22. Charles E. Mauk, Ph.D.

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OCT 1 1976

AFFIDAVIT OF CHARLES E. MAUK, PH.D.
ON BEHALF OF HOUSTON RESEARCH, INC.

Charles E. Mauk, having been duly sworn, deposes and says:

My name is Charles E. Mauk, and I reside in Houston, Texas. I am a graduate of the University of Houston with B.S.,M.S. and Ph.D. degrees in Chemical Engineering. I am a registered professional engineer in Texas, No. 29635. I have been employed by Houston Research, Inc., for twelve years and I am now Manager of Special Projects Section. I have been associated with Houston Research's ozone activity since its inception in 1970. I have been co-inventor on U.S. patent 3,920,547 for the destruction of cyanides in water by ozone-ultraviolet. I am co-inventor for patent applications for the destruction of pollutants in water, refractory to oxidation, by ozone-ultraviolet. The application numbers are: USA 572453; France 76/13453; West Germany P2618338.0; United Kingdom 16441/76. I have co-authored ten papers and reports available to the public on the oxidative destruction of various pollutants in water by ozone with ultraviolet light. A copy of my curriculum vitae is attached hereto as Exhibit A. Copies for the ozone-ultraviolet papers are attached as Exhibits B-E.

Houston Research, Inc. is a privately owned company engaged in contract research, development, engineering and system sales, primarily, but not exclusively in wastewater treatment. The company was founded in 1952,and activity in the area of ozone treatment began in 1970. Ozone, in conjunction with ultraviolet



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light, has been investigated extensively at Houston Research for the destruction of vinyl chloride in exhaust gas, and a patent application has been filed as a result of this work. $O_3$-UV for water treatment has been applied to dozens of wastewater constituents, with the resulting patents and publications memtioned in the first paragraph and is the background for the OXYPHOTOLYSIS ($O_3$-UV) wastewater treatment systems marketed by Houston Research.

HR also markets prototype wastewater treatment systems, and two examples are shown as Exhibits F and G. Exhibit F shows a coagulation-sedimentation unit used to clean water used to wash garbage trucks. Exhibit G shows the above-the-ground portion of a system used to clean water from car washing operations. The water is later reused.

Exhibit H shows a small OXYPHOTOLYSIS unit supplied by HR to the Army Medical R&D command for treating hospital wastewater. Fabrication of this unit was completed in a total of only three months.

Exhibit I shows a large OXYPHOTOLYSIS unit supplied by HR to Hughes Tool Company. Less than nine months are required for all laboratory work, engineering design, fabrication, delivery, and start-up operations. This unit incorporates three wastewater treatment operations: 1) pH control on one water stream, 2) copper pyrophosphate removal on a second water stream, and 3) oxidation of cyanide waste in the third water stream by ozone-ultraviolet.

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The reaction units in the HR ozone-ultraviolet laboratory work are liquid phase batch, continuously gas sparged, because this type of reactor permits many data points to be obtained at various times during the run, resulting in convenience and savings intime. However, in a full scale treatment system, flow reactors of the same configuration will be used. A mixer speed was used which would result in a mixing energy input of 20 horsepower per 1000 gallons in solution. The mechanical configuration of a reactor is shown in Exhibit J. This configuration satisfies existing correlations of power input, mass transfer coefficients, and interfacial area in a most predictable and reproducible fashion. Size scaleup from bench to pilot to full scale can be performed without difficulty for single stage or multistage systems. Two reactors were used during the work, both of the same mechanical configuration. The first was a 10 liter acrylic plastic reactor, stirred at 700 RPM, containing two lamps, each inserted vertically through the top and bottom of the reactor in direct contact with the liquid. Each lamp is a General Electric germicidal G15T8, a 15 watt low pressure mercury lamp with the major part of the ultraviolet energy emitted at a wavelength of 2537 Angstroms. About 60% of the electrical power to the lamp is converted to ultraviolet light in the proper frequency range, but only 74% of the ultraviolet light is transmitted through the glass walls of the lamp. The lamp is normally submerged in the liquid in the reactor for two-thirds of its length. This results in a useful ultraviolet dosage of 0.44 watts per liter

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of reactor liquid for each lamp used. The second is a 21.05 liter stainless steel reactor, stirred at 515 RPM, having two quartz lamp wells through the top. Into the wells are inserted Canrad-Hanovia high pressure mercury vapor lamps with quartz envelopes. Each lamp is completely below the liquid level. Assuming negligible attenuation by the quartz well, the 200 watt lamp contributes 0.50 watts per liter of useful UV light, and the 450 watt lamp contributes 3.97 watts per liter of useful UV light.

Of interest to the study of destruction in water of polychlorinated biphenyls (PCB) by $O_3$-UV is the study of pentachlorophenol because of the similar polychlorinated ring structure. Pentachlorophenol has a relatively high water solubility (80 mg/ℓ) and this is sufficient concentration to allow the analysis of the water for total organic carbon (TOC) and for inorganic chloride. These analyses show that as pentachlorophenol is destroyed by $O_3$-UV, all of the chlorine in the molecule is converted to inorganic chloride, and all of the carbon in the molecule is converted to carbon dioxide.

Samples of water from HR studies on pentachlorophenol, dichlorobutane, dichlorobenzene, chloroform and DDT treated by $O_3$-UV have been analyzed by Gas Chromatograph (GC) with an electron capture detector, which is extremely sensitive to chlorinated organic compounds. In none of these analyses was any chlorinated organic materials detected, other than the original molecules residual from incomplete treatment.





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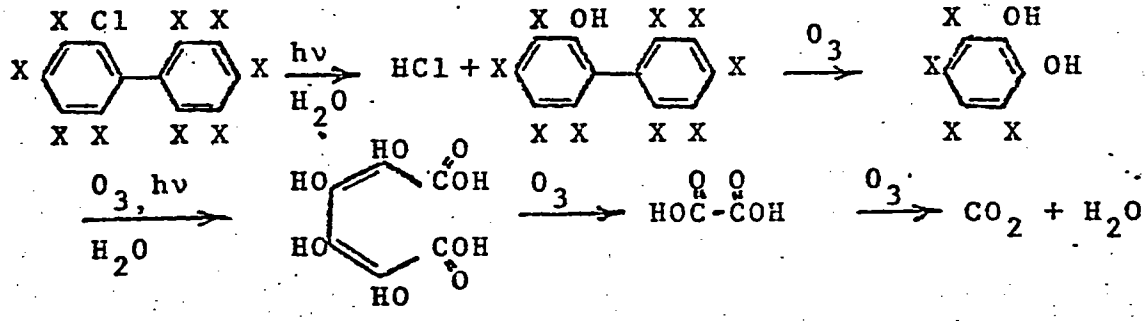
In the environment, PCB degrades via successive dechlorination steps before the biphenyl structure degrades, and this is additional evidence to support the following mechanism, postulated to be similar to that of pentachlorophenol,



For our direct experimentation, the PCB used was Aroclor 1254, primarily a mixture of isomers of pentachlorobiphenyl. Exhibit K shows the dissapearance of PCB by GC analysis. The original charge was at the 500 microgram/liter PCB level added to the water as a solution in methanol. The resulting dispersion in water was at about eight times the solubility of PCB in water. Since only the PCB in solution was being treated at any one time, the curve is also controlled by the rate at which PCB is going into solution. If the original charge had been within the solubility limit, the disappearance curve would have indicated a more effective treatment. Even so, with ozone added at the rate of 4.1 mg/(ℓ-min) the PCB concentration was reduced to 33 microgram/liter before the run was arbitrarily stopped.

To confirm a more effective treatment at lower concentrations, additional runs were made with the original charge





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at the 12 microgram/liter PCB level added to the water as a solution in methanol. The most effective of these later runs was made at 2.05 mg/(ℓ-min) ozone (half the previous dosage) and 0.88 watts/ℓ of useful UV light, one fifth of the previous intensity. When the first sample was analyzed, taken at one hour into the run, the PCB by GC/EC was found to be 0.1 microgram/liter. Since this was the limit of detection for our analytical set-up, this level may have been reached considerably before the one hour sample was taken.

In addition, total organic carbon analyses (TOC) were made on the samples. Although PCB concentration was too low to contribute a detectable amount to TOC, the methanol (solvent for PCB) in the water had a TOC equivalent to 80 mg/ℓ. By one hour, when the PCB had been reduced to 0.1 microgram/liter, ozone had been added into the solution to a total of only 35% of the theoretical requirement to oxidize methanol.

In early 1976, Versar, Inc. completed report EPA 560/6-76-006 under contract to USEPA. This report contains estimates of cost for PCB treatment by $O_3$-UV based on information made available to Versar by Houston Research in mid 1975. Our work on $O_3$-UV has continued, and we now have available additional information to make much more exact estimates of costs. In the cost calculations, the reaction rate is based on the batch run data, showing one hour to drop the PCB concentration to 0.1 microgram/liter, although we have reason to believe that the reaction is faster than this. However, the design basis is to



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reduce PCB from 50 microg./ℓ to 1.0 microg./ℓ, to be consistent with the Versar report. In addition, the design basis includes the ozone demand of 30 mg/ℓ COD, to be consistent with the Versar report. This includes a considerable safety factor, since our experimentation shows that the PCB can be destroyed while supplying ozone to destroy as little as 35% of the other organic material present.

The resulting design for treatment of PCB by $O_3$-UV calls for a multi-staged flow system. The projected costs, based on ozone generation in oxygen, are given in Exhibit L. Carbon plus pre-treatment costs are summed from Tables 3.2.2-1, 3.2.2-2, 3.3.1-2, and 3.3.1-3 of the Versar report. Exhibit L shows that $O_3$-UV has a cost advantage over carbon pre-treatment, both in capital and pre-treatment cost.

The HR OXYPHOTOLYSIS process can also be effective in destroying some of the important substitutes for PCB, so that a system installed to treat wastewater containing PCB will continue to be useful when other materials have been substituted in the various PCB uses. In askarels, chlorobenzenes have been substituted for part of the PCB, and $O_3$-UV has effectively treated dichlorobenzene, as documented in Exhibit D.

One of the leading possible substitute classes is phthalate ester. We can be sure that $O_3$-UV will be an effective treatment agent because of similarities in structure to materials successfully treated in previous work. Malathion and Baygon with ester structures, and Baygon with a non-chlorinated ring struc-



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ture, have been effectively treated (Exhibit E).

Another possible substitute class is diaryl sulfonate. This has a structure similar to alkyl nitrobenzene sulfonic acid. Treating a solution whose organic content was almost entirely alkyl nitrobenzen sulfonic acid at a total organic carbon (TOC) level near 4000 mg/l, the TOC was reduced by 59% by $O_3$-UV under unoptimized conditions, and under similar conditions, the TOC was reduced only 10% by ozone alone. From this we can conclude that diaryl sulfonate can be treated to an environmentally acceptable level by $O_3$-UV under optimized conditions.

Hydrogenated paraffin oils are long chain saturated fatty acids similar to palmetic acid. Palmetic acid has been successfully treated by HR, and the results are documented in Exhibit B. We can expect that hydrogenated paraffin oils will be as easy to treat.

Mineral oil, consisting of saturated and cyclic hydrocarbons, has a strong similarity to mixed waste oil in water treated by OXYPHOTOLYSIS. The waste oil was reduced from a TOC level of 17 mg/l to the limit of detection of the TOC analyzer. The same success can be expected for treating mineral oil in water by $O_3$-UV.

We have no direct evidence of the destruction of dimethyl silicone oil by $O_3$-UV, however, we have oxidized by $O_3$-UV other molecules containing methyl groups attached to carbon, to oxygen, and to nitrogen. In addition, Bailey's summary of ozone reactions in Ozone in Water Treatment (ed. by Evans),

reports ozone alone as able to cleave silicon-hydrogen, silicon-silicon, and silicon-carbon bonds. We may infer from this that OXYPHOTOLYSIS will successfully treat silicone oils in water.

Butylated monochlorodiphenyl oxides are in what is probably the most important class of substitutes for PCBs because of direct replacement possibilities. Bailey (Loc. Cit.) reports that the furan structure is very susceptible to destruction by ozone alone. HR has successfully treated several compounds with ring, chlorinated ring and alkyl ring structures by $O_3$-UV. Based on this evidence we can conclude that OXYPHOTOLYSIS will successfully treat butylated monochlorodiphenyl oxides.

In summary, this affidavit presents evidence for our belief that:

1) $O_3$-UV converts PCB to innocuous products; 2) $O_3$-UV can reduce PCB to a concentration less than 0.1 micrograms/liter, 3) Because of its modular (staged) construction, an $O_3$-UV system could be designed to treat to an effluent level of 1.0 microgram/liter PCB, and later have additional modular stages added to further reduce the PCB in the effluent to 0.1 microgram/liter if the discharge specifications are lowered;





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4) $O_3$-UV systems to treat PCB in wastewater can be supplied in much less than one year; 5) $O_3$-UV will just as successfully treat future substitutions for PCB.

Charles E. Mauk
Manager, Sepcial Projects
Houston Research, Inc.

Subscribed and sworn to before
me this 15th day of September, 1976

Notary Public



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Exhibit A

PERSONNEL DATA

1. Name: Charles E. Mauk, PE Texas #29635

2. Title:

   a) Manager, Special Projects
   b) Chief Engineer
   c) Computer Specialist

3. Education:

   a) B.S. in Chemical Engineering, 1959, University of Houston
   b) M.S. in Chemical Engineering, 1961, University of Houston
   c) Ph.D. in Chemical Engineering, 1964, University of Houston

4. Chronology of Experience:

   a) March 1948-August 1952 and June 1954-September 1955; Laboratory Technician, Nyotex Chemicals, Inc., Houston, Texas.
   b) August 1952-June 1954: U. S. Army (see service record below).
   c) September 1955-June 1959: Undergraduate in Chemical Engineering, University of Houston.
   d) August 1958-November 1958 and January 1959-February 1959: Laboratory Technician, Quality Electric Steel Castings, Inc., Houston, Texas.
   e) June 1959-August 1964: Graduate School, University of Houston.
   f) March 1964-Present: Houston Research, Inc.

5. U. S. Army Service:

   a) Active duty with Corps of Engineers, Ft. Leonard Wood, Missouri, and overseas service in Japan. Assignment: Chief Engineer Storage Specialist, Regional Post Engineer, Kobe, Japan.

6. Theses, Publications, and Patents:

   a) M.S. Thesis: "Exploration of the Origin of Liquid Phase Interactions in Solutions".

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b) Ph.D. Thesis: "Exploratory Work - An Investigation of Certain Intermolecular Effects on the Configurational Properties of Liquids."

c) "Thermodynamics of Solution. New Equipment for Measuring Heats of Solution. Data for Five Systems," J. Chem. Eng. Data, 6, 395 (1961).

d) "Application of Chemical Engineering Principles to Problems in Outer Space," 19th Annual Technical Meeting, South Texas Section, AIChE, Galveston, Texas, October 23, 1964.

e) "Design Data for Ablators; Part III - Mathematical Model for Decomposition of Phenol-Formaldehyde Ablators." N66-38924, National Technical Information Service, Springfield, Va. 22151 (March 1965).

f) "An Evaluation of the Kinetic and Chemical Reactions That Occur in the Degradation of the Apollo Heat Shield," X66-21437, NASA Scientific and Technical Information Facility, P. O. Box 33, College Park, Maryland 20740 (August 1966).

g) "Study, Design and Fabrication of a Real Time Chemical Simulant Sampler," AD 868 348, Defense Documentation Center, Alexandria, Va. 22314 (June 1969).

h) "Equipment for High-Pressure Infrared Measurements," Applied Spectroscopy, 24, 241 (1970).

i) "Thermal Conductivity of Filled RTV Compounds," N72-30500, National Technical Information Service, Springfield, Va. 22151 (July 1972).

j) "Advanced $O_3$-Oxidation System for Complexed Cyanides," First International Symposium on Ozone for Water and Wastewater Treatment, Washington, D. C., December 2-5, 1973, International Ozone Institute, Syracuse University Syracuse, New York (1975).

k) "Cyanide Disposal by Ozone Oxidation," AFWL-TR-73-212, AD 775 152/2GA, National Technical Information Service, Springfield, Va., 22151 (February 1974).

l) "A Management Tool to Determine Economic Feasibility of Pollution Abatement by Water Reuse in the Power Generation Industry," 78th National Meeting AIChE, Salt Lake City (August 18-21, 1974).

m) "Oxidation of Refractory Organic Materials by Ozone and Ultraviolet Light," Final Report 7184, AD/A-003 091/6GA, National Technical Information Service, Springfield, Va. 22151 (November 1974).

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n) "Computer Design of Systems for Total Recycle of Municipal Effluent," Second National Conference on Complete WateReuse, AIChE/USEPA, Chicago (May 4-8, 1975).

o) "Oxidation of Refractory Organic Materials by Ozone and Ultraviolet Light," Second International Symposium on Ozone for Water and Wastewater Treatment, Montreal, May 11-14, 1975, International Ozone Institute, Syracuse University, Syracuse, New York (1976).

p) "System for Total Direct Recycle of Secondary Municipal Wastewater. Volume 1. Design Concepts," Final Report AFWL-TR-74-235-Vol-1, AD-A011938/8GA, National Technical Information Service, Springfield. Virginia 22151 (June 1975).

q) "Chemical Oxidation of Cyanide Species by Ozone with Irradiation from Ultraviolet Light," Paper No. 75-B-310, Society of Mining Engineers of AIME Fall Meeting, Salt Lake City (September 10-12, 1975).

r) "Ozone/UV Process Effective Wastewater Treatment," Hydrocarbon Processing, 54(10), 82 (October 1975).

s) "Ozone-Based System Treats Plating Effluents," Metal Progress, 101(6) (November 1975).

t) "Method of Destroying Cyanides", U. S. Patent 3,920,547 (November 18, 1975).

u) "Ozone with Ultraviolet Provides Improved Oxidation of Water Pollutants," Pollution Engineering, 8(1). 42, (January 1976).

v) "A Novel Method for the Recovery of Metals from Complexed Cyanide Solutions," Water and Wastewater Equipment Manufacturers' Association Technical Conference, Houston (March 30-April 1, 1976).

7. Research and Laboratory Work:

a) Inorganic analysis and reactions, including, acid-base analysis, gravimetric, titrametric, colorimetric, electrolyte systems, instrumental analysis, combustion analysis.

b) Thermodynamics of non-electrolyte solutions, theoretical and experimental, including heats of solution, dielectric properties, infrared spectroscopy.

c) Computer (IBM 650, 1401, 709, 7094; UNIVAC 1107, 1108, CDC 3600, 6600) applications to engineering problems and mathematical models in FORTRAN and MAD languages.

d) Intermolecular effects including infrared absorption by liquids up to 5,000 atm. pressure, collision



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trajectories, intermolecular potential functions for spherical and non-polar shaped molecules, configurational energy of liquids, mathematical cell models, and general theory of the liquid state.

e) Kinetics of pyrolysis and design data for ablators.
f) Phase diagram development for sulfide salts.
g) Chemical plant operators' training program.
h) Recovery/separation systems for chemical process streams.
i) Relation of pore size distribution to internal surface area and gas permeability of porous materials.
j) Development of instrumentation for determination of aerosol particle size distribution.
k) Vapor pressure measurements on pyrophoric materials.
l) Development of high temperature extrusion lubricant.
m) Theory of mixing of particulate solids.
n) Chemical and physical testing of plastics and coatings.
o) Effect of cement particle size on setting properties.
p) Experimental exploration of chemical reactor model flow.
q) Heat transfer calculations.
r) Thermal cracking of hydrocarbons.
s) Vacuum outgassing.
t) Rock sawing.
u) Ozonation of wastewaters containing refractories and toxic materials.
v) Instrumentation for boat sewage monitoring.
w) Oil film sampling.
x) Chemical deposition of zinc coating.
y) Magnetic separation of oil and water.
z) Testing of fire retardant paints.
aa) Alkaline chlorination of silver cyanide.
bb) Exploration of marine sanitation waste treatment concepts.
cc) Oil spill recovery.
dd) Detection of oil in water.
ee) Design of wastewater treatment systems.

8. <u>State-of-the-Art Reviews</u>:

a) Chemical tagging of oil spills
b) Particle deagglomeration
c) Formation of chemical scales from water solutions
d) Foam as a dust suppressant



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e) Ozone for disinfection of wastewater
f) Liquid absorbing system to remove toluene from air
g) Ultimate disposal of hazardous solid wastes
h) Reaction of steam and mixed organic wastes
i) Wet oxidation of mixed organic wastes
j) Ozonation mechanisms in wastewater
k) Reuse of waste oils
l) Detection of oil in water
m) Instruments for water analyses
n) Electroplating processes
o) Plywood drying
p) Metal finishing line wastes
q) Reverse osmosis for wastewater cleanup
r) Hydrogen bonding
s) Adhesives
t) Moisture detection
u) Wet scrubbers
v) Liquid nitrogen production
w) Energy recovery from municipal refuse

9. Membership in Learned and Professional Societies:

a) Member, Tau Beta Pi (Engineering honorary)
b) Associate Member, A.I.Ch.E.
c) Junior Member, National Society of Professional Engineers
d) Member, American Chemical Society
e) Member, Society of the Sigma XI (Scientific Research honorary)

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Exhibit B

# OXIDATION OF REFRACTORY MATERIALS BY OZONE WITH ULTRAVIOLET RADIATION

H.W. Prengle, Jr., C.G. Hewes, III and C.E. Mauk

Houston Research, Inc., 7705 South Loop East, Houston, Texas

ABSTRACT - Rates of oxidation of refractory chemical species were experimentally studied with ozone and ultraviolet light. Ethanol, acetic acid, glycine, glycerol, and palmitic acid were chosen as representative of the five types of refractories found in municipal and industrial wastewater. A refractory index scale was established which ranks the compounds in order of difficulty of oxidation. Ozone alone was not particularly effective in oxidizing the subject species but activation by ultraviolet radiation resulted in substantial increases in reaction rate for all species. Also, data were collected on mass transfer and ozone autodecomposition.

RESUME - Les vitesses d'oxydation d'especes refractaires par l'ozone et par lumiere ultraviolette ont ettes edutiees experimentalement. L'ethanol, l'acide acetique, la glycocolle, le glycerol et l'acide palmitique etes ont choisis comme elements representatifs des cinq types de refractaires que l'on retrouve dans les eaux d'egouts municipaux et industriels. Nous avons etabli une echelle indexee des composes refractaires par ordre de difficulte d'oxydation. L'ozone par lui-meme ne s'est pas revele particulierement efficace, mais une activation par lumiere ultraviolette donne un accroissement substanciel de la vitesse de reaction pour toutes les especes. Des donnees numeriques sur les transports de matiere et sur l'autodecomposition de l'ozone sont egalement presentees.

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Presented at 2nd International Ozone Symposium, International Ozone Institute, May 11-14, 1975; Montreal, Canada.



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Work has been conducted during the past four years on the development of chemical oxidation with ozone as an advanced waste treatment process, specifically aimed at difficult to oxidize wastewater species, commonly referred to as refractory compounds. The program has been directed towards carrying out research, preliminary to application of ozone oxidation as a commercially feasible process for both industrial and municipal wastewater treatment, and the purpose of this paper is to present certain work completed to date on the development of the process.

In recent years, much attention has been given to tertiary treatment processes (carbon adsorption, ion exchange, reverse osmosis, chlorination, etc.), which can be added to conventional wastewater treatment processes, to provide effluents which meet projected zero discharge standards. However, results indicate that a number of tertiary processes do not remove all undesirable refractory species, some of which when chlorinated produce highly undesirable discharge species[1]. Therefore, a process is needed which will take refractory species to complete oxidation ($CO_2$, $H_2O$, $N_2$ ...); thereby making them harmless in effluent streams.

From its inception, the work has visualized 1) multi-stage reactors which permit optimization of the reaction system, 2) improved mass transfer in a hydrodynamic continuous sparged CSTR, and 3) more recently the enhancement of the reaction rate by the use of UV radiation. In-house work was carried out in 1971, and in mid-1972 a contract was obtained to study the application of ozone to cyanide removal contained in plating and photographic wastes. The most difficult components to oxidize in these wastes were complexed cyanides, e.g., potassium ferricyanide, which have very small dissociation constants



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and are almost impossible to oxidize. It was found that the photolysis reaction with ozone proceeded very rapidly; enhancement of the reaction was phenomenal, increasing the rate 10-100 fold.

Following this, an investigation was undertaken to study the oxidation of organic materials; the compounds selected for study were: 1) glycine, $NH_2CH_2COOH$, the smallest amino acid, 2) ethanol, $CH_3CH_2OH$, 3) acetic acid, $CH_3COOH$, 4) glycerol, $CH_2OHCHOHCH_2OH$, and 5) palmitic acid, $CH_3(CH_2)_{14}COOH$, the smallest of the common fatty acids. Ethanol and acetic acid were chosen over other possibilities because they both contain two carbon atoms, as does glycine, and the results would be very useful to a future study. The results obtained were outstanding; probably the most striking example is that of the oxidation of acetic acid, by far the most refractory compound studied. In the absence of UV radiation, acetic acid is essentially unoxidized by $O_3$; however, with UV radiation the oxidation proceeds rapidly at room temperature.



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REFRACTORY INDEX, RFI

For purposes of comparison of different refractory species, a "Refractory Index (RFI)" was defined which is a measure of the difficulty of oxidation of a given molecular species; i.e., the larger RFI, the more difficult the species is to oxidize.

Standard Run Conditions

$O_3$ is used as the oxidant, the run is conducted at room temperature (25-27°C), the initial concentration of the reactant is 50-100 mg/l, and the reactor is operated in the good to excellent mixing regime. No ultraviolet radiation is used.

Definition

$$\text{RFI (hrs)} \equiv \frac{B_c^o \text{ (mg/l)} \; t_{\frac{1}{2}} \text{ (hrs)}}{A_o \text{ (mg/l)}} \qquad (1)$$

$$B_c^o \text{ (mg/l)} \equiv \frac{\dot{m}_B \text{ (mg/min)} \; t_{\frac{1}{2}} \text{ (min)}}{V \text{ (ℓ)}} \qquad (2)$$

where $B_c^o$ is the cumulative $O_3$ pumped into the liquid phase from t = 0 to t = $t_{\frac{1}{2}}$, per liter of liquid.

$t_{\frac{1}{2}}$ is the time required for 50% complete conversion of the reactant component, as measured by TOC for organic species, and an appropriate method for inorganic species.

$A_o$ is the initial amount of reactant component

$\dot{m}_B$ is the $O_3$ mass feed rate to the reactor

V is the liquid volume in the reactor

Values of RFI of the various compounds studied are shown in Table 1. It will be noted that of all compounds studied, acetic acid is most refractory, with complexed ferricyanide, ethanol, and glycerol in the highly refractory category.



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TABLE 1

RFI VALUES FOR VARIOUS COMPOUNDS

| | Compound | RFI-Value | Qualitative Scale |
|---|---|---|---|
| 1) | KCN | 0.41 | Slightly Refractory (RFI < 1) |
| 2) | Complexed Cd-Cyanide | 0.96 | Slightly Refractory (RFI < 1) |
| 3) | Glycine | 19.7 | Refractory (RFI, 1 → 100) |
| 4) | Palmitic Acid (as $NH_4$-Salt) | 27.3 | Refractory (RFI, 1 → 100) |
| 5) | Glycerol | 112 | Highly Refractory (RFI > 100) |
| 6) | Ethanol | 245 | Highly Refractory (RFI > 100). |
| 7) | Complexed Ferricyanide | 270 | Highly Refractory (RFI > 100) |
| 8) | Acetic Acid | > 1000 | Very Highly Refractory |

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CHEMICAL REACTION DATA

Prior to considering the experimental chemical reaction data for individual compounds, it must be recalled that there is a theoretical (stoichiometric) amount of ozone necessary to completely oxidize the molecular species to $CO_2$, $H_2O$ ... Typical oxidation ratios, based on one reactive oxygen atom per ozone molecule, are given in Table 2.

TABLE 2

THEORETICAL OZONE REQUIREMENT*

| | Compound | $b \equiv \frac{\text{moles } O_3}{\text{moles compound}}$ | $\frac{\text{mass } O_3}{\text{mass compound}}$ |
|---|---|---|---|
| 1) | Acetic Acid | 4.0 | 3.20 |
| 2) | Ethanol | 6.0 | 6.26 |
| 3) | Glycerol | 7.0 | 3.65 |
| 4) | Glycine (to $NH_3$) | 3.0 | 1.92 |
| | (to $N_2$) | 4.5 | 2.88 |
| 5) | Palmitic Acid | 46.0 | 8.62 |
| 6) | Carbon | 2.0 | 8.00 |
| 7) | Cyanide, $CN^-$ to $CNO^-$ | 1.0 | 1.85 |

* Based on one reactive oxygen atom per ozone molecule.

The experimental runs were carried out in a continuously sparged batch stirred tank reactor of 9.92 liter volume, using sparging gas of oxygen with 1 to 5 w% ozone. When conducting experiments of this type, in some instances the chemical reaction rate is very rapid and the $O_3$ molecules are used as rapidly as they are transferred into the liquid phase, i.e., the mass transfer of



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the $O_3$ from the gas into the liquid is reaction rate controlling. Under these circumstances, the disappearance of the reactant is given by,

$$\left(\frac{m_A}{m_{Ao}}\right) = 1 - \left(\frac{\dot{m}_B}{b m_{Ao} V}\right) t \qquad (3)$$

a straight line function falling off from unity at t = 0, which in effect is the "limiting line" oxidation time profile; determined by the ozone feed rate $\dot{m}_B$, the initial concentration of the reactant, $m_{Ao}$, and the theoretical ozone requirement, b. The limiting lines are shown on the subsequent plots. The degree to which the actual time profile is removed to the right of the limiting line, 1) indicates that the oxidation is chemical reaction rate controlled, and 2) measures the ozone use efficiency. The mass transfer controlling situation is the most desirable since it leads to essentially 100% $O_3$ utilization.

1. Potassium Cyanide

The oxidation of $CN^-$ to $CNO^-$ by ozone is well known, having been studied by numerous investigators[2,3], and is used commercially as a waste treatment process. Some studies in the past have assumed that the chemical reaction was rate controlling; however, controlled experiments now indicate that mass transfer is controlling. The $O_3$ molecules are utilized essentially as soon as they are transferred into the liquid phase, as indicated in Figure 1. In fact, by comparison with other reactions the $KCN/O_3$ reaction can be considered a classic case of mass transfer controlling.

2. Potassium Ferricyanide

In the study[4] on nickel stripping, copper plating, photographic bleach, and photographic fixer wastes, containing cyanide and complexed cyanide ions, it was found that the

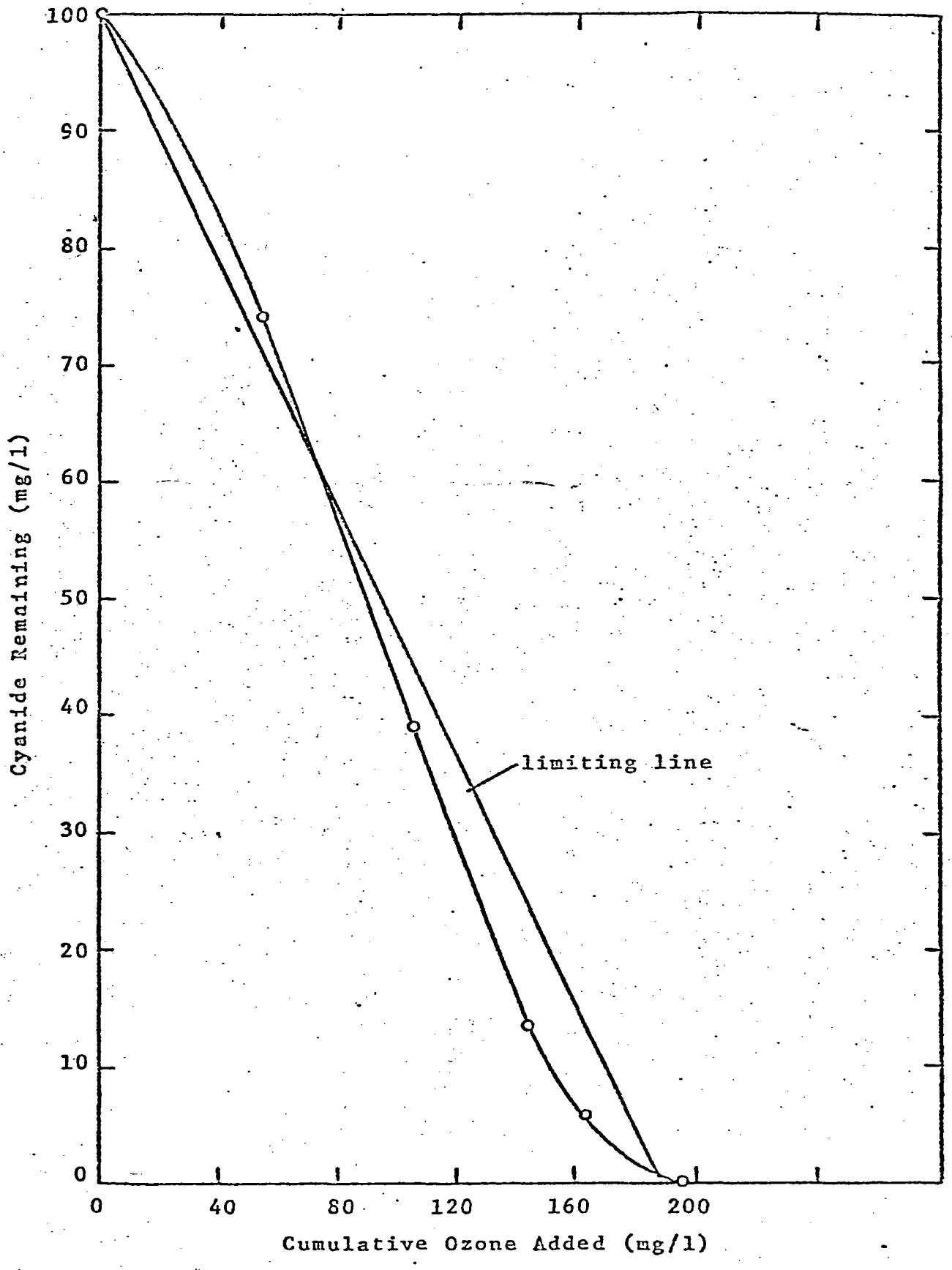


FIGURE 1. Ozonation of Dilute Free Cyanide



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most difficult to oxidize species was complexed ferricyanide ion (e.g., $K_3[Fe(CN)_6]$). In Figure 2, the upper two curves with 1% and 5% ozone indicate very slow reaction, and an apparent equilibrium, probably between $CN^-$ and $CNO^-$. Experiments with $O_3$ and UV substantially improved the reaction rate and with 5% $O_3$ the reaction moved into the mass transfer controlled regime; also, it appears that the $CNO^-$ was completely destroyed.

