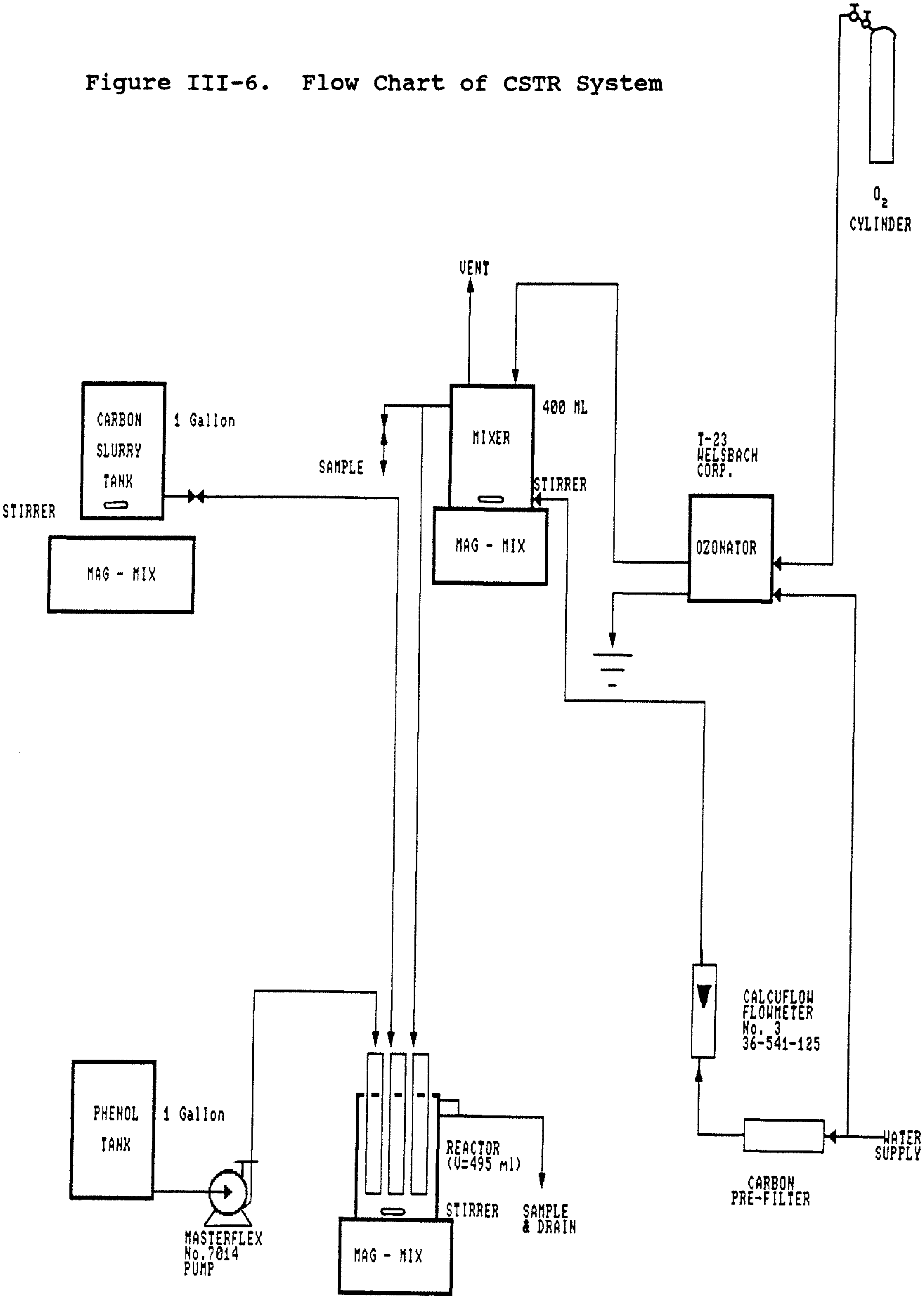


Figure III-5 Standard Curves for TCE and Chloroform

Figure III-6. Flow Chart of CSTR System



RESULTS AND DISCUSSION

Oxidation of organic pollutants by ozone was carried out in aqueous solutions simulating waste waters. The pollutants which were investigated in this study include eight compounds as follow:

1) Amine compounds -- Aniline, Pyridine;
2) Amide compounds -- Acetamide, N,N-dimethyl formamide;
3) Phenolic compounds -- O-cresol, Phenol;
4) Volatile compounds -- Trichloroethylene, Chloroform.

Reactions were conducted on all of compounds at 25°C and operated at atmospheric pressure. For each compound, experiments of combined ozone plus carbon and ozone-only were both performed. Two initial concentrations were studied for each compound and each concentration study had 10 residence time measurement points at time intervals from 1 to 6 minutes. The effective volume of the reactor was 400 ml for all the experiments in the semi-batch runs. Concentrations of ozone and charcoal are listed in Table IV-1.

Powdered activated carbon (PAC, mesh No.50-200, 84%; >No.50 2%; <No.200 14% by weight) was used in the experiments dealing with TCE, Chloroform and Phenol, while granular activated carbon (GAC, mesh No.10-30, 80%; No.30-50 20% by weight) was used in all experiments with the rest of the compounds. Constant dosage of GAC was maintained at 3

grams. 0.01 gram PAC was added to the system in TCE and Chloroform runs.

Experimental results on decomposition of pollutants are illustrated in Figure IV-1 through IV-8, which show normalized concentration (C/Co) as a function of the average residence time for the two different initial concentrations. It is seen that target compound concentration consistently decreased with increasing reaction time for all the reactions. One might notice that for some carbon catalyzed reactions the pollutants decayed much quicker than in the experiments without carbon but ozone only.

The reactor results were analyzed by fitting the following rate model to the data:

$$-\frac{d[M]}{dt} = k' * [M] * [O_3] * [C] \qquad (1)$$

where [M], $[O_3]$ and [C] are the concentrations of target compound, ozone and carbon respectively.

The concentrations of ozone and carbon during the reaction are assumed to be constant. Equation (1) will remain in the same format:

$$-\frac{d[M]}{dt} = k * [M] \qquad (2)$$

where $k = k' * [O_3] * [C]$ (unit: 1/Time) (3)

When dosages of ozone or/and carbon were changed, pseudo-first order rate constant k in Equation (3) was changed as:

$$\frac{k_1}{k_2} = \frac{k'_1 * [O_3]_1 * [C]_1}{k'_2 * [O_3]_2 * [C]_2} \qquad (3a)$$

Equation (3a) shows that k is directly proportional to both concentrations of ozone and carbon. Constant k increases with increasing the dosages of ozone and/or carbon if k' is assumed constant.

Pseudo-first order kinetics was then assumed in order to analyze the mechanism of pollutants decomposition by ozone and ozone-carbon systems from the integrated rate Equation (2):

$$[M] = [M]o * \exp(-k * t) \qquad (4)$$

rearrange Equation (4):

$$\mathrm{Ln}\,([M]/[M]o) = -k * t \qquad (5)$$

where [M]o: initial concentration of target compound;
[M]: concentration of target compound at time t;
k: reaction rate constant for pseudo-first order;
t: contact time of reaction.

The fractional conversion X of target compound as reactant is defined as the fraction of reactant converted into product or

$$X = 1 - ([M]/[M]o) \qquad (6)$$

So Equation (5) becomes:

$$\mathrm{Ln}\,(1-X) = -k * t \qquad (7)$$

Defining the half-life of the reaction, $t_{1/2}$, as the time for the concentration of reactants to drop to one-half the original value:<7>

$$[M] = 1/2\ [M]o \tag{8}$$

then from Equations (5) and (8), the Half-life time is given by:

$$t_{1/2} = \frac{Ln\ 2}{k} \tag{9}$$

Plots of integrated rate Equation (5), -Ln([M]/[M]o) verses time, are shown in Figures IV-9 through IV-16 for a range of initial concentration and conversions. Those plots for all compounds except pyridine show good linearity and indicate that the process is pseudo-first order. Tables IV-2 through IV-6 are the summary of rate constants and half-lifes for ozone and ozone-carbon runs on each compound. These runs include varied ozone levels as well as initial pollutant level for each pollutant.

A. Ozone in Liquid Phase

When ozone was bubbled into the aqueous solution, absorption takes place from the gas phase into liquid phase at the bubble surface, and then diffusion in the liquid phase from the bubble surface to the bulk liquid. The mass balance of ozone over the liquid gives:<46>

$$V * \frac{dC_{O3}l}{dt} = Kl_{O3} * a * V * (C_{O3}i - C_{O3}l) \tag{10}$$

where kl_{O3}: mass transfer coefficient for O_3 gas absorption

a: bubble surface area

V: reaction volume

Ci: O_3 concentration at H_2O-O_3 bubble interface

Cl: O_3 concentration of O3 in solution

Ci is assumed constant and integrating the Equation(10) at the boundary conditions: t=0, $C_{O3}l=0$; t=t, $C_{O3}l=C_{O3}l$:

$$1 - (C_{O3}l/C_{O3}i) = \mathrm{Exp}(-Kl_{O3} * a * t) \qquad (11)$$

this equation is solved by linear regression of experimental data of $C_{O3}l$ verses time. Figure IV-17<47> shows the plot of ozone concentration verse time at room temperature. The value of mass transfer coefficient (combined with interfacial surface area a) is found to be 0.6363 min^{-1}.<47>

B. Destruction of Pollutants with Ozone

Figures IV-1 through IV-5 show best fit first order decay plots for the reaction of aniline, acetamide, pyridine, n,n-dimethyl formamide and o-cresol in both ozonation and charcoal catalyzed ozonation systems. Data for first order decay for aniline fit the experimental data very well, particularly in the lower initial reagent (target organic) concentration runs. For almost every lower initial concentration set of experiments with acetamide and dimethyl formamide, pseudo-first order decay is obeyed. Degradation of pyridine and o-cresol are, however, not well fit by the pseudo-first order decay curves.

1. Degradation Rate of Target Compounds

Of the eight chemicals studied, decomposition was most rapid for aniline with contact time 10 min, and slowest for acetamide and N,N-dimethyl formamide with contact times of 60 min and 30 min respectively, as shown in Tables IV-2,5. Degradation of aniline, acetamide and n,n-dimethyl formamide to X=0.5 requires 2.1, 30.3 and 33.4 minutes respectively. Here it is also seen that acetamide and N,N-dimethyl formamide are not reactive with ozone alone to a significant extent.

This is probably due to oxidation selectivity of system.<25> Since ozone oxidations are generally classified into two types: a) mass transfer controlled and b) chemical reaction rate controlled. Mass transfer controlled oxidations with ozone such as aniline and o-cresol occur so rapidly that the rate is limited only by the speed at which ozone can be added to the solution. We observe here that only these mass transfer controlled ozonation reactions react to completion in our system.

On the other hand, some ozone oxidations proceed very slowly, e.g. cyclophosphamide, dimethylnitrosamine and kepone.<44> This is shown to be independent of the concentration of ozone, and the presence of excess ozone over the minimum amount required to maintain a measurable ozone residual has no influence upon the rates of such reactions. The organic chemicals oxidize only until the residual ozone concentration has been depleted.<25>

2. Changes of PH Values in the Reactions

In Table IV-7, one may notice that pH values at the end of the destruction process were lower than 7, that means pH values decrease during the reaction. This agrees with Bader and Hoigne who proposed two mechanisms of ozonation: 1) direct reaction of the O_3 molecule; 2) reaction with the OH radical formed by the decomposition of O_3. PH values influenced the speed of decomposition of ozone to form hydroxyl free radical, which is initiated and catalyzed by hydros ions (OH^-)<31>. Therefore hydros ion was consumed in the reaction:

$$O_3 + OH^- \text{----->} O_2^- + HO_2$$

The hydros free radical reactions dominate over the direct ozone reactions. In high pH value reaction system, decomposition of ozone in water increased with more hydros ion disappearing to form highly reactive secondary oxidants (e.g. OH)<31,45>. Thus the destruction of pollutant by ozone was increased. Because OH^- was consumed, the values of pH in the system decreased in our system.

It should be pointed out that TCE and Chloroform have a high volatility and low solubilities, their concentrations in liquid phase may easily change by evaporation or/and stripping. Therefore the effect of purging with inert gas (stripping) is a required calibration process for determination of rate constants.

C. Effect of Activated Carbon

In the reaction systems that have had carbon added, the reaction rates have been significantly increased.

Figure IV-2 and IV-4 indicated that appreciable conversion of N,N-dimethyl formamide (0.365 in 30 min) and acetamide(0.61 in 60 min) have been observed when the reaction system was changed to ozone plus carbon from ozone oxidation alone on the same time scale. This also applies to all the other target compounds: aniline, TCE, chloroform and o-cresol which decomposed more quickly in ozone plus charcoal experiments. As mentioned before, the conversion rate of formamide and acetamide were lower than that of other compounds studied, this combination of ozone plus carbon technology provides an effective and useful method for destroying these organics in water.

Two forms of activated carbon: GAC and PAC were utilized in experiments on the different target compounds. For typical runs on aniline, acetamide, pyridine, dimethyl formamide and cresol, 3 grams of GAC were added to 400 Ml reagent volume and the average reaction rates were accelerated 21, 68, 12, 59 and 17 percent, respectively. Much smaller doses of PAC (0.1 G / 400 Ml reagent volume) was applied in the TCE and Chloroform experiments. Here the rate of reaction had been increased 11%-14% by addition of the small quantity of PAC.

Usually, GAC has 1200-1500 M^2/G and PAC has 1500-2000 M^2/G.<1> Therefore PAC possesses more surface area than GAC for the surface reactions. It is obvious that PAC is more effective than GAC based on the same mass dosage added to the system.

When the dose of O_3 was held constant and PAC levels increased, one can see from Figure IV-8 that conversion of phenol increases 14% by increasing the concentration of PAC five times in the system. Clearly the lower amount of PAC in the experiment, the slower observed decay of phenol.

The rate constant and half-life is shown in Table IV-4. From Equation (3a):

$$\frac{k'_1}{k'_2} = \frac{k_1 * [C]_2}{k_2 * [C]_1} = \frac{0.1525 * 0.125}{0.1739 * 0.025} = 4.38 > 1$$

so $k'_1 > k'_2$ where k' in $(\text{Conc.}^{-2} * \text{Time}^{-1})$

This means increasing the PAC dosage then leads to pseudo first order rate constant k increases, but k' decreases. Because in this case the increase of constant k (a factor of 1.14) is smaller than the increase of the dosage of carbon (a factor of 5). This phenol system favored (kinetically) the lower amounts of PAC.

D. Oxidant Dosages

Figure IV-8 gives a good example on the effect of O_3 dose level in phenol reaction to show that dosage of ozone is an important factor in this process. A pseudo-first order plot is shown in Figure IV-11 for different ozone levels. Table IV-4 gives a summary of phenol experiments.

The rate constants in Table IV-4 show that when the output from ozonator is increased from 70 volts to 90 volts, dosage of O_3 available for the process of destruction of phenol increased from 23 Mg/L to 43 Mg/L, a factor of 1.87. This leads to an increase in the pseudo-first order reaction rate of a factor of 2. Here the change was from a rate of 0.1525 to 0.3068 min^{-1}. The increase of rate constant k (the factor of 2) was over the increase of ozone dosage (the factor of 1.87) when two sides of Equation (3a) were compared. Then:

$(k'_1/k'_2) = 0.94 < 1$

so $k'_2 > k'_1$ where k' in $(Conc.^{-2}*Time^{-1})$

This proves that increasing the dose of ozone is effective in ozone oxidation process.

On the other hand, half-life time for degradation of phenol decreased a factor of 2, from 4.54 min to 2.25 min. The same results has been obtained in CSTR runs, which will be described below.

It is observed from Figure IV-8 and IV-11 that for the different doses of O_3 and activated carbon the data fit the integrated first order rate equation well.

E. Efficiency of CSTR runs

CSTR studies were carried out by using kinetic data from the semi-batch system described in this work as initial design input. The values of pseudo-first order rate constants obtained from the semi-batch experiments were used to estimate the values of the flow rate required in CSTR reactor in order to get a desired target conversion. Operating conditions for this mixed flow reaction system were at room temperature and under atmospheric pressure, the phenol system was studied in mixed flow reactor.

To make a material balance for phenol, reactant density is assumed to remain constant. The performance equation obtained is:<7>

Input = Output + Disappearance + Accumulation

or $$Q * Cin = Q * Cout + (-r) * V + \left(-V * \frac{dC}{dt}\right) \tag{12}$$

where Q: total flow rate
V: reactor volume
Cin: mixing concentration for phenol input the system
Cout: mixing concentration for phenol output from the system
r: reaction rate for phenol

Accumulation at steady-state is zero (dc/dt=0), so Equation (12) can be rearranged to:

$$-r = Q / V * (Cin - Cout) \tag{13}$$

for a pseudo-first order reaction,

$$-r = k * Cout \qquad (\text{ k in min}^{-1}) \tag{14}$$

then from Equations (13) and (14), k is calculated.

Table IV-4 is a summary of mixing concentration for each stream into the reactor. A total of 10 experiments were conducted, of which 3 runs were performed directly with ozone at different ozone dosages and varied target flow rates. Another 3 runs with carbon only at different carbon levels. 4 additional runs focused on ozone plus carbon experiments. Activated carbon in this system was PAC because as it was shown to be more effective than GAC in the catalyzed oxidation semi-batch experiments.

Table IV-6 summarizes the experimental results calculated by Equation (13) on CSTR reaction of phenol. Reaction rate constants, half-lifes and process conversion rates are all illustrated. The combination of ozone plus carbon brought about phenol degradation at the fastest rate. The destruction was slowest when carbon alone was employed. Direct ozonation process, as expected, was much faster than carbon adsorption, but slower than carbon plus ozone reaction.

1. Effect of Oxidant Level

At the same O_3 dosage, the degradation rate of phenol in combined ozone and charcoal system was two times faster than in ozonation system. The conversion rate of phenol increased dramatically in the presence of carbon. Carbon adsorption for removing phenol proceeded very slowly. The conversion of phenol disappearance in the carbon-only solution was only 0.09 on average.

The increase of ozone dosage in the ozone-carbon system suggested that a faster disappearance of phenol could be ac at higher $[O_3]$ levels. As shown in cases 7 and 6, when increasing ozone levels (ozonator output from 90 volts to

110 volts), the rate constant increased from 0.0481 to 0.0706 1/min and conversion of phenol increased from 0.227 to 0.32.

2. Effect of Initial Phenol Concentration

In the ozone oxidation system, lower phenol concentration yields higher destruction rates of phenol. As described early in this chapter (section B), this might be due to the fact that phenol is attacked very rapidly by ozone. The limitation of mass transfer of ozone from gas phase to liquid phase leads to rapid ozone consumption and less phenol conversion (on a relative scale) at the higher phenol levels.<25>

3. Residence Time

As seen in cases 1, 2 and 3; cases 4 and 6; cases 5 and 7 from Tables IV-5 and IV-6 as well as Table III-6, the smaller the overall flow rate or the longer the residence time, the higher the conversion of parent phenol. Long residence time will increase the unit cost operation of the system, the optimum for the flow rate and the conversion of reaction then depends on the total cost effectiveness.

Compared with semi-batch system, the mixed flow system showed lower efficiency over the same reaction period. The largest conversion rate for an individual experiment in the mixed flow reactor was 0.46 because mixed flow reactions are known to be less efficient. This was, however, far beyond our expectation. Selection of system parameters became more important in the flow system because each streams flow directly influenced the reaction velocity, and further affected the system efficiency. More investigation is needed to find optimal operating conditions for an economic system in a continuous flow mode.

F. Heterogeneous Catalytic Oxidation

Charcoal catalyzed ozonation is a heterogeneous process, in which carbon is a solid and ozone and target compound are in gas and liquid phase. The presence of a carbon surface for the reactive ozone molecule and hydros radical in the liquid solution promotes the oxidation by ozone. This is illustrated in the results of Tables IV-2 through IV-6.

For an ozonation with species A, the reaction is represented by the following equation:

$$A + O_3 \text{ ----> decomp. prod.} \qquad (13)$$

Oxidation by ozone with organics usually occurs in liquid phase. The reaction depends on the rate of collision of the reactants and the rate of ozone reaction with the organic molecules in water. Compared with the liquid phase reaction, catalytic reaction occurs at the liquid-solid interphase. The overall process by which heterogeneous catalytic reactions proceed can be broken down into the sequence of individual steps:<46>

1. Mass transfer of species A and O_3 from the bulk solution to the external surface of the carbon pellet

2. Internal diffusion of species A and O_3 in the porous carbon surface
3. Adsorption of reactant A and O_3 onto the carbon surface
4. Reaction on the surface of carbon as Equation (13)
5. Desorption of the decomposing products from the surface
6. Diffusion of the products from the interior pellet to the external surface
7. Mass transfer of the products from the external surface to the bulk solution

Activated carbon adsorbs both ozone and parent organics on its large surface area. It supplies sites where the oxidation reaction may occur faster. The oxidation can also lead to regenerating of the carbon surface, which is then available for additional adsorption of organics. This increases the efficiency of carbon utilization. Decomposition of A by ozone on the carbon surface is thereby faster than in the liquid phase.

If species A is an aromatic compound such as aniline, cresol and phenol, when A is adsorbed on the surface of carbon, pi-orbital complex formed with the carbon surface. Then ozone attacks the adsorbed complex more easily and degradation of parent compound is accelerating.<46>

Table IV-1

Concentrations of Ozone and Charcoal for Semi-batch Runs

Volume of Reaction: 400 Ml

Flow Rate of Ozone: 1.06 L/Min

COMPOUND	Initial Conc.	$[O_3]$ Mg/L	[GAC] or [PAC] * G/L
Aniline	1000 ppm 500 ppm	50.9	7.5
Pyridine	2000 ppm 1000 ppm	50.9	7.5
N,N-Dimethyl Formamide	2000 ppm 1000 ppm	50.9	7.5
O-Cresol	2000 ppm 1000 ppm	50.9	7.5
Acetamide	2000 ppm 1500 ppm	50.9	7.5
Trichloro-ethylene	500 ppm	50.9	0.25 *
Chloroform	500 ppm	50.9	0.25 *

Note: Concentrations of GAC or PAC only for the Combined Ozone-Carbon Experiments

Table IV-2

Reaction Constants for Semi-batch Runs

V:400 Ml; $[O_3]$:50.9 Mg/L; [C]:7.5 G/L (*:0.25 G/L)

COMPOUND	Initial Conc.	k Value (1/Min)	
		O_3	O_3 + Charcoal
Aniline	1000 ppm	0.247	0.344
		0.279	0.320
	500 ppm	0.331	0.394
		0.383	0.432
Pyridine	2000 ppm	0.0225	0.0280
		0.0270	0.0278
	1000 ppm	0.0349	0.040
		0.0353	0.039
N,N-Dimethyl Formamide	2000 ppm	8.98×10^{-3}	0.0128
		0.0124	0.0139
	1000 ppm	7.06×10^{-3}	0.0131
		7.13×10^{-3}	0.0143
O-Cresol	2000 ppm	0.108	0.127
		0.117	0.154
	1000 ppm	0.32	0.33
		0.32	0.36
Acetamide	2000 ppm	7.59×10^{-3}	0.0156
		7.87×10^{-3}	0.0164
	1500 ppm	9.62×10^{-3}	0.0146
		0.0132	0.0150
Trichloroethylene*	500 ppm	0.1493	0.1707
Chloroform*	500 ppm	0.1478	0.1631

Table IV-3

Half-Lifes for Semi-batch Runs

V: 400 Ml; [O_3]:50.9 Mg/L; [C]:7.5 G/L (*:0.25 G/L)

COMPOUND	Initial Conc.	$T_{1/2}$ (Min.) O_3	$T_{1/2}$ (Min.) O_3 + Charcoal
Aniline	1000 ppm	2.801 2.484	2.015 2.165
	500 ppm	2.094 1.810	1.759 1.605
Pyridine	2000 ppm	30.81 25.67	24.76 24.93
	1000 ppm	19.86 19.64	17.33 17.77
N,N-Dimethyl Formamide	2000 ppm	77.19 55.90	54.15 49.87
	1000 ppm	98.18 97.22	52.91 48.47
O-Cresol	2000 ppm	6.42 5.92	5.46 4.50
	1000 ppm	2.17 2.17	2.10 1.93
Acetamide	2000 ppm	91.32 88.08	44.43 42.27
	1500 ppm	72.05 52.51	47.48 46.21
Trichloro-ethylene *	500 ppm	4.64	4.05
Chloroform *	500 ppm	4.69	4.25

Table IV-4

Rate Constants and Half-life for Phenol

[Phenol]o = 0.01063 Mol/L

Reaction Time: 14 Min

Volume of Reaction: 400 Ml

Flow Rate of O_3: 1.06 L/Min

Expt. No.	Description	[C] G/L	[O_3] Mg/L	k Min^{-1}	$T_{1/2}$ Min
1.	70 Volts	0.125	23	0.1739	3.99
2.	90 Volts	0.025	43	0.3068	2.25
3.	70 Volts	0.025	23	0.1525	4.54

Table IV-5

Mixing Concentrations in CSTR Runs

V (hold-up) = 495 ml

(ppm)

Case	Description	(Phenol) in	(Phenol) out	O_3 in Water	Carbon
1.	O_3 90 Volts	750	640	6.95	--
2.	O_3 90 Volts	645	544	4.76	--
3.	O_3 110 Volts	492.6	404	4.1	--
4.	O_3 + Carbon 90 Volts	245	131	4.9	83.3
5.	O_3 + Carbon 110 Volts	252	157	5.1	103.3
6.	O_3 + Carbon 90 Volts	316.3	244.5	2.88	66.3
7.	O_3 + Carbon 110 Volts	405.4	275.2	7.2	76
8.	Carbon	188	170.9	---	57.9
9.	Carbon	140.8	126.2	---	57.3
10.	Carbon + O_2	625	547	---	59.4

Table IV-6

Rate Constants, Half-lifes and Conversion Rates in CSTR Runs

V (hold-up) = 495 ml

see Table IV-5 for concentrations

Case No.	Description	k values 1 /Min	T 1/2 Min	X Fraction
1.	O_3 90 Volts	0.0278	24.9	0.147
2.	O_3 90 Volts	0.0233	29.7	0.157
3.	O_3 110 Volts	0.0180	38.5	0.18
4.	O_3 + Carbon 90 Volts	0.0633	11	0.46
5.	O_3 + Carbon 110 Volts	0.0425	16.3	0.38
6.	O_3 + Carbon 90 Volts	0.0481	14.4	0.227
7.	O_3 + Carbon 110 Volts	0.0706	9.8	0.32
8.	Carbon	8.09E-03	85.7	0.091
9.	Carbon	0.0108	64.2	0.104
10.	Carbon + O_2	0.0174	39.8	0.080

Table IV-7

PH Values for Semi-batch Runs

Volume of Reaction: 400 Ml

Flow Rate of Ozone: 1.06 L/Min

Compoound	Initial Conc. (ppm)	Expt. Time (Min)	[O_3] Mg/L	[GAC] or [PAC] * G/L	pH Values Start	pH Values End
Aniline	1000	10	50.9	---	7.0	5.0
				7.5	7.0	4.9
	500			---	7.0	4.5
				7.5	7.0	4.3
Acetamide	2000	60	50.9	---	7.0	5.7
				7.5	7.0	5.4
	1500			---	7.1	4.5
				7.5	7.0	4.1
Pyridine	2000	15	50.9	---	7.0	5.2
				7.5	7.0	5.2
	1000			---	7.0	4.6
				7.5	7.0	4.1
N,N-dimethyl Formamide	2000	30	50.9	---	6.9	4.5
				7.5	7.1	2.3
	1000			---	7.1	4.5
				7.5	7.0	2.2
O-cresol	2000	30	50.9	---	7.0	2.8
				7.5	7.0	2.7
	1000			---	7.0	2.9
				7.5	7.0	2.8

Table IV-7

PH Values for Semi-batch Runs

(Cont.)