The amount of UV used is also a factor, and can be seen in Figure 3, c.f. 4 watts and 16 watts at 77°F.

3. Acetic Acid

As noted previously, this compound was the most difficult to oxidize with ozone, RFI > 1000. Since acetic acid is a partial oxidation product of many organic molecules, and represents a "dead end" in oxidation with air and $O_2$, a substantial number of runs were made to delineate its reaction characteristics.

Figure 4 shows that for oxidation without UV, there is no loss of TOC even after several hours, but analysis for acetic acid shows a sudden drop of about 16% to a plateau that lasts indefinitely. This oxidation without carbon loss implies the formation of an acid peroxide,

$$2\ CH_3\overset{\overset{O}{\|}}{C}OH + O_3 \rightarrow CH_3\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}CH_3 + H_2O + O_2 \qquad (4)$$

possibly explaining the disappearance of acid without a disappearance of TOC. The acid concentration drops to an equilibrium point at which the rate of formation of peroxide is equal to the rate of its autodecomposition back into acid. This phenomena was not observed with UV activation of the reaction.

The use of UV substantially enhances the reaction at room temperature and at 50°C, as indicated in Figure 5. The only

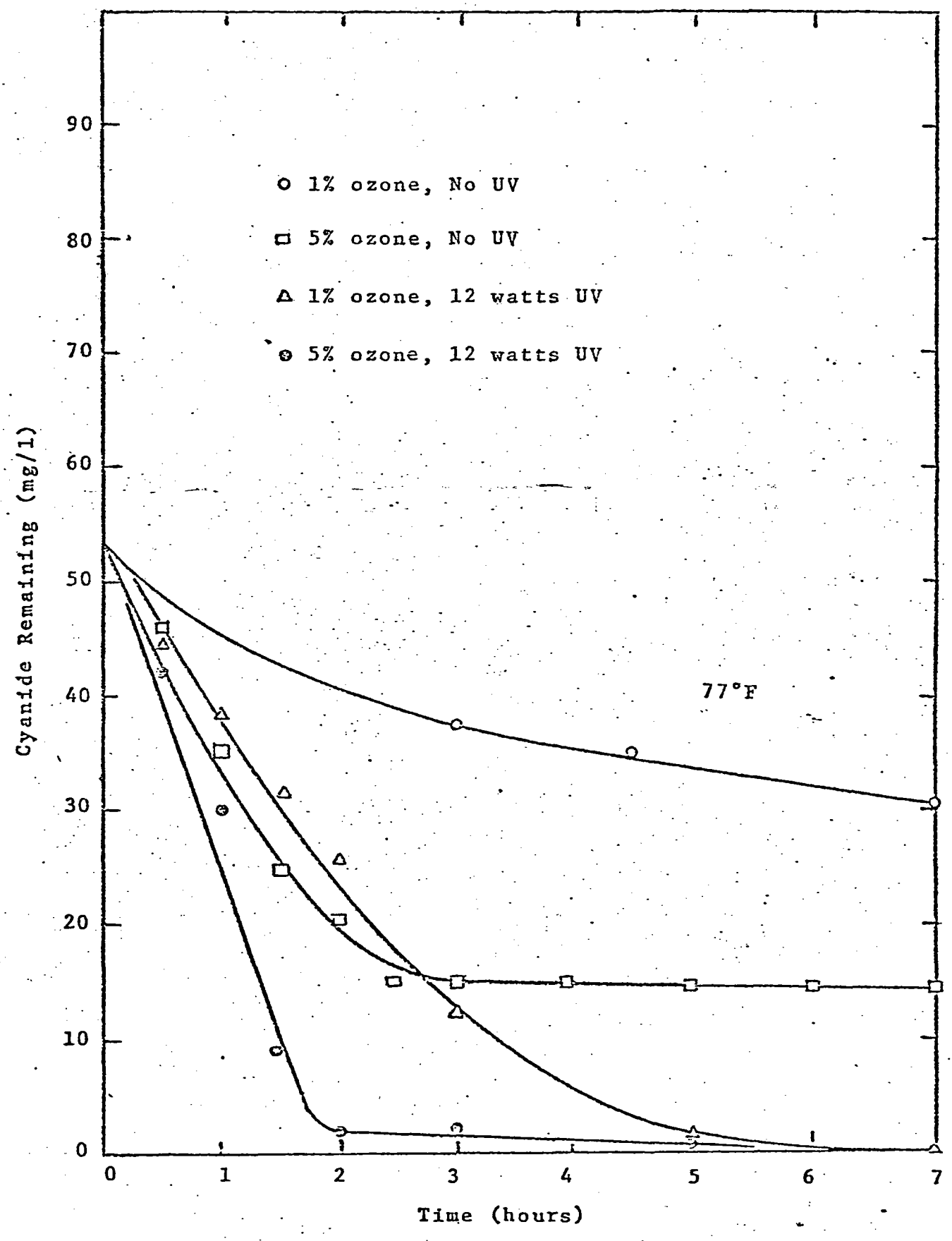


FIGURE 2. Effect of UV and $O_3$-Concentration on Oxidation of Ferricyanide



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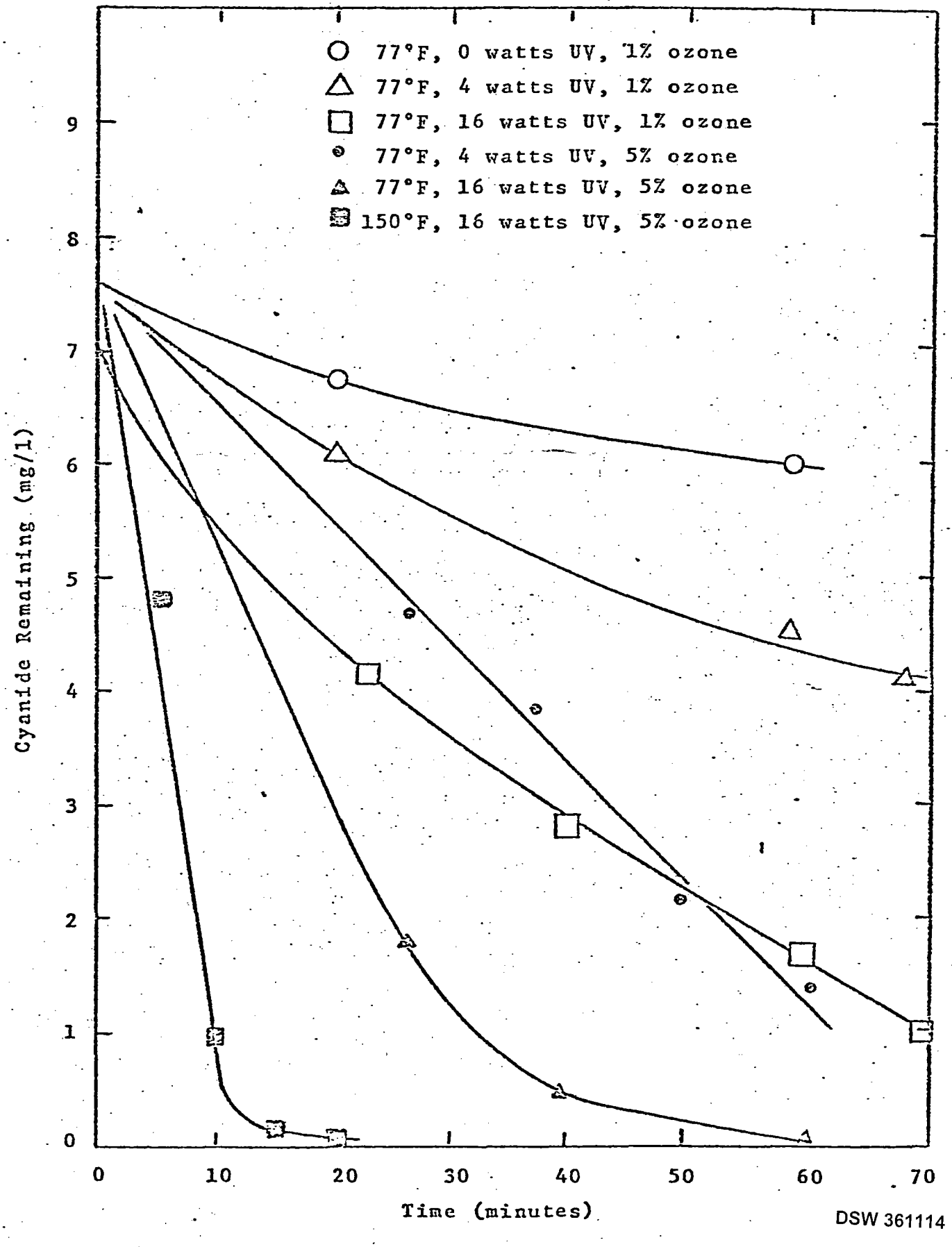


FIGURE 3. Effect of UV, $O_3$-Concentration, and Temperature on Oxidation of Complexed Cyanides.

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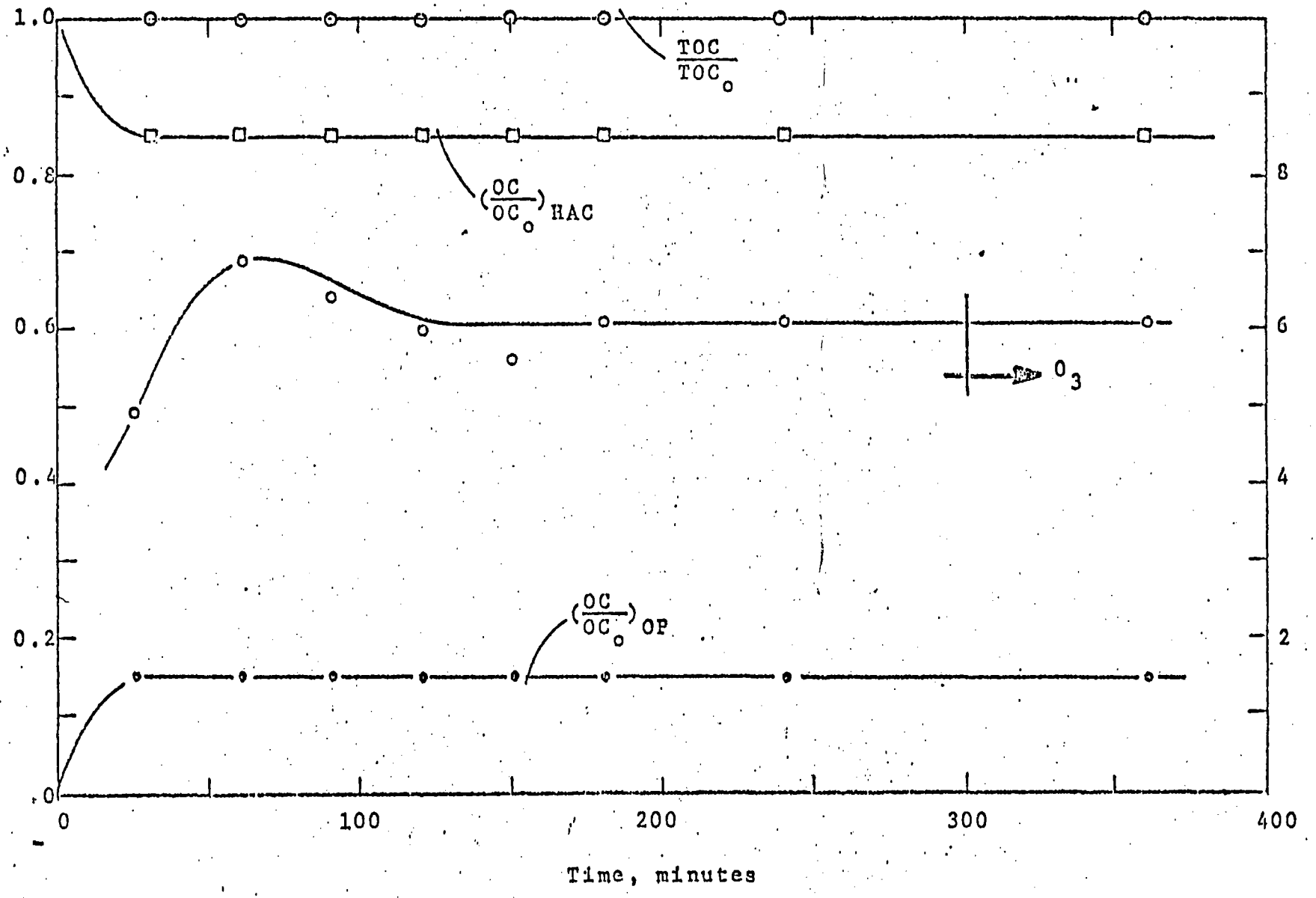


FIGURE 4. Ozone Oxidation of Acetic Acid
[27-31°C, Initial $CH_3COOH$ = 105 mg/l]



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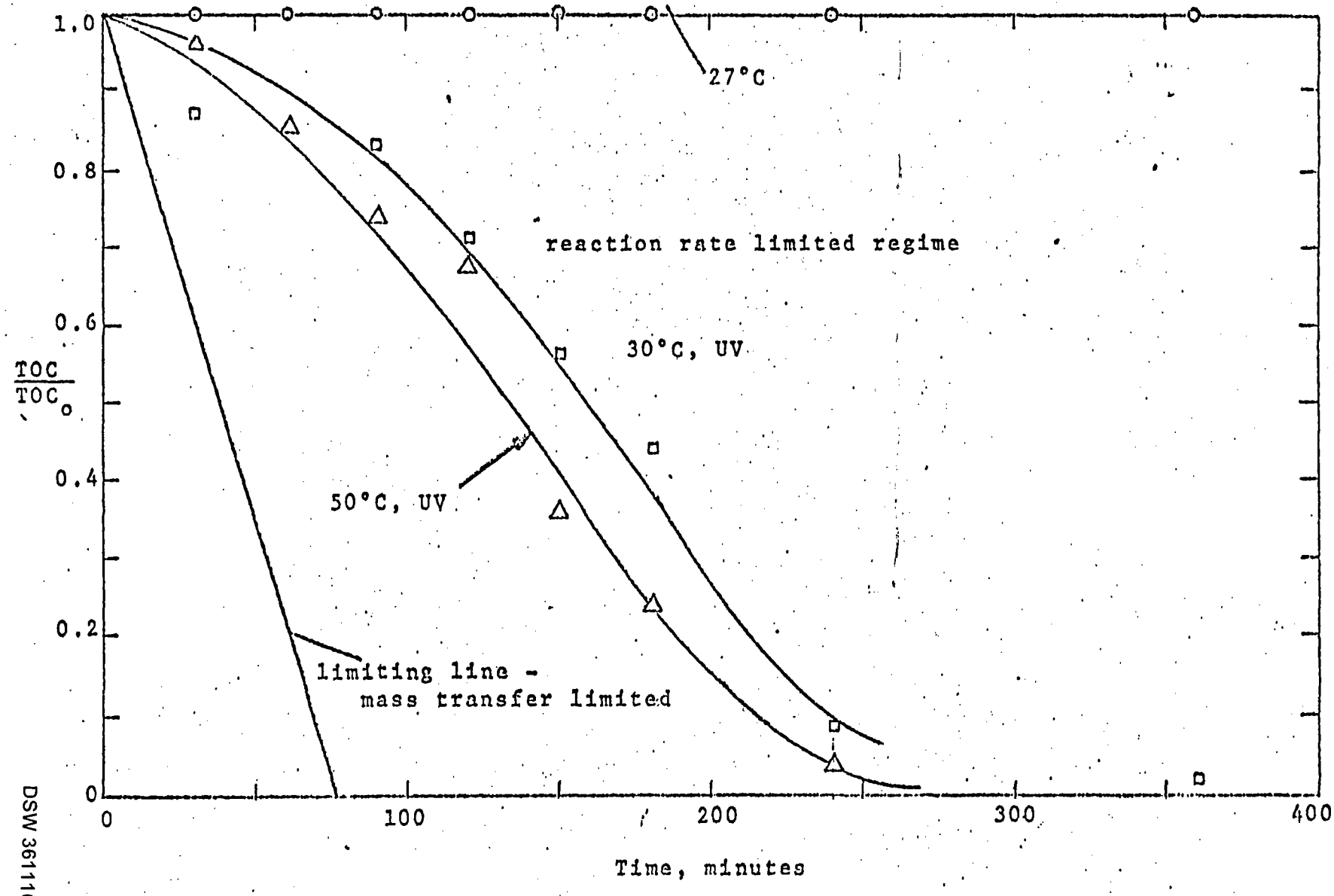


FIGURE 5. Ozone Oxidation of Acetic Acid, Effect of UV and Temperature [Initial $CH_3COOH$ = 105 mg/l, $O_3(\ell)$ = 3.5 mg/l]



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slight increase from 30°C to 50°C indicates that further enhancement by higher temperature is not encouraging. The time profiles presented in Figure 6 map out the disappearance of the acetic acid, the build up and disappearance of intermediate oxidation products (OP), and the final evolution of $CO_2$, as well as the disappearance of total organic carbon.

The enhancement of the oxidation rate by increased UV is shown in Figure 7, indicating that at a given set of conditions there will be a particular or critical amount of UV necessary to make the reaction mass transfer controlled.

4. Ethanol

Figure 8 compares the disappearance of TOC for ethanol with and without UV and at elevated temperature. The 50°C-UV curve is very close to the limiting line, and the use of somewhat more UV would be more effective than additional temperature. The time profiles given in Figure 9 indicate a very rapid disappearance of ethanol at 30°C with UV, i.e., a conversion to intermediate oxidation species which oxidize more slowly. The latter control the disappearance of TOC, but their total oxidation can be accelerated by the use of more UV.

5. Glycerol

Figure 10 shows the disappearance of TOC for glycerol with temperature and UV. The data for 30°C-UV and 50°C-UV fall close together; little improvement would be expected for additional temperature increase. Comparison of Figures 10 and 8 indicates that at all temperatures and UV conditions, glycerol reacts much faster than ethanol; undoubtedly because the glycerol molecule has three active hydroxyl sites for oxidation while ethanol has only one.

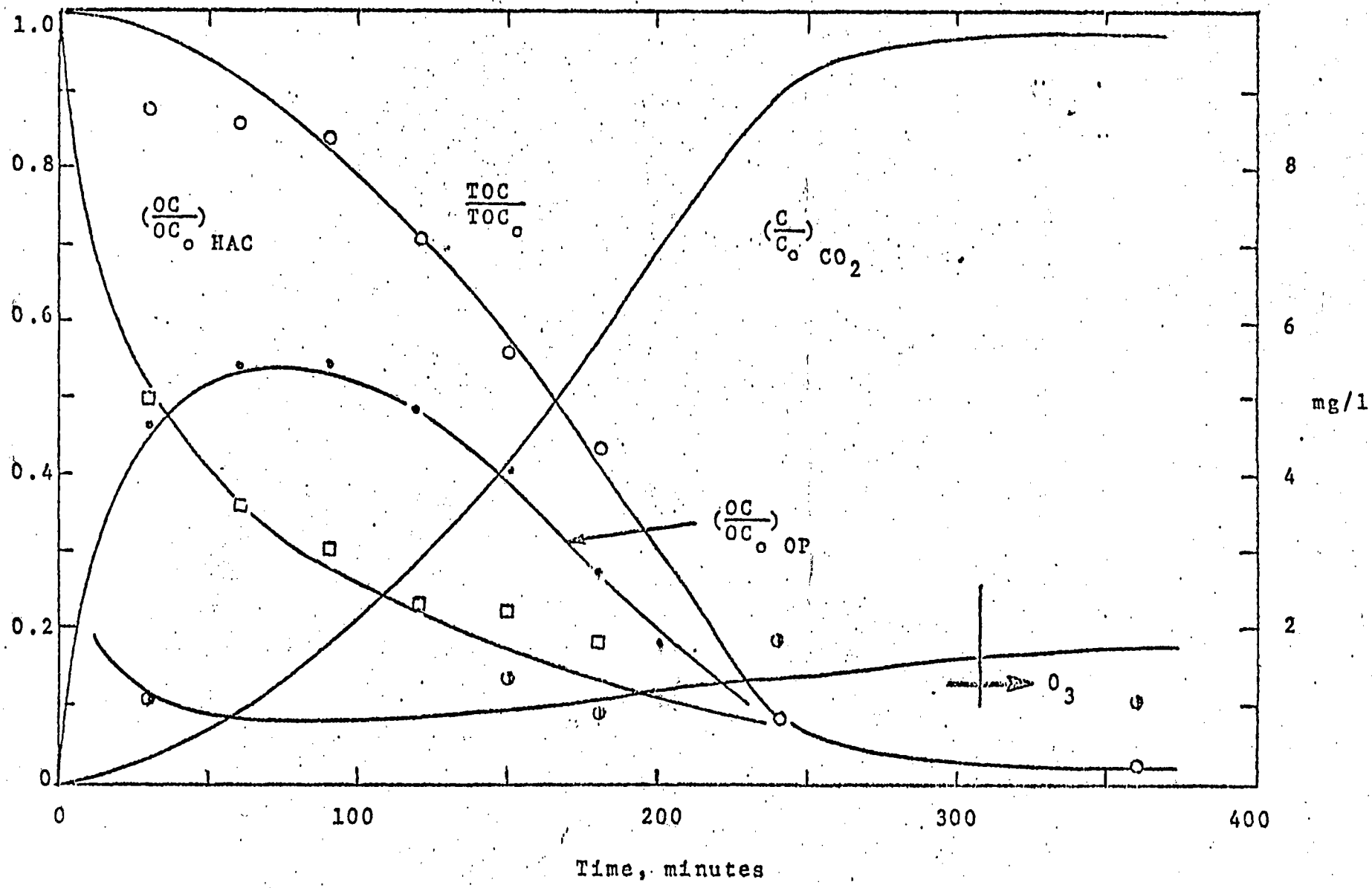


FIGURE 6. Ozone Oxidation of Acetic Acid with UV
[30°C, Initial $CH_3COOH$ = 105 mg/l]



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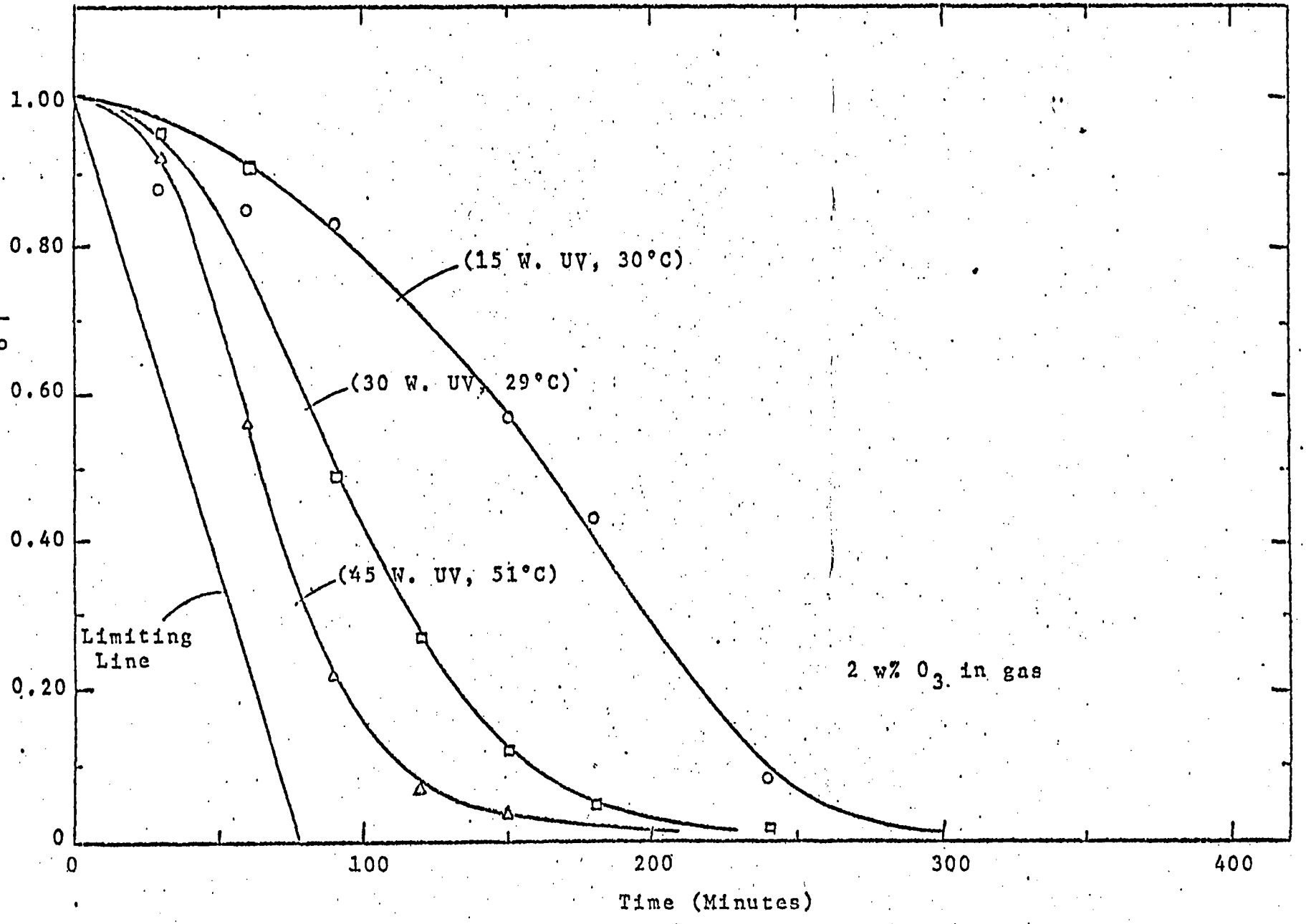


FIGURE 7. Ozone w/UV Oxidation of Acetic Acid

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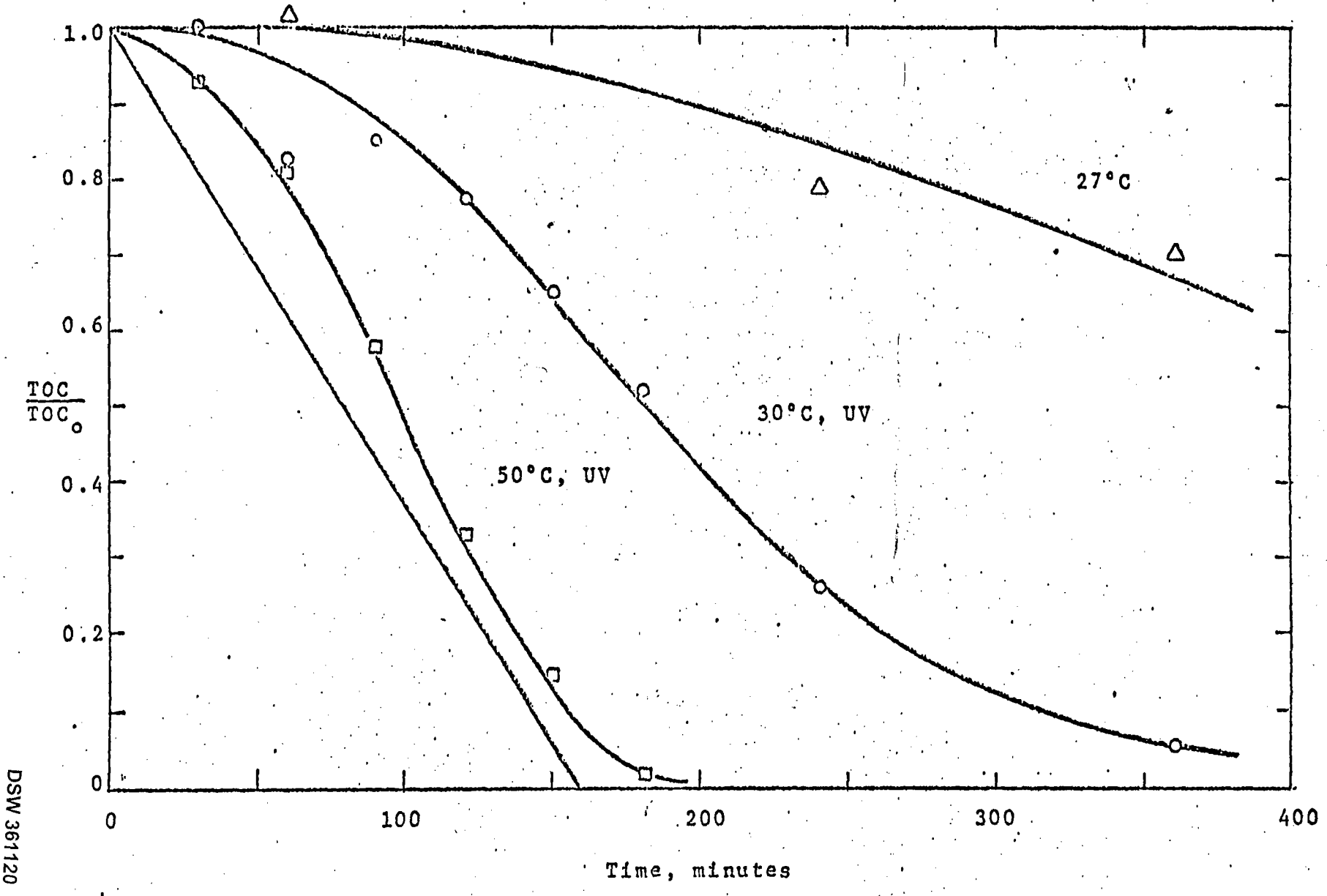


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FIGURE 8. Ozone Oxidation of Ethanol, Effect of UV and Temperature
[Initial $C_2H_5OH$ = 116 mg/l, $O_3(\ell)$ = 2-4 mg/l]

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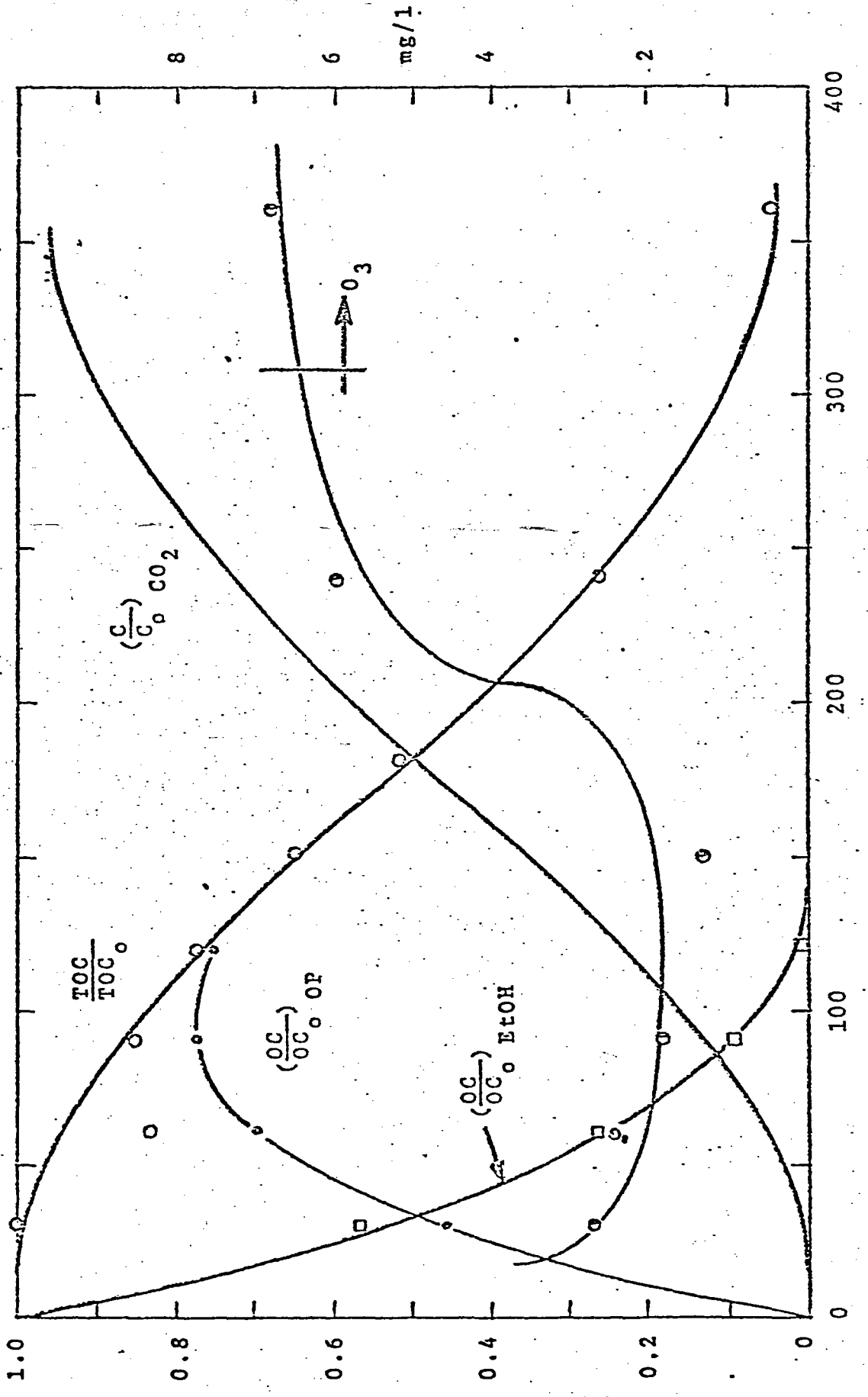


FIGURE 9. Ozone Oxidation of Ethanol with UV [30°C, Initial $C_2H_5OH$ = 115 mg/l].