Trichloro-ethylene	500	12	50.9	---	7.0	2.2
				0.25 *	7.0	2.3
Chloroform	500	12	50.9	---	7.0	2.9
				0.25*	7.0	3.1
Phenol	1000	14	23@	0.025*	7.0	7.0#
			43@	0.025*	7.0	7.0#
			23@	0.125*	7.0	7.0#

Reaction in pH 7 buffer

@ Flow rate of ozone: 0.6 L/Min

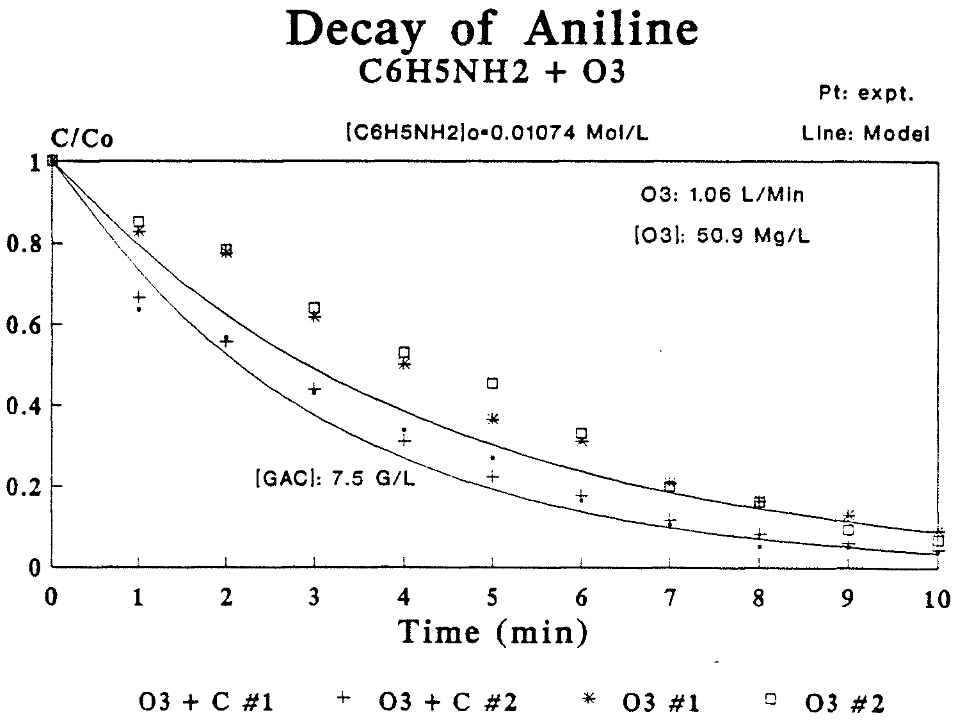


Figure IV-1a Ozone Decomposition of Aniline

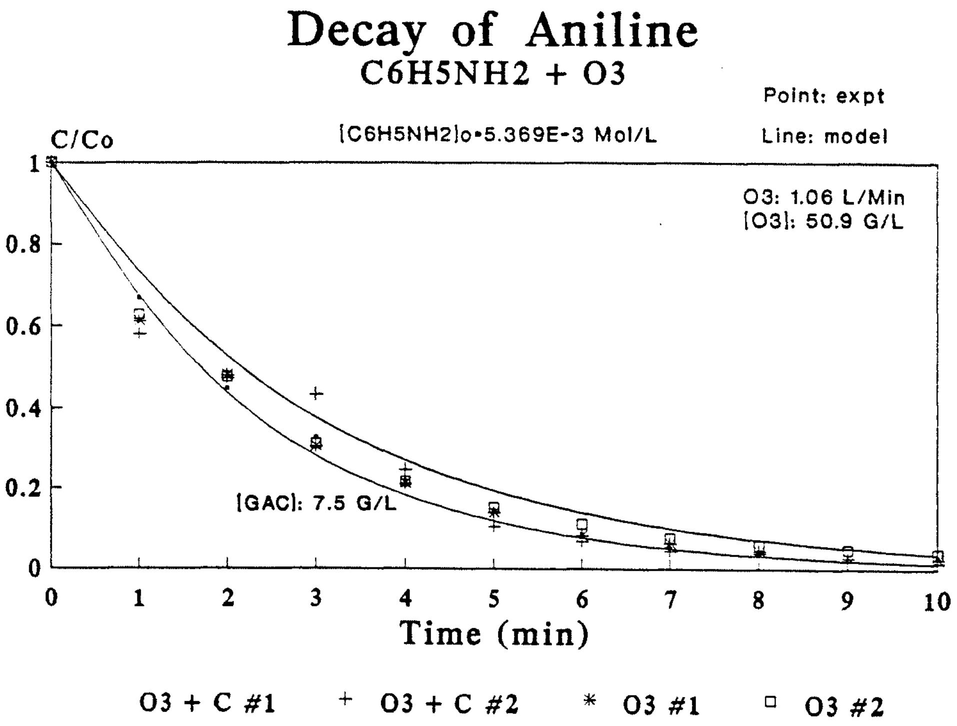


Figure IV-1b Ozone Decomposition of Aniline

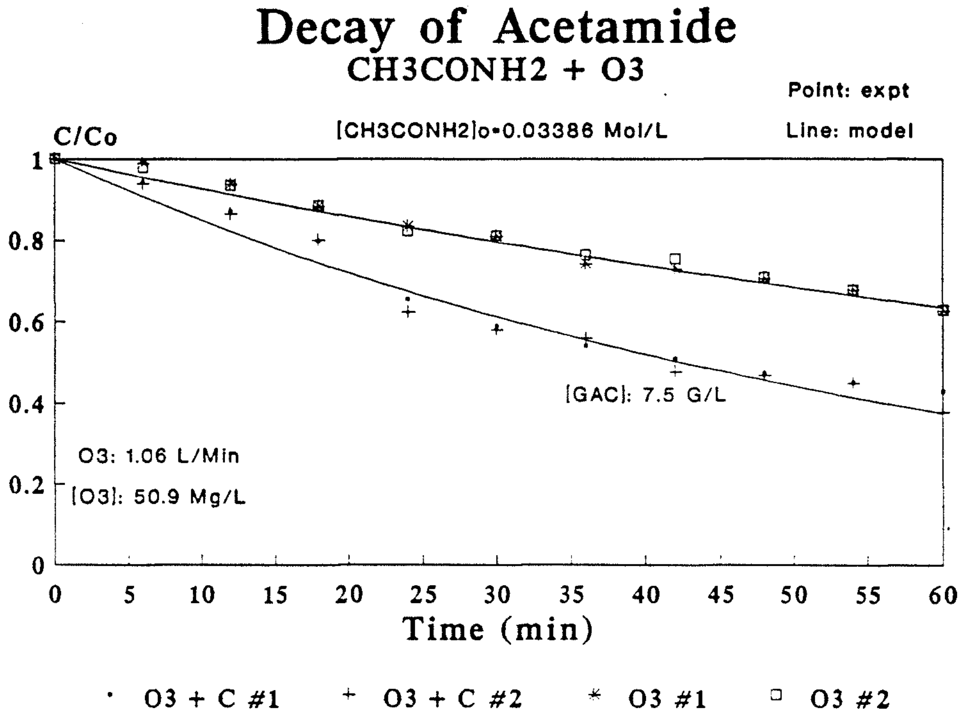


Figure IV-2b Ozone Decomposition of Acetamide

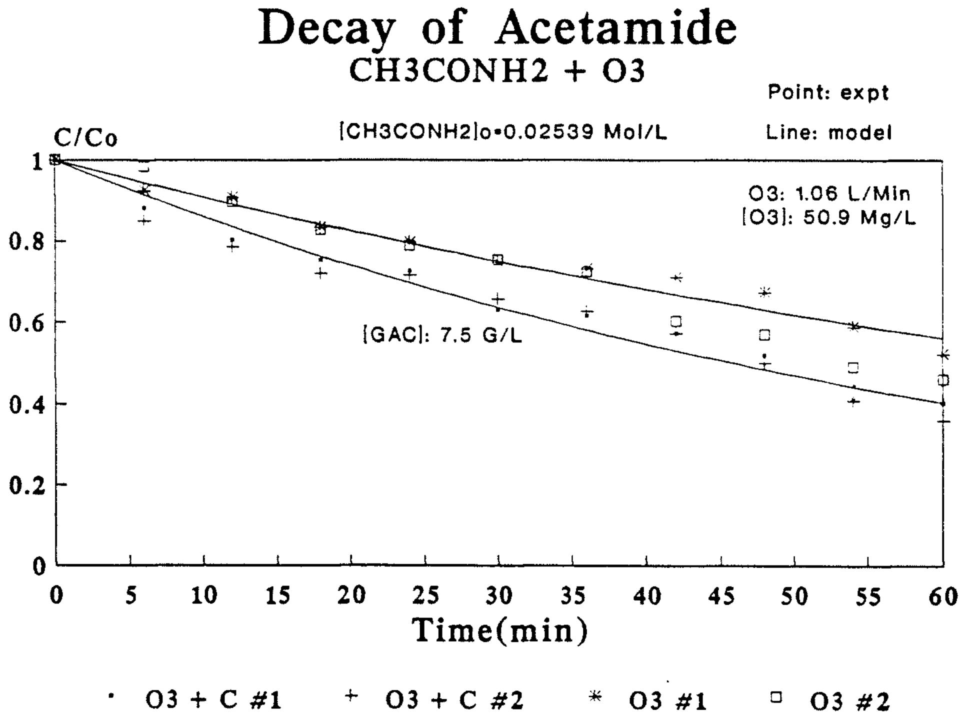


Figure IV-2a Ozone Decomposition of Acetamide

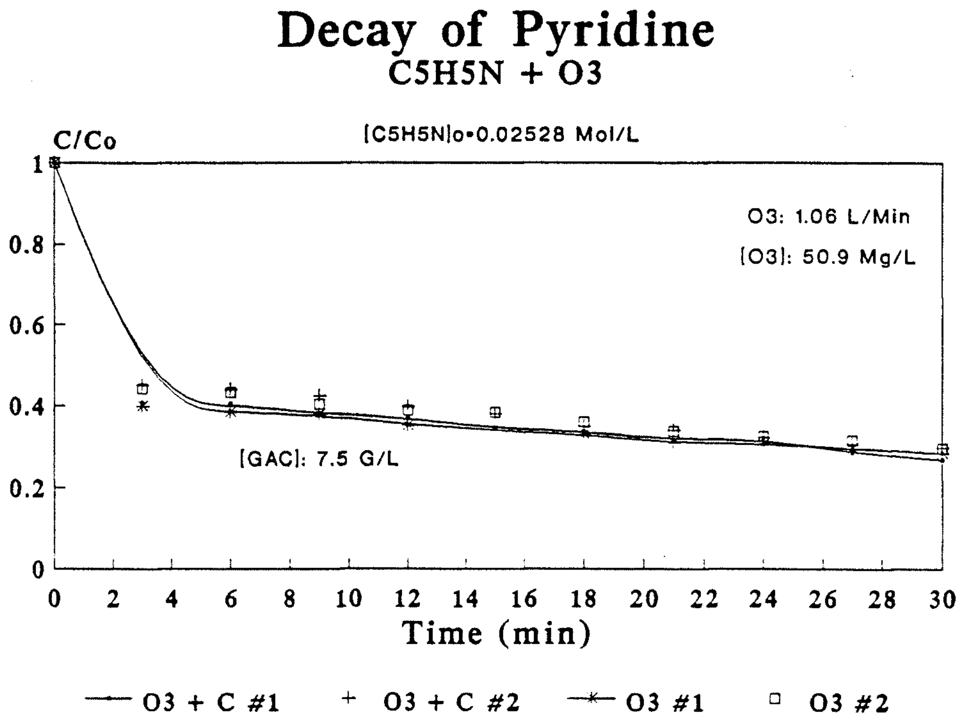


Figure IV-3a Ozone Decomposition of Pyridine

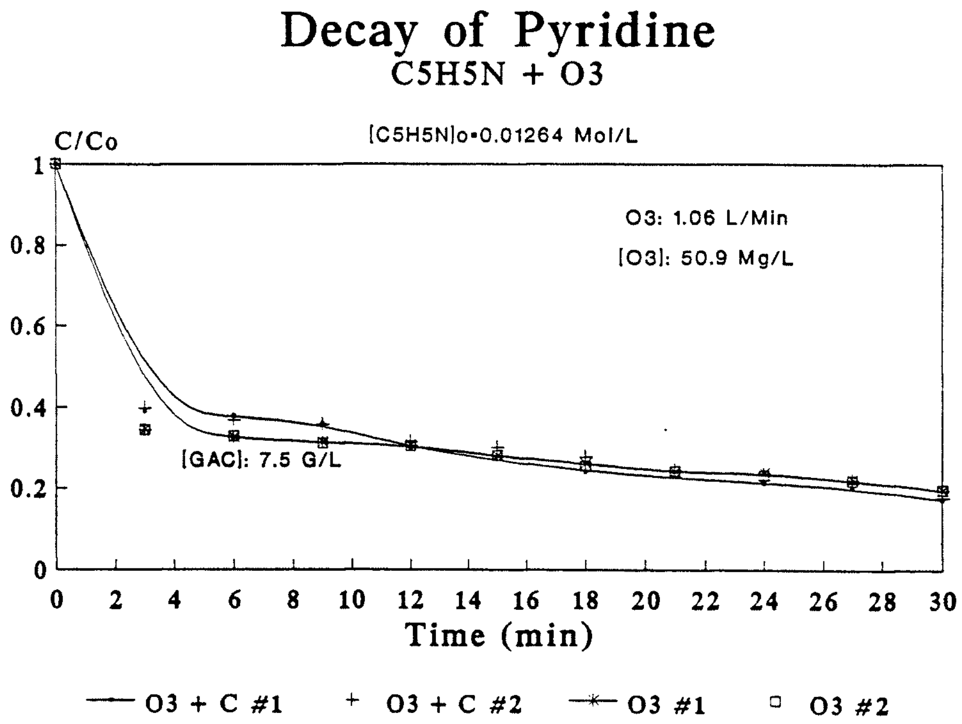


Figure IV-3b Ozone Decomposition of Pyridine

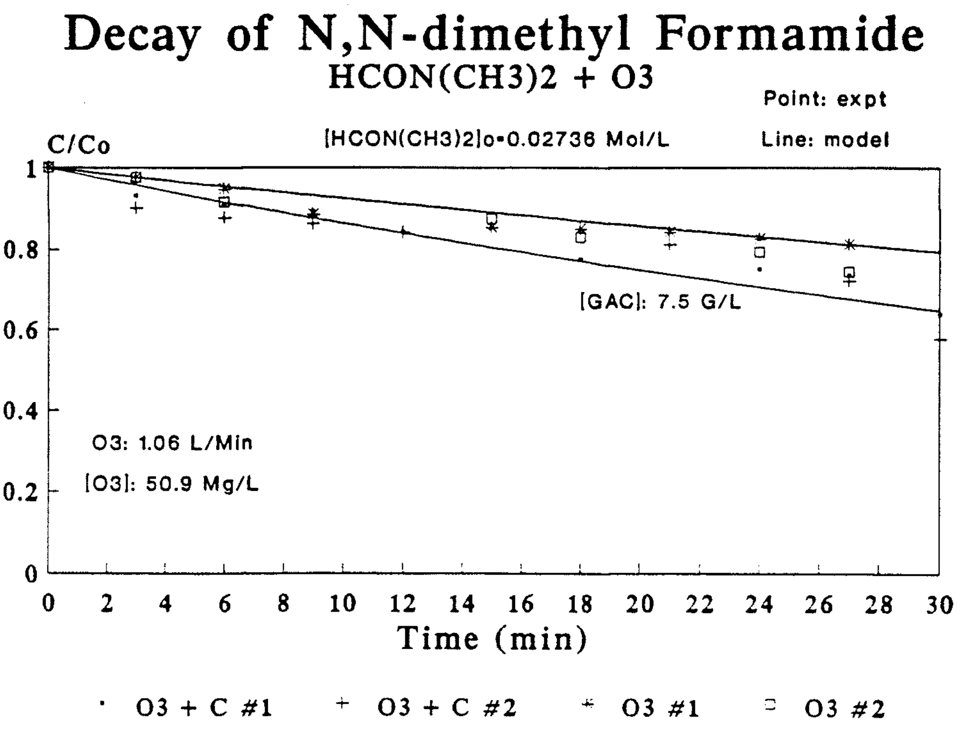


Figure IV-4a Ozone Decomposition of N,N-dimethyl Formamide

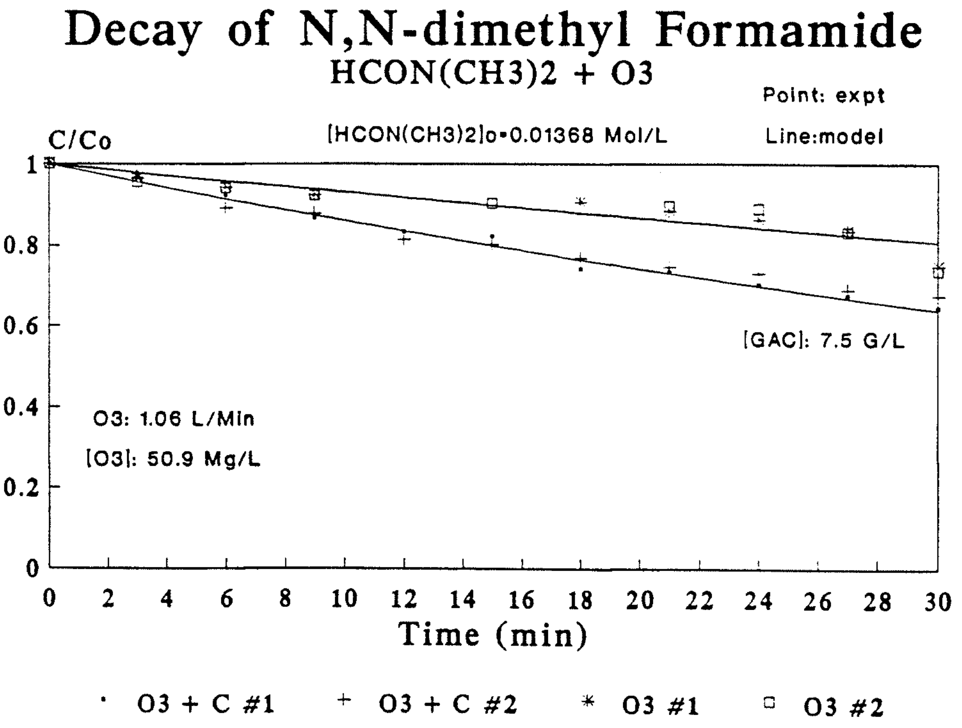


Figure IV-4b Ozone Decomposition of N,N-dimethyl Formamide

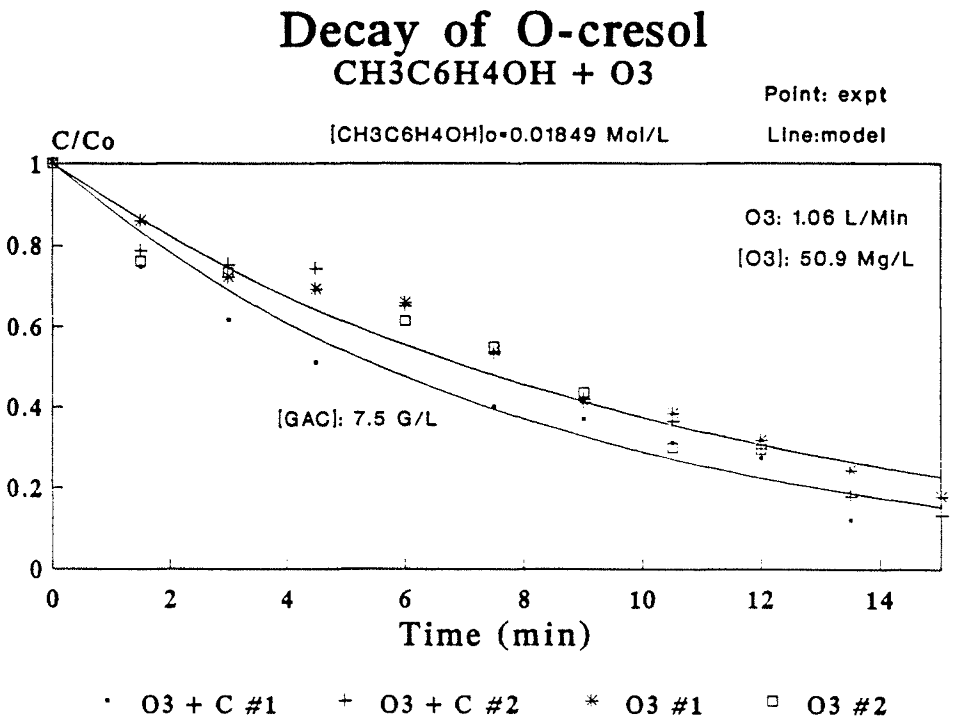


Figure IV-5a Ozone Decomposition of O-cresol

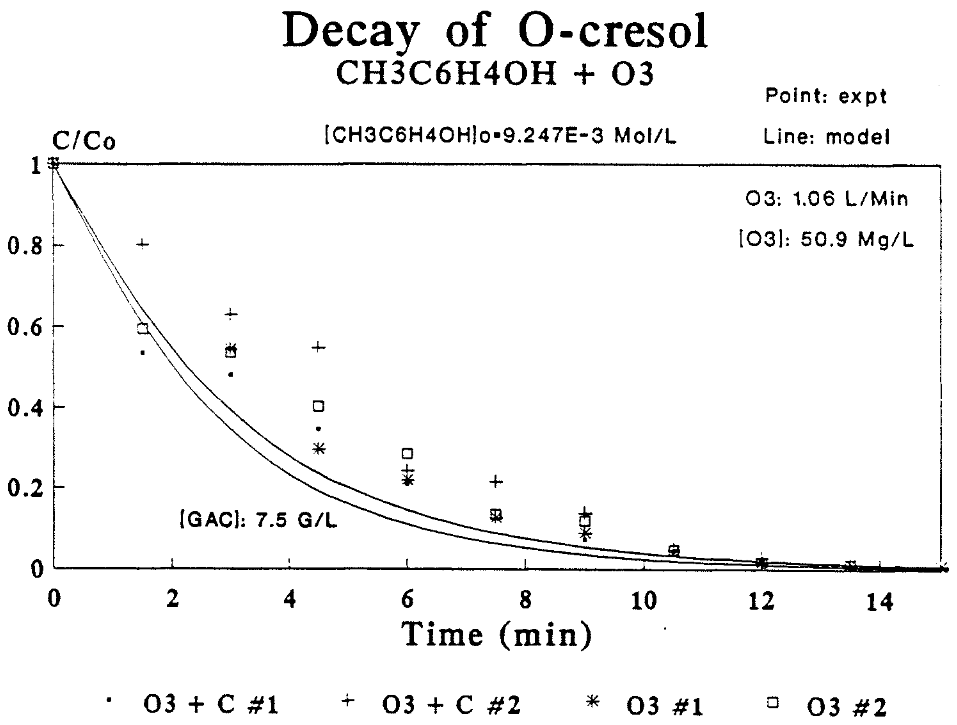


Figure IV-5b Ozone Decomposition of O-cresol

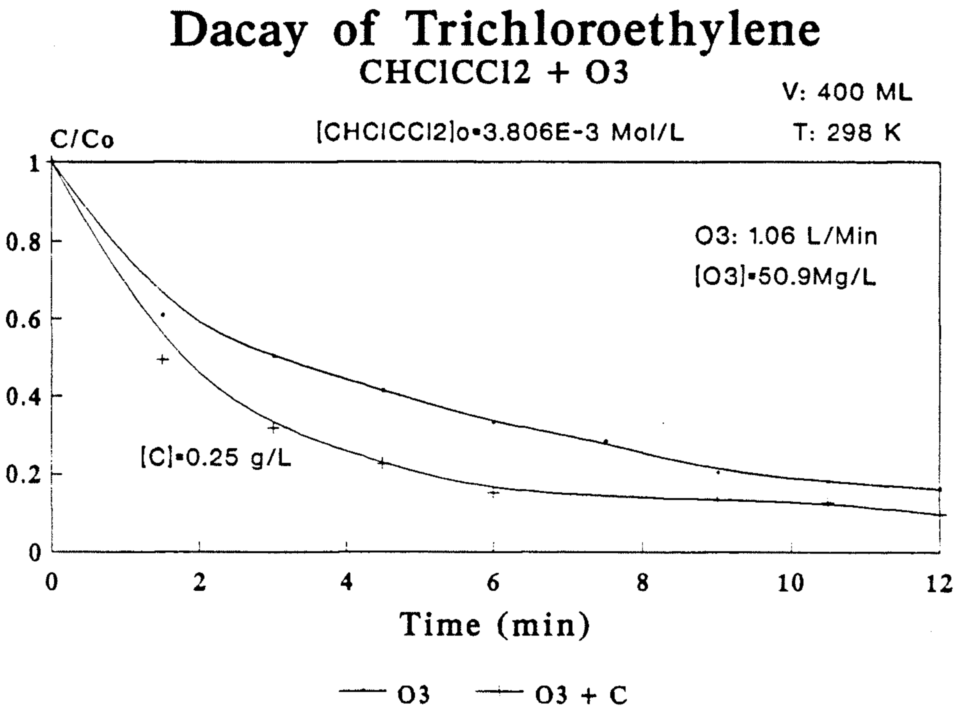


Figure IV-6 Ozone Decomposition of Trichloroehylene

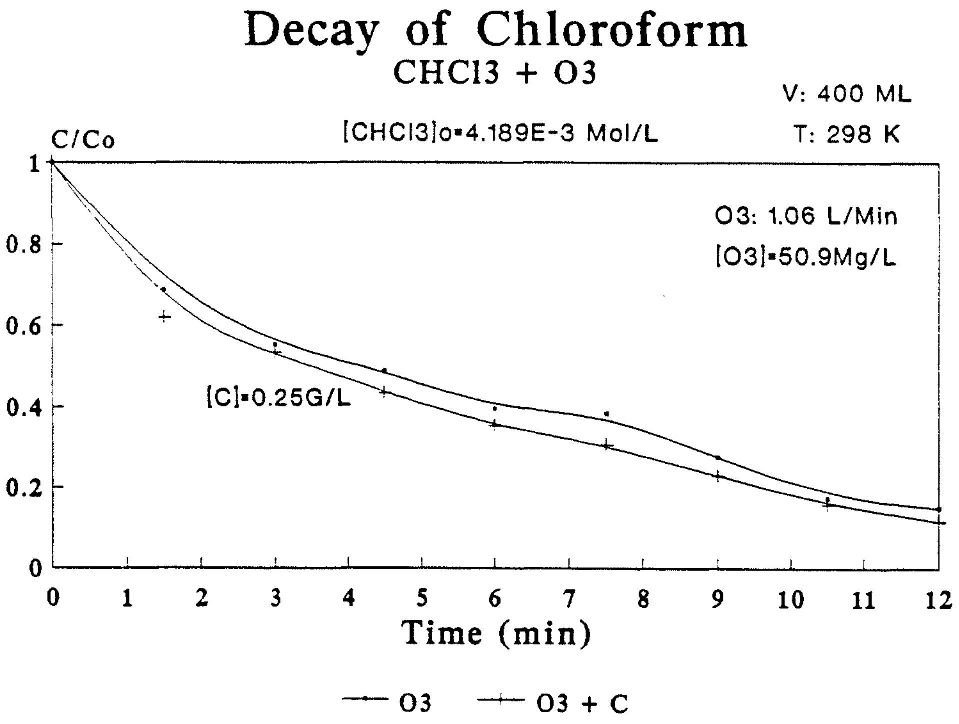


Figure IV-7 Ozone Decomposition of Chloroform

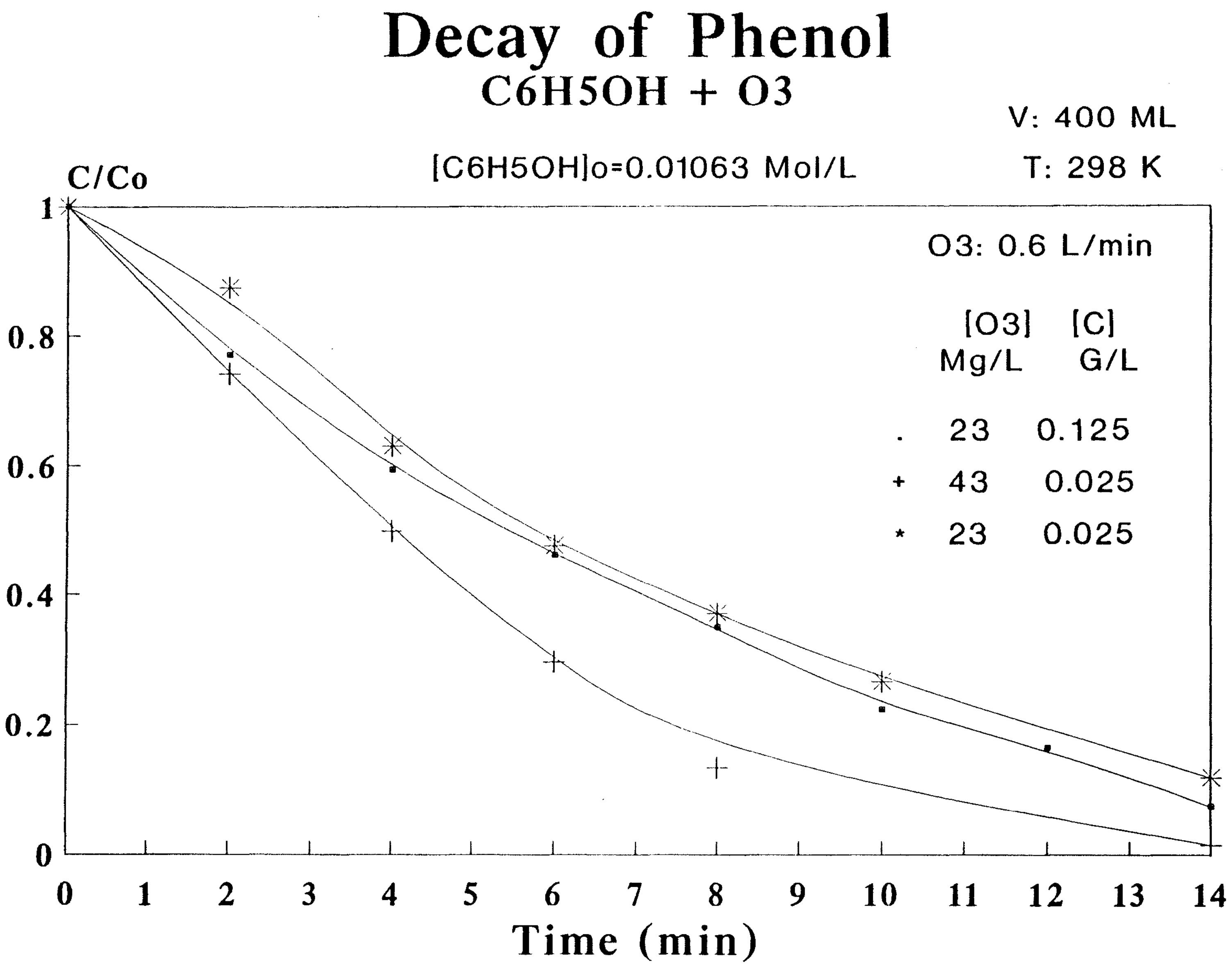


Figure IV-8 Ozone Decomposition of Phenol

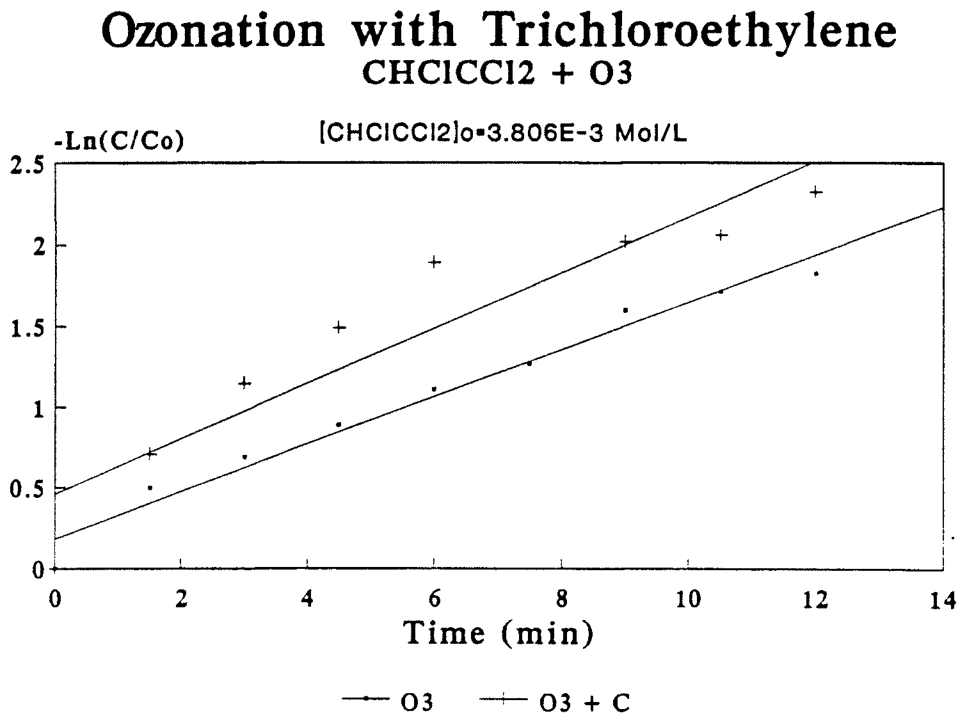


Figure IV-9 First Order fit fot TCE

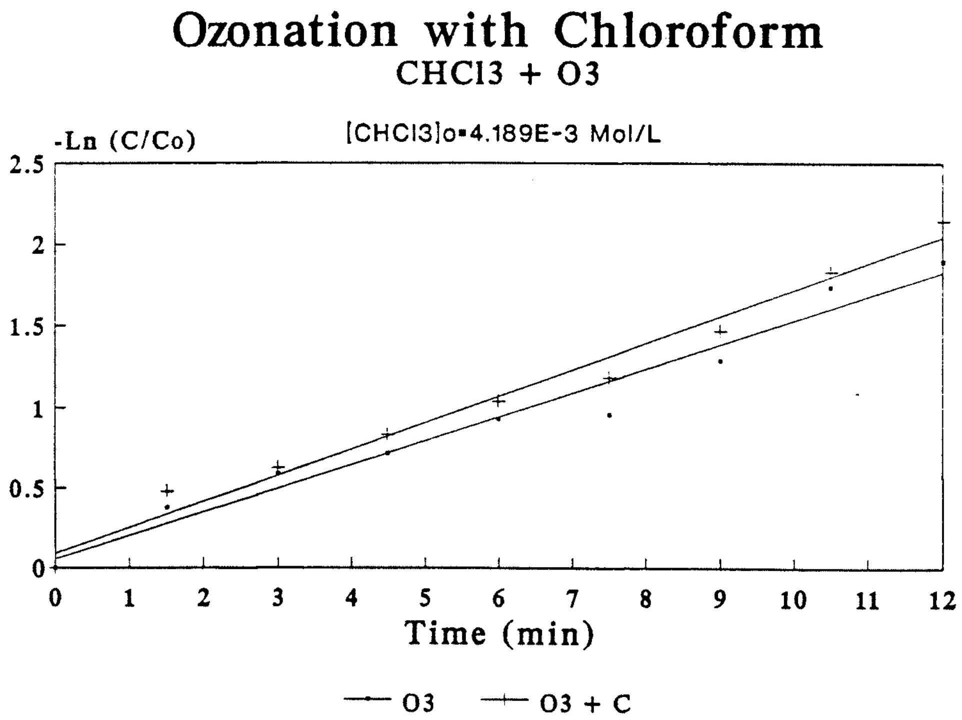


Figure IV-10 First Order Fit for Chloroform

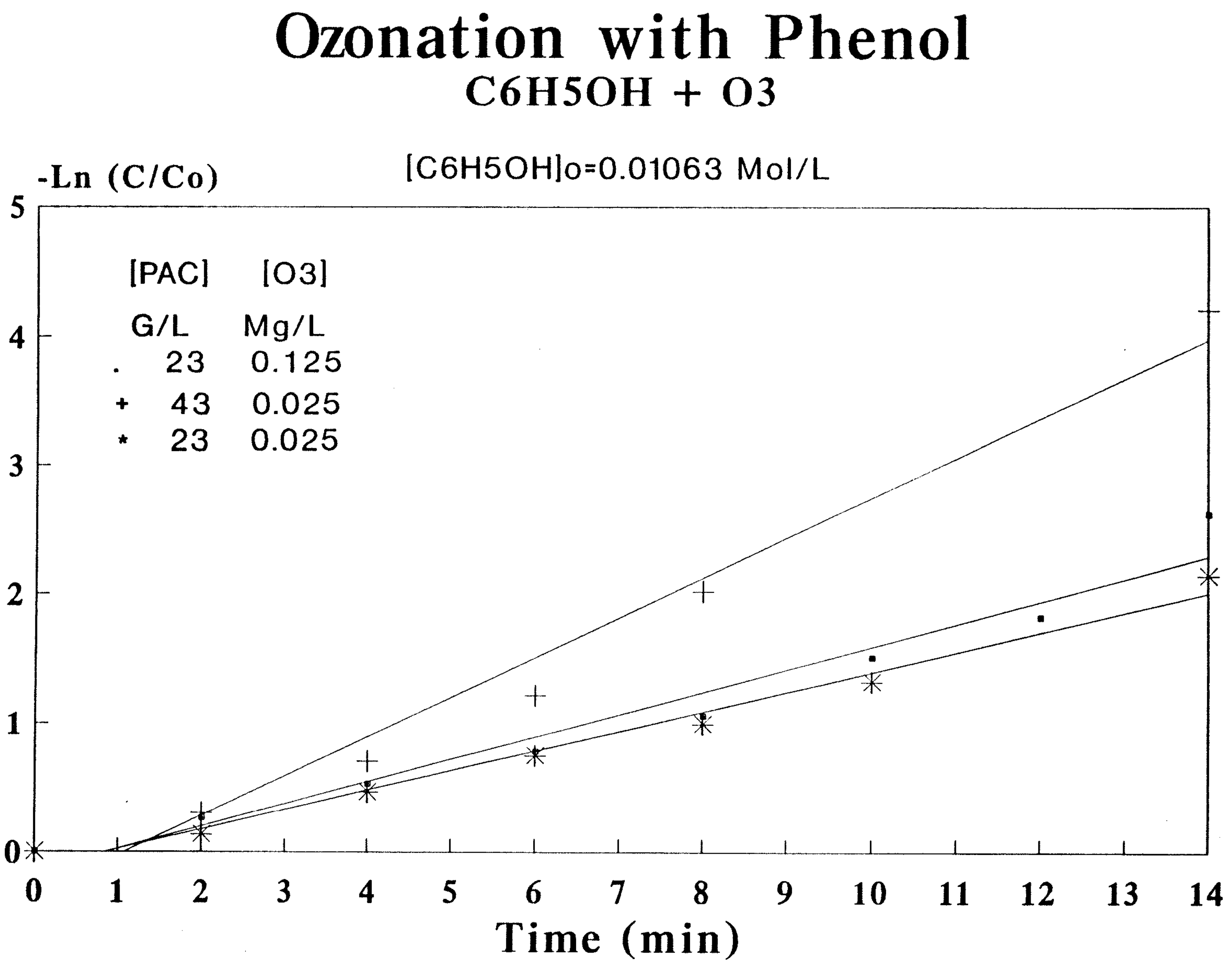


Figure IV-11 First Order Fit for Phenol

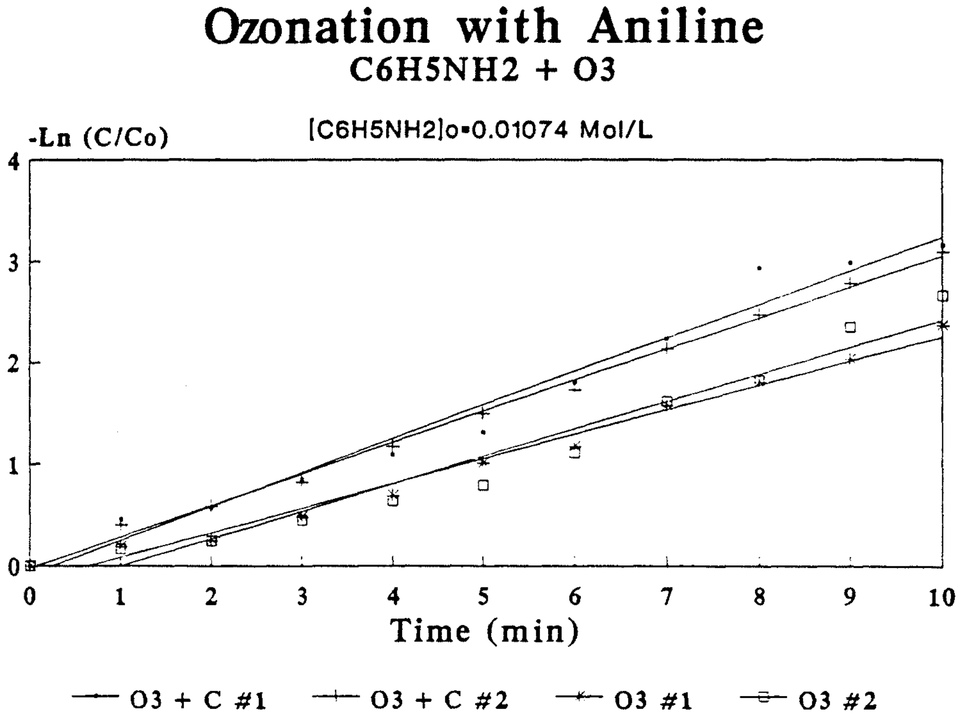


Figure IV-12a First Order Fit for Aniline

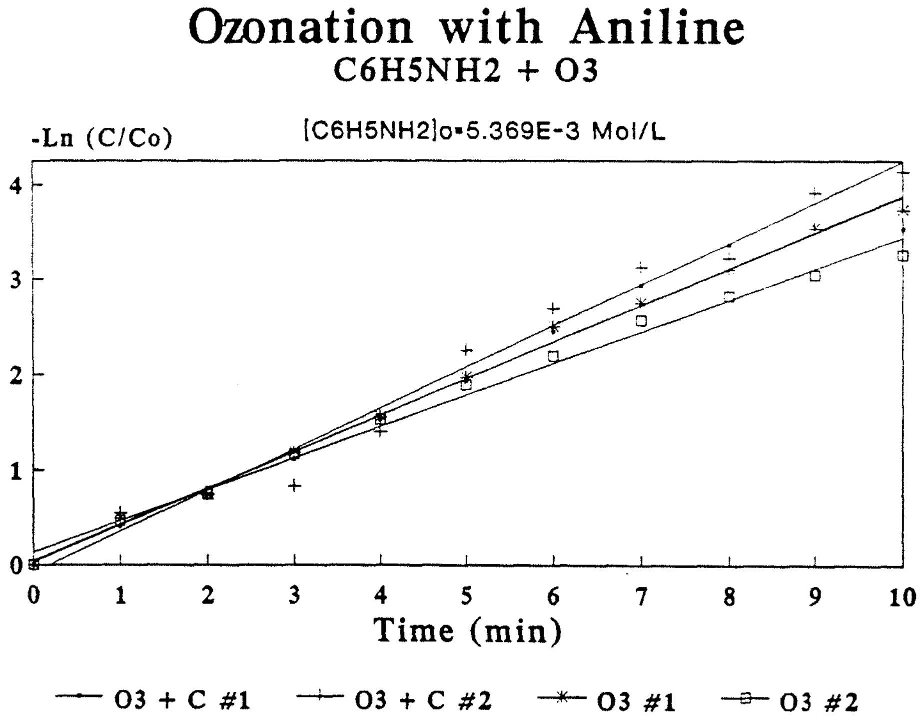


Figure IV-12b First Order Fit for Aniline

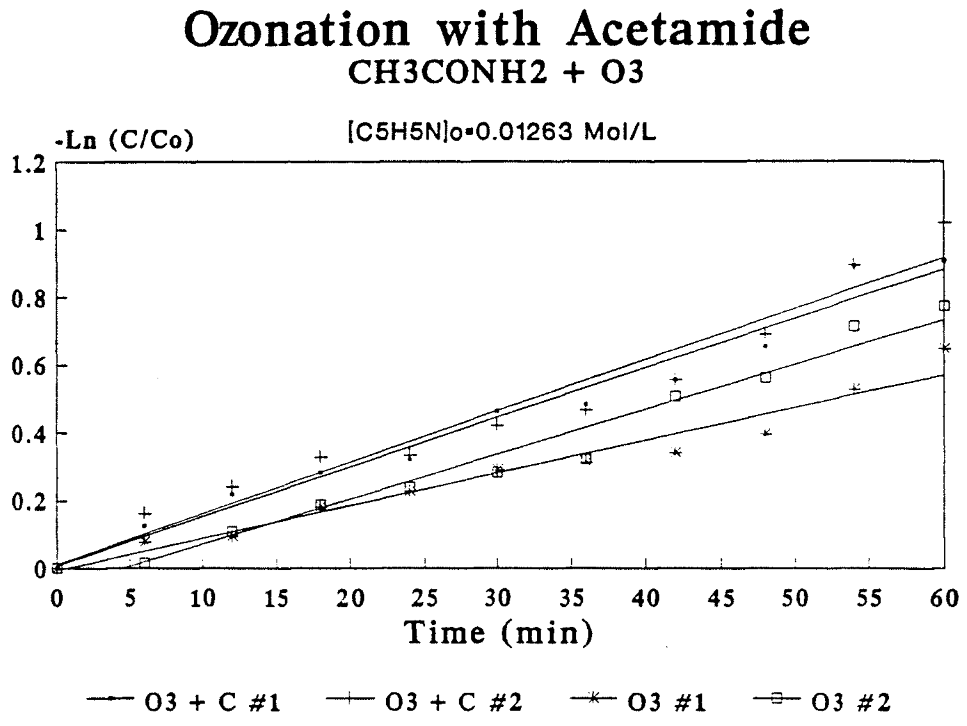


Figure IV-13a First Order fit for Acetamide

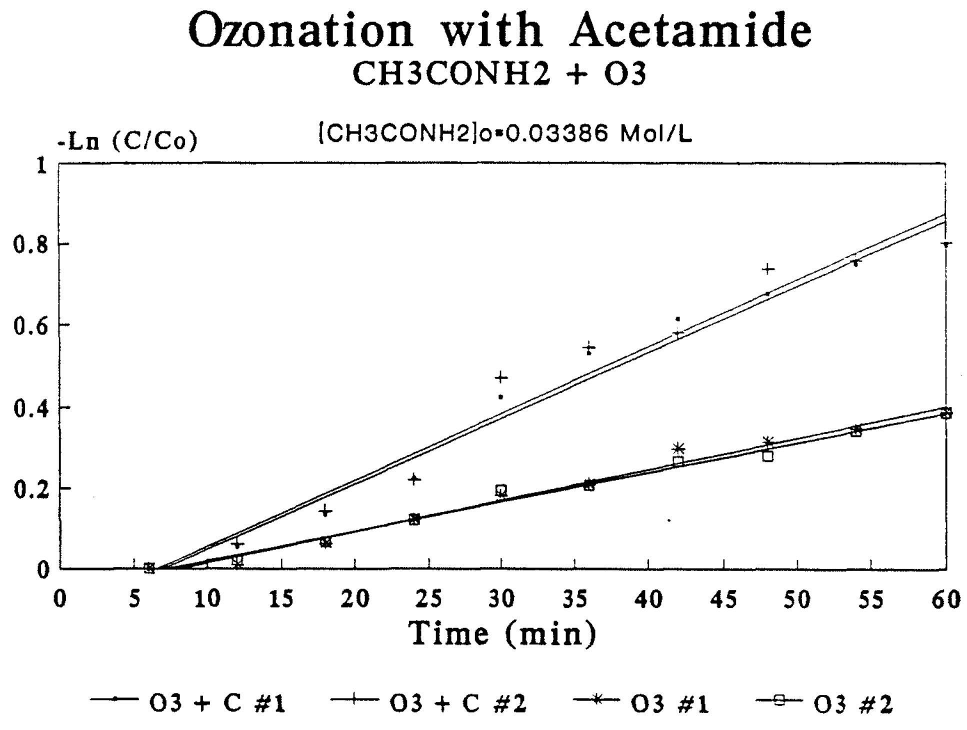


Figure IV-13b First Order Fit for Acetamide

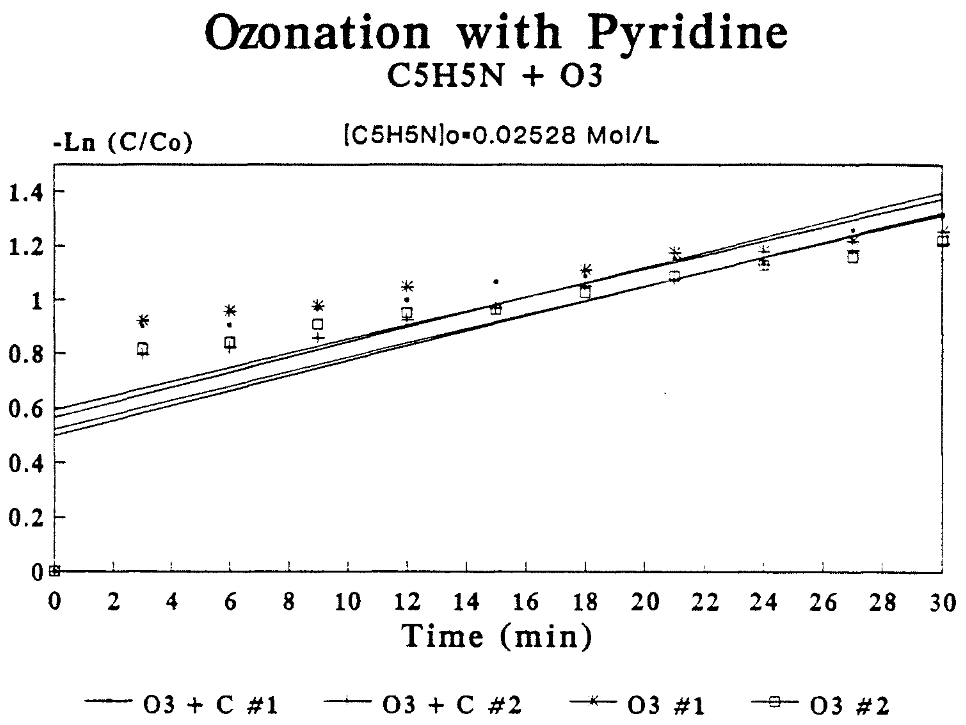


Figure IV-14a First Order Fit for Pyridine

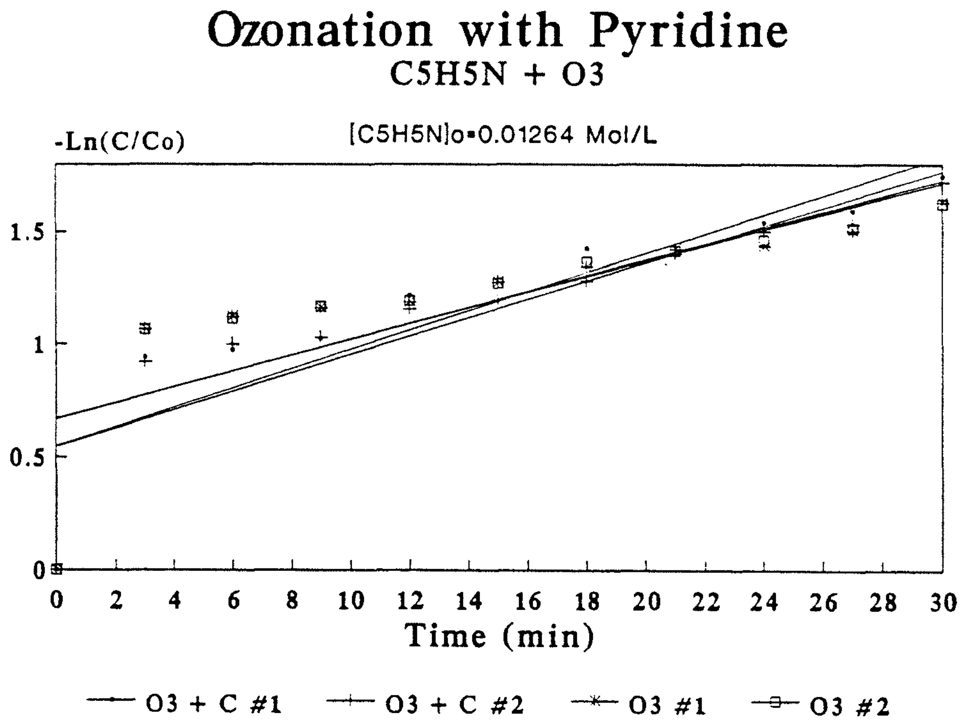


Figure IV-14b First Order Fit for Pyridine

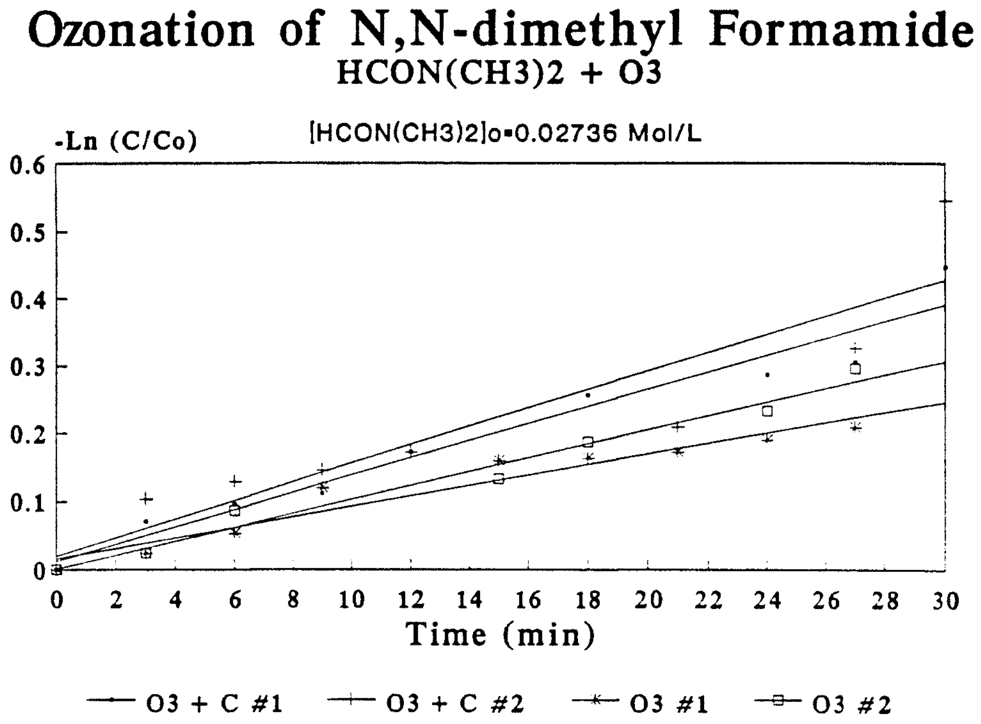


Figure IV-15a First Order Fit for N,N-dimethyl Formamide

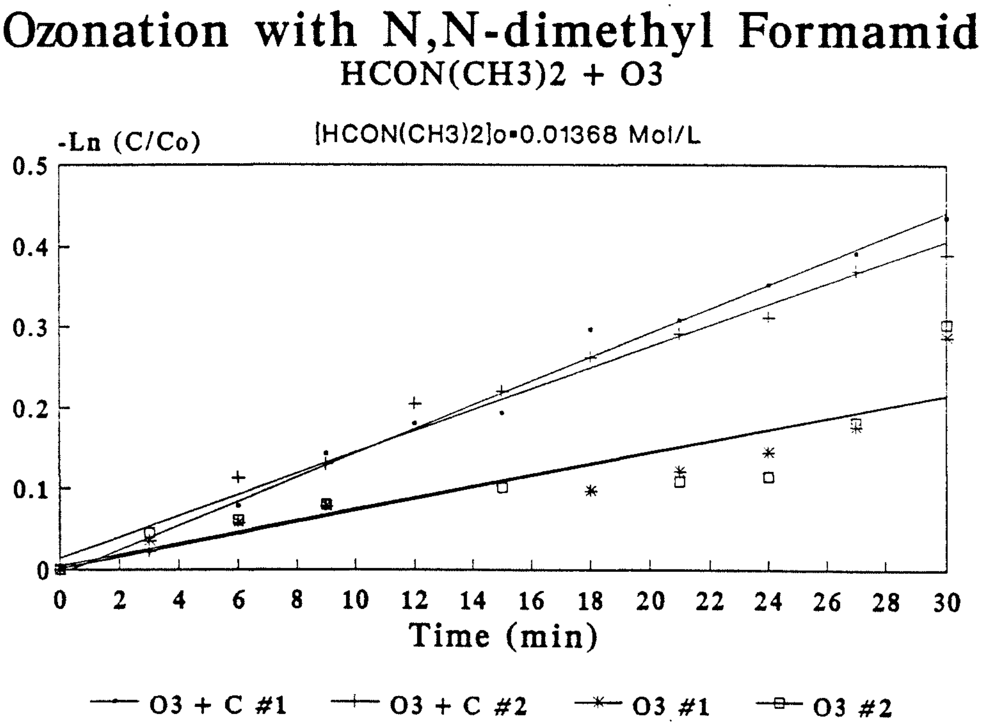


Figure IV-15b First Order Fit for N,N-dimethyl Formamide

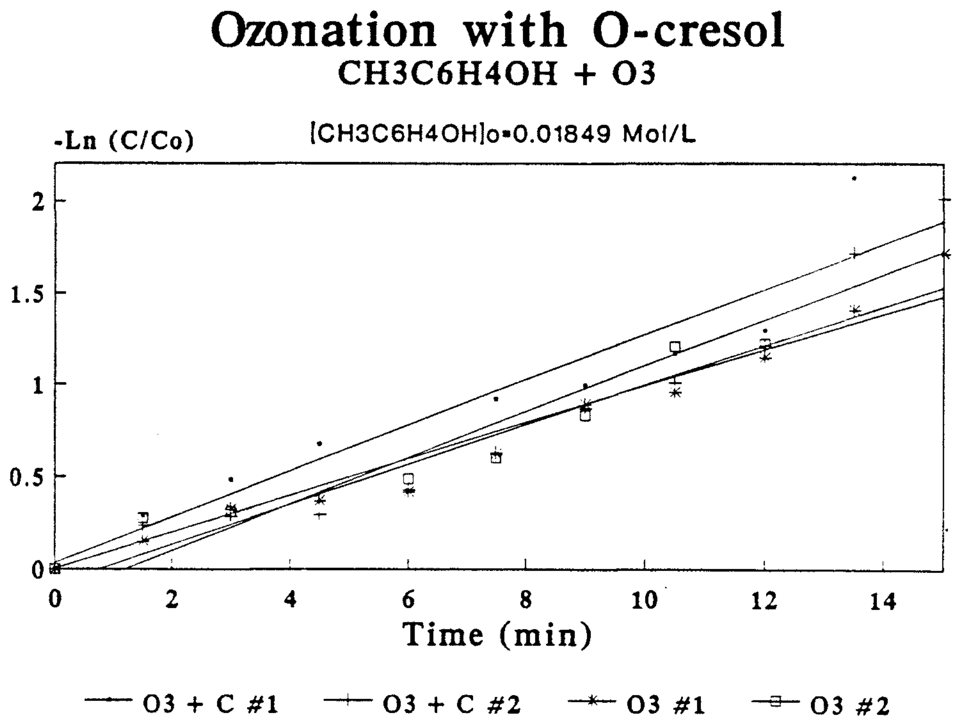


Figure IV-16a First Order Fit for O-Cresol

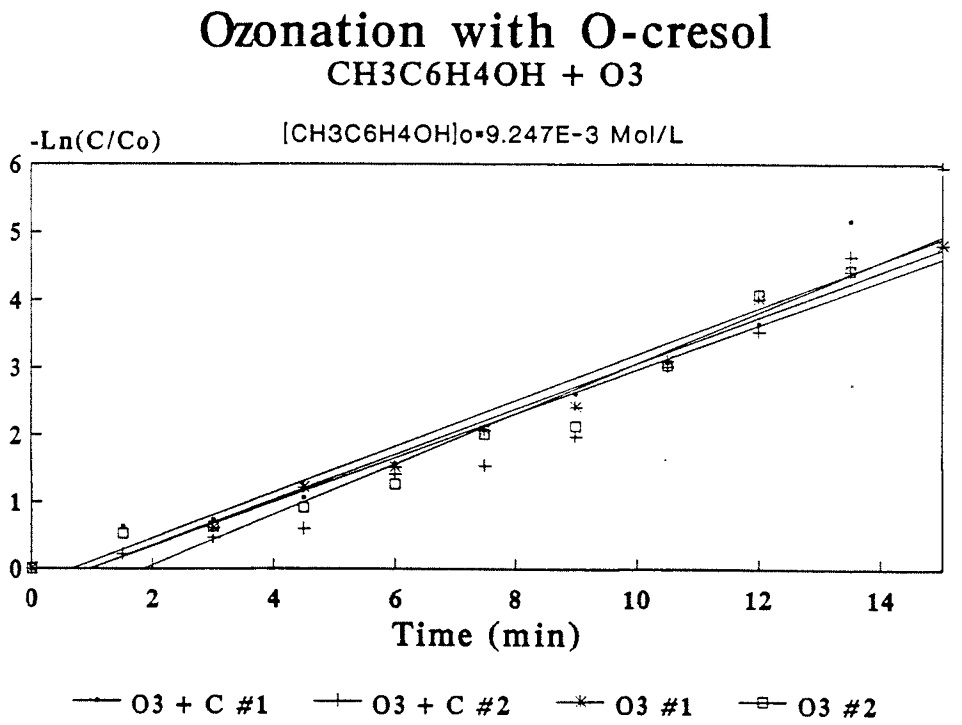
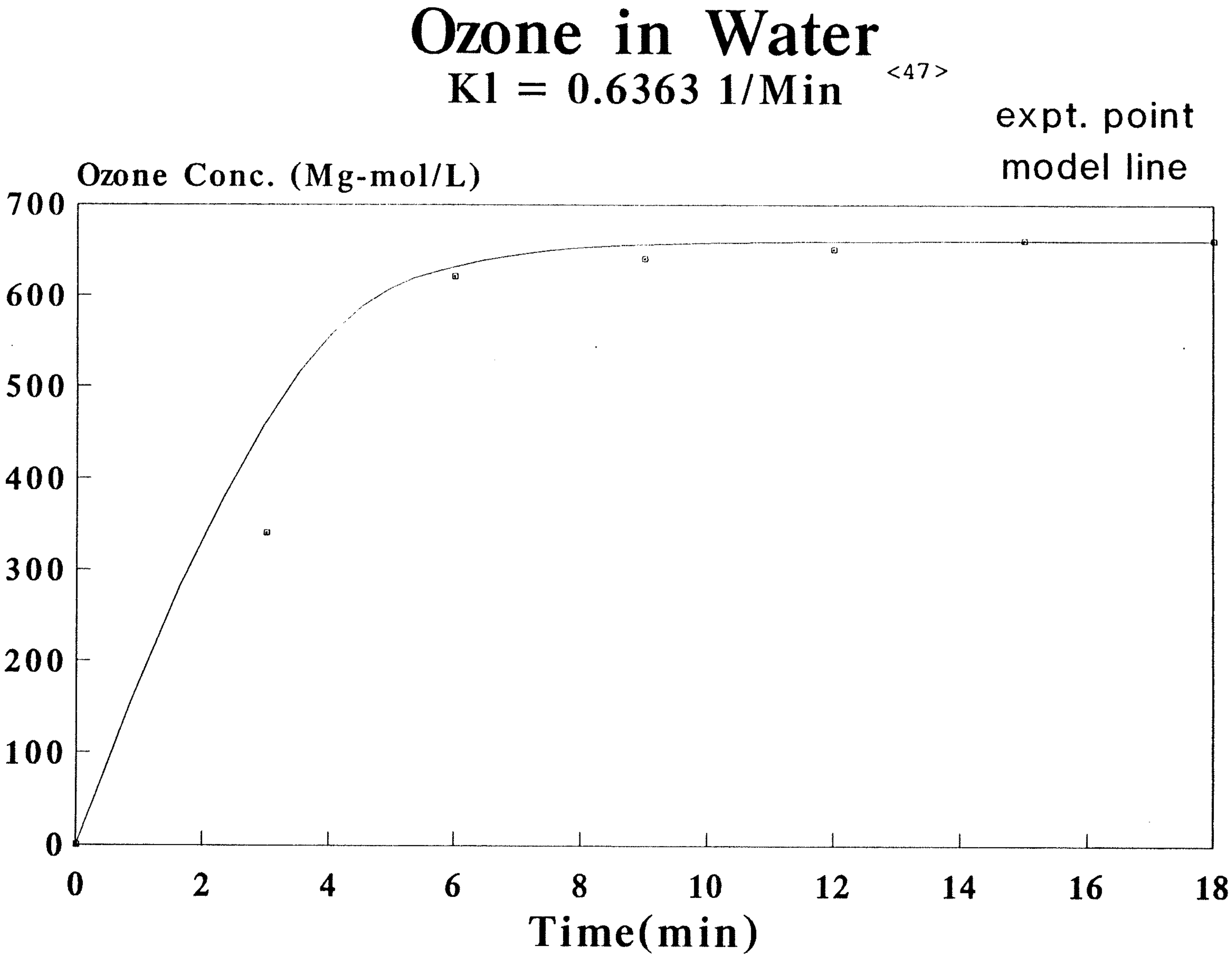


Figure IV-16b First Order Fit for O-cresol



298 K

Figure IV-17 Ozone Concentration at Room Temperature

KINETIC MECHANISM

Ozone decomposition of methanol in water is being analyzed for kinetic reaction modeling. According to recent mechanistic studies, the autodecomposition of ozone may be considered as its most fundamental aqueous phase reaction. The reaction forms many secondary oxidants that catalyze further decomposition. <49,50> When ozone and these active radical products react with methanol, methanol will be decomposed through two pathways: yielding CH_3O and CH_2OH radicals. They finally form carbon dioxide and water. Ozone and other reactive species reacting with methanol and its by-products to form carbon dioxide and water are discussed below.

A. Ozone Decomposition in Water

Hoigne and his coworker reported<29,30> that in pure water the decomposition of ozone is initiated by:

$$O_3 + OH^- \text{--->} O_2^- + HO_2$$

where the superoxide anion O_2^- and the hydroperoxyl radical HO_2 are in equilibrium (pKa at 4.8):

$$HO_2 \quad \text{<==>} O_2^- + H^+$$

During propagation, the superoxide ion immediately transfers an electron to O_3 forming the ozonide anion(O_3^-) and molecular oxygen(O_2)

$$O_2^- + O_3 \text{--->} O_3^- + O_2$$

O_3^- is then protonated and subsequently decomposes to OH radical, which is ready to react indiscriminately with virtually any solute.

$O_3^- + H^+ \Longleftrightarrow HO_3$

$HO_3 \longrightarrow OH + O_2$