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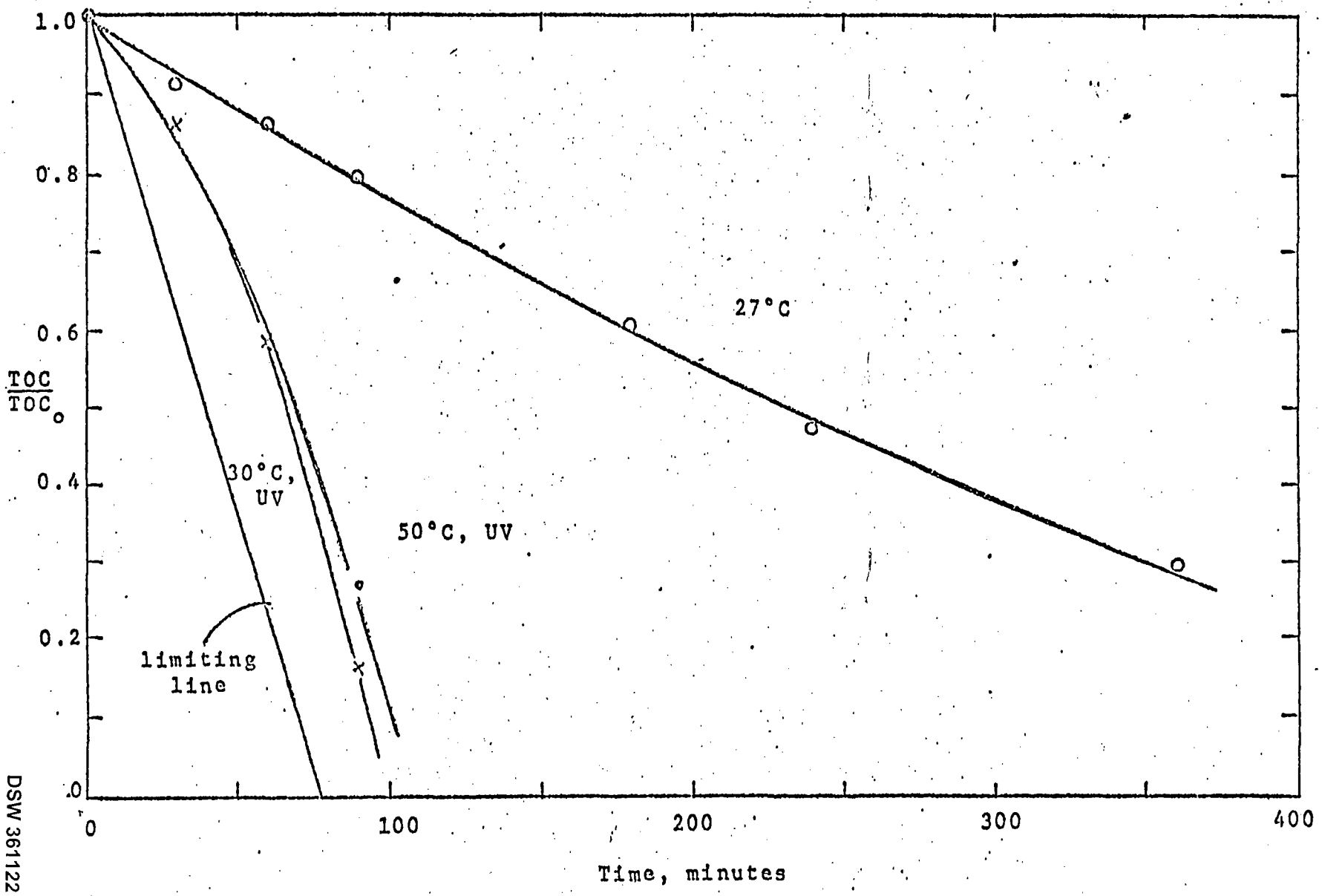


FIGURE 10. Ozone Oxidation of Glycerol, Effect of UV and Temperature [Initial $CH_2OHCHOHCH_2OH$ = 106 mg/1, $O_3(\ell)$ = 1.4 mg/1]



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## 6. Glycine

Figure 11 shows TOC disappearance for glycine with and without UV and elevated temperature. Limiting lines are shown both for oxidation to nitrogen and to ammonia; although no direct experimentation was undertaken to determine which is formed, the tendency of the glycine runs to remain near neutral pH implies that ammonia is not being formed. At low concentration and near neutral, it is unlikely that if ammonia were formed it would be stripped from solution by the oxygen flow. Although the 30° and 50° data fall together during most of the run time period, they are satisfactorily close to the theoretical limiting line for nitrogen formation.

## 7. Palmitic Acid

Because of the low solubility of palmitic acid, it was simulated by the more soluble ammonium palmitate, as shown in Figure 12. The reaction at all temperatures and UV conditions was surprisingly fast. One can speculate that since the molecule is long, there are numerous places on the chain where oxidation can begin, which compensates for the reluctance of C-C or C-H structure to be oxidized. The 30° and 50° data fall together and in the early part of the runs are very close to the limiting line. Increased UV would insure complete oxidation following the theoretical line.

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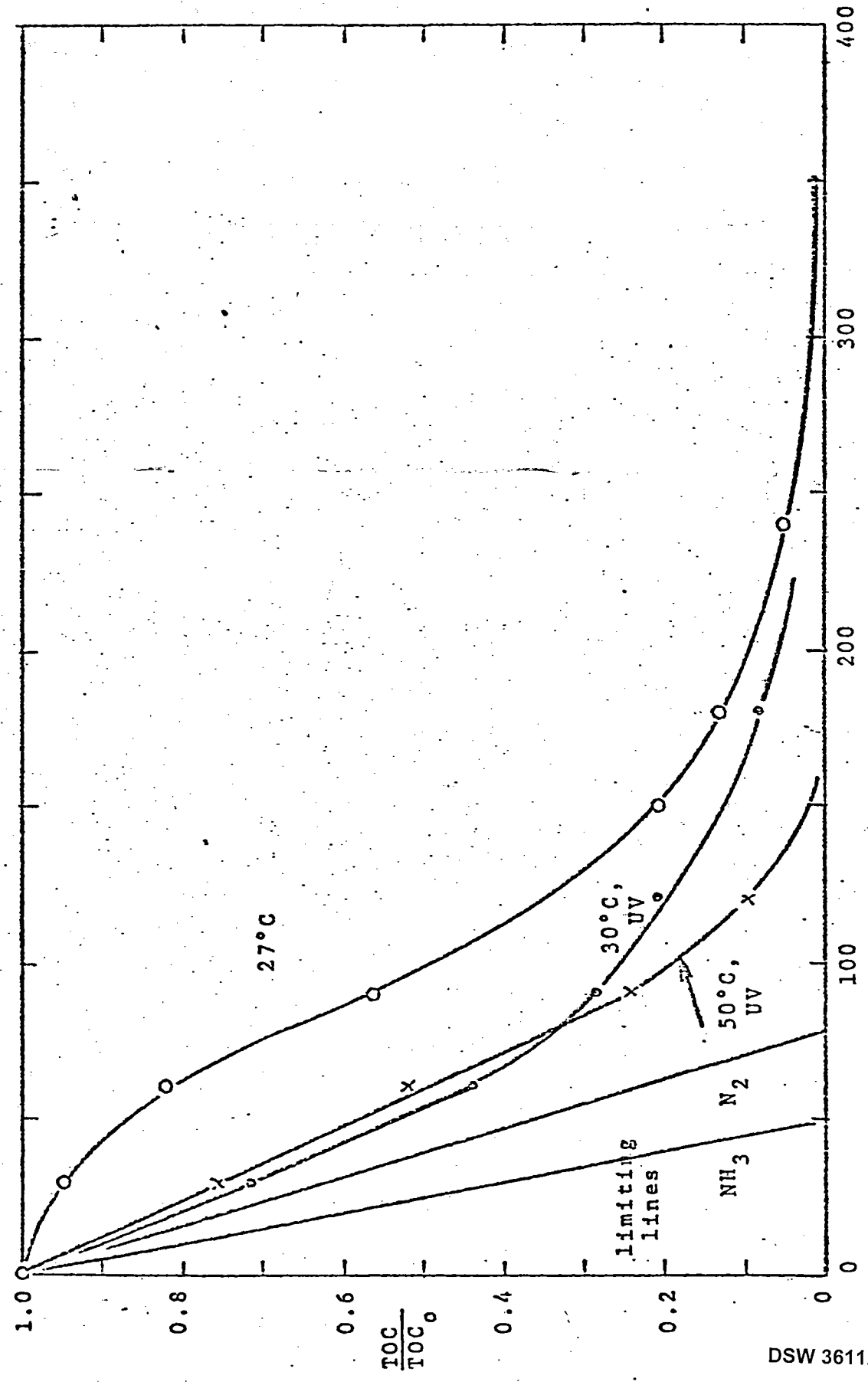


FIGURE 11. Ozone Oxidation of Glycine, Effect of UV and Temperature [Initial $NH_2CH_2COOH$ = 117 mg/l. $O_3$(g) = 1.4 mg/l]



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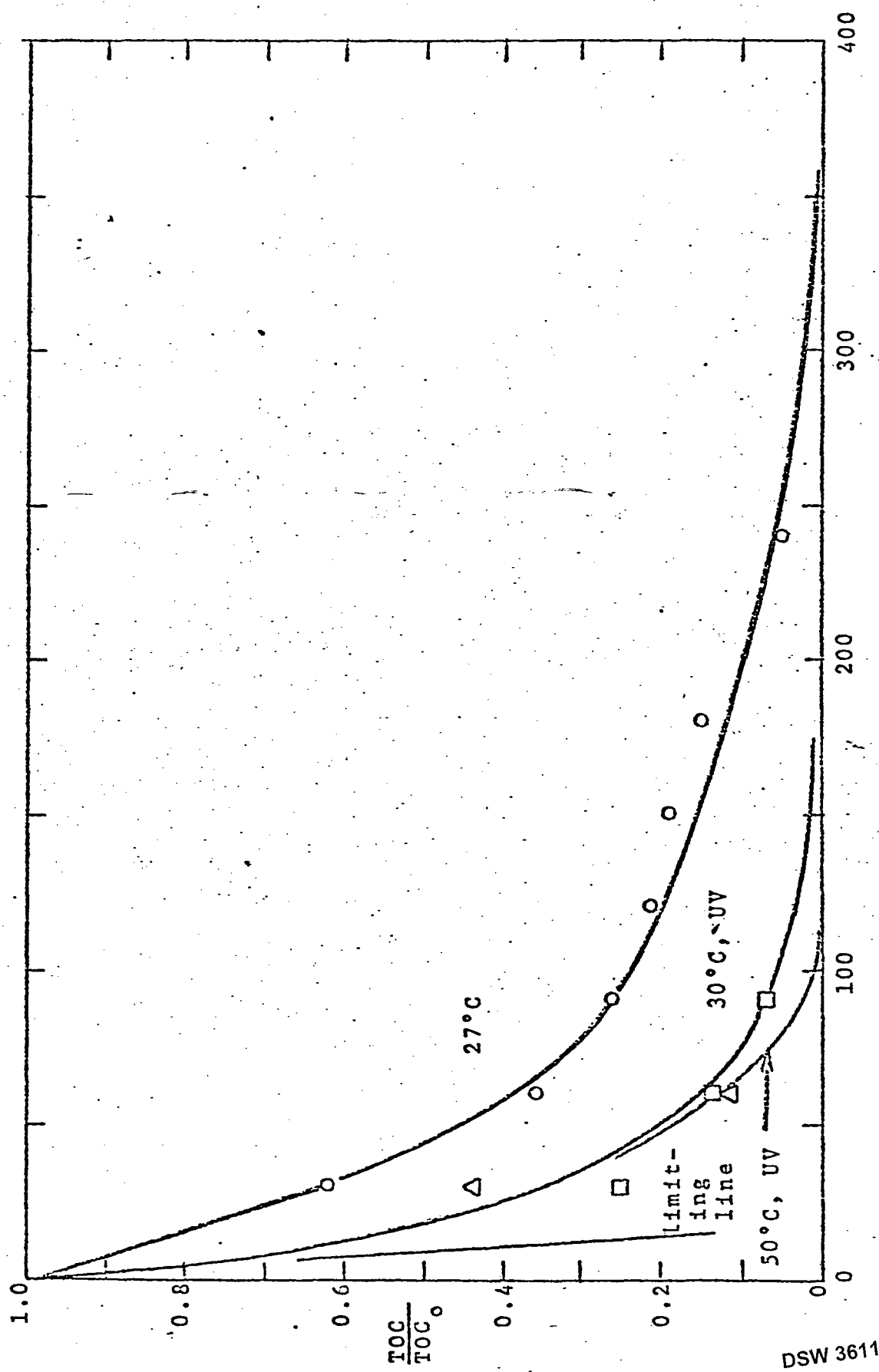


FIGURE 12. Ozone Oxidation of Ammonium Palmitate, Effect of UV and Temperature



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## CHEMISTRY AND KINETICS

There are two distinct aspects of the chemistry involved in the oxidation of the compounds in the concentration ranges studied: 1) the photochemical excitation of the molecules by the UV radiation, followed by 2) oxidation by the ozone. The data shows that oxidation by ozone alone, for refractory type species, is relatively slow, the overall process being reaction rate controlled, and, hence, the ozone not fully utilized. On the other hand, the photochemical processes of the species and the water, in the absence of ozone, were not sufficient to bring about appreciable reaction - there was some evidence that the ferricyanide concentration decreased slightly after a very long time. Consequently, the process takes advantage of the combination of the UV and the ozone. Excitation of the molecules occurs and free radicals are produced which are highly reactive in the presence of ozone. The excited state and free radical species provide more thermodynamically feasible reaction paths[5] as well as increased driving forces for enhancement of reaction rates.

Consider the first step, photochemical excitation or sensitization of the molecular species: Calvert and Pitts[6] provide background on the primary photochemical processes involved; a summary of pertinent information is presented in Table 3. It will be noted that generally the primary photochemical processes lead to production of free radicals and other smaller neutral molecules including CO and $CO_2$. The former being the primary step leading to more rapid subsequent oxidation reactions with ozone. Some of the smaller neutral molecules are more readily oxidizable (e.g., olefins), and all can in turn absorb UV for further activation.

Ozone oxidation reactions have been studied by numerous investigators: Criegee[13], and Bailey and coworkers[14]



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TABLE 3

PHOTOCHEMICAL DATA ON REFRACTORY COMPOUNDS

| Compound/(RFI) | Structure | UV Absorption Range (nm) | Primary Photochemical Processes | Reference |
|---|---|---|---|---|
| Acetic Acid (>1000) | $H_3C-C(=O)-OH$ | Peak: 205<br>180-230 | 1) $R + CO_2H^{++}$ (or $CO_2 + H$)<br>2) $RCO_2^{++}$ (or $R + CO_2$) + H<br>3) $RCO^{++}$ (or $R + CO$) + OH<br>4) $RH + CO_2$ | C&P (428,431)* |
| Ferricyanide (270) | $[Fe(CN)_6]^{-3}$ | 230 | Electron transfer to water of hydration | C&P (270) |
| Ethanol (245) | $H_3C-C(H)-OH$ (H) | Peak: 182, 152<br>150-200 | 1) $C_2H_5^{++}$ (or $C_2H_4 + H$) + OH<br>2) $CH_3CH_2O^{++}$ (or $CH_3 + CH_2O$) + H<br>3) $C_2H_4 + H_2O$<br>4) $CH_3CHO + H_2$<br>5) $CH_4 + CH_2O$ | C&P (442,444) |
| Glycerol (112) | $H_2C(OH)-C(H)(OH)-CH_2(OH)$ | Peak: 210, 260<br>190-280 | Free radical and intramolecular photodissociative processes | (7) |
| Palmitic Acid ($NH_3$ Salt, 27) | $H_3C-(CH_2)_{14}-C(=O)-OH$ | Peak: 215<br>180-250 | 1) Acid type processes, and<br>2) Alcohol type | (8,9) |
| Glycine (20) | $H_2N-C(H)-C(=O)-OH$ | Peak: 240, 210<br>190-240 | 1) Acid type processes, and<br>2) Amine type, RNH + H | C&P (455 ff)<br>(10) |

* C&P (428,431) ≡ Calvert & Pitts, p. 428, p. 431

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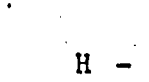
TABLE 3 (Continued)

PHOTOCHEMICAL DATA ON REFRACTORY COMPOUNDS

| Compound/(RFI) | Structure | UV Absorption Range (nm) | Primary Photochemical Processes | Reference |
|---|---|---|---|---|
| Chloroform |  | Peak: 285, 180<br>>250, >240 | 1) Free radicals (similarly for $CCl_4$) | C&P (526,527)<br>(11) |
| Water | $H_2O$ | Peak: 167, 130<br>100-180 | 1) $H(^2S_{1/2}) + OH(^2\pi)$<br>2) $H(^2S_{1/2}) + OH(^2\Sigma^+)$<br>3) $H_2 + O(^1D)$ | C&P (200,442) |
| Ozone | $O_3$ | Peak: 260<br>150-300 | 1) $O_3(S_o) \rightarrow O_3(S_1)$<br>2) $O_3(S_1) \rightarrow O_2(^1\Delta_g) + O(^1D)$<br>$\searrow O_2(^1\Sigma_g^+) + O(^1D)$<br>3) $O_3(S_o) \rightarrow O_3(T_1) \rightarrow O_2(^3\Sigma_g^-) + O(^3P)$ | C&P (207-209)<br>(12) |

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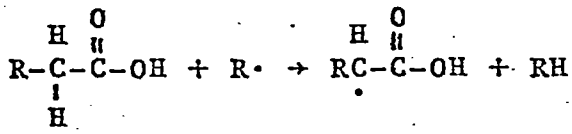
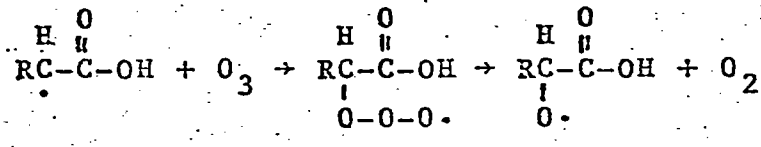
olefins; Schubert and coworkers[15,16] - saturated hydrocarbons; and Bailey[17,18] and coworkers - free radical formation. The classical chain propagation mechanism of free radical reactions starts with the abstraction of a hydrogen atom from a molecule by a second radical, as illustrated by the following for a carboxylic acid,



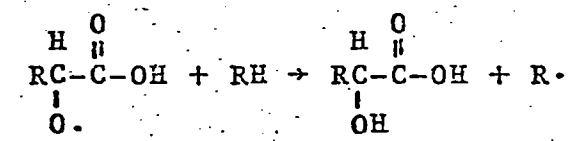
(5)

Ozone additions typically result in the addition of all three oxygen atoms to the radical, followed by rapid release of an oxygen molecule,



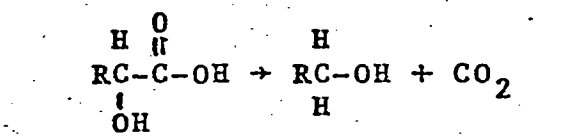
(6)

The cycle of the chain propagation is then closed by the free radical removing a hydrogen from a neutral molecule,



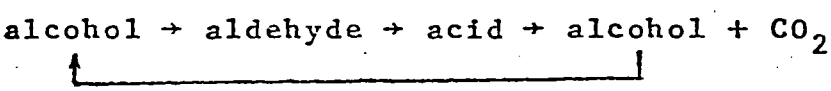
(7)

with the unstable molecule immediately rearranging to release $CO_2$,



(8)

In a similar manner, the alcohol formed is oxidized to an aldehyde, which is in turn oxidized to an acid. Therefore, for long chain molecules a cycle results,



and in the limiting case of a one-carbon-chain, water (not alcohol) is formed on oxidation of the acid.



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The use of UV radiation produces substantially more free radicals than the use of ozone alone; the radicals initiate many more propagation chains similar to those described above, and causes the overall reaction to proceed much, much faster. The overall photochemical-oxidation process to produce $CO_2$, $H_2O$, $N_2$, etc., can be represented schematically as shown in Figure 13. The two step initiation process, 1) primary photochemical process, and 2) initial $O_3$ oxidation, is followed by the propagation chains which produce additional free radicals, neutral molecules, and some $CO_2$, $H_2O$ ... by a termination step.

It is obvious from the foregoing discussion that the sequence of events is quite complex, and, therefore, the derivation of a mathematical model for the kinetics based on theory would be extremely involved. On the other hand, it is possible to construct a kinetic model, keeping in mind the following predominant processes which occur:

1) – in an organic reaction the disappearance of TOC is a reversed sigmoid shaped function when conditions of reaction rate controlling prevail.

2) – predominantly initial species oxidize to intermediates which finally oxidize to $CO_2$, $H_2O$, ... etc.

3) – with increased amount of UV radiation, the reaction passes from reaction rate controlled to mass transfer controlled (re: Figure 7); there being some critical input of UV which causes the total oxidation to follow the $O_3$ input limiting line.

The reaction may be visualized as follows:

$$A + h\nu \rightarrow R\cdot's \qquad (10a)$$

$$R\cdot's + O_3 \rightarrow P_1 \qquad (10b)$$

$$P_1 + h\nu + O_3 \rightarrow P_2 \qquad (10c)$$

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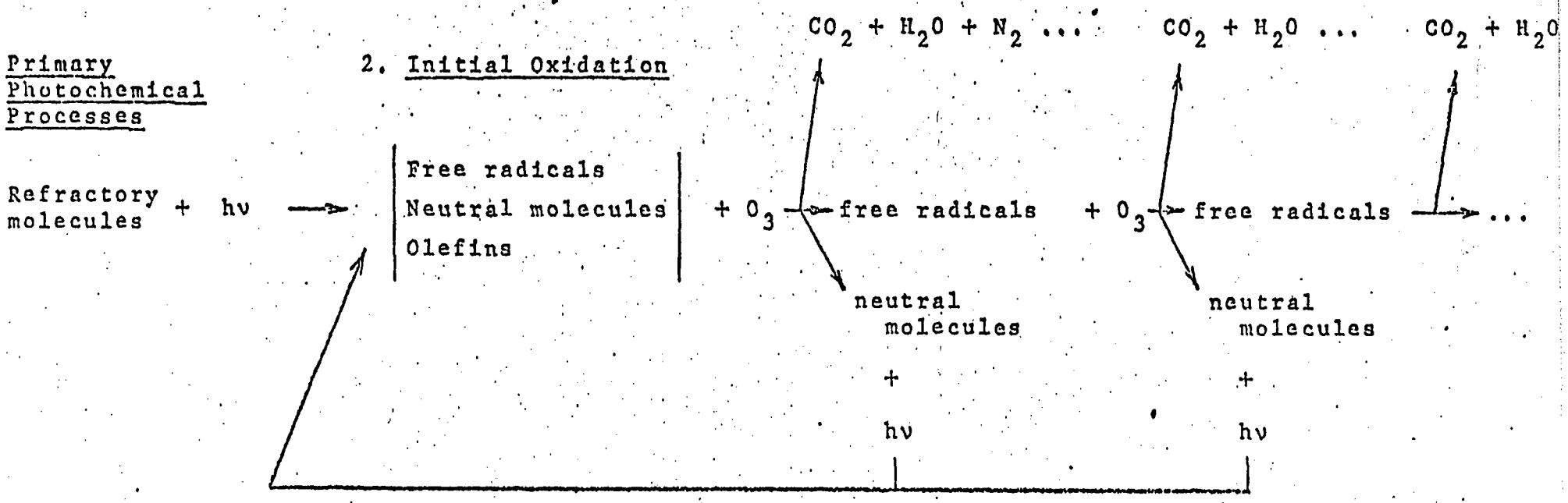


FIGURE 13. Overall Photochemical/Oxidation Process to Produce $CO_2$, $H_2O$, etc.

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$$P_2 + h\nu + O_3 \rightarrow CO_2 + H_2O + \cdots \quad (10d)$$

---

$$\text{Overall: } A + h\nu + O_3 \rightarrow CO_2 + H_2O + \cdots \quad (10e)$$

where, R·'s are the free radicals, and $P_1$, $P_2$ are the intermediate species.

When the amount of UV radiation is small, and the chemical reactions are rate controlling, the reaction can be visualized as being predominantly a three step sequence,

$$A \xrightarrow[h\nu, O_3]{k_o} P_1 \xrightarrow[h\nu, O_3]{k_1} P_2 \xrightarrow[h\nu, O_3]{k_2} P_3 \quad (CO_2 + H_2O + \cdots) \quad (11a)$$

and for this mechanism, it can be shown that,

$$\left(\frac{TOC}{TOC_o}\right) = \Omega_o e^{-\omega_o t} - \Omega_1 e^{-\omega_1 t} - (\Omega_o - \Omega_1 - 1) e^{-\omega_2 t} \quad (11b)$$

where, $\omega_o$, $\omega_1$, $\omega_2$ are the reaction rate moduli containing $k_o$, $k_1$, $k_2$, and,

$$\Omega_o \equiv \frac{\omega_1 \omega_2}{(\omega_1 - \omega_o)(\omega_2 - \omega_o)} \; ; \; \Omega_1 \equiv \frac{\omega_o \omega_2}{(\omega_1 - \omega_o)(\omega_2 - \omega_1)} \quad (11c)$$

When the amount of UV is larger, i.e., the critical amount, the reaction becomes mass transfer controlled, and many more smaller free radicals are produced which go directly to $CO_2$, $H_2O$, etc.

$$A + h\nu \rightarrow R\cdot\text{'s} \quad (12a)$$

$$R\cdot\text{'s} + O_3 \rightarrow CO_2 + H_2O + \cdots \quad (12b)$$

By the first law of photochemistry[19]

$$\dot{R}\cdot\text{'s} = \frac{\mu \phi a \dot{I}_\nu}{N_o h\nu} = k_\nu a \dot{I}_\nu \quad (12c)$$

where, the radiation transfer coefficient is defined as,

$$k_\nu a \equiv \frac{\mu \Phi a}{N_o h\nu} \quad , \left(\frac{\text{mols/vol}}{\text{time,watt}}\right) \text{ or } \left(\frac{\text{mass/vol}}{\text{time,watt}}\right) \tag{12d}$$

Then at critical UV input $\dot{I}_{\nu c}$ and mass transfer limiting, the disappearance of TOC is given by;

$$\left(\frac{TOC}{TOC_o}\right) = 1 - \left(\frac{\dot{m}_B}{b m_{Ao} V}\right) t = 1 - \left(\frac{k_\nu a V \dot{I}_{\nu c}}{m_{Ao}}\right) t \tag{12e}$$

$$= 1 - \theta t$$

where $\theta$ is defined as the radiation modulus, with dimensions as follows:

$$\theta \equiv k_\nu a \left(\frac{V}{m_{Ao}}\right) \dot{I}_{\nu c} \tag{12f}$$

$$\frac{1}{\text{time}} = \left(\frac{\text{mols/vol}}{\text{time,watt}}\right) \left(\frac{\text{vol}}{\text{mols/vol}}\right) \left(\frac{\text{watts}}{\text{vol}}\right)$$

For all cases, the limits as well as intermediate situations, one can construct a function,

$$\left(\frac{TOC}{TOC_o}\right) = f_1(t)\, f_2(t) \tag{13a}$$

where $f_1(t)$ is function (12e) and $f_2(t)$ is function (11b), then,

$$\left(\frac{TOC}{TOC_o}\right) = (1-\theta t)[\Omega_o e^{-\omega_o t} - \Omega_1 e^{-\omega_1 t} - (\Omega_o - \Omega_1 - 1) e^{-\omega_2 t}] \tag{13b}$$

in the limits,

a) when UV input is small, $f_1(t) \approx 1$ and $\left(\frac{TOC}{TOC_o}\right) = f_2(t)$

b) when UV input is large, t is small, $f_2(t) \approx 1$ and $\left(\frac{TOC}{TOC_o}\right) \approx f_1(t)$.

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The model is illustrated by the following example. For a particular reaction, the chemical reaction moduli are, $\omega_o = 2.30\ hr^{-1}$, $\omega_1 = 0.72$, and $\omega_2 = 12.0$; and the ozone feed rate gives $(\dot{m}_B/bm_{Ao}) = 1.0\ hr^{-1}$. Time profiles $(TOC/TOC_o)$ are desired for different values of input radiation from low level to critical level, $\theta = 0.01, 0.20\ 0.50, 1.00$. The function is,

$$\left(\frac{TOC}{TOC_o}\right) = (1-\theta t)[1.549e^{-0.72t} - 0.564e^{-2.3t} + 0.015e^{-12.0t}] \quad (13c$$

Figure 14 shows the time profiles. From experimental runs it would be necessary to determine $\dot{I}_{vc}$ (watts/vol) and calculate the radiation transfer coefficient $k_v a$.

A summary of $\omega$-values for the various compounds studied, with and without UV (low level) is presented in Table 4. A typical situation might be that $A \rightarrow P_1$ is fairly rapid ($\omega_o$ is relatively large), $P_1 \rightarrow P_2$ is slow ($\omega_1$ is small) and $P_2 \rightarrow P_3$ is very rapid ($\omega_2$ is large); the oxidation of ethanol follows this pattern. In addition, it must be kept in mind that highly refractory species, like acetic acid which shows little tendency to oxidize with ozone alone, can be moved into the rapid reaction regime with UV and, in fact, can be moved all the way to the limiting line by the proper amount of UV radiation, representing an enhancement of $10^2$ to $10^4$ times.

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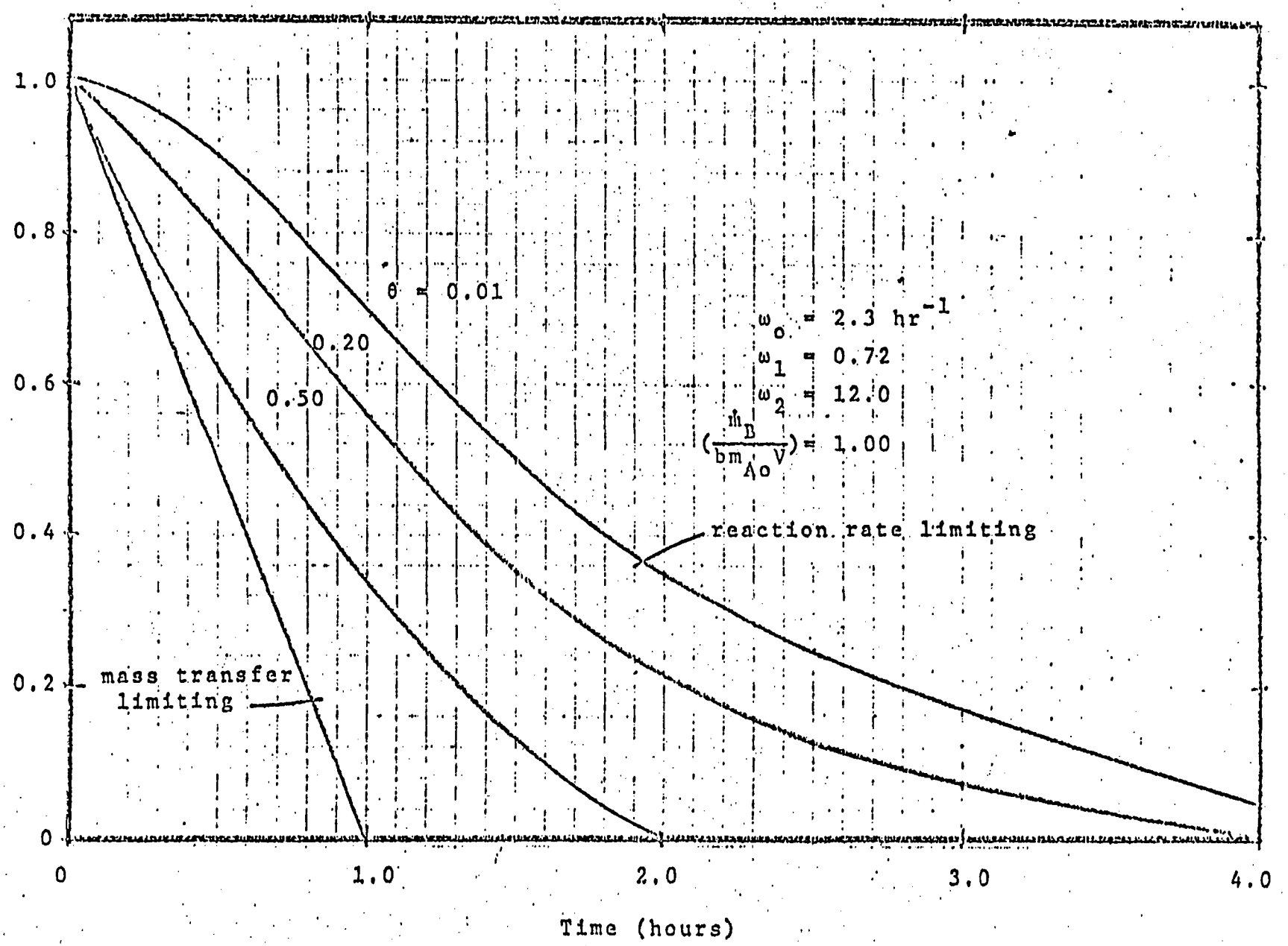


FIGURE 14. Calculated Time Profiles From Kinetic Model

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TABLE 4 - SUMMARY OF CHEMICAL REACTION MODULI

| Compound | T, °C | UV | $\omega_o$, $hr^{-1}$ | $\omega_1$, $hr^{-1}$ | $\omega_2$, $hr^{-1}$ |
|---|---|---|---|---|---|
| Acetic Acid | 30 | Yes | 2.290 | 0.717 | 11.700 |
| Acetic Acid | 50 | Yes | 1.466 | 1.254 | 4.078 |
| Ethanol | 27 | No | 0.388 | 0.117 | 1.861 |
| Ethanol | 30 | Yes | 1.009 | 0.886 | 1.013 |
| Ethanol | 50 | Yes | 2.355 | 1.830 | 6.525 |
| Gylcerol | 27 | No | 1.081 | 0.251 | 11.79 |
| Glycerol | 30 | Yes | 6.462 | 1.613 | 5.307 |
| Glycerol | 50 | Yes | 4.521 | 1.302 | 4.649 |
| Glycine | 27 | No | 2.519 | 0.964 | 2.909 |
| Glycine | 30 | Yes | 6.688 | 0.913 | 33.439 |
| Glycine | 50 | Yes | 2.660 | 2.781 | 2.657 |
| Am. Palmitate | 27 | No | 5.067 | 0.784 | 25.336 |
| Am. Palmitate | 30 | Yes | 9.077 | 2.335 | 83.308 |
| Am. Palmitate | 50 | Yes | 8.394 | 2.497 | 35.591 |

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## REACTOR AND MASS TRANSFER

Laboratory reaction units commonly used to study heterogeneous, gas-liquid reactions are of two types:

a) batch continuously sparged reactors (BCSR), i.e., liquid phase is batch, gas flow is continuous; or
b) continuous reactors (CSTR), liquid and gas continuously fed to the reactor.