The radicals O_2^- and OH act as chain carriers. The production of OH radicals leads to rapid conversion to HO_4 radicals:

$OH + O_3 \Longleftrightarrow HO_4$

Consequently, HO_4 radicals behave as chain carrier reservoirs within the chain cycle slowing down the overall rate of reaction.<50>

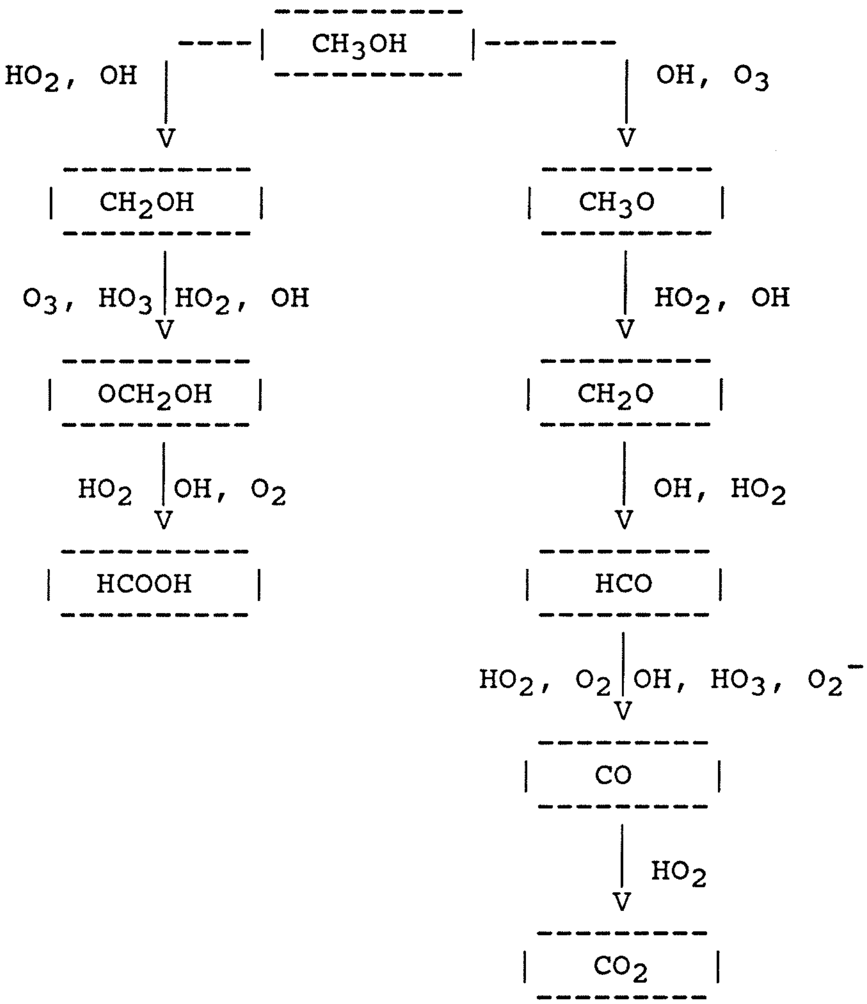
B. Decomposition of Methanol by Ozone and the Active Species

Methanol in water may be destroyed by ozone and the active species such as OH, HO_2, O_2, O_3, HO_3 and O_2^-. The decomposition reaction in liquid phase is divided into two pathways. One is to form CH_2OH, which is further oxidized to formic acid (HCOOH):

$HCOOH \Longleftrightarrow H^+ + HCOO^-$ (Keq = 1.77×10^{-4} Mol/L)<55>

another pathway is to form CH_3O radical. The radical then continues loss of hydrogen to form CH_2O, CHO in order when reacts with the active species. At last the products of the system are carbon monoxide, carbon dioxide and water.

A block diagram is illustrated as follow:



The reaction mechanism system is shown in Table B in Appendix along with the reaction rate constants of each reaction. The description of the reaction mechanism in Table B consists of 64 elementary reactions and 27 species.

C. Thermodynamic Data in Liquid Phase

The thermodynamic data in liquid phase is developed for the species in this oxidation system. The properties of parent species are from references <51,52,53>. For the species which data are not available in literature, their enthalpies of formation, entropies and heat capacities in the liquid phase were calculated from:

1) the group activity method of Benson<54> utilized for the same species in gas phase, using current bond energy data in the literature and computer code THERM.

2) assumptions that the species have the same heats of liquification to known similar hydrocarbon species and their known vapor phase heats of formation.

The thermodynamic properties of species for ozone decomposition of methanol in water system are listed in Appendix -- Table A.

CONCLUSIONS

Decomposition of dilute (500-2000 ppm in water) aniline, acetamide, pyridine, dimethyl formamide, o-cresol, trichloroethylene, chloroform and phenol solutions by ozone (O_3) oxidation and by Integrated Adsorption-Ozonation (charcoal-ozone) systems have been investigated at room temperature. Two reaction configurations: semi-batch and CSTR reactor system were studied with the compounds interest.

Direct ozonation of aniline and o-cresol in water are fast, while direct ozonation of acetamide and dimethyl formamide are relatively slow process. Adding activated carbon significantly accelerated the oxidation of acetamide by a factor of 1.68 and of dimethyl formamide by a factor of 1.59. For amine compounds (aniline and pyridine) as well as o-cresol, the increases were 1.21, 1.13 and 1.17 respectively for the integrated adsorption ozonation process. Experiments on volatile compounds: TCE and chloroform were also performed. Their acceleration factor were 1.14 and 1.11.

Activated carbon is shown to possess catalytic effect when existing in the system of ozone oxidation. Of two forms of activated carbon, investigated PAC was more effective than GAC from the experimental data.

Rate enhancement was observed at higher ozone dosage. The experiment result was consistent with it.

A single compound phenol was chosen to obtain more additional information in CSTR system. In ozone-carbon system, the reaction rate increased a factor of two over direct ozone oxidation alone. Of the two individual treatments alone, ozonation is more effective for phenol degradation in water than charcoal treatment. Further research will be necessary to optimize the system in order to obtain higher efficiency.

It is concluded from the results of this study that charcoal catalyzed ozonation is an effective treatment and can be employed usefully to handle a variety of industrial wastes to remove organic pollutants. The process has demonstrated its applicability, and the effectiveness can be enhanced by further engineering and optimizing the process.

REFERENCES