Data from the second type simulate prototype reactors and operation, but are very time consuming for collecting experimental data since essentially only one point can be obtained per run. On the other hand, a BCSR offers the advantages of convenience and savings in time, since many data points can be obtained per run.

A BCSR was used to obtain the data reported in this investigation and was described previously[4].

The ultraviolet lamp used was a General Electric germicidal lamp, No. G15T8; a 15 watt low pressure mercury lamp with the major part of the UV energy emitted at a wavelength of 254 nm. About 60% of the electrical power to the lamp is converted to ultraviolet light in the proper frequency range, but only 74% of the ultraviolet light is transmitted through the lamp wall and the lamp is normally submerged about two-thirds of its length. This results in a useful ultraviolet input of 0.44 watts per liter of reactor liquid.

In using a BCSR, it is essential that the configuration used permits scaleup. Principles of design have been described and discussed previously[20], and additional work by Prengle and co-workers[21], indicates that the standard reactor configuration shown in Figure 15 satisfies existing correlations



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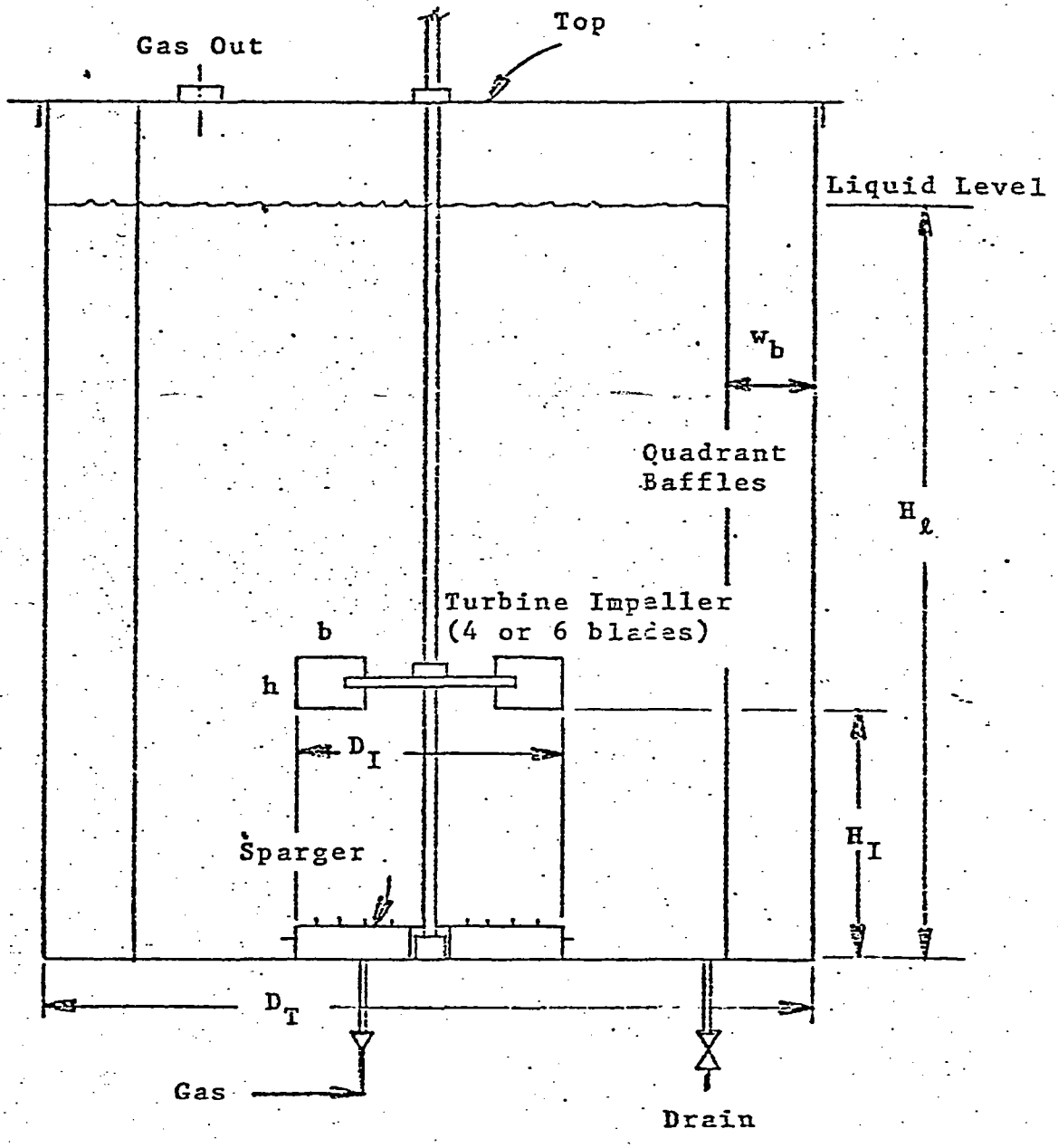


FIGURE 15. Standard Hydrodynamic Reactor Configuration

Dimensions: $H_\ell = D_T$, $w_b = D_T/10$, $D_I = D_T/3$, $H_I = D_I$

Sparger Holes: 3 - 1/16" holes/in$^2$ of sparger cross-section

Impellers: $b = D_I/4$, $h = D_I/5$

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of power input, mass transfer coefficients, and interfacial area, in the most predictable and reproducible fashion. Adopting the standard configuration permits scaleup from bench scale to pilot scale to full scale; for a single stage or multistaged system, without difficulty. Also, the reactor can be readily fit with UV-tubes for photolysis runs.

Mass transfer data were independent of chemical reaction in order to obtain certain base values, and the time profiles are presented as Figure 16, both with and without UV radiation. The data were analyzed, determining the following parameters:

$k_L a$, the mass transfer coefficient;

$k_o$, the $O_3$ auto-decomposition rate constant, previously studied by Hewes and Davidson[22];

$\eta \equiv (1 + \frac{k_o}{k_L a})$, the inhibition coefficient; and

$C_{Be}$, the $O_3$ equilibrium concentration (plateau value).

The reactor was operated in the "complete-mixing" regime (500-800 rpm).

Table 5 presents the results. It will be noted that,

1) Without UV, the equilibrium $O_3$ concentration is 12-14 mg/l. The mass transfer coefficient is approximately 1.4 (lb mols $O_3/ft^3$ min) and the auto-decomposition constant is in the range of 5% to 20% of the mass transfer coefficient.

2) With UV, the equilibrium $O_3$ concentration is much lower, at about 2 mg/l, and assuming the mass transfer coefficient to be about the same (i.e., 1.4), the auto-decomposition constant is approximately five times the mass transfer coefficient.

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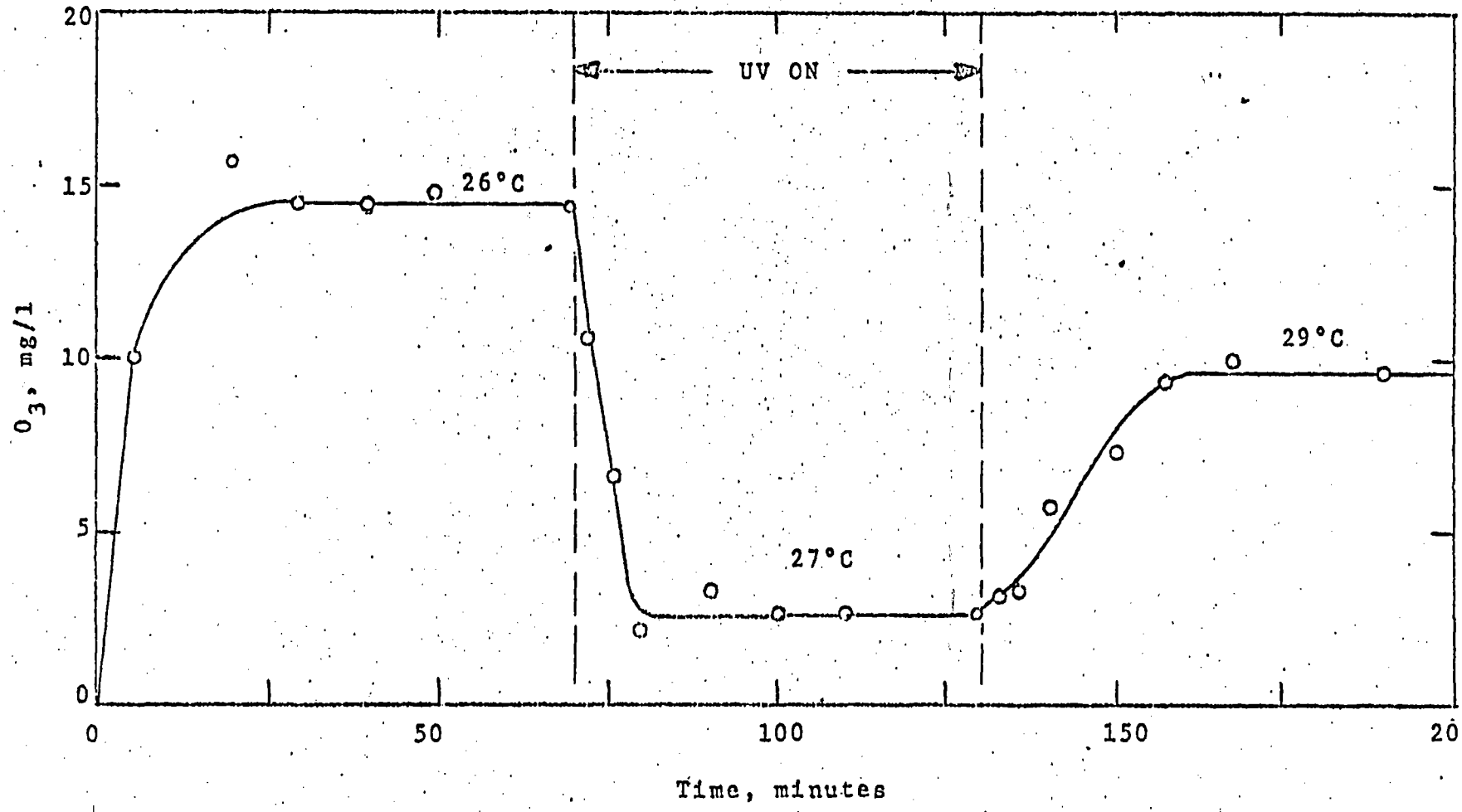


FIGURE 16. Mass Transfer; Equilibrium Ozone in Water
[Effect of UV and T]



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TABLE 5. Mass Transfer Data

| T °C | Stirring (RPM) | Gas $\left(\frac{ft^3}{min\ ft^2}\right)$ | w% $O_3$ | $C_{Be}$ (mg/l) | $\eta \equiv \frac{C_B^*}{C_{Be}}$ | $k_La$ $\left(\frac{lb\ mols}{ft^3\ min}\right)$ | $k_o$ $\left(\frac{lb\ mols}{ft^3\ min}\right)$ | $\left(\frac{k_o}{k_La}\right)$ |
|---|---|---|---|---|---|---|---|---|
| Without UV | | | | | | | | |
| 26 | 548 | 0.0774 | 3.15 | 14.4 | 1.055 | 1.33 | 0.0734 | 0.0550 |
| 26 | 720 | 0.0774 | 3.15 | 12.5 | 1.22 | 1.43 | 0.307 | 0.215 |
| With UV (1.51 watts/liter) | | | | | | | | |
| 27 | 548 | 0.0774 | 3.15 | 2.50 | 5.34 | (1.38) | 6.00 | 4.35 |
| 28 | 720 | 0.0774 | 3.15 | 1.90 | 7.75 | (1.38) | 9.17 | 6.65 |

$C_B^*$ ≡ Henry's Law equilibrium solubility value

$C_{Be}$ ≡ Equilibrium plateau value = $C_{Be}^*/\eta$



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The latter point raises the obvious question: if auto-decomposition of $O_3$ is so much greater with UV, why is reaction rate enhanced so greatly with UV? Several points are pertinent to a possible explanation:

1) In general, for the chemical reaction case three rate constants are competing, k, $k_o$, and $k_L a$; for a given $k_L a$, k and $k_o$ compete.

2) UV attenuates very rapidly as a function of distance in a liquid, therefore, it can be presumed that the reaction is occurring primarily in the liquid film as it is swept by the UV transfer surface (exterior of the bulb).

3) UV enhancement of the reaction rate is so great, $10^2$ to $10^4$ times, that $O_3$ is used up as soon as it appears in the liquid and has very little time to auto-decompose.

The above suggests that UV input should be dispersed in the reactor via several UV tubes, rather than a single tube, for best results.

CONCLUSIONS

1. A refractory index (RFI) was established in order to compare the difficulty of oxidation of various compounds. The compounds studied fell in the range from slightly refractory to highly refractory on the RFI scale.

2. For refractory compounds, the use of UV enhances reaction with ozone $10^2$ to $10^4$ fold, and drives the reaction to completion, $CO_2$, $H_2O$, etc.; whereas without UV the final products, in some instances, are stable compounds, e.g., ozonides.

3. Acetic acid, an end product of bio-oxidation, was the most refractory of the compounds studied. The use of UV substantially enhances the oxidation rate, and, in fact, moves the rate from the reaction controlled to the mass transfer

controlled regime. Elevated temperature also enhances the reaction rate, but not as dramatically as additional UV.

4. Ethanol, less refractory than acetic acid, was oxidized readily by ozone with UV. Also, temperature enhanced the rate.

5. Glycerol, glycine, and palmitic acid were less refractory than acetic acid or ethanol, and their reaction rates were enhanced substantially by UV. The existence of multiple oxidation sites in these molecules also accelerated the reaction rate. Operation in the mass transfer controlled regime, using ozone with UV, is not difficult to achieve.

6. Of the types of refractory compounds found in municipal wastewater, alcohols and acids are the most difficult to oxidize; while amino acids, fatty acids, and polyhydroxy alcohols are relatively easy to oxidize. For the acids, the difficulty does not arise from decomposition of the acids themselves, but from decomposition of partial oxidation products. Alcohols convert quickly to acids; the acids formed are constantly reacting as they build up, but concentrations are always considerably less than the corresponding initial concentration. The resulting refractory effect is, therefore, not as extreme for the alcohols as for the acids. Amino acids, fatty acids, and polyhydroxy alcohols also form acids on oxidation, but at a much slower rate than alcohols and refractory effect is less than for alcohols.

7. At room temperature, without UV radiation and with good reactor mixing, an equilibrium ozone concentration of 14 mg/l was reached. The ozone mass transfer coefficient, $k_L a$, was 1.4 lb mole/ft$^3$-min and the ozone autodecomposition rate constant was 0.2 lb mole/ft$^3$-min. In the presence

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of UV radiation the equilibrium ozone concentration in the liquid fell to approximately 2.0 mg/l, giving an increase in the autodecomposition rate constant to approximately 8 lb mole/ft$^3$-min. This substantial increase in the autodecomposition rate is not detrimental since the use of UV also enhances the reaction rate, and if one operates in the mass transfer controlled region, the ozone is used as rapidly as it is transferred into the liquid phase.

8. Based on these results, a properly designed multistaged reactor system, with ozone and ultraviolet radiation can accomplish essentially complete removal of refractory materials. Prototype units can be designed for field applications.

ACKNOWLEDGEMENT

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NOTE: Standard chemical and algebraic symbols are used throughout the text or are defined in the body of the text.

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Exhibit C

# Ozone/UV process effective wastewater treatment

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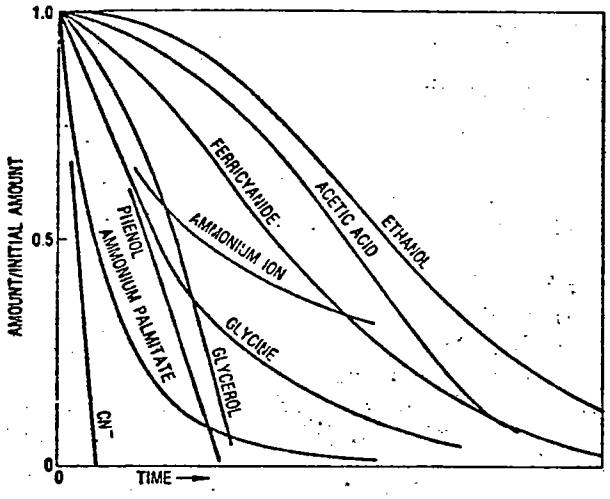


Fig. 1—Typical removal curves for refractory compounds by ozone with UV near 30° C.

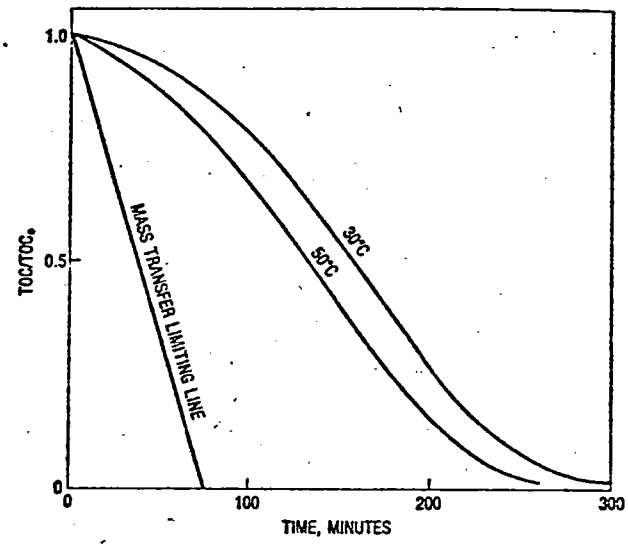


Fig. 2—Ozone oxidation of acetic acid, effect of temperature at low UV intensity.

phase from $t = 0$ to $t = t_{½}$, per liter of liquid

$t_{½}$ is the time required for 50 percent complete conversion of the reactant component, as measured by TOC for organic species and an appropriate method for inorganic species

$A_o$ is the initial amount of reactant component

$\dot{m}_B$ is the $O_3$ mass feed rate to the reactor

$V$ is the liquid volume in the reactor.

Values of *RFI* of various compounds studied are shown in Table 1. Potassium cyanide (free cyanide) is least refractory of all compounds studied; acetic acid is most refractory, with complexed ferricyanide, ethanol and glycerol in the highly refractory category.

## OZONE OXIDATION WITH UV

Although the Ozone-UV process was initially developed for treatment of complexed cyanides,[2] it is successfully applied to treatment of many other wastewater species some of which are represented in Fig. 1. Curves of Figs. 1, 2 and 3 result from experimental studies in a batch, continuously sparged and stirred mix reactor. Reactor design permits direct size scaleup without difficulty.[3,4]

Acetic acid, which is an important intermediate oxidation product of most organic materials, is also one of the more difficult to oxidize species (Fig. 1). However, a slight elevation in temperature has a marked effect on acetic acid destruction (Fig. 2). The mass transfer limiting line is the theoretical stoichiometric limit based on the rate at with ozone is added to the liquid. Improvement up to this limiting line by elevating temperatures alone is impractical.

Ultraviolet light can be used to further improve ozone oxidation of acetic acid (Fig. 3). No reduction of TOC

**TABLE 2—Photochemical data on refractory compounds**

| Compound/(RFI) | Structure | UV absorption range (nm) | Primary photochemical processes | Reference |
|---|---|---|---|---|
| Acetic acid (>1,000) | $H_3C-C(=O)-OH$ | Peak: 205<br>180–230 | 1) $R + CO_2H^{++}$ (or $CO_2 + H$)<br>2) $RCO_2^{++}$ (or $R + CO_2$) + H<br>3) $RCO^{++}$ (or $R + CO$) + OH<br>4) $RH + CO_2$ | [5](p. 428 and 431) |
| Ferricyanide (270) | $[Fe(CN)_6]^{-3}$ | 230 | Electron transfer to water of hydration | [5](p. 270) |
| Ethanol (245) | $H_3C-CH_2-OH$ | Peak: 182, 152<br>150–200 | 1) $C_2H_5^{++}$ (or $C_2H_4 + H$) + OH<br>2) $CH_3CH_2O^{++}$ (or $CH_3 + CH_2O$) + H<br>3) $C_2H_4 + H_2O$<br>4) $CH_3CHO + H_2$<br>5) $CH_4 + CH_2O$ | [5](p. 442, 444) |
| Glycerol (112) | $H_2C(OH)-CH(OH)-CH_2(OH)$ | Peak: 210, 260<br>190–280 | Free radical and intramolecular photodissociative processes | [6] |
| Glycine (20) | $H_2N-CH_2-C(=O)-OH$ | Peak: 240, 210<br>190–240 | 1) Acid type processes, and<br>2) Amine type, RNH + H | [5](p. 455 ff) |
| Chloroform | $HCCl_3$ | Peak: 285, 180<br>250, 240 | 1) Free radicals (similarly for $CCl_4$) | [5](p. 526, 527) |
| Ozone | $O_3$ | Peak: 260<br>150–300 | 1) $O_3(S_o) \rightarrow O_2(S_1)$<br>2) $O_3(S_1) \rightarrow O_2(^1\Delta_g) + O(^1D)$<br>3) $O_3(S_o) \rightarrow O_3(T_1) \rightarrow O_2(^3\Sigma_g^-) + O(^3P)$ | [5](p. (207-209) |

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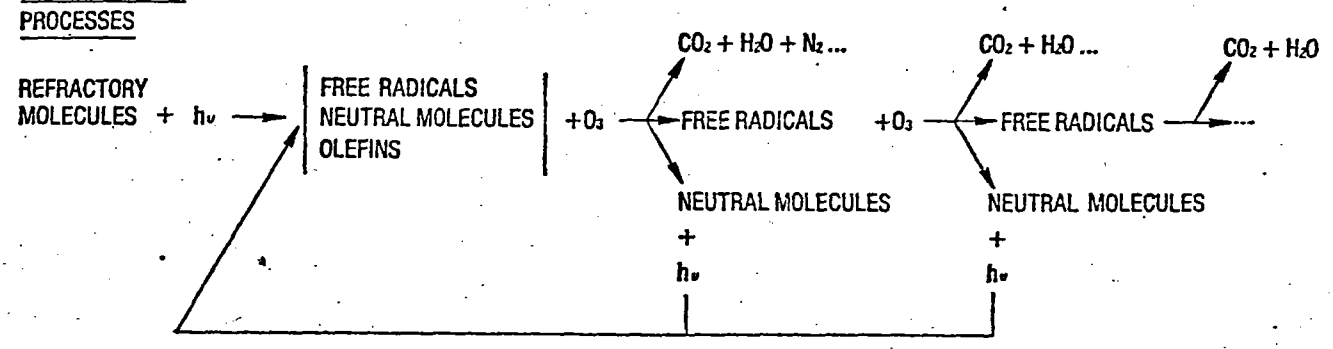


**Fig. 5**—Over-all photochemical/oxidation process to produce $CO_2$, $H_2O$, etc.

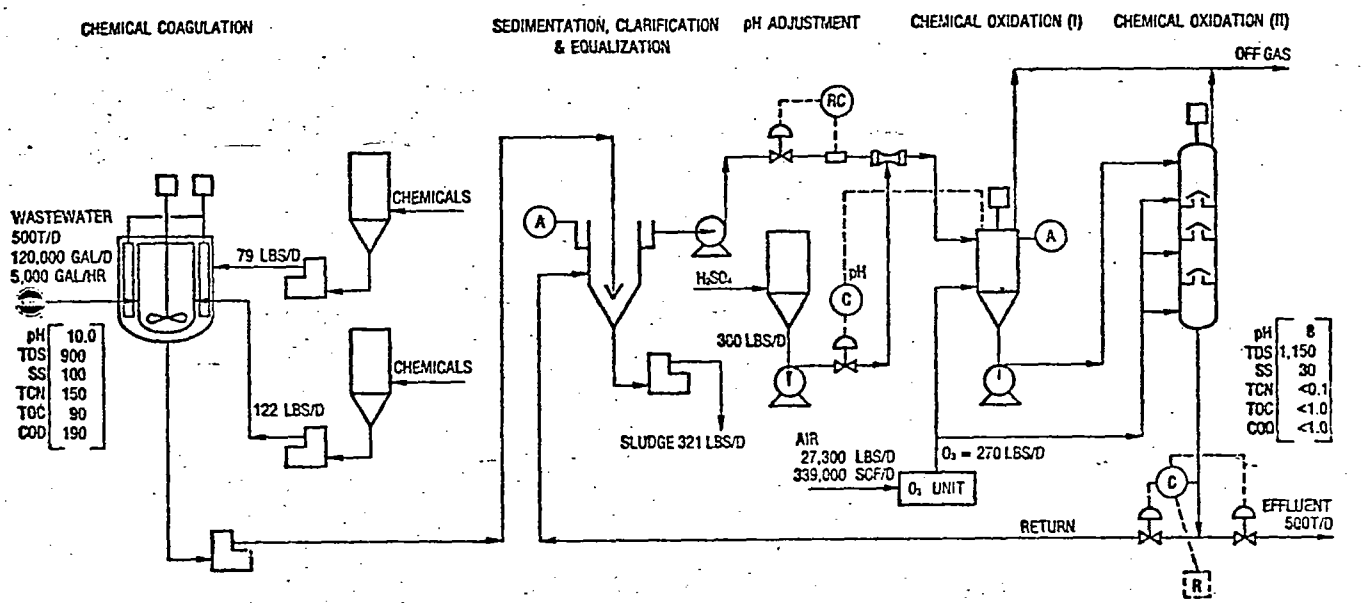


**Fig. 6**—Process flow for mixed cyanides plus organic refractories oxidation.

$$RC(H)(O)-C(=O)-OH + O_3 \rightarrow RC(H)(O)-C(=O)-OH \rightarrow RC(H)(O)-C(=O)-OH + O_2 \qquad (3)$$

The cycle of the chain propagation is then closed by the free radical removing a hydrogen from a neutral molecule

$$RC(H)(O\cdot)-C(=O)-OH + RH \rightarrow RC(H)(OH)-C(=O)-OH + R\cdot \qquad (4)$$

with the unstable molecule immediately rearranging to release $CO_2$

$$RC(H)(OH)-C(=O)-OH \rightarrow RC(H)(H)-OH + CO_2 \qquad (5)$$

In a similar manner, alcohol formed is oxidized to an aldehyde, which is in turn oxidized to an acid. Therefore, for long chain molecules a cycle results,

*alcohol → aldehyde → acid → alcohol + $CO_2$*

and in the limiting case of a one-carbon-chain, water (not alcohol) is formed on oxidation of the acid.

UV radiation produces substantially more free radicals than ozone alone; the radicals initiate many more propagation chains and cause the over-all reaction to proceed much, much faster. The over-all photochemical process to produce $CO_2$, $H_2O$, $N_2$, etc., can be represented schematically (Fig. 5). The two-step initiation process (primary photomechanical process and initial $O_3$ oxidation) is fol-

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alum, activated silica and polyelectrolyte, followed by sedimentation, clarification and equalization. The pH is adjusted to 7-8 by acid addition for best results in the chemical oxidation reactors. A single-stage reactor (I) to oxidize front end RFI compounds is followed by a multistage reactor for final oxidation of high RFI compounds. Multistaging permits more effective oxidation, reduces total reactor volume and thereby capital cost. Ozone is supplied by a commercially available ozonator. The unit operates on air.

Installed plant cost is $590,000 and operating cost, including amortization, is approximately $500/day.

► Removal of ammonia, cyanide and organic nitrogen compounds (Fig. 7).

Wastewater treatment processing 700 tons/day (117.4 gpm) containing ammonia, cyanide and organic nitrogen compounds with a total nitrogen content of 1,000 mg/l. The objective of the plant is to reduce the ammonia, cyanide and organic materials to a dischargeable level. The first step is to adjust pH to basic and strip out ammonia with steam. Afterward, pH is further adjusted to near neutral for best results in two chemical oxidation reactors. Ozone is provided by generators using recycled oxygen. Installed facility cost is $334,000 and operating cost (including amortization) is approximately $225/day.

► Tertiary treatment to specifically oxidize refractory organics which would produce toxic compounds if chlorinated (Fig. 8).

Potentially toxic refractory organic compounds remaining after secondary treatment and carbon adsorption are removed in this facility. A stream of 1 million gallons/day contains 10 mg/l of TOC which must be reduced to a concentration of less than 0.1 mg/l. The influent stream from the previous units is flow controlled to the multistage reaction unit where compounds undergo complete oxidation to carbon dioxide and water. Ozone is supplied by commercially available ozonation unit operating on air. Ozone concentration is adjusted automatically by an effluent monitor. Installed cost of the entire facility is $505,000.

## PROCESS ECONOMICS

Effective reactor staging results in lower total amortized capital and operating costs (Table 3) where the optimum cost is less than a third of the single-stage treating cost. A similar cost analysis can be prepared for any wastewater species for which reaction rate data are available. Indication of the cost contribution for a reactor with mixer and ultraviolet lights is given in Fig. 9. Costs of ozone generated from air and from oxygen (Fig. 10) include the cost of oxygen.


### ACKNOWLEDGMENT

Houston Research, Inc., wishes to acknowledge the U.S. Air Force Contract (AFSC/AFWL), F29601-73-C-0065, and U.S. Army Contract (MERDC), DAAK02-74-C-0239, under which substantial development of this process was carried out.


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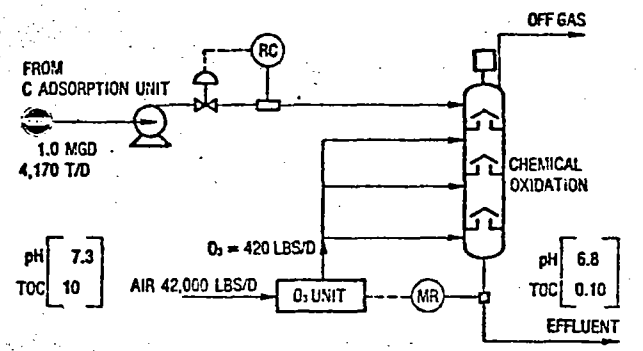


Fig. 8—Process flow for oxidation of refractory organics.

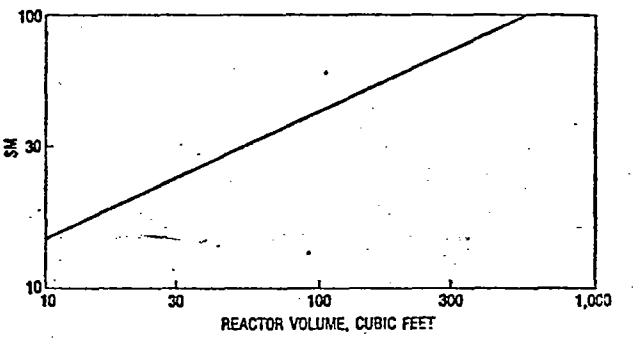


Fig. 9—Installed cost of stainless steel reactor, mixer and UV lights.

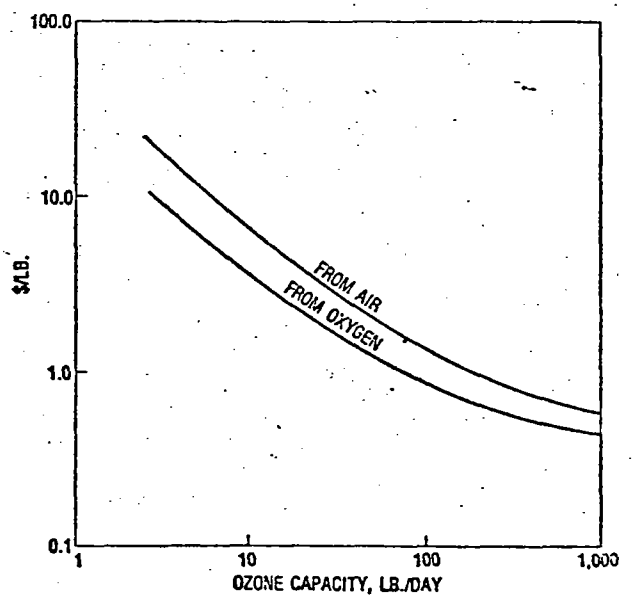


Fig. 10—Cost of producing ozone, including 10-year amortization.

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EXHIBIT 5

# OZONE/UV OXIDATION OF CHLORINATED COMPOUNDS IN WATER*

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ABSTRACT

The presence of chlorinated compounds in source water as possible carcinogens is of considerable current interest; therefore, an examination of the oxidation of these compounds is pertinent. Preliminary work on the ozone and ozone/UV oxidation rates, mechanisms, and intermediate and final products for: pentachlorophenol, dichlorobenzene, dichlorobutane, chloroform, and polychlorinated biphenyls is presented. Oxidation rates are substantially enhanced by ozone/UV, as compared to ozone alone, and can be made to go approximately stoichiometrically. Analytical methods were used to track the disappearance of the compounds, appearance of intermediates, and the production of chloride ion and chlorine. For compounds with large UV absorption the chlorine atoms are released very rapidly to form chloride ion; whereas for low level UV absorbers dechlorination occurs by oxidation releasing the atoms as chlorine and thence to hypochlorous acid. Pentachlorophenol is a strong UV absorber and releases chlorine by the former mechanism; whereas chloroform is a weaker absorber and both dechlorination mechanisms occur.

*Presented at the International Ozone Institute Forum on Ozone Disinfection; Chicago, Illinois, June 2-4, 1976.

(For Reference Only)


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Table 1. RFI Values for Compounds

Table 2. Molecular Characteristics

Figure 1. Pentachlorophenol UV-Spectrogram

Figure 2. Destruction of Pentachlorophenol TOC

Figure 3. Related Time Profiles -- Oxidation of Pentachlorophenol

Figure 4. Destruction of 1. Dichlorobenzene; 2. Dichlorobutane

Figure 5. Destruction of Polychlorinated Biphenyls

Figure 6. Destruction of Chloroform TOC




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## INTRODUCTION

As a result of substantial recent interest in the presence of chlorinated compounds, as possible or suspected carcinogens, in source waters and municipal water supplies[1,2,3], Houston Research, Inc. is currently investigating the oxidation of a number of chlorinated compounds by ozone, and ozone or oxygen with UV radiation. The work is a continuation of previously reported work[4,5,6] on the development of an advanced chemical oxidation water treatment system for the destruction of hazardous and refractory materials.