<1> Chermisinoff, P.N. and Morresi, A.C., Carbon Adsorption Applications, Carbon Adsorption Handbook, Ann Arbor Science Publishers, Inc. (1978)

<2> McKay, G., and McAleavey, G., Ozonation and Carbon Adsorption in a Three-phase fluidized Bed for Color Removed from Peat Water, Chem. Eng. Res. Des. Vol.66, 531-36, Nov. (1988)

<3> Birdsalt, Jenkins and Spadinger, Analytical Chemistry, Vol.24, 662, (1952)

<4> Staehelin, J. and Hoigne, J.; Decomposition of ozone in Water: Rate of Initiation by Hydroxide Ions and Hydrogen Peroxide; Environ. Sci. Technol., Vol.16, 676-81, (1982)

<5> Glaze, W.H.; Drinking Water Treatment with Ozone, Environ. Sci. Technol., Vol.21, 224-30, (1987)

<6> Hoigne, J. and Bader H.; Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water--I; Water Res.; Vol.17, 173-83, (1983)

<7> Levenspiel, Chemical Reaction Engineering, 2nd Ed., John Wiley & Sons, Inc., (1972)

<8> Rice, R.G., Ozone Oxidation Products -- Implications for Drinking Water Treatment, Biohazards of Drinking Water Treatment, Lewis Publishers, (1989)

<9> Singer, P., American Water Works Association Journal, Vol.82, No.10, 78-88 (1990)

<10> Stopka, K., Pollution Engineering, Vol.22, No.9, 101, (1990)

<11> Ozone Is Primary Disinfectant, Water/Engineering & Management, Vol.137, No.6, 19, (1990)

<12> Echols, J. and Mayne, S., ASHRAE Journal, Vol.32, No.6, 34, (1990)

<13> Echols, J. and Mayne, S., Chemical Engineering, Vol.97, No.5, 163, (1990)

<14> Wang, Y., Water Research, Vol.24, No.2, 185-90, (1990)

<15> Jacangelo, J.G.; Patania, N.L. and Kevin, M.; Ozonation: Assessing its Role in the Formation and Control of Disinfection By-products; American Water Works Association Journal, Vol.81, No.8, 74-84, (1989)

<16> Ozone Technology Removes Organics from Groundwater, American Water Works Association Journal, Vol.81, No.6, 124, (1989)

<17> Glaze,W.H.; Koga, M. and Cancilla, D.; Ozonation Byproducts. Improvement of an Aqueous-phase Derivatization Method for the Detection of Formaldehyde and other Carbonyl Compounds Formed by the Ozonation of Drinking Water; Environ. Sci. & Technol.; Vol.23, No.7, 838-47, (1989)

<18> Oehlshlaeger, H.F., Reactions of Ozone with Organic Compounds, Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, (1978)

<19> Gould, J.P. and Weber, W.J., Oxidation of Phenols by Ozone; Jour. Water Poll. Control Fed., Vol.48, No.1, 47, (1976)

<20> Buhler, R.E.; Staehelin, J. and Hoigne, J.; Ozone Decomposition in Water Studied by Pulse Radiolysis; J. of Phys. Chem., Vol.88, 2560-4, (1984)

<21> Hoigne, J. and Bader, H., Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water--II, Water Res., Vol.17, 185-94, (1983)

<22> Giamalva, D.H.; Church, D.F. and Pryer, W.A.; Kinetics of Ozonation. 5. Reactions of Ozone with Carbon-Hydrocarbon Bonds, (1986)

<23> Genhringer, P.; Proksch, E.; Szinovats, W. and Eschweiler, H.; Decomposition of Trichloroethylene and Tetrachloroethylene in Drinking Water by a combined Radiation/Ozone Treatment; Wat. Res.; Vol.22, No.5, 645-46, (1988)

<24> Eisenhauer, H.R.; Jour of Wat. Poll. Control Federation, Vol.40, No.11, 1887, (1968)

<25> Rice, R.G., Ozone for the Treatment of Hazardous Materials, AICHE Symposium Series, Water, (1980)

<26> Weiss, J., Transactions Faraday Society, Vol.31, 668, (1935)

<27> Alder, G.A. and Hill, G.R., Jour. Ameri. Chem. Soc., Vol.72, 1884, (1950)

<28> Preley, M., Water Research, Vol.10, 361-65, (1976)

<29> Buhler, R.E. and Hoigne, J., Ozone Decomposition in Water Studied by Pulse Radiolysis. 1. HO_2/O_2^- and HO_3/O_3^- as Intermediates, J. Phys. Chem. Vol.88, 2560-64, (1984)

<30> Staehelin, J. and Hoigne, J., Ozone Decomposition in Water Studied by Pulse Radiolysis. 2. OH and HO_4 as Chain Intermediates, J. Phys. Chem., Vol.88, 5999-6004, (1984)

<31> Hoigne, J. and Bader, H., The Role of Hydroxyl Radical Reactions in Ozonation Process in Aqueous Solutions, Water Res., Vol.10, 377-86, (1976)

<32> Maloney, S.W.; Suffet, T.H. and Bancroft, K.; Ozone-GAC Following Conventional US Drinking Water Treatment, American Water Works Association Jour., Vol.77, 66-73, Aug. (1985)

<33> Glaze, W.H. and Wallace, J.L., Americ. Water Association Jour., Vol.76, 68-75, Feb. (1984)

<34> Ozone Contact Pretreatment, Water/Engineering & Management, Vol.137, 18, Nov. (1990)

<35> DeWaters, J.E. and Digiano, F.A., The Influence of Ozonated Natural Organic Matter on the Biodegradation of a Micropollutant in a GAC Bed, Americ. Water Works Association Jour., Vol.82, 69-75, Aug. (1990)

<36> Smith, J.M., Chemical Engineering Kinetics, McGraw Hill Book Co.

<37> Skoog, D., Principles of Instrumental analysis, 3rd Ed., Saunders College Publishing, (1985)

<38> Battino, R.; Rettich, T.R. and Tominage, T.; The Solubility of Oxygen and Ozone in Liquids, J. Phys. Chem. Ref. Data, Vol.12, No.2, (1983)

<39> Standard Methods for the Examination of Water and Wastewater, 15th Ed., APHA, Washington, D.C. (1980)

<40> Bader, H. and Hoigne, J., Determination of Ozone in Water by the Indigo Method, Water Resources, Vol.15, 449, (1981)

<41> Bozzelli, J.W.; Experiment on "Atmospheric Oxidants--5. Ozone"; Handout for NJIT Course: Air Pollution Analysis, Chem 662, (1990)

<42> Harrington, G.W.; Organics' Adsorbability after ozonation; Public Works; Vol.120, 205-6, Sep. (1989)

<43> Kool, H.J.; Van Kreeiji, C.P. and Hrubec, J.; Mutagenic and Carcinogenic Properties of Drinking Water, Water Chlorination Chemistry, Environmental Impact and Health Effects; Vol.5, 187-206, Lewis Publishers, Inc., (1985)

<44> Bailey, P.S.; Ozonation in Organic Chemistry, Vol.1, Olefinic Compounds; Academic Press, Inc., New York, N.Y., (1978)

<45> Taube, H. and Bray, W.C.; Chain Reactions in Aqueous Solutions Containing Ozone, Hydrogen Peroxide and Acid; Jour. of Am. Chem. Soc.; Vol.62, 3553-73; (1940)

<46> Fogler, H.S.; Elements of Chemical Reaction Engineering; Prentice-Hall, Inc.; New Jersey, (1986)

<47> Khan, S.R.; Huang, C.R.; Bozzelli, J.W., Park, A.Y. and Shih, T.; Oxidation of 2-Chlorophenol Using Ozone and Ultraviolet Radiation, (1987)

<48> Jain, K.K. and Bryce, A.J.; Feasibility of Munitions Wastewater Treatment by Adsorption-oxidation; Carbon Adsorption Handbook; Ed. by Chermisinoff, P.N. and Ellerbusch, F.; Ann Arbor Science Publishers, Inc.; (1978)

<49> Hoigne, J.; Mechanisms, Rates and Selectivities of Oxidations of Organic Compounds Initiated by the Ozonation of Water; Handbook of Oozne Technology and Application; Ed. by Rice, R.G. and Netzer, A.; Ann Arbor Science, Ann Arbor, MI.; (1982).

<50> Chelkowska, K. and Grasso, D.; Early Aqueous Ozone Decomposition - Progeny Speciation; (1989).

<51> Stull, D. R.; Westrum, Jr. and Sinke,; The Chemical Thermodynamics of Organic Compounds; Wiley, (1969)

<52> Pedley, J.B.; Naylor and Kirby; Thermochemical Data of Organic Compounds;

<53> Domalski, E.S.; Evans, W.H. and Hearing, E.D.; Heat Capacities and Entropies of Organic Compounds in the Condensed Phase; J. of Phys. Chem. Ref. Data; Suppl.1; (1984)

<54> Benson, S.W.; Thermochemical Kinetics; 2nd Ed.; Wiley; New York, (1976)

<55> Boikess, R.S. and Edelson, E.; Chemical Principles; 3rd Ed.; Harper & Row, Publishers; New York; (1985)

APPENDIX

Table A

Thermodynamic Properties of Ozone Decomposition of Methanol in Water

Units: cal

Species	Hf(298)x10^3	S(298)	Cp(300)
OH^-	-54.95	-2.51	17.03
H_2O	-68.13	16.72	18.07
O_3	23.59	28.38	19.46
O_2^-	-32.25	6.36	17.34
HO_2	-7.01	26.35	18.42
O_2	-10.51	20.63	17.07
O_3^-	1.85	14.45	19.73
HO_3	6.59	36.47	19.44
OH	-1.02	15.50	17.21
H^+	0.00	0.00	15.02
HO_4	21.29	45.87	23.14
H_2O_2	-32.53	55.69	10.33
HO_2^-	-60.94	8.34	18.26
CH_3OH	-57.02	30.30	19.39
CHOOH	-101.52	30.82	23.67
CH_2O	-32.86	22.53	16.31
CH_3O	-4.00	33.65	18.37
HCO	5.24	23.93	16.13
$HCOO^-$	-122.22	32.02	25.14
$HCO(O)_2H$	-56.22	42.57	28.98
CH_2OH	-15.00	34.46	18.37

Table B

Reaction Mechanism for Ozone Decomposition of Methanol in Water

Reaction	k (cm^3/mol-sec)	Sourc
1. $O_3 + OH^- = O_2^- + HO_2$	7.00E04	a,
2. $HO_2 = O_2^- + H^+$	7.61E05	c
3. $O_2^- + H^+ = HO_2$	4.80E13	d
4. $O_2^- + O_3 = O_3^- + O_2$	1.60E12	a
5. $O_3^- + H^+ = HO_3$	5.20E13	a
6. $HO_3 = H^+ + O_3^-$	3.70E02	a
7. $HO_3 = OH + O_2$	1.40E05	a
8. $OH + O_3 = HO_4$	2.00E12	a,
9. $HO_4 = HO_2 + O_2$	2.80E04	a
10. $OH + O_2^- = OH^- + O_2$	1.00E13	a
11. $HO_3 + O_2^- = OH^- + O_2 + O_2$	1.00E13	a
12. $HO_4 + O_2^- = OH^- + O_3 + O_2$	1.00E13	a
13. $OH + OH = H_2O_2$	5.00E12	a
14. $OH + HO_3 = H_2O_2 + O_2$	5.00E12	a
15. $HO_3 + HO_3 = H_2O_2 + O_2 + O_2$	5.00E12	a
16. $HO_4 + HO_4 = H_2O_2 + O_3 + O_3$	5.00E12	a
17. $HO_4 + OH = H_2O_2 + O_3$	5.00E12	a
18. $HO_4 + HO_3 = H_2O_2 + O_3 + O_2$	5.00E12	a
19. $H_2O_2 = HO_2^- + H^+$	1.12E-1	c
20. $HO_2^- + H^+ = H_2O_2$	5.00E13	c
21. $HO_2^- + O_3 = OH + O_2^- + O_2$	2.20E09	e

22. $HO_4 + HO_2 = O_3 + O_2 + H_2O$	1.00E13	a
23. $H_2O = H^+ + OH^-$	2.50E-5	f
24. $H^+ + OH^- = H_2O$	1.40E14	f
25. $CH_3OH + OH = CH_3O + H_2O$	2.85E11	g
26. $CH_3OH + O_3 = CH_3O + HO_3$	3.38E08	g
27. $CH_3OH + HO_2 = CH_3O + H_2O_2$	2.87E01	g
28. $CH_3OH + OH = CH_2OH + H_2O$	2.58E11	g
29. $CH_2OH + HO_2 = OCH_2OH + OH$	1.81E13	g
30. $CH_2OH + HO_2 = H_2O_2 + CH_2O$	6.05E12	g
31. $CH_2OH + HO_3 = OCH_2OH + HO_2$	1.81E13	g,h
32. $CH_2OH + O_3 = OCH_2OH + O_2$	6.21E08	g,i
33. $CH_2OH + OH = H_2O + CH_2O$	1.21E13	g
34. $OCH_2OH + O_2 = HO_2 + HCOOH$	4.05E10	g,j
35. $OCH_2OH + OH = H_2O + HCOOH$	4.05E10	g,j
36. $OCH_2OH + HO_2 = H_2O_2 + HCOOH$	4.05E10	g,j
37. $HCOOH = H^+ + HCOO^-$	8.60E06	k,f
38. $HCOO^- + H^+ = HCOOH$	5.00E13	k,f
39. $HCOOH + OH^- = HCOO^- + H_2O$	3.00E09	l
40. $HCOOH + OH = HCOO + H_2O$	1.45E11	g
41. $HCOOH + HO_2 = HCOO + H_2O_2$	1.43E11	g,m
42. $HCOO + O_2^- = O_2 + HCOO^-$	1.00E13	n
43. $HCOO^- + O_3 = HCO_3^- + O_2$	1.60E12	o
44. $HCOO^- + HO_2 = HCO_3^- + OH$	1.60E12	o
45. $HCOO^- + HO_3 = HCO_3^- + HO_2$	1.60E12	o
46. $HCO_3^- + OH^- = CO_3^{-2} + H_2O$	6.00E12	l
47. $HCO_3^- + H^+ = H_2CO_3$	4.70E13	k,f
48. $H_2CO_3 = H^+ + HCO_3^-$	8.00E06	k,f

49. $H^+ + CO_3^{-2} = HCO_3^-$	4.70E13	p
50. $HCO_3^- = H^+ + CO_3^{-2}$	2.36E03	q
51. $OH + CO_3^{-2} = OH^- + CO_3^-$	4.20E11	e
52. $OH + HCO_3^- = OH^- + HCO_3$	1.50E10	e
53. $CH_3O + HO_2 = H_2O_2 + CH_2O$	1.51E11	g
54. $CH_3O + OH = H_2O + CH_2O$	9.05E12	g
55. $CH_2O + OH = H_2O + HCO$	3.04E12	g
56. $CH_2O + HO_2 = H_2O_2 + HCO$	2.27E03	g
57. $HCO + HO_2 = HCOO + OH$	1.51E13	g
58. $HCO + O_2 = HCO_3$	1.21E12	g
59. $HCO + HO_3 = HCO_2 + HO_2$	1.51E13	g, r
60. $HCO + HO_2 = CO + H_2O_2$	9.06E12	g
61. $HCO + OH = CO + H_2O$	1.51E13	g
62. $HCO + O_2 = CO + HO_2$	1.94E12	g
63. $HCO + O_2^- = CO + HO_2^-$	1.94E12	g,s
64. $CO + HO_2 = CO_2 + OH$	1.43E14	g

Sources

a) References <30> and <50>

b) Reference <29>

c) Desai, V.Y. and Bozzelli, J.W.; Aqueous Phase Kinetic Model Computer Integration; (1989)

d) Bielski, B.H.j.; Cabell, D.E.; Arudi, R.L. and Ross, A.B.; Reactivity of HO_2/O_2^- Radicala in Aqueous Solution; J. Phys. Chem. Ref. Data; Vol.14, No.4, 1063,(1985)

e) Reference <4>

f) Hague, D.N.; Fast Reactions; London, New York, Wiley-Interscience, (1971)

g) for $OH + OH = H_2O_2$;

liquid phase: k=5.00E12 cm^3/mol-sec

gas phase: k=(2.50E17)*(4.0E-5)=1.0E13 cm^3/mol-sec at 1 atm

R = kg / kl = 2

then: $kl = kg / R = \frac{kg}{2}$

where kg from NIST

h) same as Equation (29)

i) from NIST: $CH_3O + O_3 \text{ ---> products}$ kg < 1.2E09

j) from NIST: $CH_3CH_2O + O_2 = CH_3CHO + HO_2$ kg=8.10E10

k) Boikess, R.S. and Edelson, E; Chemical Principles; 3rd Ed.; Harper & Row, Publishers; New York; (1985)

l) Gardiner, W.C.; Rates and Mechanisms of Chemical Reactions;

m) from Equation (40): $HCO_2H + OH \text{ ---> product}$

A: 2.89E11   Ea=0

for Equation (41): Ea=7 then kg=2.86E11

n) from $OH + O_2^- \text{ ---> } OH^- + O_2$ kl=1.00E13

o) from $OH + O_2^- \text{ ---> } O_3^- + O_2$ kl=1.60E12

p) from $H^+ + HCO_3^- = H_2CO_3$ kl=4.70E13

q) Ka = kf / kr

pKa = 10.3, kf = 4.7E13, then: kr = 2.36E+3

r) from $HCO + HO_2 \text{ ---> } HCOO + OH$ kl = 1.51E13

s) from $HCO + O_2 \text{ ---> } CO + HO_2$ kl = 1.94E12