The work reported herein examined oxidation rates, under a wide variety of conditions, and reaction mechanisms and products, for the following five compounds:

Pentachlorophenol
O-dichlorobenzene
Dichlorobutane
Chloroform
Polychlorinated Biphenyls

These were specifically chosen to insure a wide spread of organic molecular types which may be encountered. A crucial aspect of the work relates to the question of what are the subsequent products as the oxidation proceeds from the initial species to completion? Do the intermediates represent a greater potential hazard, and in particular, what happens to the chlorine atoms? In general, none of the five compounds are oxidized to the desired lower limits of concentration by ozone treatment alone, but require more severe treatment, viz ozone with UV.



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## CHARACTERIZATION OF COMPOUNDS

Previously, we have established a quantitative scale for refractory compounds[5]; the refractory index (RFI) was defined which measures the difficulty of oxidation of a given compound by ozone. Table 1 presents the latest list and indicates the five compounds relative to others that have been studied. It will be noted that the five compounds range from slightly refractory to highly refractory -- chloroform being the least refractory and polychlorinated biphenyls highly refractory.

As a result of recent work, the correlation of the amount and the spectral distribution of the UV absorption, over the range 180-450 nm, with reaction characteristics and rates is emerging. Consequently, such information is important in determining the particular UV radiators to be used in the reactor design. Table 2 presents some molecular characteristics of the compounds related to this matter. It will be noted that the integrated specific absorbance values range from $10^{+1}$ to $10^{+5}$ $cm^2$/millimoles, and have peaks generally at 180-240, 240-290, and 290-360 nm, which approximately correspond to the radiation ranges of commercially available UV radiators.



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TABLE 1. RFI VALUES FOR COMPOUNDS

| Compound | RFI* Value | Qualitative Scale |
|---|---|---|
| 1) Potassium cyanide (KCN) | 0.41 | Slightly Refractory (RFI < 1.0) |
| 2) Phenol | 0.44 | |
| 3) Chloroform | 0.53 | |
| 4) Color (α-units) | 0.66 | |
| 5) Complexed Cd-cyanide | 0.96 | |
| 6) Pentachlorophenol | 1.6 | Refractory (RFI = 1 → 100) |
| 7) Ammonium ion | 8. | |
| 8) Simulated Medical Waste | 13. | |
| 9) Glycine | 19.7 | |
| 10) Palmitic Acid ($NH_4$Salt) | 27.3 | |
| 11) Dichlorobutane | 56. | |
| 12) Glycerol | 112 | Highly Refractory (RFI = 100 → 1000) |
| 13) O-dichlorobenzene | 113 | |
| 14) Polychlorinated Biphenyls | 200 (est.) | |
| 15) Ethanol | 245 | |
| 16) Complexed Ferricyanide | 270 | |
| 17) Acetic Acid | >1000 | Very Highly Refractory (RFI > 1000) |

*RFI $\equiv \frac{B_c^o \, t_{1/2}}{A_o}$ ; [$B_c^o \equiv O_3$ supplied to $t_{1/2}$; $t_{1/2} \equiv$ time for 1/2 conversion of $A_o$; $A_o \equiv$ initial amount of compound.]

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TABLE 2. MOLECULAR CHARACTERISTICS

| Compound | Structure | Molecular Weight Solubility, mg/ℓ | UV-Specific Absorbance ($cm^2$/m mol) (λ, nm) |
|---|---|---|---|
| 1) Phenol | $C_6H_5OH$ | 94<br>$\cong 8.2\times10^4$ (15°C) | 1) $1.805\times10^{+3}$ (180-240 nm)<br>2) $0.543\times10^{+3}$ (240-290 nm) |
| 2) Pentachlorophenol | $C_6Cl_5OH$ | 266.5<br>80. | 1) $41.5\times10^3$ (200-236 nm)<br>2) $17.8\times10^3$ (236-275 nm)<br>3) $5.65\times10^3$ (275-355 nm) |
| 3) O-dichlorobenzene | $C_6H_4Cl_2$ | 147 | 1) $1.70\times10^3$ (180-240 nm)<br>2) $0.0419\times10^3$ (240-285 nm) |
| 4) Dichlorobutane | $Cl(CH_2)_4\ Cl$ | 127 | 1) $0.203\times10^3$ (180-220 nm)<br>2) $0.0165\times10^3$ (220-280 nm) |
| 5) Chloroform | $CH\ Cl_3$ | 119.5<br>$8.2\times10^3$ (20°C) | 1) $0.058\times10^3$ (180-220 nm)<br>2) $0.0028\times10^3$ (220-270 nm)<br>3) $0.018\times10^3$ (270-350 nm) |
| 6) Polychlorinated Biphenyls | $C_6H_aCl_5C_6H_cCl_d$ | 321<br>$5.6\times10^{-2}$ (20°C) | 1) $58\times10^3$ (180-250 nm) |



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## OXIDATION OF THE INDIVIDUAL COMPOUNDS

The experimental ozonation runs were carried out in stirred batch, continuously sparged gas, liquid phase reactors. The equipment and experimental procedures have been described previously[4,5]. The ultraviolet input (UV) levels referred to are given as watts of useful UV light per liter. A stoichiometric limiting line represents the theoretical maximum rate at which a compound could be oxidized for the particular $O_3$ rate to the reactor.

GC analyses were made to follow the disappearnce of the original species; TOC analyses to follow the destruction of intermediate oxidation products; and turbimetric chloride analyses to determine whether the chlorine atoms went to chloride or some other form. The pH measurements followed the formation and destruction of organic acids and the permanent formation of hydrochloric and hypochlorous acids.

### Pentachlorophenol (PCP)

Pentachlorphenol shows strong absorption of UV over a wide range of wavelength, as indicated by Figure 1. This makes it very susceptible to oxidation by ozone and typically the compound, as determined by gas chromatographic analysis, has reacted in less than 15 minutes residence time. The PCP was charged to the reactor at a concentration level of 70 mg/ℓ. The further oxidation of intermediate oxidation products, as indicated by total organic carbon (TOC) analysis, takes place less rapidly as shown by Figure 2. With the proper amount of UV input, the oxidation to completion proceeds essentially stoichiometrically.



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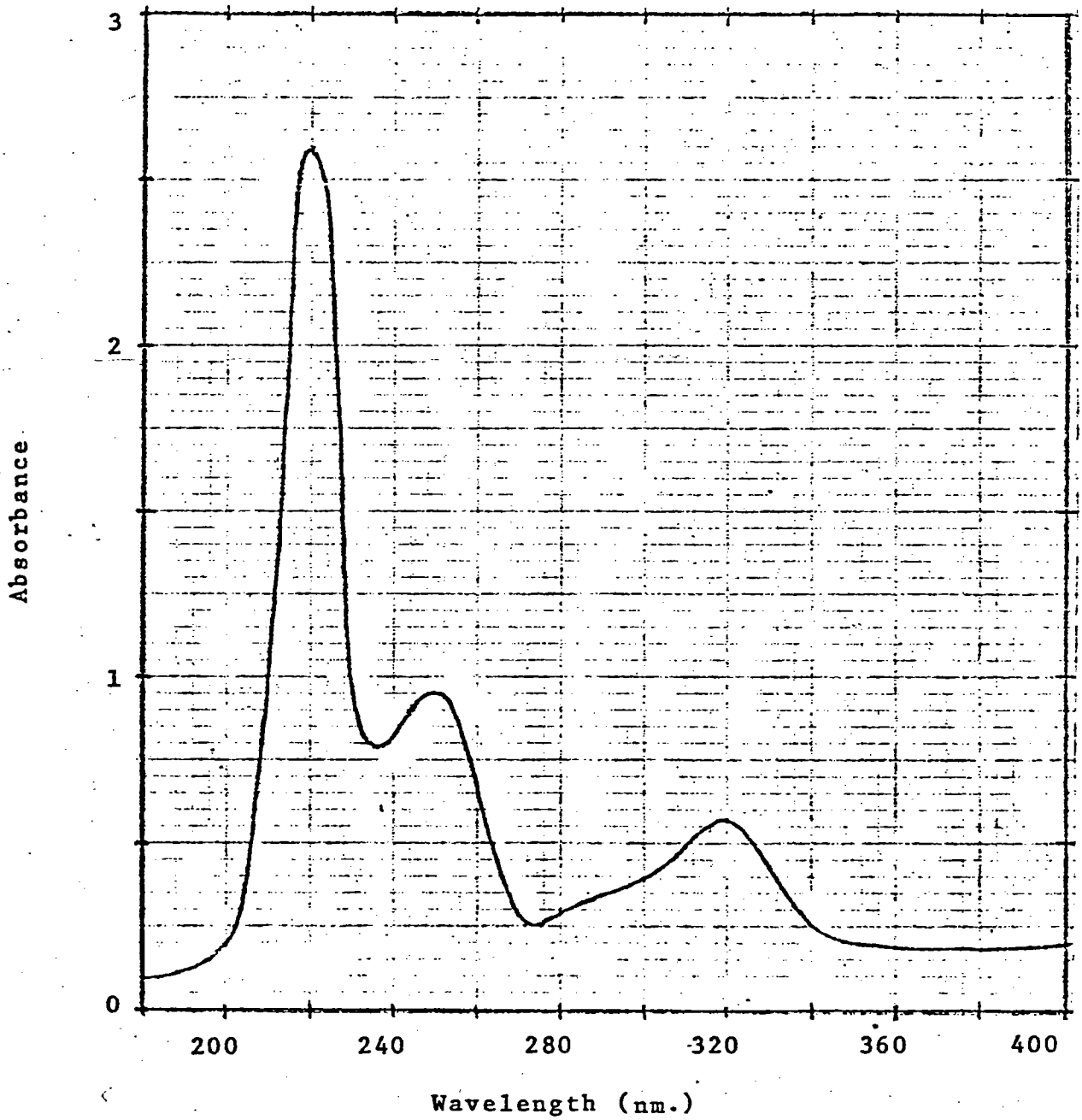


FIGURE 1. Pentachlorophenol UV-Spectrogram (7.0 mg/ℓ)

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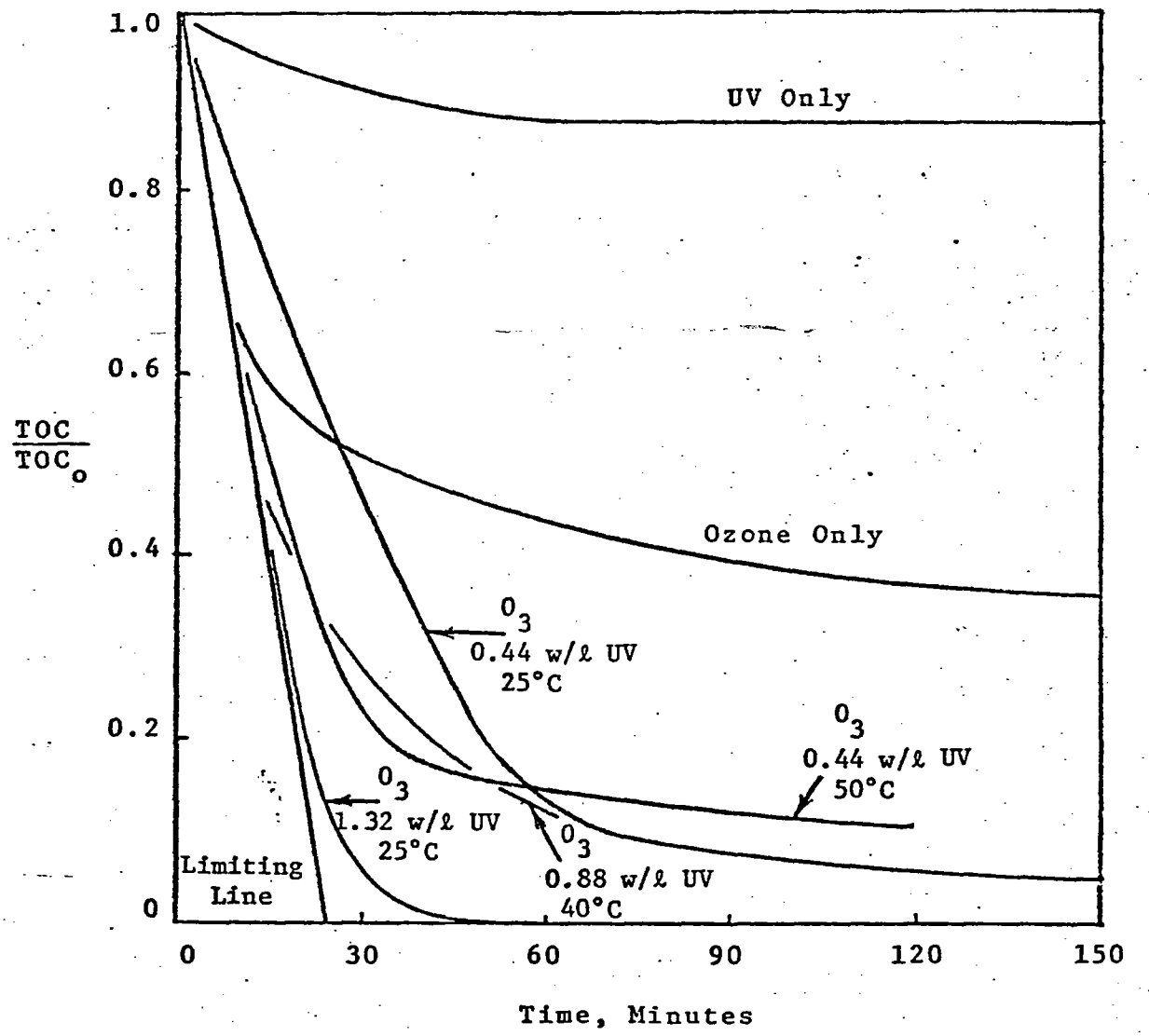


FIGURE 2. Destruction of Pentachlorophenol TOC (initial PCP, 70 mg/ℓ)

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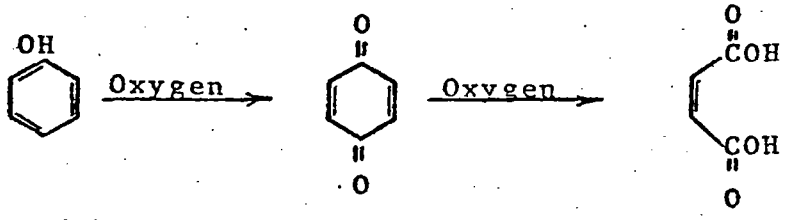
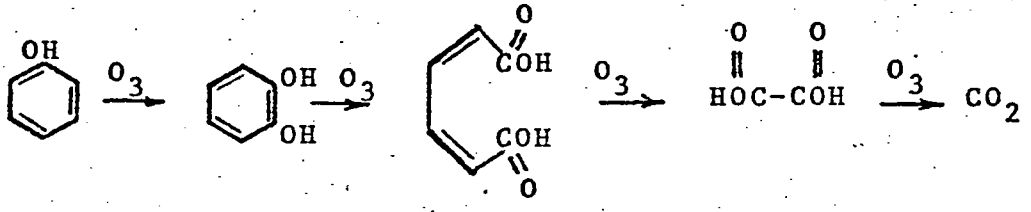
Because of similarity of structure, it is appropriate to consider first the oxidation of phenol. The classical oxidation is first to quinone, which further oxidizes to maleic acid,




Bailey[7] has reviewed the ozone oxidation of phenol, and he concludes that the major pathway is through catechol to muconic acid. Since oxalic acid is found as an intermediate oxidation product, it appears that the ozone attacks muconic acid at the double bonds. Following the carbon structure only, this gives,




As evidenced by TOC, phenol is converted to $CO_2$ by ozone-UV at essentially the stoichiometric rate. Because much of the conversion of pentachlorophenol to $CO_2$ is also at essentially the stoichiometrically limited rate, there is justification for assuming a similar oxidation mechanism. But in addition, the pentachlorophenol by gas chromatographic analysis disappears much faster than does the TOC; at the same time, the pH of the water drops drastically and a chloride concentration corresponding to more than half the stoichiometric amount suddenly appears and then slowly increases. With UV alone, the pentachlorophenol disappearance, PH drop, and chloride appearance is extensive, but much slower than with ozone-UV; with UV alone,



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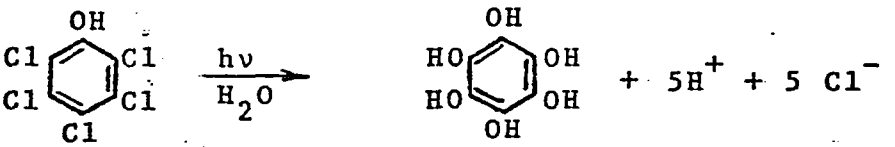
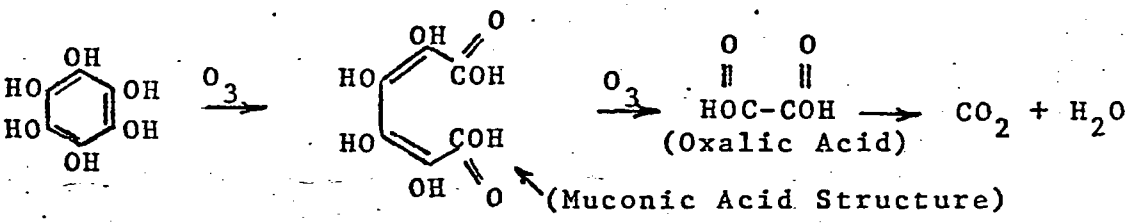
TOC disappearance is small. This implies an initial chlorine loss caused by UV,




(Catechol Structure)

followed by oxidation of the ring,




(Muconic Acid Structure)

It appears unlikely that the chlorine is released from the ring as free chlorine which would produce hypochlorous acid in aqueous medium; whereas analyses of the apparent ozone content of the water gives no indication of transient hypochlorite.

Confirmation of this mechanism can be made by examining the time profiles in Figure 3. As the UV rapidly removes the chlorine atoms from the compounds, the PCP drops to zero very rapidly, and the chloride ion concentration rapidly reaches a plateau. The pH drops rapidly from 9.6 because of the formation of HCl and phenolic compounds of an acidic nature. Then the pH drops more slowly as the phenolics are converted to the more acidic organic acids. As the TOC shows the organic acids being destroyed, the pH rises to a plateau near 5, resulting only from the unoxidizable HCl.

Dichlorobenzene (DCBZ)

O-dichlorobenzene is a strong absorber of UV, and by GC analysis disappears rapidly. When UV is used with ozone,



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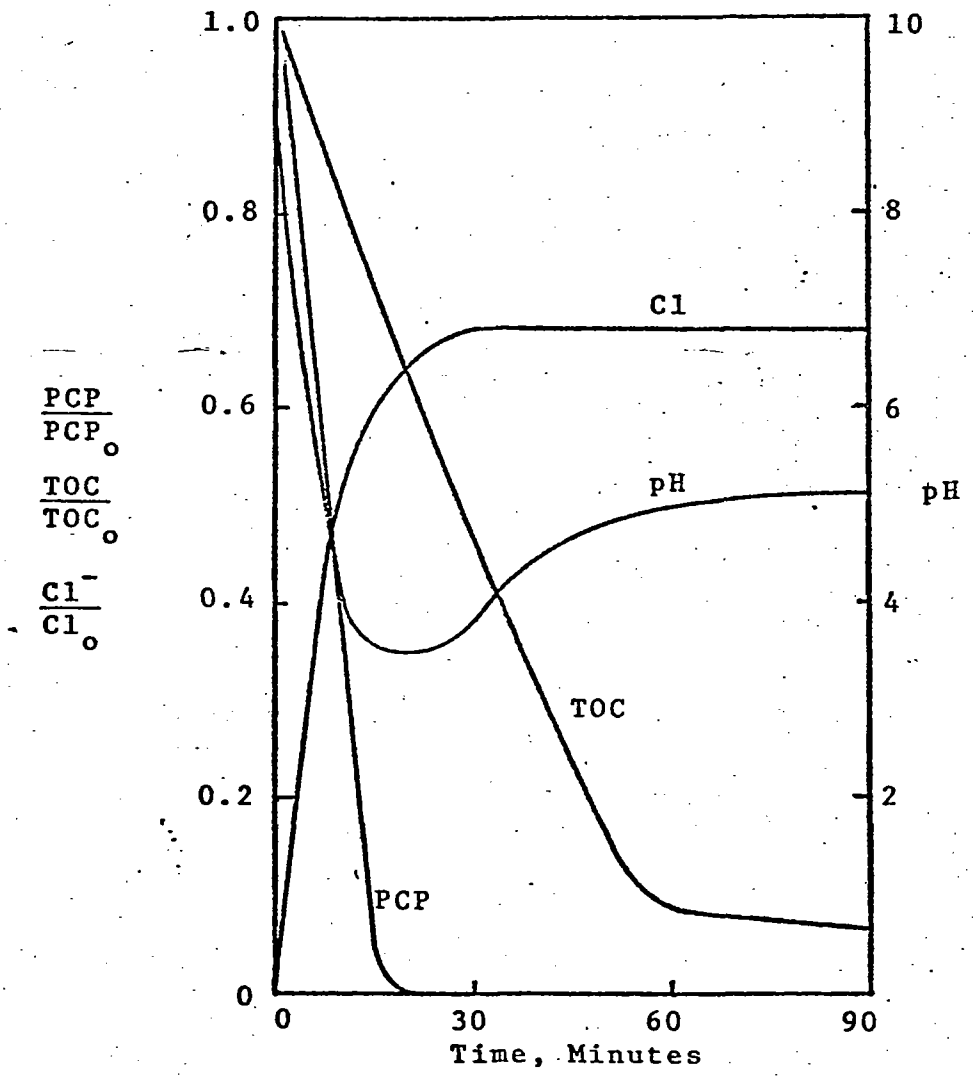


FIGURE 3. Related Time Profiles, Oxidation of Pentachlorophenol. (Re: Figure 2.)

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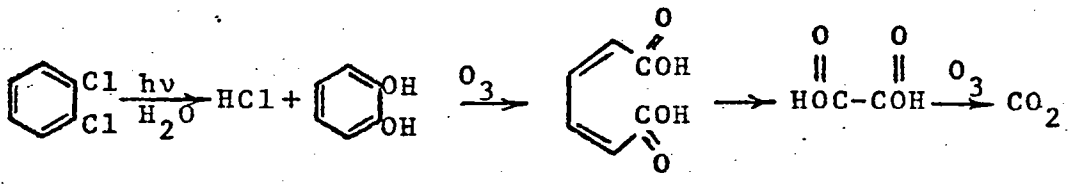
the chloride jumps to a value corresponding to about half of the chlorine in the molecule; suggesting an oxidation mechanism similar to pentachlorophenol,



DCBZ was charged to the reactor at the 100 mg/ℓ level, and by GC analysis was 95% destroyed in the first 15 minutes; destruction was complete by 30 minutes.

The destruction of TOC from intermediate oxidation products was not as rapid, as shown in Figure 4.

Dichlorobutane (DCB)

With ozone alone, the oxidation of 1,4 dichlorobutane proceeds relatively slowly and almost no chloride is formed. The molecule has a relatively low absorbance of UV, but when UV is used with ozone, the disappearance by GC is twice as fast, and a stoichiometric production of chloride is obtained, suggesting the oxidation mechanism to be,

$$Cl(CH_2)_4\,Cl \xrightarrow[H_2O]{h\nu} HCl + HO(CH_2)_4\,OH \xrightarrow{O_3} HOOC(CH_2)_2COOH$$

(dihydroxybutane) (Succinic Acid)

$$\xrightarrow{O_3} HOOC\text{-}COOH \xrightarrow{O_3} CO_2 + H_2O$$

(Oxalic Acid)

Dichlorobutane was charged to the reactor at the 50 mg/ℓ level, and by GC analysis was destroyed with $O_3$-UV by 50% at 15 minutes, and completely by 60 minutes. With $O_3$ alone, more than 60 minutes for 50% destruction and more than 240



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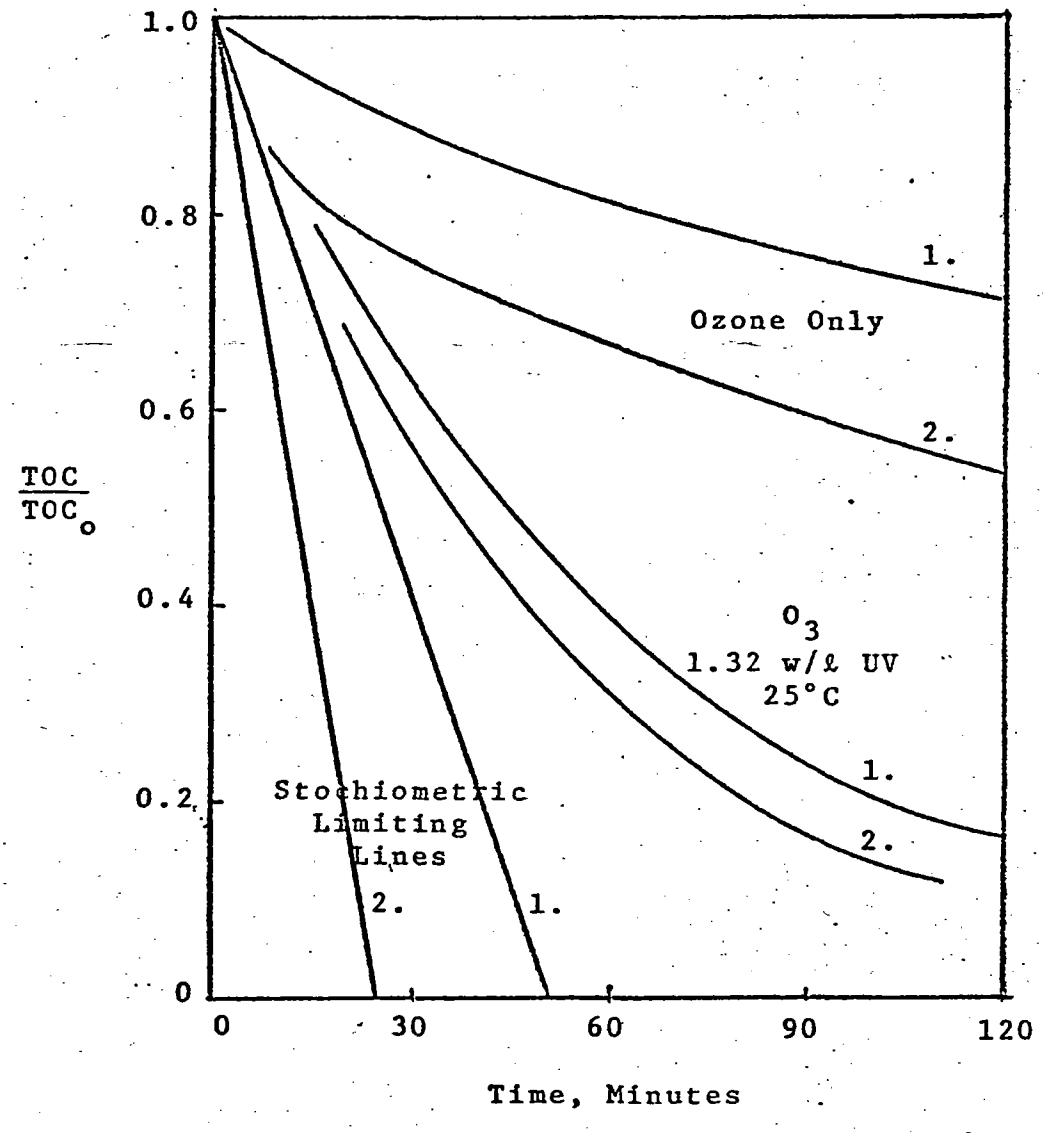


FIGURE 4. Destruction of 1. Dichlorobenzene (initial, 100 mg/ℓ). 2. Dichlorobutane (initial, 50 mg/ℓ).

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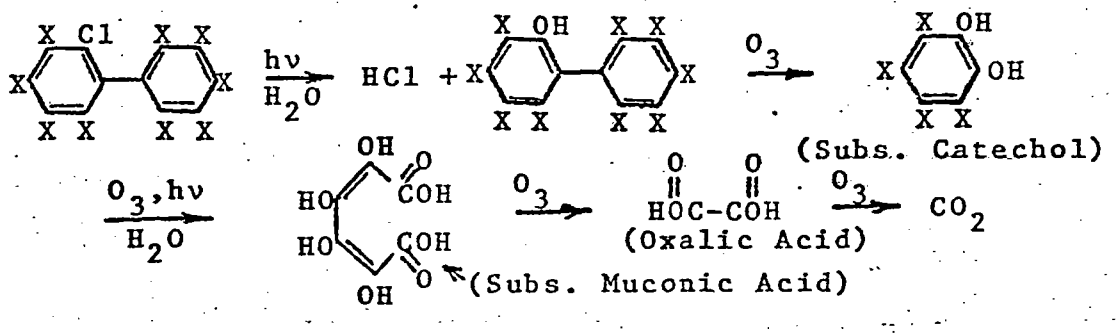
minutes for complete destruction is required. Destruction of TOC from dichlorobutane and intermediate oxidation products proceeds less rapidly, as shown in Figure 4.

Polychlorinated Biphenyl

The polychlorinated biphenyl (PCB) used was Aroclor 1254, essentially a mixture of isomers of pentachlorobiphenyl. In the environment, PCB degrades via successive dechlorination steps before the biphenyl structure degrades, by a mechanism which can be postulated to be similar to that of pentachlorophenol,




In the above structures, for the commercial product, X is undetermined and may be H, Cl, or OH.

Figure 5 shows the disappearance of PCB by GC analysis. The original charge was at the 0.5 mg/ℓ PCB level added to the water as a solution in methanol. The resulting dispersion in water was at about eight times the solubility of PCB in water. Since only the PCB in solution was being treated, the curve is also controlled by the rate at which the PCB is going into solution; even so, it will be noted that the rate of disappearance was fairly rapid!

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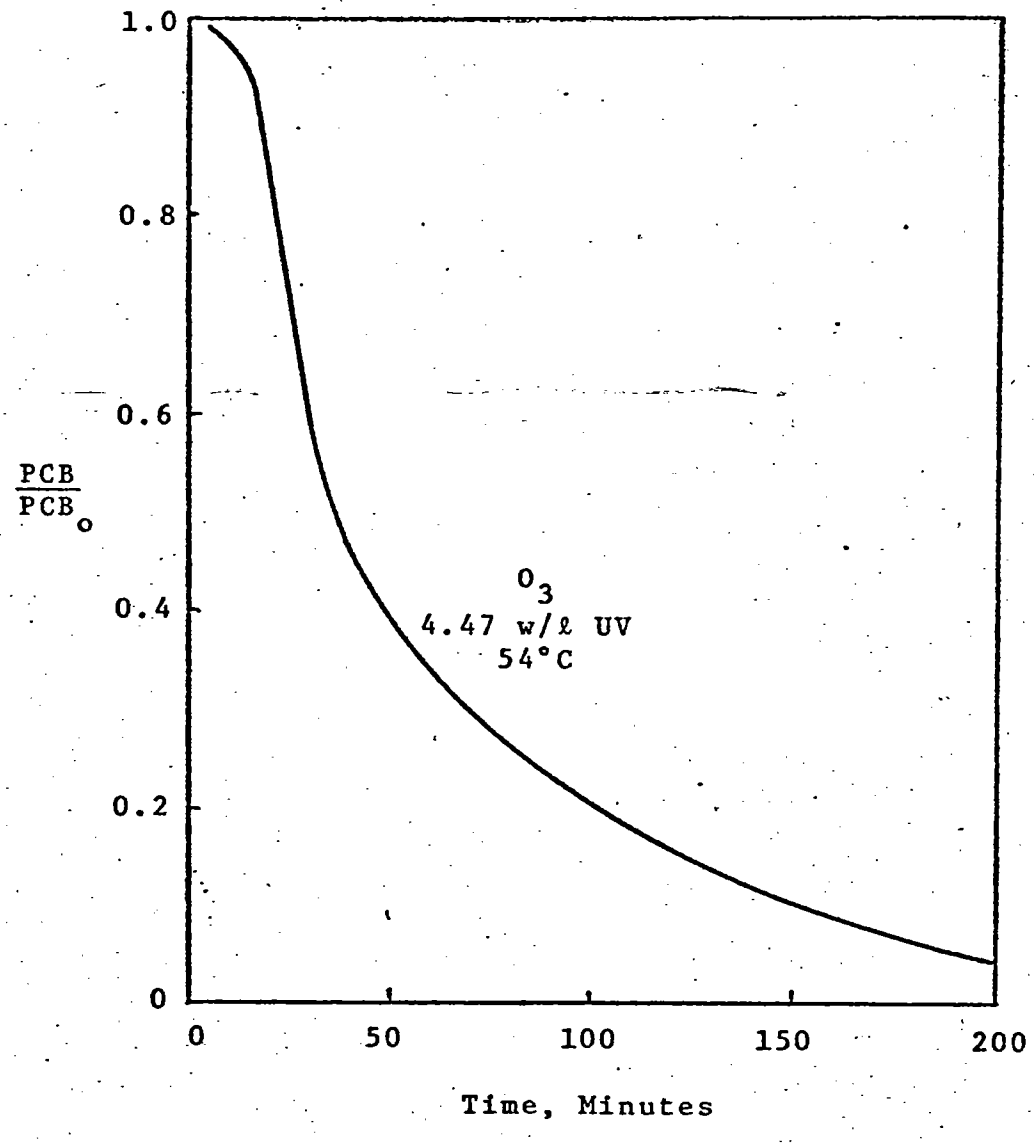


FIGURE 5. Destruction of Polychlorinated Biphenyls (PCB) (initial, 0.5 mg/ℓ)

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Chloroform

Chloroform was charged to the reactor at the 600 mg/ℓ level, and the disappearance was followed by GC. Using $O_3$-UV, disappearance was 50% in 60 minutes and 80% in 120 minutes. Using $O_3$, disappearance was 50% in 75 minutes, and 70% in 120 minutes. Because of the volatility of the compound, a large portion of the loss results from the sweeping of the solution by the flow of gas. It is estimated that at least one fourth of the original charge was destroyed by $O_3$-UV because the chloride content in solution rises to a level equivalent about a fourth of the chlorine in the original charge. The disappearance of TOC from the original compound and intermediate oxidation products is almost as rapid as the disappearance of the chloroform, implying few and fast intermediate oxidation steps. TOC disappearance is shown in Figure 6.

The classical oxidation mechanisms for chloroform are[8]:

$$HCCl_3 \xrightarrow[\text{Oxidizer}]{\text{Strong}} HCO_2Cl_3 \xrightarrow{H_2O} Cl_3CHO + H_2O_2$$

$$Cl_3CHO \longrightarrow COCl_2 + HCl$$

and for air with or without light[9, 10],

$$HCCl_3 \xrightarrow{O_2} HCO_2Cl_3 \longrightarrow Cl_2 + CO_2 + HCl$$

$$HCO_2Cl_3 \longrightarrow COCl_2 + HCl + 1/2\ O_2$$

the carbonyl chloride (phosgene) decomposing thermally by,



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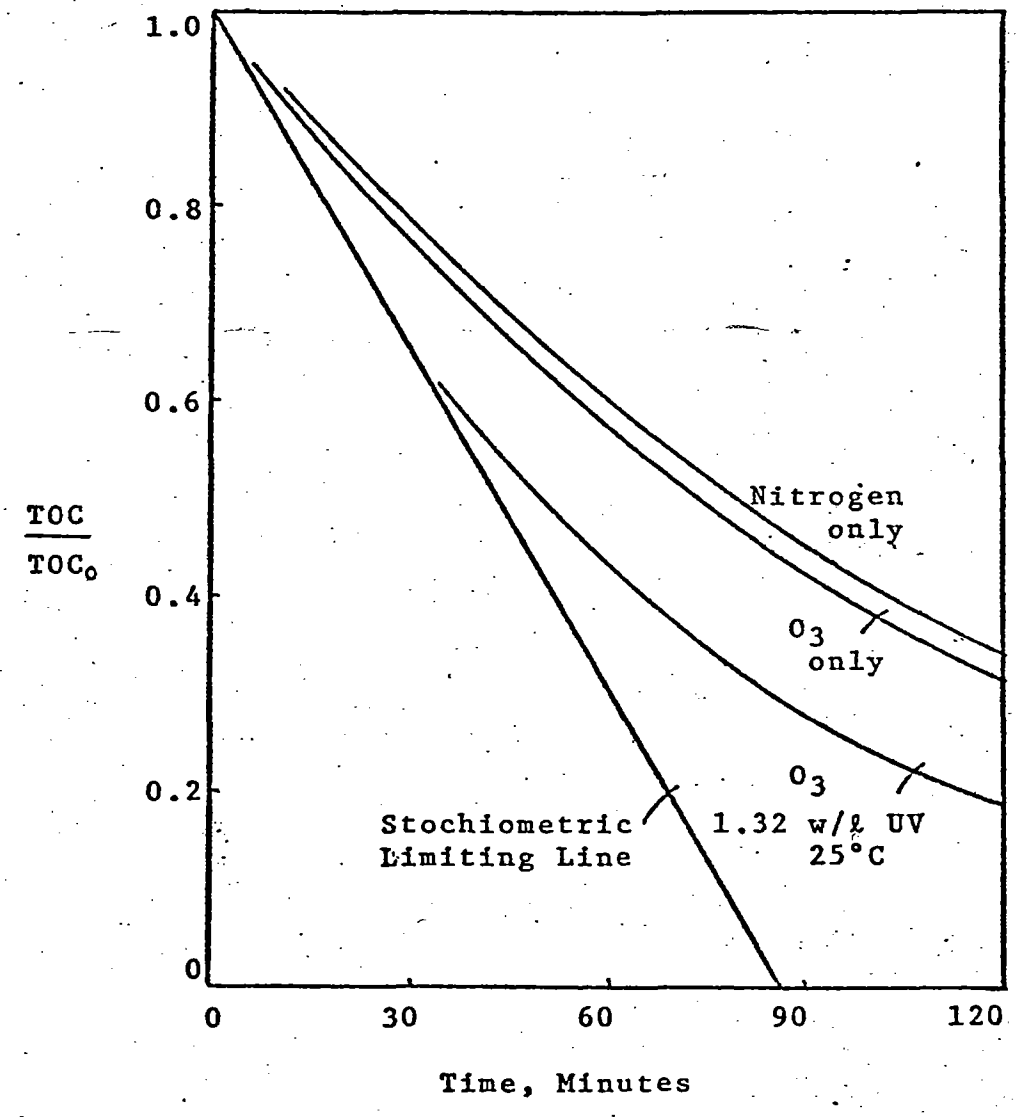


FIGURE 6. Destruction of Chloroform TOC (initial chlororm, 600 mg/ℓ)

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$$COCl_2 \longrightarrow CO + Cl_2$$

or by hydrolysis in water,

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl.$$

For oxidation with $O_3$-UV, chloroform by GC does not disappear abruptly, but instead at a rate comparable to the disappearance of TOC. Unlike the aromatics, chloroform is not a strong absorber of UV, but without UV little chloride is formed, and with UV, only about a quarter of the chlorine atoms go to chloride; suggesting the mechanism to be,

$$HCCl_3 + \begin{cases} O_3 \\ H_2O \end{cases} \longrightarrow HO_2CCl_3$$

$$\downarrow$$

$$Cl_2\underset{H}{C}OCl + H_2O_2$$

$$\downarrow h\nu$$

$$COCl_2 + H^+ + Cl^-$$

$$\downarrow O_3$$

$$CO_2 + Cl_2$$

The question of whether the presence of phosgene represents a potential hazard arises. The compound is slightly soluble in water and hydrolyzes slowly. At low initial concentrations of chloroform, it is unlikely that the solubility will be exceeded, and in the presence of ozone and UV, the compound should react very rapidly.



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## CONCLUSIONS

Based on the preliminary investigation of oxidation of the subject compounds, it appears that:

1. $O_3$-UV oxidation is highly effective for chlorinated compounds in water; the original and partial oxidation species completely oxidize to stable forms, such as $Cl^-$, $Cl_2$, $CO_2$, and $H_2O$.

2. UV absorption produces activated species, free radicals, excited state species, etc., from the organic compounds as well as from ozone. UV absorption correlates with reactivity and reaction rate, e.g. aromatics absorb more UV and are more reactive than aliphatic compounds.

3. Dechlorination occurs primarily by two mechanisms leading to: a) chloride ion, and b) chlorine and thence to hypochlorous acid. When UV absorption is substantial, initial rapid dechlorination occurs to form chloride ion, viz. pentachlorophenol, dichlorobenzene, dichlorobutane, and polychlorinated biphenyls. When UV absorption is small, initially oxidation occurs setting free chlorine. The latter occurs to a lessor degree, but some compounds exhibit both mechanisms, viz. chloroform.

4. As indicated previously[5], increased UV input is more effective than elevated temperature.

5. Performance of the Ozone/UV process, in a properly designed reaction system, is unequaled in accomplishing essentially complete removal of chlorinated compound from water; resulting in simple innocuous species.



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Ultraviolet scans were made by Dr. R. A. Geanangel of the University of Houston Chemistry Department.

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Exhibit E

AD

# REPORT NO. 7206
# OXIDATION OF PESTICIDES BY OZONE AND ULTRAVIOLET LIGHT

DA Project Number
1T76270D048-07

Charles E. Mauk
H. William Prengle, Jr.
Jack E. Payne

July 1976

Sanitary Sciences Division
U. S. Army Mobility Equipment
Research and Development Command
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Contract DAAG53-76-C-0089

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## SUMMARY

This work was undertaken to establish the feasibility of the oxidative destruction in water of five pesticides: malathion, Baygon, Vapam, pentachlorophenol, and DDT, by ozone with ultraviolet light. Each separate pesticide was treated by ozone with various combinations of ultraviolet intensities and temperatures in a sparged stirred tank reactor. Not only was the pesticide destroyed, as indicated by gas chromatographic analysis, but also the total organic content of the water, with contributions from the pesticide and from intermediate oxidation products, was reduced to the limit of detectability. A mathematical model was developed, and constants were calculated from the data to characterize the reactions. Data resulted which will permit the design of prototype treatment equipment to remove pesticide from potable water or from effluent.




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# PREFACE

This work was authorized by DA Project Number 1T7620D048-07, entitled "Environmental Quality", as a part of MERADCOM's general program of pollution abatement and waste treatment studies.

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# I. INTRODUCTION

In the past, the extensive unrestricted use of insecticides and herbicides has resulted in persistent pollution of water bodies, with accompanying danger to humans and desirable water life. Of particular interest are organic compounds containing phosphorous, sulfur, and chlorine which fall into the classifications organophosphorus, carbamate, chlorinated hydrocarbons, and phenolic.

Because of extensive success in the oxidation of hazardous and difficult to oxidize materials by ozone with ultraviolet light, this project was undertaken as part of MERADCOM's general program of pollution abatement and waste treatment studies to extend the $O_3$/UV technology to selected representatives of these classes of pesticides and obtain data which will permit the design of prototype treatment equipment for drinking water or for effluent.

The specific objectives of this work were to experimentally study the ozone oxidation of malathion (organophosphorus), Baygon (carbamate), Vapam (thiocarbamate), pentachlorophenol, and DDT (chlorinated hydrocarbon), at ambient and elevated temperatures, with and without the presence of ultraviolet light. Constants to characterize each reaction were calculated from the data.



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## II. INVESTIGATION

### A. EQUIPMENT

The laboratory reaction units used in this work are liquid batch, continuously gas sparged, because this type of reactor permits many data points to be obtained at various times during the run, resulting in convenience and savings in time. A wide variety of conditions and feed stocks can be explored without modifications to the reactors. A schematic diagram of the apparatus is shown in Figure 1. Automatic temperature control, manual pH monitoring, and ultraviolet light were used on some of the runs. A mixer speed was used which would result in a mixing energy input of 20 horsepower per 1000 gallons of solution.

The mechanical configuration of a reactor is shown in Figure 2. This configuration satisfies existing correlations of power input, mass transfer coefficients, and interfacial area in a most predictable and reproducible fashion.(1,2) Size scaleup from bench to pilot to full scale can be performed without difficulty for single stage or multistage systems. Two reactors were used during the work, both of the same mechanical configuration. Most of the runs were made in a 10 liter acrylic plastic reactor, stirred at 700 RPM, containing three lamps, each inserted vertically through the top and bottom of the reactor and in direct contact with the liquid. Each lamp is a General Electric germicidal G15T8, a 15 watt low pressure mercury lamp with the major part of the ultraviolet energy emitted at a wavelength of 2537 Angstroms. About 60% of the electrical power to the lamp is converted to ultraviolet light in the proper frequency range, but only 74% of the ultraviolet light is transmitted through the glass wall of the lamp. The lamp is normally submerged in the liquid in the reactor for two-thirds of its length. This results in a useful ultraviolet dosage of 0.44 watts per liter of reactor liquid for each lamp used.

The second is a 21.05 liter stainless steel reactor, stirred at 515 RPM, having two quartz lamp wells through the top. Into the wells can be inserted Canrad-Hanovia high pressure mercury vapor lamps with quartz envelopes. The characteristics of the lamps are given by Table I. Each lamp is completely below the liquid level. Assuming negligible attenuation by the quartz well, the 100 watt lamp contributes 0.22 watts per liter of UV light, the 200 watt lamp contributes 0.50 watts per liter of UV light, and the 450 watt lamp contributes 3.97 watts per liter of UV light.

Ozone was produced from a W. R. Grace & Co. Model LG-2-L2 air cooled generator. The generator capacity is 2-1/2 pounds per day from oxygen feed, or one pound per day from air feed, with the output adjustable by varying power input (by changing



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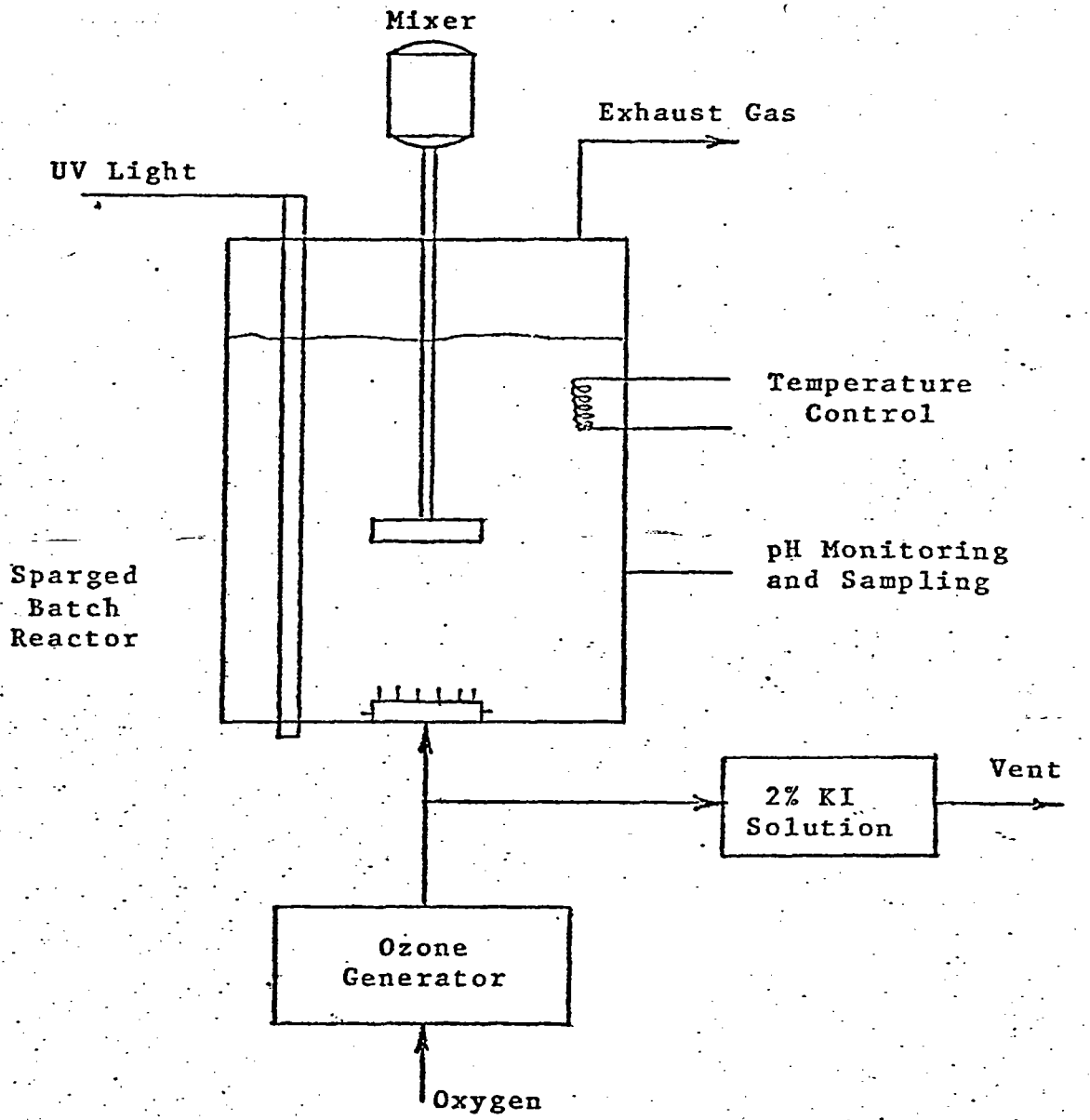


FIGURE 1. Schematic Diagram of Apparatus for Ozonation Runs



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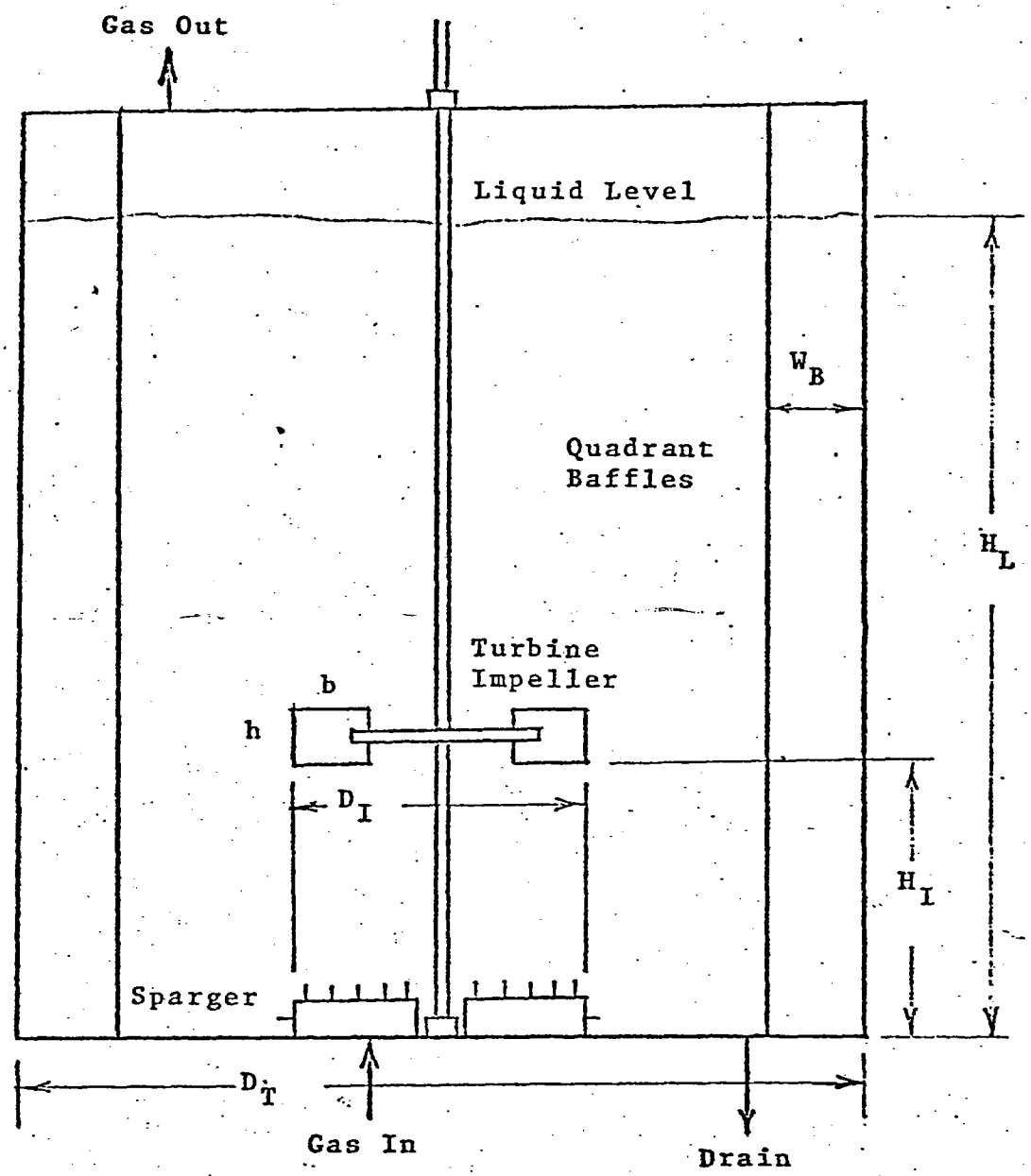


FIGURE 2. Reactor Configuration

Dimensions: $H_L = D_T$, $W_B = D_T/10$, $D_I = D_T/3$, $H_I = D_I$

Sparger
Holes: Three 1/16" holes/in$^2$

Impeller: Six blades, $b = D_I/4$, $h = D_I/5$



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TABLE I

SPECTRAL CHARACTERISTICS OF HIGH PRESSURE LAMPS

| Lamp No. | Electrical Watts | Ultraviolet Watts 2200A-2800A | 2800A-3200A | 3200A-4000A | Total |
|---|---|---|---|---|---|
| 608A | 100 | 1.14 | 1.97 | 1.53 | 4.64 |
| 654A | 200 | 2.88 | 4.14 | 3.46 | 10.48 |
| 679A | 450 | 27.0 | 28.7 | 28.0 | 83.7 |

operating frequency) with a 10-turn potentiometer. The ozone generator produces ozone in two plate type corona discharge cells. It is designed for operation at gas pressures from atmospheric to 15 psig. The concentration of ozone produced can be varied over the range of 0.5% to 10% by weight simply by varying the ratio of power input to feed gas input. The optimum concentration from the standpoint of ozone production costs alone is about 1% by weight when the feed gas is air, or about 2% by weight when the feed gas is oxygen. In this work, all ozone was produced from oxygen and used at a nominal 2% concentration. The ozone dosage to the reactor was determined by the gas flow rate and was typically 2-3% of the production capacity. The output of the ozone generator can be affected somewhat by variations in line input voltage and pressure, therefore, a constant voltage transformer and 2-stage pressure regulation were employed. The gas supplied to the ozone generator was extra dry, commercial grade oxygen, with a dew point of about -70°F, and the hydrocarbon content was negligible.

B. EXPERIMENTATION

The reactor was filled with laboratory de-ionized water to an appropriate level, a weighed amount of pesticide was added, and the reactor was stirred until all material was in solution. If elevated temperature was to be used, the controller was activated and the solution brought to the selected temperature. A sample was taken for time zero, a precalibrated ozone stream was sparged into the reactor, the necessary UV lamps were switched on, and the reaction time was started. Samples were drawn for analysis at various times during the run; typically 15, 30, 60, 90, and 120 minutes, but sampling was extended several hours more if the reaction were expected to be slow. Separate samples were drawn for ozone content of the liquid. Temperature and pH were recorded at each sample time.



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The ozone concentration in the gas stream from the ozone generator to the reactor was determined by passing the gas through a gas scrubbing bottle containing a 2% solution of potassium iodide. After a specific volume of gas was passed through the gas scrubbing bottle, the sample was acidified with sulfuric acid. The liberated iodine was titrated with a standardized sodium thiosulfate solution in order to determine the concentration.

Residual ozone in the aqueous reaction solutions was determined by the same type of iodometric method. In cases where high ozone concentration was encountered, the titration was carried out potentiometrically using an automatic titrator. Where low concentrations were encountered, the analyses were carried out using a starch indicator and standard volumetric procedure was followed.

Total Organic Carbon Analysis

The Total Organic Carbon (TOC) content of solutions was determined using a modified Beckman Model 915 Total Organic Carbon Analyzer. The method of determining total organic carbon is indirect. The instrument is so designed that the total carbon content (organic carbon and carbonates) is determined. Then a second channel on the instrument is used to determine only the carbon present in the inorganic form of carbonates. The TOC is then obtained by subtracting the inorganic carbon content from the total carbon content. The total carbon and inorganic carbon are catalytically combusted in a way as to form carbon dioxide, which is measured quantitatively by a non-dispersive infrared detector.

Early in the study, it was determined that very low concentrations of inorganic carbon existed in either the water used to make up the solutions or the samples taken at various reaction times. Therefore, the standards prepared for the total carbon analyses contained only organic materials. Potassium acid phthalate was used as the standard for Total Organic Carbon.

A plot of concentration versus peak height at a given setting on the non-dispersive infrared detector was made, using concentrations ranging from 10 ppm to 100 ppm total carbon. The plot is obtained by making three injections of each standard using an automatic syringe. Each sample is then injected three separate times at the same volume as the standard.

Gas Chromatographic Analyses

The concentration of unreacted original species was followed in the reaction mixtures by the use of gas liquid chromatography using a Hewlett-Packard 5700A Gas Chromatograph. A dual flame ionization detector was used for malathion, Baygon, and Vapam. An electron capture detector was used for pentachlorophenol and





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DDT. All columns were glass with on-column injection parameters. The column packing for all analyses consisted of 5% OV-101 on 90-100 mesh ABS polymer beads.

The following instrument parameters were used for the analysis of all substances:

| | Baygon, Malathion, and Vapam | Pentachlorophenol and DDT |
|---|---|---|
| Detector | FID | EC |
| Detector Temperature | 200°C | 300°C |
| Injection Inlet Temperature | 200°C | 300°C |
| Column Oven Temperature | 150°C | * |
| Carrier Gas Flow Rate | 75 ml/min Helium | 120 ml/min dry $N_2$ |
| Hydrogen Flow Rate | 60 ml/min | None |
| Air Flow Rate | 300 ml/min | None |
| Column Length | 6 ft | 6 ft |
| Column Diameter | 4 mm ID | 4 mm ID |
| Column Material | Glass | Glass |
| Sample Size | 2 µl | 2 µl |

The samples were prepared for analysis as follows:

1. Malathion was extracted from water solution with n-hexane. A standard of 100 mg/l malathion in n-hexane was used.

2. Baygon was extracted from water solution with chloroform. A standard of 50 mg/l Baygon in chloroform was used.

3. Vapam water solutions were acidified with nitric acid and the resultant solution extracted with chloroform. A standard solution of 100 mg/l Vapam in water was acidified and extracted with chloroform. The chloroform extract was used as standard.

4. Pentachlorophenol water solutions were extracted with benzene. A standard of 70 mg/l pentachlorophenol in benzene was used. The extracts and standards were dried with calcium chloride.

5. DDT water solutions were extracted with benzene. A standard solution of 5 mg/l DDT in benzene was used. The standard and extracts were dried with calcium chloride.

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* 275°C for pentachlorophenol and 245°C for DDT.



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The standards and extracts were syringe injected into the gas chromatograph and peak areas were obtained for each pesticide. Quantitative calculations were made as follows:

$$\text{mg/l in sample} = \frac{(\text{Vol. Extractant})(\text{Peak Area Sample})(\text{mg/l Standard})}{(\text{Vol. Sample Water Solution})(\text{Standard Peak Area})}$$

Auxiliary Analyses

Malathion samples were analyzed quantitatively for orthophosphate content by the stannous chloride method, No. 223E, of Standard Methods for the Examination of Water and Wastewater, 13th Edition. Sulfate content of Vapam samples and chloride content of pentachlorophenol samples were determined turbidimetrically with a Bausch & Lomb Spectronic 20 spectrophotometer.

C. RAW DATA

Forty runs were included in this work, 10 on malathion (M1-M10), 8 on Baygon (B1-B8), 7 on Vapam (V1-V7), 8 on pentachlorophenol (P1-P8), and 7 on DDT (D1-D7). Table II summarizes the run conditions, and Tables III-XLII present the data. The ozone in liquid values are of use only as general guidelines, since they may contain contributions from organic peroxides.



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TABLE II

SUMMARY OF RUN CONDITIONS

| Table | Run Number | Nominal Temperature, °C | Ozone | UV Lamps, Electrical Watts | UV Light, Watts/Liter |
|---|---|---|---|---|---|
| III | M1 | Room | Yes | 45 | 1.32 |
| IV | M2 | Room | No | 45 | 1.32 |
| V | M3 | Room | Yes | Zero | Zero |
| VI | M4 | Room | Yes | 15 | 0.44 |
| VII | M5 | 50 | Yes | 15 | 0.44 |
| VIII | M6 | Room | No | 45 | 1.32 |
| IX | M7 | Room | Yes | Zero | Zero |
| X | M8 | Room | Yes | 300 | 0.72 |
| XI | M9 | 40 | Yes | 30 | 0.88 |
| XII | M10 | 50 | Yes | 45 | 1.32 |
| XIII | B1 | Room | Yes | 45 | 1.32 |
| XIV | B2 | Room | Yes | Zero | Zero |
| XV | B3 | Room | No | 45 | 1.32 |
| XVI | B4 | Room | Yes | 15 | 0.44 |
| XVII | B5 | 50 | Yes | 15 | 0.44 |
| XVIII | B6 | 37 | Yes | 300 | 0.72 |
| XIX | B7 | Room | Yes | 15 | 0.44 |
| XX | B8 | Room | Yes | 45 | 1.32 |
| XXI | V1 | Room | Yes | Zero | Zero |
| XXII | V2 | Room | Yes | 45 | 1.32 |
| XXIII | V3 | Room | No | 45 | 1.32 |
| XXIV | V4 | Room | Yes | 15 | 0.44 |
| XXV | V5 | 50 | Yes | 15 | 0.44 |
| XXVI | V6 | Room | Yes | Zero | Zero |
| XXVII | V7 | Room | Yes | 100 | 0.22 |
| XXVIII | P1 | Room | Yes | 45 | 1.32 |
| XXIX | P2 | 30 | Yes | Zero | Zero |
| XXX | P3 | 30 | No | 45 | 1.32 |
| XXXI | P4 | 30 | Yes | 15 | 0.44 |
| XXXII | P5 | 55 | Yes | 15 | 0.44 |
| XXXIII | P6 | 30 | Yes | 45 | 1.32 |
| XXXIV | P7 | 40 | Yes | 30 | 0.88 |
| XXXV | P8 | 30 | Yes | 450 | 3.97 |
| XXXVI | D1 | Room | Yes | 45 | 1.32 |
| XXXVII | D2 | Room | Yes | Zero | Zero |
| XXXVIII | D3 | Room | No | 45 | 1.32 |
| XXXIX | D4 | 50 | Yes | 15 | 0.44 |
| XL | D5 | 40 | Yes | 30 | 0.88 |
| XLI | D6 | Room | Yes | 450 | 3.97 |
| XLII | D7 | Room | No | 45 | 1.32 |



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TABLE III

MALATHION DATA RUN M1

0.87 gm commercial malathion into 10ℓ reactor
Three 15 watt UV lamps
Two ℓ/min of 2.39% ozone

| Time, Minutes | TOC, mg/l | $O_3$,* mg/l | pH | Temp., °C | Malathion mg/l | Ortho-phosphate as P, mg/l |
|---|---|---|---|---|---|---|
| 0 | 24 | 0 | 8.9 | 21 | 55 | 0.0 |
| 30 | 23 | 50. | 3.2 | 24.5 | <0.1 | |
| 60 | 19 | 152. | 3.2 | 25.5 | | |
| 90 | 11 | 98. | 3.1 | 27.5 | | 0.7 |
| 120 | 0 | 3.5 | | 29. | | |

TABLE IV

MALATHION DATA RUN M2

1.03 gm commercial malathion into 10ℓ reactor
Three 15 watt UV lamps
Zero ozone

| Time, Minutes | TOC, mg/l | pH | Temp., °C | Malathion, mg/l | Ortho-phosphate as P, mg/l |
|---|---|---|---|---|---|
| 0 | 19 | 4.6 | 22 | 62 | 0.0 |
| 120 | 19 | 3.4 | 26 | 6 | 0.0 |

* Apparent ozone in water concentrations in this and following tables may contain contributions from organic peroxides.



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TABLE V

MALATHION DATA RUN M3

Treated water from Run M2 in 10ℓ reactor
Zero UV
Two ℓ/min of 2.2% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Malathion, mg/l | Ortho-phosphate as P, mg/l |
|---|---|---|---|---|---|---|
| 0 | 19 | 0 | 3.4 | 26 | 6 | 0.0 |
| 30 | 19 | | 3.0 | 26 | <1 | |
| 60 | 19 | 19.5 | 3.0 | 26 | | |
| 90 | 19 | 24.1 | 3.0 | 26 | | |
| 120 | 19 | 25 | 3.0 | 26 | | 0.2 |

TABLE VI

MALATHION DATA RUN M4

1.00 gm commercial malathion into 10ℓ reactor
One 15 watt UV lamp
Two ℓ/min of 2.48% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Malathion, mg/l | Ortho-phosphate as P, mg/l |
|---|---|---|---|---|---|---|
| 0 | 33 | 0 | 4.6 | 18 | 82 | 0.0 |
| 15 | 33 | | 3.0 | | <1 | 0.0 |
| 30 | 33 | | 3.0 | | | 0.1 |
| 60 | 33 | | 3.0 | | | 0.3 |
| 90 | 33 | 67. | 2.95 | 25.5 | | 1.0 |
| 150 | 26 | 69.75 | 2.90 | 27.0 | | 2.0 |
| 240 | 6 | 7.25 | 2.90 | 27.0 | | |



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TABLE VII

MALATHION DATA RUN M5

1.19 gm commercial malathion into 10ℓ reactor
One 15 watt UV lamp
Two ℓ/min of 2.59% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Malathion, mg/l | Ortho-phosphate as P, mg/l |
|---|---|---|---|---|---|---|
| 0 | 40 | 0 | | 49 | 94. | 0.0 |
| 15 | 40 | 11.16 | | 49 | <1 | 0.3 |
| 30 | 39 | 16.74 | | 49 | | 0.7 |
| 60 | 37.5 | 21.20 | | 49 | | 1.8 |
| 90 | 24.5 | 21.20 | | 49 | | 6.2 |
| 120 | 6 | 5.58 | | 49 | | 8.8 |

TABLE VIII

MALATHION DATA RUN M6

1.00 gm commercial malathion into 10ℓ reactor
Three 15 watt UV lamps
Zero ozone

| Time, Minutes | TOC, mg/l | pH | Temp., °C | Malathion, mg/l | Ortho-phosphate as P, mg/l |
|---|---|---|---|---|---|
| 0 | 17 | | 21 | 58 | 0.0 |
| 15 | 16 | | | 23 | |
| 30 | 15 | | | 12 | |
| 60 | 15 | | | 5 | |
| 90 | 15 | | | 2 | 0.0 |
| 120 | 15 | | 29.5 | <1 | |



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TABLE IX

MALATHION DATA RUN M7

1.12 gm commercial malathion into 10ℓ reactor
Zero UV
Two ℓ/min of 2.53% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | Temperature, °C | Malathion, mg/l | Ortho-phosphate as P, mg/l |
|---|---|---|---|---|---|
| 0 | 38 | 0 | 22.0 | 90 | 0.0 |
| 15 | 38 | | | <1 | |
| 30 | 38 | 22.5 | | | |
| 60 | 38 | 23.5 | 23.0 | | |
| 90 | 38 | | | | |
| 120 | 38 | 24.0 | 24.0 | | 0.2 |

TABLE X

MALATHION DATA RUN M8

2.11 gm commercial malathion into 21ℓ reactor
100 watt UV lamp and 200 watt UV lamp
Three ℓ/min of 2.44% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Malathion, mg/l | Ortho-phosphate as P, mg/l |
|---|---|---|---|---|---|---|
| 0 | 28.0 | 0 | - | 23.0 | 80 | 0.1 |
| 15 | 30.8 | 1.75 | 3.4 | 24.0 | 54 | 0.1 |
| 30 | 42.8 | 6.98 | 3.05 | 25.0 | ≤0.5 | 0.2 |
| 60 | 29.1 | 18.47 | 3.15 | 27.0 | | 0.7 |
| 90 | 21.8 | 9.98 | 3.05 | 32.0 | | 3.2 |
| 120 | 6.9 | 3.50 | 2.8 | 34.0 | | 3.7 |



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TABLE XI

MALATHION DATA RUN M9

1.00 gm commercial malathion into 10ℓ reactor
Two 15 watt UV lamps
Two ℓ/min of 2.02% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C |
|---|---|---|---|---|
| 0 | 27.0 | 0 | 5.5 | 40.0 |
| 15 | 28.0 | 5.4 | 3.0 | 40.2 |
| 30 | 26.3 | 8.7 | 2.95 | 40.5 |
| 60 | 19.0 | 15.3 | 2.90 | 41.0 |
| 90 | 1.5 | 3.0 | 2.90 | 41.5 |
| 120 | 0.0 | 1.2 | 2.95 | 42.0 |

TABLE XII

MALATHION DATA RUN M10

1.00 gm commercial malathion into 10ℓ reactor
Three 15 watt UV lamps
Two ℓ/min of 2.06% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C |
|---|---|---|---|---|
| 0 | 34.5 | 0 | 3.73 | 51.0 |
| 15 | 34.3 | 6.0 | 2.90 | 51.0 |
| 30 | 30.2 | 10.2 | 2.80 | 51.0 |
| 60 | 10.0 | 1.8 | 2.80 | 51.0 |
| 90 | 0.5 | 1.5 | 2.80 | 51.0 |
| 120 | 0.0 | 1.5 | 2.80 | 51.0 |



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TABLE XIII

BAYGON DATA RUN B1

2.96 gm of 13.9% Baygon in solvent into 10ℓ reactor
Three 15 watt UV lamps
1.25 ℓ/min of 3.02% ozone

| Time, Minutes | $O_3$, mg/l | pH | Temp., °C | Baygon, mg/l |
|---|---|---|---|---|
| 0 | 0 | 3.8 | 25 | 49 |
| 30 | 17.8 | 3.1 | 26.5 | <0.1 |

TABLE XIV

BAYGON DATA RUN B2

0.50 gm of CSI Baygon into 10ℓ reactor
Zero UV
Two ℓ/min of 1.44% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Baygon, mg/l |
|---|---|---|---|---|---|
| 0 | 32.5 | 0 | 5.3 | | 44 |
| 15 | 23.0 | | 4.0 | | <0.5 |
| 30 | 22.0 | | 3.85 | 26 | |
| 60 | 22.0 | 10.0 | 3.80 | 28 | |
| 90 | 20.5 | 18.7 | 3.80 | | |
| 120 | 18.0 | 14.9 | 3.80 | 28 | |



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TABLE XV

BAYGON DATA RUN B3

0.50 gm of CSI Baygon into 10ℓ reactor
Three 15 watt UV lamps
Zero ozone

| Time, Minutes | TOC, mg/l | pH | Temp., °C | Baygon, mg/l |
|---|---|---|---|---|
| 0 | 26.5 | 6.1 | 24.0 | 49 |
| 15 | 24.3 | 6.1 | | 22 |
| 30 | 25.5 | 6.1 | | 22 |
| 60 | 25.8 | 6.25 | 28.0 | 21 |
| 90 | 25.8 | 6.25 | | 12 |
| 120 | 25.3 | 6.25 | 28.0 | 12 |

TABLE XVI

BAYGON DATA RUN B4

0.50 gm of CSI Baygon into 10ℓ reactor
One 15 watt UV lamp
Two ℓ/min of 2.0% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Baygon, mg/l |
|---|---|---|---|---|---|
| 0 | 113 | 0 | 4.7 | 23.0 | 34 |
| 15 | 106 | 15.0 | 4.0 | 23.0 | 4 |
| 30 | 114 | 39.9 | 3.8 | | <0.5 |
| 60 | 102 | 24.9 | 3.6 | | |
| 90 | 98 | 59.9 | 3.4 | 30.0 | |
| 120 | 98 | 89.9 | 3.3 | 30.0 | |



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TABLE XVII

BAYGON DATA RUN B5

0.50 gm of CSI Baygon into 10ℓ reactor
One 15 watt UV lamp
Two ℓ/min of 2.13% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Baygon, mg/l |
|---|---|---|---|---|---|
| 0 | 30 | 0 | 5.1 | 50 | 38 |
| 15 | 32.25 | 16.47 | 3.2 | 50 | <0.5 |
| 30 | 18.0 | 19.97 | 3.0 | 50 | |
| 60 | 10.5 | 11.48 | 3.3 | 50 | |
| 90 | 3.0 | 4.99 | 4.4 | 50 | |
| 120 | 2.0 | | 3.8 | 50 | |

TABLE XVIII

BAYGON DATA RUN B6

1.05 gm of CSI Baygon into 21ℓ reactor
100 watt UV lamp and 200 watt UV lamp
Two ℓ/min of 2.08% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Baygon, mg/l |
|---|---|---|---|---|---|
| 0 | 39.75 | 0 | 5.7 | 24 | 51 |
| 15 | 24.75 | 0.5 | 4.55 | 26 | 5 |
| 30 | 21.5 | 0.5 | 4.7 | 28 | 1 |
| 60 | 17.2 | 0.5 | 5.25 | 34 | <0.5 |
| 90 | 13.2 | 0.5 | 4.95 | 40 | |
| 120 | 11.5 | 0.5 | 5.3 | 50 | |



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TABLE XIX

BAYGON DATA RUN B7

0.50 gm of CSI Baygon into 10ℓ reactor
One 15 watt UV lamp
Two ℓ/min of 1.95% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Baygon mg/l |
|---|---|---|---|---|---|
| 0 | 24.5 | 0 | 4.8 | 24.5 | 43 |
| 15 | 21.4 | 33.2 | 3.85 | 25.0 | <1 |
| 30 | 20.9 | 57.9 | 3.75 | 26.0 | |
| 60 | 18.4 | 24.9 | 3.5 | 27.5 | |
| 90 | 13.4 | 19.9 | 3.35 | 29.5 | |
| 120 | 11.3 | 15.97 | 3.6 | 29.5 | |

TABLE XX

BAYGON DATA RUN B8

0.50 gm of CSI Baygon into 10ℓ reactor
Three 15 watt UV lamps
Two ℓ/min of 2.29% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Baygon mg/l |
|---|---|---|---|---|---|
| 0 | 25.6 | 0 | 5.6 | 23.5 | 53 |
| 15 | 21.3 | 8.5 | 3.5 | 24 | <1 |
| 30 | 18.2 | 9.24 | 3.3 | 25 | |
| 60 | 8.8 | 2.5 | 5.7 | 28 | |
| 90 | 5.1 | 2.0 | 5.9 | 31 | |
| 120 | 5.3 | 2.4 | 5.8 | 34 | |



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TABLE XXI

VAPAM DATA RUN V1

1.00 gm of CSI Vapam into 10ℓ reactor
Zero UV
Two ℓ/min of 2.09% ozone

| Time, Minutes | TOC, mg/l | pH | Temp., °C | Vapam, mg/l | Sulfate, mg/l |
|---|---|---|---|---|---|
| 0 | 10.8 | 7.6 | 26 | 58 | 4 |
| 15 | 8.2 | 2.6 | 27 | 6 | 48 |
| 30 | 8.0 | 2.6 | 28 | <0.5 | 50 |
| 60 | 8.2 | 2.5 | 29 | | 58 |
| 90 | 7.6 | 2.5 | 30.5 | | 52 |
| 120 | 7.6 | 2.5 | 31.0 | | 68 |
| 180 | 7.4 | 2.5 | 34.0 | | 76 |

TABLE XXII

VAPAM DATA RUN V2

1.00 gm of CSI Vapam into 10ℓ reactor
Three 15 watt UV lamps
Two ℓ/min of 2.0% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Vapam, mg/l | Sulfate, mg/l |
|---|---|---|---|---|---|---|
| 0 | 7.5 | 0 | 8.8 | 23.0 | 70 | 9 |
| 15 | 7.05 | 11.15 | 3.25 | 25.5 | 2 | 62 |
| 30 | 6.29 | 22.9 | 3.20 | 26.0 | <0.5 | 76 |
| 60 | 1.88 | 1.4 | 3.15 | 29.0 | | 80 |
| 90 | .86 | 2.25 | 3.15 | 32.0 | | 68 |
| 120 | .84 | 1.99 | 2.75 | 34.0 | | 60 |
| 180 | .41 | 2.0 | 2.75 | 39.5 | | 100 |



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TABLE XXIII

VAPAM DATA RUN V3

1.00 of CSI Vapam into 10ℓ reactor
Three 15 watt UV lamps
Zero ozone

| Time, Minutes | TOC, mg/l | pH | Temp., °C | Vapam, mg/l | Sulfate, mg/l |
|---|---|---|---|---|---|
| 0 | 9 | 8.48 | 24.0 | 71 | 13 |
| 15 | 9 | 8.50 | 25.0 | 66 | 16 |
| 34 | 9 | 7.55 | 26.5 | 66 | 16 |
| 60 | 9 | 7.78 | 28.5 | 66 | 16 |
| 90 | 9 | 6.60 | 31.0 | 66 | 14 |
| 120 | 9 | 5.07 | 33.0 | 53 | 36 |
| 180 | 9 | 3.90 | 37.0 | 27 | 34 |
| 240 | 9 | 3.62 | 40.0 | 8 | 36 |

TABLE XXIV

VAPAM DATA RUN V4

1.00 gm of CSI Vapam into 10ℓ reactor
One 15 watt UV lamp
Two ℓ/min of 1.99% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Vapam, mg/l | Sulfate, mg/l |
|---|---|---|---|---|---|---|
| 0 | 8 | 0 | 7.92 | 25.0 | 88 | 7 |
| 15 | 8 | 4.8 | 3.20 | 25.5 | 50 | 30 |
| 30 | 8 | 11.0 | 3.03 | 26.3 | <0.5 | 50 |
| 60 | 7 | 26.8 | 2.98 | 28.0 | | 50 |
| 90 | 4 | 5.5 | 2.93 | 30.0 | | 68 |
| 120 | 3 | 3.5 | 2.92 | 31.5 | | 64 |
| 180 | 2 | 3.2 | 2.89 | 34.0 | | 58 |



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TABLE XXV

VAPAM DATA RUN V5

1.00 gm of CSI Vapam into 10ℓ reactor
One 15 watt UV lamp
Two ℓ/min of 2.2% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Vapam, mg/l | Sulfate, mg/l |
|---|---|---|---|---|---|---|
| 0 | 9.9 | 0 | 10.55 | 50.8 | 75 | 7 |
| 20 | 9.5 | | 6.32 | 50.8 | <0.5 | 34 |
| 30 | 8.7 | 9.5 | 6.30 | 50.8 | | 42 |
| 60 | 6.4 | 6.0 | 6.25 | 50.8 | | 50 |
| 90 | 2.8 | 2.0 | 6.25 | 50.8 | | 84 |
| 120 | 2.4 | 2.5 | 6.25 | 50.8 | | 60 |
| 180 | 2.1 | 2.8 | 6.22 | 50.8 | | 60 |

TABLE XXVI

VAPAM DATA RUN V6

1.00 gm of CSI Vapam into 10ℓ reactor
Zero UV
Two ℓ/min of 1.31% ozone

| Time, Minutes | TOC, mg/l | $O_3$, mg/l | pH | Temp., °C | Vapam, mg/l | Sulfate, mg/l |
|---|---|---|---|---|---|---|
| 0 | 11.1 | 0 | 9.3 | 26.0 | 20 | 13 |
| 15 | 8.3 | 2.5 | 3.34 | 26.5 | 20 | 24 |
| 30 | 6.8 | 6.0 | 3.17 | 27.0 | 6 | 44 |
| 60 | 6.8 | 7.5 | 3.15 | 28.0 | <0.5 | 44 |
| 90 | 6.0 | 8.5 | 3.13 | 29.0 | | 88 |
| 120 | 6.0 | 8.0 | 3.13 | 29.8 | | 84 |
| 180 | 5.8 | 8.0 | 3.13 | 31.0 | | 86 |



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TABLE XXVII

VAPAM DATA RUN V7

2.11 gm of CSI Vapan into 21ℓ reactor
100 watt UV lamp
Four ℓ/min of 2.44% ozone

| Time, Minutes | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | Vapam, mg/ℓ | Sulfate, mg/ℓ |
|---|---|---|---|---|---|---|
| 0 | 8.2 | 0 | 9.08 | 24.0 | 84 | 5 |
| 15 | 7.1 | 3.0 | 3.63 | 24.5 | 17 | 104 |
| 30 | 7.4 | 8.5 | 3.90 | 25.5 | 1 | 100 |
| 60 | 7.7 | 9.0 | 4.15 | 27.5 | <0.5 | 92 |
| 90 | 4.3 | 10.0 | 4.03 | 29.0 | | 104 |
| 120 | 2.4 | 6.0 | 3.97 | 30.5 | | 135 |

TABLE XXVIII

PENTACHLOROPHENOL DATA RUN P1

1.14 gm of Penta 40 solution into 10ℓ reactor
Three 15 watt UV lamp
1.25 ℓ/min of 3.14% ozone

| Time, Minutes | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | Chloride, mg/ℓ |
|---|---|---|---|---|---|
| 0 | 25 | 0 | 3.3 | 20 | 0 |
| 30 | 24 | 10.8 | 3.0 | 21.0 | 7 |
| 60 | 23 | 48.5 | 3.2 | 22.0 | 7 |
| 90 | 18 | 17.5 | 3.0 | 23.0 | 7 |
| 120 | 10 | 4.5 | 2.8 | 25.0 | 7 |
| 150 | 5 | | | 26.5 | 7 |
| 165 | 3 | 3.6 | | 27.0 | 7 |



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STLCOPCB4097813

TABLE XXIX

PENTACHLOROPHENOL DATA RUN P2

0.70 gm purified pentachlorophenol into 10ℓ reactor
Zero UV
Two ℓ/min of 2.10% ozone

| Time, Min. | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | Pentachlorophenol, mg/ℓ | Chloride, mg/ℓ |
|---|---|---|---|---|---|---|
| 0 | 31.7 | 0 | 10.15 | 31.0 | 71 | 3 |
| 15 | 18.7 | 9.0 | 3.70 | 31.3 | <0.5 | 30 |
| 30 | 16.1 | 10.0 | 3.60 | 32.0 | | 30 |
| 60 | 14.1 | 10.0 | 3.53 | 32.5 | | 30 |
| 90 | 12.7 | 9.5 | 3.48 | 33.0 | | 36 |
| 120 | 12.6 | 9.5 | 3.45 | 33.5 | | 40 |
| 180 | 11.0 | 9.5 | 3.45 | 34.5 | | 40 |
| 240 | 11.0 | 9.0 | 3.35 | 35.0 | | 43 |

TABLE XXX

PENTACHLOROPHENOL DATA RUN P3

0.70 gm purified pentachlorophenol into 10ℓ reactor
Three 15 watt UV lamps
Zero ozone

| Time, Min. | TOC, mg/ℓ | pH | Temp., °C | Pentachloropheonol, mg/ℓ | Chloride, mg/ℓ |
|---|---|---|---|---|---|
| 0 | 32.0 | 10.03 | 31.0 | 63 | 6 |
| 15 | 29.5 | 9.90 | 32.5 | 46 | 7 |
| 30 | 28.5 | 9.88 | 33.5 | 36 | 9 |
| 60 | 28.3 | 9.23 | 36.0 | | 14 |
| 90 | 30.2 | 6.55 | 37.5 | 16 | 21 |
| 120 | 29.3 | 5.90 | 39.0 | 4 | 30 |
| 180 | 26.7 | 4.33 | 41.5 | <0.5 | 38 |
| 240 | 24.9 | 4.05 | 43.5 | | 38 |



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TABLE XXXI

PENTACHLOROPHENOL DATA RUN P4

0.70 gm purified pentachlorophenol into 10ℓ reactor
One 15 watt UV lamp
Two ℓ/min of 1.99% ozone

| Time, Min. | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | Pentachlorophenol, mg/ℓ | Chloride, mg/ℓ |
|---|---|---|---|---|---|---|
| 0 | 16.4 | 0 | 9.6 | 33.0 | 40 | 2 |
| 15 | 11.5 | 7.0 | 3.65 | 33.3 | 1.8 | 30 |
| 30 | 7.7 | 5.5 | 3.75 | 34.0 | <0.5 | 20 |
| 60 | 1.5 | 2.3 | 5.0 | 35.0 | | 20 |
| 90 | 1.2 | 2.3 | 5.15 | 36.0 | | 20 |
| 120 | 0.8 | 1.8 | 5.10 | 37.0 | | 20 |
| 180 | 0.8 | 1.8 | 4.90 | 38.0 | | 21 |

TABLE XXXII

PENTACHLOROPHENOL DATA RUN P5

0.63 gm purified pentachlorophenol into 9ℓ water in 10ℓ reactor
One 15 watt UV lamp
Two ℓ/min of 2.00% ozone

| Time, Min. | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | Pentachlorophenol, mg/ℓ | Chloride, mg/ℓ |
|---|---|---|---|---|---|---|
| 0 | 35.8 | 0 | 9.95 | 60.5 | 70 | 6 |
| 15 | 17.8 | 2.4 | 3.40 | 59.5 | <0.5 | 35 |
| 30 | 7.9 | 2.4 | 3.45 | 58.0 | | 20 |
| 60 | 4.6 | 3.0 | 3.50 | 56.0 | | 21 |
| 90 | 4.7 | 4.2 | 3.50 | 53.5 | | 21 |
| 120 | 4.7 | 3.6 | 3.55 | 53.0 | | 34 |



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TABLE XXXIII

PENTACHLOROPHENOL DATA RUN P6

0.63 gm purified pentachlorophenol into 9ℓ water in 10ℓ reactor
Three 15 watt UV lamps
Two ℓ/min of 1.94% ozone

| Time, Min. | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | Pentachlorophenol, mg/ℓ | Chloride, mg/ℓ |
|---|---|---|---|---|---|---|
| 0 | 20.4 | 0 | 10.0 | 31.0 | 47 | 4 |
| 15 | 8.2 | 1.8 | 3.42 | 32.0 | <0.5 | 18 |
| 30 | 1.1 | 1.8 | 4.62 | 33.0 | | 33 |
| 60 | 0.2 | 1.8 | 4.40 | 35.0 | | 30 |
| 90 | 0 | 1.8 | 4.22 | 37.0 | | 30 |
| 120 | 0 | 2.4 | 4.18 | 39.0 | | 52 |

TABLE XXXIV

PENTACHLOROPHENOL DATA RUN P7

0.63 gm purified pentachlorophenol into 9ℓ water in 10ℓ reactor
Two 15 watt UV lamps
Two ℓ/min of 2.02% ozone

| Time, Min. | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | Pentachlorophenol, mg/ℓ | Chloride, mg/ℓ |
|---|---|---|---|---|---|---|
| 0 | 35.7 | 0 | 10.13 | 40.0 | 67 | 8 |
| 15 | 16.5 | 5.4 | 3.40 | 40.3 | <0.5 | 48 |
| 30 | 10.7 | 3.6 | 3.43 | 40.6 | | 54 |
| 60 | 4.4 | 3.3 | 3.88 | 41.0 | | 50 |
| 90 | 2.8 | 3.3 | 3.85 | 41.7 | | 33 |
| 120 | 2.2 | 3.9 | 3.85 | 42.0 | | 33 |



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TABLE XXXV

PENTACHLOROPHENOL DATA RUN P8

1.48 gm CSI pentachlorophenol into 21ℓ reactor
450 watt UV lamp
Four ℓ/min of 2.04% ozone

| Time, Min. | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | Pentachlorophenol, mg/ℓ |
|---|---|---|---|---|---|
| 0 | 25.7 | 0 | 10.10 | 26.0 | 62 |
| 15 | 2.0 | 1.2 | 5.90 | 27.5 | 1.3 |
| 30 | 1.3 | 1.2 | 6.15 | 30.5 | <0.5 |
| 60 | 1.3 | 0.6 | 6.50 | 34.4 | |
| 90 | 2.0 | 0.6 | 6.50 | 39.0 | |
| 120 | 0.9 | 0.6 | 6.50 | 44.0 | |

TABLE XXXVI

DDT DATA RUN D1

0.50 ml of 1.0 gm DDT/liter methanol into 10ℓ reactor
Three 15 watt UV lamps
Two ℓ/min of 2.04% ozone

| Time, Min. | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | DDT, mg/ℓ |
|---|---|---|---|---|---|
| 0 | 15.5 | 0 | 5.75 | 27.0 | 0.057 |
| 15 | | 8.4 | | 28.0 | 0.014 |
| 30 | | 13.4 | | 29.0 | 0.0007 |
| 60 | | 2.1 | | 31.5 | <0.0005 |
| 90 | | 1.2 | | 34.0 | |
| 120 | 1 | 1.2 | 5.1 | 36.0 | |
| 180 | 1 | 1.2 | 4.6 | 39.0 | |



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TABLE XXXVII

DDT DATA RUN D2

0.50 ml of 1.0 gm DDT/liter methanol into 10ℓ reactor
Zero UV
Two ℓ/min of 1.98% ozone

| Time, Min. | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | DDT, mg/ℓ |
|---|---|---|---|---|---|
| 0 | 16.0 | 0 | 4.15 | 26 | 0.026 |
| 15 | 15.8 | 7.2 | 3.8 | 26.5 | 0.005 |
| 30 | 15.8 | 6.9 | 3.9 | 27.0 | 0.004 |
| 60 | 14.75 | 6.3 | 4.0 | 28.0 | 0.003 |
| 90 | 14.75 | 6.3 | 4.05 | 29.0 | 0.0025 |
| 120 | 12.3 | 6.0 | 4.1 | 29.5 | 0.0023 |
| 180 | 9.0 | 5.4 | 4.0 | 31.0 | 0.0015 |
| 240 | 4.0 | 5.4 | 4.05 | 33.0 | <0.0015 |

TABLE XXXVIII

DDT DATA RUN D3

0.50 ml of 1.0 gm DDT/liter methanol into 10ℓ reactor
Three 15 watt UV lamps
Zero Ozone

| Time, Min. | TOC, mg/ℓ | pH | Temp., °C | DDT, mg/ℓ |
|---|---|---|---|---|
| 0 | 16 | 5.9 | 25.3 | 0.022 |
| 15 | 17 | 5.3 | 26.3 | 0.007 |
| 30 | 17 | 4.9 | 27.3 | 0.0008 |
| 60 | 17 | 4.2 | 30.0 | 0.0005 |
| 90 | | 4.05 | 32.0 | <0.0005 |



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TABLE XXXIX

DDT DATA RUN D4

0.50 ml of 1.0 gm DDT/liter methanol into 10ℓ reactor
One 15 watt UV lamp
Two ℓ/min of 2.05% ozone

| Time | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | DDT, mg/ℓ |
|---|---|---|---|---|---|
| 0 | 22.0 | 0 | 4.3 | 50.0 | 0.0070 |
| 15 | 19.5 | 2.7 | 4.0 | 50.0 | 0.0014 |
| 30 | 15.5 | 2.7 | 3.7 | 50.0 | <0.0005 |
| 60 | 4.0 | 3.6 | 3.9 | 50.0 | |
| 90 | 0 | 1.2 | 4.1 | 50.0 | |

TABLE XL

DDT DATA RUN D5

0.50 ml of 1.0 gm DDT/liter methanol into 10ℓ reactor
Two 15 watt UV lamps
Two ℓ/min of 2.02% ozone

| Time | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | DDT, mg/ℓ |
|---|---|---|---|---|---|
| 0 | 19.0 | 0 | 4.05 | 40.0 | 0.013 |
| 15 | 14.2 | 1.5 | 3.75 | 40.3 | 0.002 |
| 30 | 8.05 | 3.0 | 3.70 | 40.8 | <0.0005 |
| 60 | 1.25 | 1.5 | 4.4 | 41.3 | |
| 90 | 0.85 | 1.2 | 4.4 | 42.0 | |



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TABLE XLI

DDT DATA RUN D6

1.05 ml of 1.0 gm DDT/liter methanol into 21ℓ reactor
One 450 watt UV lamp
Four ℓ/min of 2.14% ozone

| Time | TOC, mg/ℓ | $O_3$, mg/ℓ | pH | Temp., °C | DDT, mg/ℓ |
|---|---|---|---|---|---|
| 0 | 14.8 | 0 | 5.0 | 25 | 0.044 |
| 15 | 9.8 | 1.8 | 3.2 | 27 | 0.008 |
| 30 | 7.5 | 2.2 | 4.4 | 30 | 0.005 |
| 60 | 0 | 1.2 | 4.4 | 35 | 0.001 |
| 90 | 0 | 0.6 | 5.3 | 39 | 0.0008 |
| 120 | 0 | 0.6 | 5.9 | 42 | 0.0008 |

TABLE XLII

DDT DATA RUN D7

0.50 ml of 1.0 gm DDT/liter methanol into 10ℓ reactor
Three 15 watt UV lamps
Zero ozone

| Time | TOC, mg/ℓ | pH | Temp., °C | DDT, mg/ℓ |
|---|---|---|---|---|
| 0 | 16.5 | 3.9 | 26 | 0.021 |
| 15 | 16.3 | 5.5 | 27 | 0.0017 |
| 30 | 16.0 | 3.9 | 28 | <0.0005 |
| 60 | 17.7 | 3.8 | 30.5 | |





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## D. MATHEMATIC MODEL

Based on the extensive research conducted thus far on the $O_3$-UV process, the following assumptions can be made for purposes of deriving a mathematical model for the overall heterogeneous process.

$$A + O_3 + H_2O + h\nu \rightarrow CO_2 + H_2O + \begin{Bmatrix}\text{other}\\ \text{simple}\\ \text{species}\end{Bmatrix} \qquad (1)$$

1. - the reactor is operated in an optimum manner with regard to stirring rate thereby producing high interacial area so that the ozone is transferred into the liquid phase at the same rate it is supplied; i.e. high mass transfer coefficient.

2. - sufficient UV radiation is supplied to cause the disappearance of the reactant and subsequent products to approach the stiochiometric limiting line: i.e. approach approximately complete utilization of the $O_3$.

3. - the differential rate of reaction is determined by the concentration of the activated species produced by absorption of UV by the reactant and by the ozone.

For purposes of mathematical model the following nomenclature and symbols are defined:

Upper Case

| | |
|---|---|
| $A, A_o$ | reactant species; and at t = 0, (mg/ℓ) |
| $B, B^\circ, \bar{B}$ | ozone; standard state value (1 mg/ℓ); average value, (mg/ℓ) |
| $E_a, E_{aa}$ | activation energy; and for autodecomposition, (k cals/mole) |
| $K_\nu^\circ$ | UV radiation transfer coefficient, (ℓ/nm- watt) |
| $N, N_s$ | stirrer rpm; standard value (700 rpm), (rev/min) |
| $\bar{R}, R^\circ$ | activated species; standard state value (1 mg/ℓ), (mg/ℓ) |
| $T, T_o, \Delta T$ | temperature; reference temperature (298°K): $\Delta T = (T-T_o)$, (°K) |
| V | reactor liquid volume, (liters) |



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Lower Case

| | |
|---|---|
| $b$ | stiochiometric coefficient to complete oxidize A, (mols $O_3$/mol A or mass $O_3$/mass A) |
| $f_\nu$ | fraction of useful UV watts per input watt, ($\nu$-watts/watt) |
| $k$ | reaction rate constant, (mg/$\ell^2$min) |
| $k_a$ | auto-decomposition reaction rate constant, (mg/$\ell$-min) |
| $\dot{m}_B, \dot{m}_{BT}$ | ozone feed rate to reactor; and out the top of the reactor, (mg/min) |
| $n$ | stirring rate exponent, ($n = 1/2$) |
| $n_B$ | number of UV bulbs in reactor |
| $t$ | time, (min) |
| $U_\nu$ | UV-input parameter, (nanometer-watts/liter) |
| $w$ | total watts/bulb-liter, (watts/$\ell$-bulb) |

Greek

| | |
|---|---|
| $\alpha$ | fraction of ozone utilized by reaction |
| $\lambda$ | wavelength of useful UV radiation, (nanometers) |
| $\xi$ | fraction conversion of A |
| $\omega$ | composite rate parameter, (mg A conv./mg B-nm-watt) |

The Derivation

For the continuously sparged batch reactor the differential rate equation for the disappearance of the reactant species can be represented by,

$$\dot{\xi} = \frac{-\dot{A}}{A_o} = \left(\frac{k}{A_o}\right) V \left(\frac{\bar{B}}{B^o}\right) \left(\frac{\bar{R}}{R^o}\right) \qquad (2a)$$

$$\min^{-1} = \left(\frac{\text{mg}}{\ell^2 \text{min}}\right)\left(\frac{\ell}{\text{mg}}\right) (\ell)\ (1)(1)$$



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The average ozone concentration is given by the material balance,

$$\bar{B}\Big]_o^t = \begin{pmatrix}\text{total } O_3\\ \text{supplied}\end{pmatrix} - \begin{pmatrix}O_3 \text{ used by}\\ \text{reaction}\end{pmatrix} - \begin{pmatrix}O_3 \text{ auto-}\\ \text{decomposed}\end{pmatrix} - \begin{pmatrix}O_3 \text{ out of}\\ \text{the top of}\\ \text{reactor}\end{pmatrix}$$

$$\bar{B} = \frac{\dot{m}_B t}{V} - bA_o\xi - k_a \frac{\bar{B}t}{B^o} - \frac{\dot{m}_{BT} t}{V} \qquad (2b)$$

(mg/ℓ)

$$\bar{B}t \left(\frac{1}{t} + \frac{k_a}{B^o}\right) = \left(\frac{\dot{m}_B t}{V}\right) \left[1 - \frac{bA_o\xi V}{\dot{m}_B t} - \frac{\dot{m}_B t}{\dot{m}_B}\right]$$

Let, $\alpha \equiv \dfrac{bA_o\xi V}{\dot{m}_B t}$, the fraction of $O_3$ utilized by reaction.

$\dfrac{\dot{m}_{BT}}{\dot{m}_B} \simeq 0$, the loss out the top of the reactor.

Assume, $\dfrac{1}{t} << \dfrac{k_a}{B^o}$ for moderate and long times.

Then, $$\frac{\bar{B}}{B^o} = \frac{\dot{m}_B (1-\alpha)}{Vk_a} \qquad (2c)$$





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The concentration of activated species ($R/R^o$) in the liquid phase will depend on the efficiency of transfer of ν-photons into the liquid and their quantum yield. The overall UV radiation transfer process can be represented by.

$$\underset{(mg/\ell)}{\bar{R}} = \frac{10^{-4}}{2} K_\nu f_{\nu\lambda} N_{B\nu} \frac{N^n}{N_o} \qquad (3a)$$

let, $$U_\nu \equiv f_\nu \lambda \eta_B \omega \left(\frac{N}{N_o}\right)^n ; \quad n = 1/2 \qquad (3b)$$

then, $$\frac{\bar{R}}{R^o} = \frac{10^{-4} K_\nu U_\nu}{2R^o} = \frac{10^{-4} K_\nu^o U_\nu}{2} \qquad (3c)$$

Subtracting (2c) and (3c) into the rate equation (2a) gives,

$$\dot{\xi} = \frac{kV}{A_o} \frac{\dot{m}_B (1-\alpha)}{Vk_a} \frac{10^{-4} K_\nu U_\nu}{2} \left(\frac{b}{}\right) \qquad (4a)$$

$$\dot{\xi} = \frac{10^{-4}}{2} \frac{K_\nu^o kV}{k_a} \frac{\dot{m}_B (1-\alpha)}{bV A_o} bU_\nu \qquad (4b)$$

Let, $$\frac{k}{k_o} = \left(\frac{k}{k_a}\right)_{T_o} \exp\left(E_a \Delta T / RT_o^2\right) \qquad (4c)$$

then, $$\dot{\xi} = \left(\frac{10^{-4}}{2}\right) K_\nu^o \left(\frac{k}{k_a}\right)_{T_o} V \exp\left(E_a \Delta T / RT_o^2\right) \left[\frac{\dot{m}_B (1-\alpha)}{bV A_o}\right] bU_\nu$$



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Let,

$$\left(\frac{K_\nu^o k}{k_a}\right)_{T_o} \equiv \omega$$

Finally,

$$\dot{\xi} = \frac{10^{-4}}{2} \omega b V U_\nu \exp\left(E_a \Delta T / T_o^2\right) \left[\frac{\dot{m}_B (1-\alpha)}{b V A_a}\right] \qquad (4d)$$

Experimental Evaluation of the Constants

For the UV-oxidation of a particular substance there are five characteristic constants:

$$b,\ k,\ k_a,\ K_\nu^o,\ \text{and}\ E_a$$

The half conversion point was chosen to evaluate these parameters. Applying (4d) for $t = t_{1/2}$, $\xi$ 1/2, $T_o = 298°K$

then,

$$\xi = \frac{1}{2} = \frac{10^{-4} w b V U_\nu}{2} \exp\left(E_a \Delta T / 176\right) \left[\frac{\dot{m}_B\ (1-\alpha)}{b V A_o}\right] t_{1/2}$$

$$1 = \frac{10^{-4} \omega b V U_\nu}{2} \exp\left(E_a \Delta T / 176\right) \left[\frac{2 m_B t_{1/2}}{b V\ A^o}\right] (1-\alpha)$$

$$1 = \frac{10\text{-}4_{\omega b V U_\nu}}{2} \left(\frac{1-\alpha}{\alpha}\right) \exp\left(E_a \Delta T / 176\right) \qquad (5a)$$

which can be regrouped,

$$\frac{2 \cdot 10^4 \alpha}{b V U_\nu (1-\alpha)} = \omega \exp\left(E_a \Delta T / 176\right)$$

and

$$\ln\left[\frac{2 \cdot 10^4 \alpha}{b V U_\nu (1-\alpha)}\right] = \ln\omega + \left(\frac{E_a}{176}\right) \Delta T \qquad (5b)$$



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For a particular experimental run, the quantities on the left are all known as well as $\Delta T$; consequently for a series of runs with different $U_\nu$ and $\Delta T$ values, $\omega$ and $E_a$ can be determined by linear regression. In addition $k_a$ can be determined, since,

$$k_a = k_{ao} \exp (E_{aa} \Delta T/176) = \frac{\dot{m}_B B^o(1-\alpha)}{V\bar{B}}$$

$$\ln \left[\frac{\dot{m}_B B^o(1-\alpha)}{V\bar{B}}\right] = \ln k_{ao} + (E_{aa}/176)\Delta T$$

leading to the final set of characteristic constants:

$$b,\ k_{ao},\ (k\ K_\nu^o)_o,\ E_a,\ E_{aa}$$



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## III. DISCUSSION

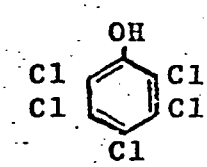
### A. CHARACTERIZATION OF COMPOUNDS

Previously, we have established a quantitative scale for refractory compounds (3,4); the refractory index (RFI) was defined which measures the difficulty of oxidation of a given compound by ozone. Table XLIII presents the latest list and indicates the five compounds relative to others that have been studied. It will be noted that the five compounds are all in the range from refractory to highly refractory.

Using the mathematical model presented in the previous section the characteristic kinetic parameters were determined for each substance, and are presented in Table XLIV. Also UV-Spectrograms were obtained over the range of 180-450 nm and the integrated specific absorbances are shown in the same Table; such information is important in determining the particular UV radiators to be used in the reactor design. It will be noted that the absorbances range from $10^2$ to $10^5$ $cm^2/m.mole$, and have peaks generally at 180-240,240-290, and 290-360 nm.

### B. PENTACHLOROPHENOL

Pentachlorophenol is,




The material used for gas chromatographic standard was 97.8% purified by Chem Services, Inc. Run P8 was made with CSI material, run P1 was made with a 47% commercial mixture (Penta 40) in an unspecified solvent, and the remainder of the runs were made with pentachlorophenol purified by HR from Penta 40.

Tables XXVIII - XXXV present the data on the eight pentachlorophenol runs. Pentachlorophenol shows strong absorption of UV over a wide range of wavelength, as indicated by Figure 3. This makes it very susceptible to oxidation by ozone and typically the compound, as determined by gas chromatographic analysis, has reacted in less than 15 minutes residence time. The PCP was charged to the reactor at a concentration level of 70 mg/ℓ. The further oxidation of intermediate oxidation products, as indicated by total organic carbon (TOC) analysis, takes place less rapidly as shown by Figure 4. With the proper amount of UV input, the oxidation to completion proceeds essentially stoichiometrically. However, it appears that 1.32 watts/ℓ UV is as much as is useful, since the curve for 3.97 watts/ℓ UV (not shown) simply overlays the 1.32 watts/ℓ line. The stoichiometric limiting line shown in Figure 4 represents the theoretical maximum reaction rate as ozone





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TABLE XLIII. RFI VALUES FOR COMPOUNDS

| Compound | RFI* Value | Qualitative Scale |
|---|---|---|
| 1) Potassium cyanide (KCN) | 0.41 | Slightly Refractory (RFI < 1.0) |
| 2) Phenol | 0.44 | |
| 3) Chloroform | 0.53 | |
| 4) Color (α-units) | 0.66 | |
| 5) Complexed Cd-cyanide | 0.96 | |
| 6) Pentachlorophenol | 1.6 | Refractory (RFI = 1 → 100) |
| 7) Ammonium ion | 8. | |
| 8) Simulated Medical Waste | 13. | |
| 9) Glycine | 19.7 | |
| 10) Palmitic Acid ($NH_4$Salt) | 27.3 | |
| 11) Nitrosodimethylamine | 31. | |
| 12) Baygon | 37. | |
| 13) Dichlorobutane | 56. | |
| 14) Methanol | 88. | |
| 15) Vapam | 102. | Highly Refractory (RFI = 100 → 1000) |
| 16) Glycerol | 112. | |
| 17) O-dichlorobenzene | 113. | |
| 18) Polychlorinated Biphenyls | 200 (est.) | |
| 19) Ethanol | 245 | |
| 20) Complexed Ferricyanide | 270 | |
| 21) DDT | 297 | |
| 22) Acetic Acid | > 1000 | Very Highly Refractory (RFI > 1000) |
| 23) Malathion | > 1000 | |

*RFI $\equiv \frac{B_c^{\circ}\, t_{1/2}}{A_o}$ ; [$B_c^{\circ} \equiv O_3$ supplied to $t_{1/2}$; $t_{1/2} \equiv$ hours for 1/2 conversion of $A_o$; $A_o \equiv$ initial amount of compound.]



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TABLE XLIV. VALUES OF KINETIC PARAMETERS AND UV ABSORBANCES

| Compound | Formula<br>M. W. | $b\left(\frac{mgO_3}{mgA}\right)$ | $\omega_1\left(\frac{}{nm\ watts}\right)$ | $E_a\left(\frac{k\ cals}{mole}\right)$ |
|---|---|---|---|---|
| 1) Pentachlorophenol | $C_6Cl_5OH$ | | 9.90 | -6.53 |
| | 266.5 | 2.07 | (r = -0.64) | |
| 2) Malathion | $(CH_3O)_2(PS)SCH(CH_2COOC_2H_5)COOC_2H_5$ | | 0.734 | 14.6 |
| | 330 | 4.65 | (r = 0.99) | |
| 3) Baygon | $CH_3NH(CO)OC_6H_4OCH(CH_3)_2$ | | 0.818 | 8.21 |
| | 198 | 6.08 | (r = 0.98) | |
| 4) Vapam | $CH_3NH(CS)SNa\cdot 2H_2O$ | | 2.02 | 3.66 |
| | 129 | 3.63 | (r = 0.77) | |
| 5) DDT | $ClC_6H_4(CHCCl_3)C_6H_4Cl$ | | 0.0291 | -8.51 |
| | 354.5 | 4.40 | (r = -0.94) | |

r = correlation coefficient, [(slope) (standard deviation in X)/(standard deviation in Y)]



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TABLE XLIV. VALUES OF KINETIC PARAMETERS AND UV ABSORBANCES (Continued)

| Compound | $k_{ao}$ $(\frac{mg}{\ell\ min})$ | $E_{aa}$ $(\frac{k\ cals}{mole})$ | $\bar{A}(\lambda)$ $(\frac{cm^2}{m.mole})$ | $\Delta\lambda$ (nm) |
|---|---|---|---|---|
| 1) Pentachlorophenol | 0.923 | -3.51 | $41.5 \times 10^3$; | 200 - 236 |
| | | | $17.8 \times 10^3$; | 236 - 275 |
| | (r = 0.58) | | $5.65 \times 10^3$; | 275 - 355 |
| 2) Malathion | 1.23 | 6.08 | $1.86 \times 10^3$; | 200 - 270 |
| | (r = 0.87) | | | |
| 3) Baygon | 0.550 | 6.68 | $4.23 \times 10^3$; | 180 - 240 |
| | (r = 0.97) | | $0.561 \times 10^3$; | 240 - 290 |
| 4) Vapam | 1.01 | 4.70 | $1.42 \times 10^3$; | 180 - 210 |
| | | | $0.078 \times 10^3$; | 210 - 300 |
| | (r = 0.80) | | | |
| 5) DDT | 2.68 | 4.27 | $153 \times 10^3$; | 190 - 280 |
| | (r ~ 1.00) | | | |

r = correlation coefficient, [(slope) (standard deviation in X)/(standard deviation in Y)]



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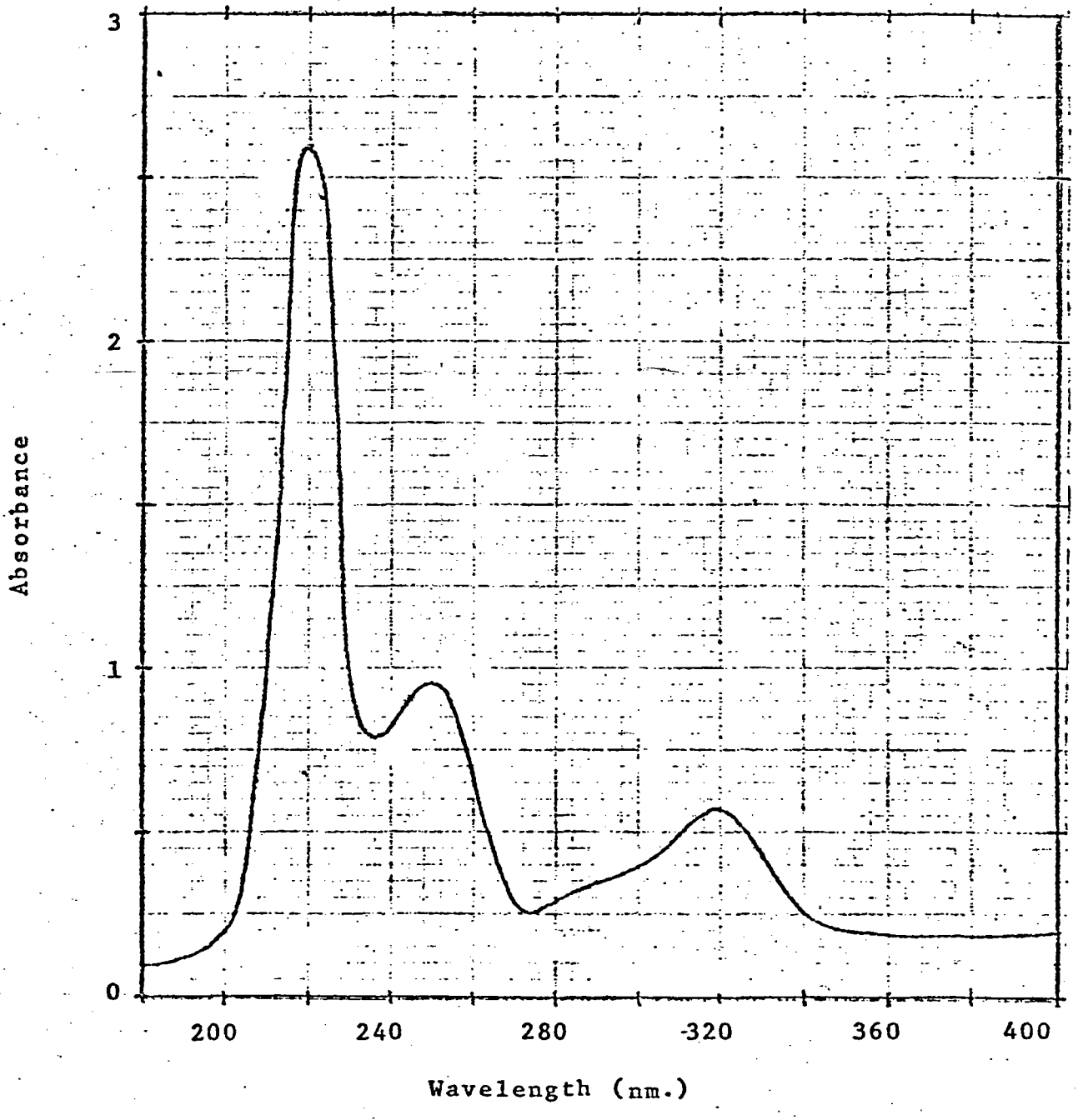


FIGURE 3. Pentachlorophenol UV-Spectrogram (7.0 mg/ℓ)



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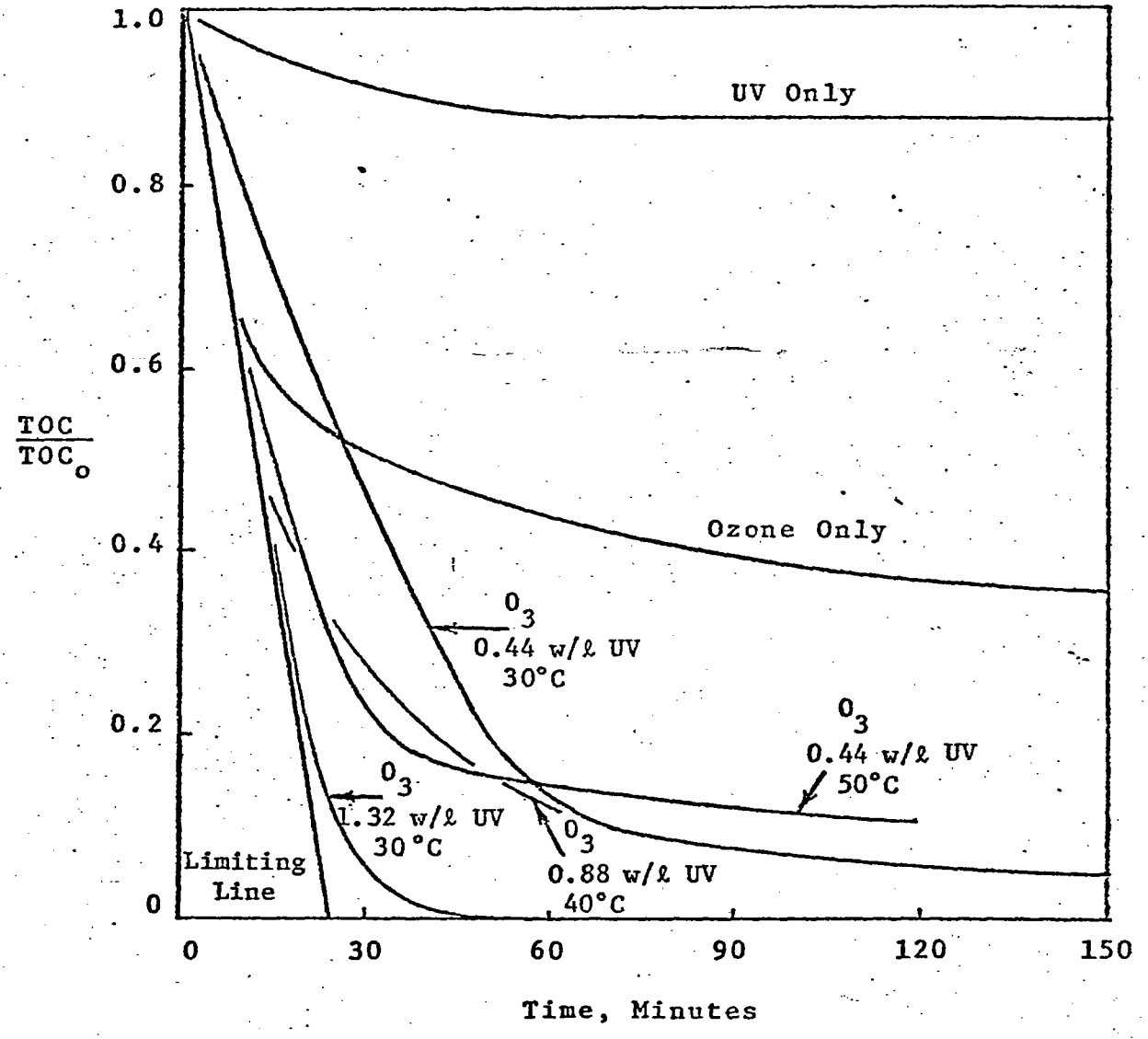


FIGURE 4. Destruction of Pentachlorophenol TOC (initial PCP, 70 mg/ℓ)



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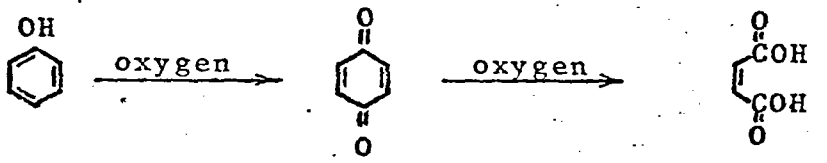
is added into the reactor, in accordance with,

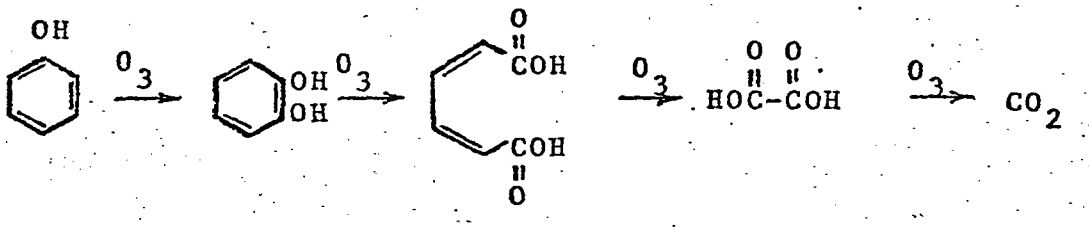
$$2\ C_6OHCl_5 + 23O_3 \longrightarrow 12CO_2 + H_2O + 23O_2 + 5Cl_2$$

which corresponds to b=2.07 mg ozone per mg pentachlorophenol.

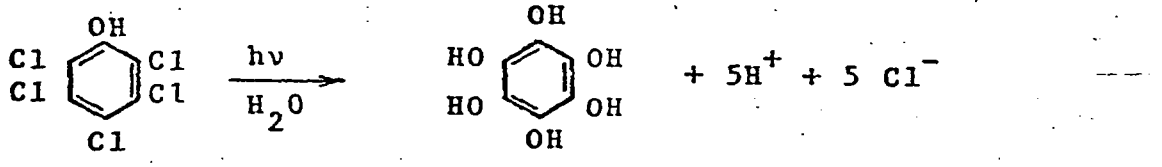
Because of similarity of structure, it is appropriate to consider first the oxidation of phenol. The classical oxidation is first to quinone, which further oxidizes to maleic acid,




Bailey (5) has reviewed the ozone oxidation of phenol, and he concludes that the major pathway is through catechol to muconic acid. Since oxalic acid is found as an intermeidate oxidation product, it appears that the ozone attacks muconic acid at the double bonds. Following the carbon structure only, this gives,




As evidenced by TOC, phenol is converted to $CO_2$ by ozone-UV at the stoichiometric rate at which ozone is added into the reactor. Because much of the conversion of pentachlorophenol to $CO_2$ is also at essentially the stoichiometrically limited rate, there is justification for assuming a similar oxidation mechanism. But in addition, the pentachlorophenol by gas chromatographic analysis disappears much faster than does the TOC; at the same time, the pH of the water drops drastically and a chloride concentration corresponding to more than half the stiochiometric amount suddenly appears and then slowly increases. With UV alone, the pentachlorophenol disappearance, pH drop, and chloride appearance is extensive, but much slower than with ozone-UV; with UV alone, TOC disappearance is small. This implies an initial chlorine loss caused by UV,



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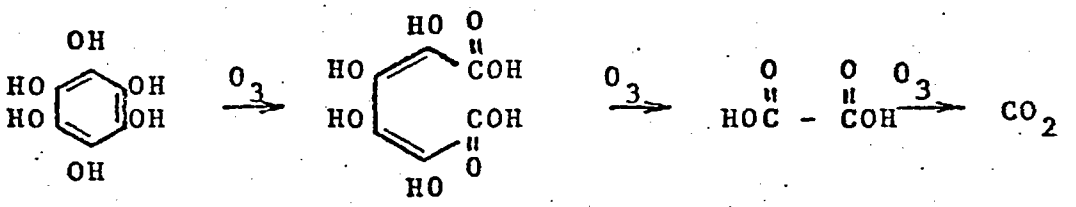
followed by oxidation of the ring,

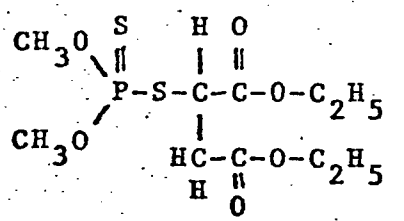


It appears unlikely that the chlorine is released from the ring as free chlorine which would produce hypochlorous acid in aqueous medium; whereas analyses of the apparent ozone content of the water gives no indication of transient hypochlorite.

Confirmation of this mechanism can be made by examining the time profiles in Figure 5. As the UV rapidly removes the chlorine atoms from the compounds, the PCP drops to zero very rapidly, and the chloride ion concentration rapidly reaches a plateau. The pH drops rapidly from 9.6 because of the formation of HCl and phenolic compounds of an acidic nature. Then the pH drops more slowly as the phenolics are converted to the more acidic organic acids. As the TOC shows the organic acids being destroyed, the pH rises to a plateau near 5, resulting only from the unoxidizable HCl.

C. MALATHION

Malathion is S-[1,2-dicarbethoxy ethyl]-o,o dimethyl dithio phosphate,



The material used for gas chromatographic standard was 95% purified by Chem Services, Inc. Runs were made with commercial 95% from Redwood Chemicals, Inc.

Tables III-XII present the run data on the ten malathion runs. The data show that any ozone run has essentially destroyed the malathion by the time the first sample of a run was taken, even when no UV was used. Malathion is also destroyed by UV alone, but this takes about two hours for complete destruction, while ozone or $O_3$/UV combination requires only 15 minutes for complete destruction of the malathion. Of course, complete destruction of the malathion decomposition products, as evidenced by the TOC, takes both ozone and UV together.



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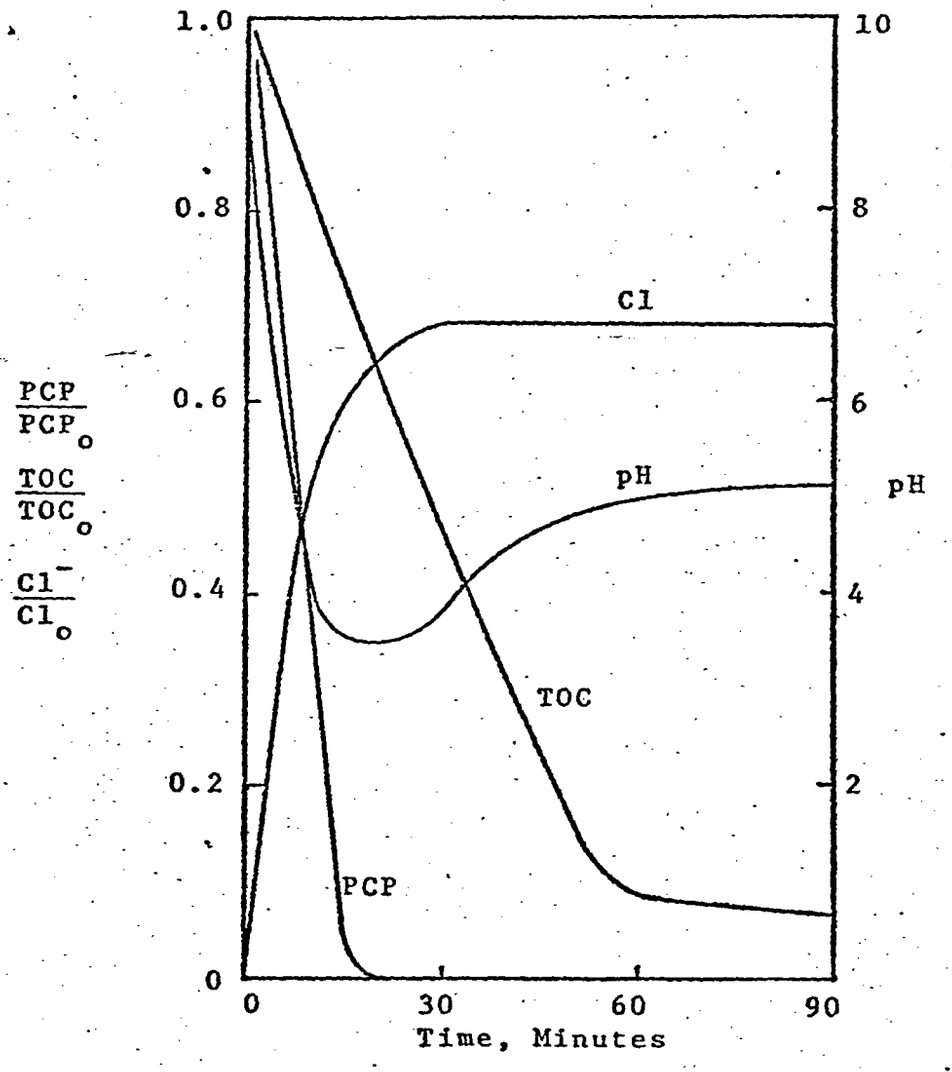


FIGURE 5. Related Time Profiles, Oxidation of Pentachlorophenol (Re: Figure 4.)



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Phosphorous makes up 9.4% by weight of the malathion molecule. The orthophosphate results indicate that if there is no significant destruction of organic material, as represented by TOC, then there is no significant formation of orthophosphate. As would be expected in runs M4, M5, and M8 where there is significant destruction of organic material, the amount of orthophosphate formed seems to correspond to the phosphorous associated with the TOC destroyed.

Figure 6 summarizes some of the malathion runs. The stoichiometric limiting line represents the theoretical rate at which TOC could be destroyed as ozone is added into the reactor, in accordance with the following chemical reaction,

$$C_{10}H_{19}S_2PO_6 + 64\ O_3 \longrightarrow 19H_2O + 20CO_2 + 4\ SO_3 + P_2O_5 + 64\ O_2$$

This indicates that b= 4.65 mg $O_3$/mg malathion.

Figure 6 shows that no TOC is destroyed if ozone alone is used or if UV alone is used, but TOC is slowly destroyed if only a small amount of UV is used with the ozone. The rate of TOC destruction can be greatly enhanced by elevated temperature, but greater enhancement can be obtained by additional UV without elevated temperature. The greatest enhancement can be obtained by elevated temperature and high UV together.

The malathion molecule contains two ester linkages, and when they hydrolyze, two ethanol molecules and an iso-substituted succinic acid will be formed. The succinic acid molecule is similar to two acetic acid molecules stuck back-to-back. Figures 7 and 8 compare the destruction by ozone-UV of TOC from malathion, ethanol and acetic acid at room temperature and at 50°C. Data on ethanol and acetic acid are from references 3 and 4. It is interesting to note that of the many materials to which this process has been applied, only malathion and acetic acid show no redution of TOC by ozone alone. As would be expected, Figure 7 shows the carbon loss from malathion at 25°C to be slowest of the three, because it must first go to ethanol and acidic forms, and the ethanol slower than acetic acid because it oxidizes to form acetic acid. However, Figure 8 indicates that at elevated temperature some other mechanism becomes more active, with malathion fastest, ethanol next, and acetic acid the slowest. One possibility is that ethanol starts to loose significant carbon through the path: ethanol to ethylene glycol to oxalic acid to carbon dioxide. In addition, malathion can loose carbon through the grouping $H_3COP$ going to methanol, which is then furthur oxidized.



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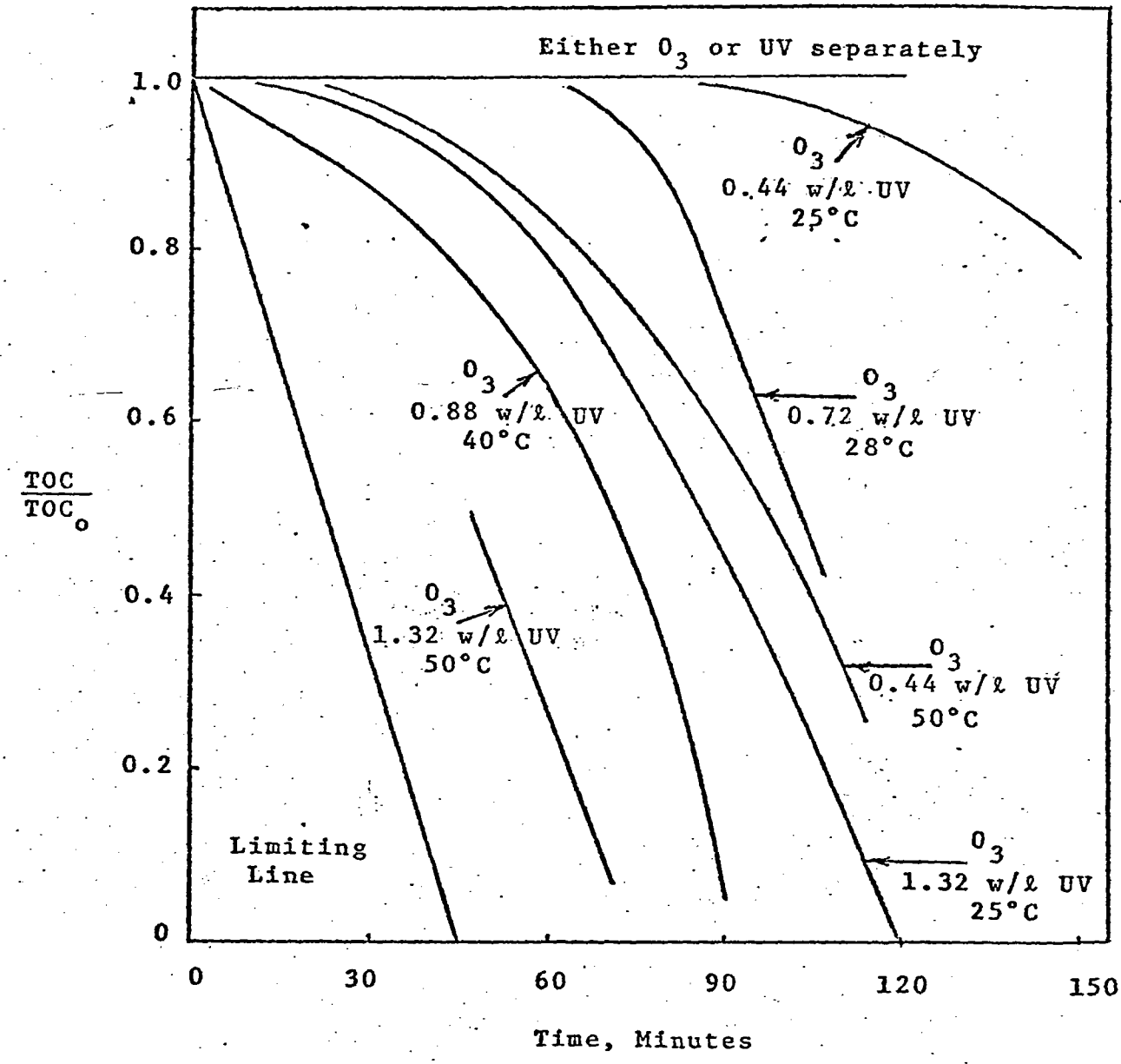


FIGURE 6. Destruction of Malathion TOC



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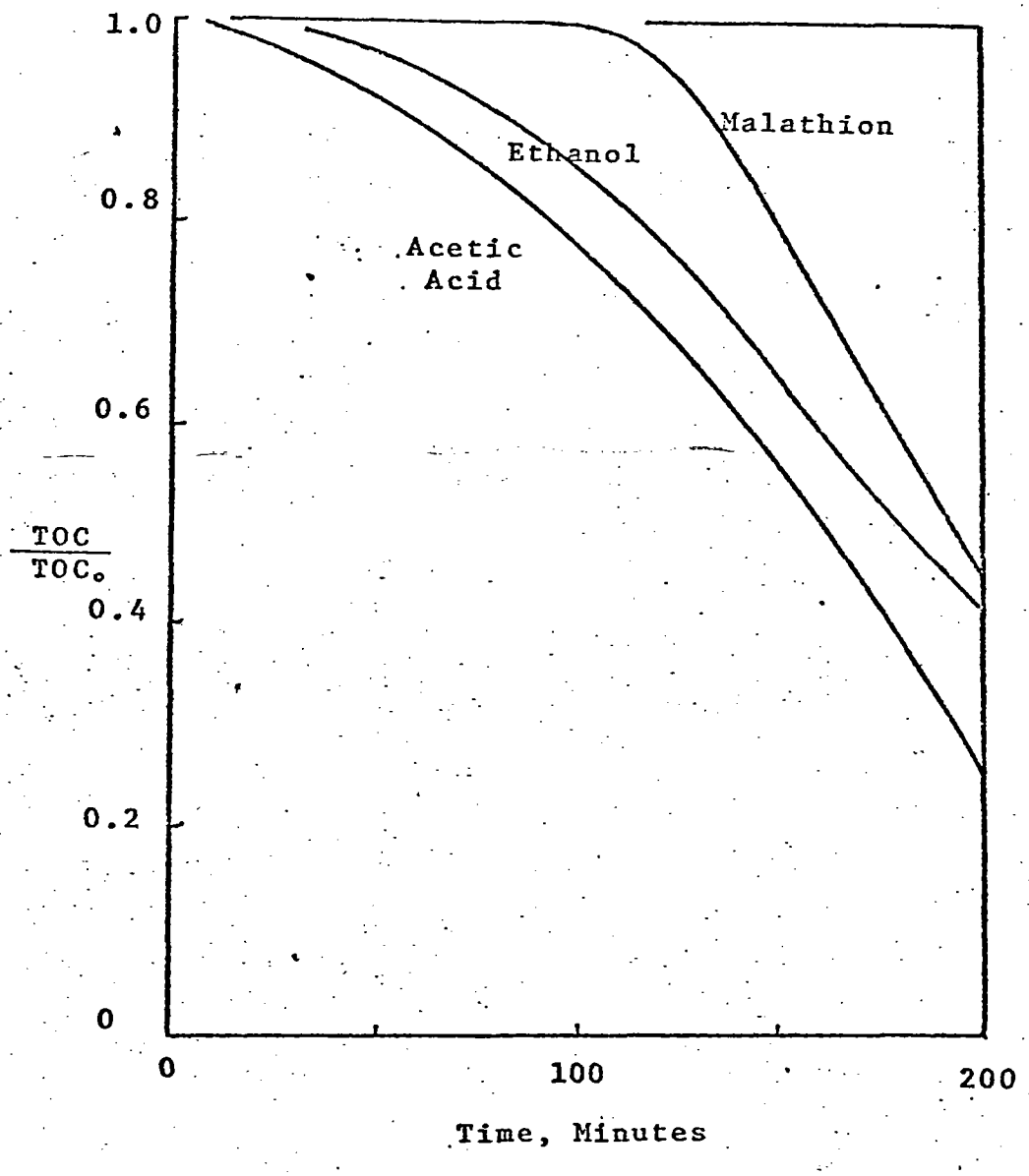


FIGURE 7. TOC Destruction for Malathion, Ethanol and Acetic Acid at 0.44 watts/liter UV and 25°C

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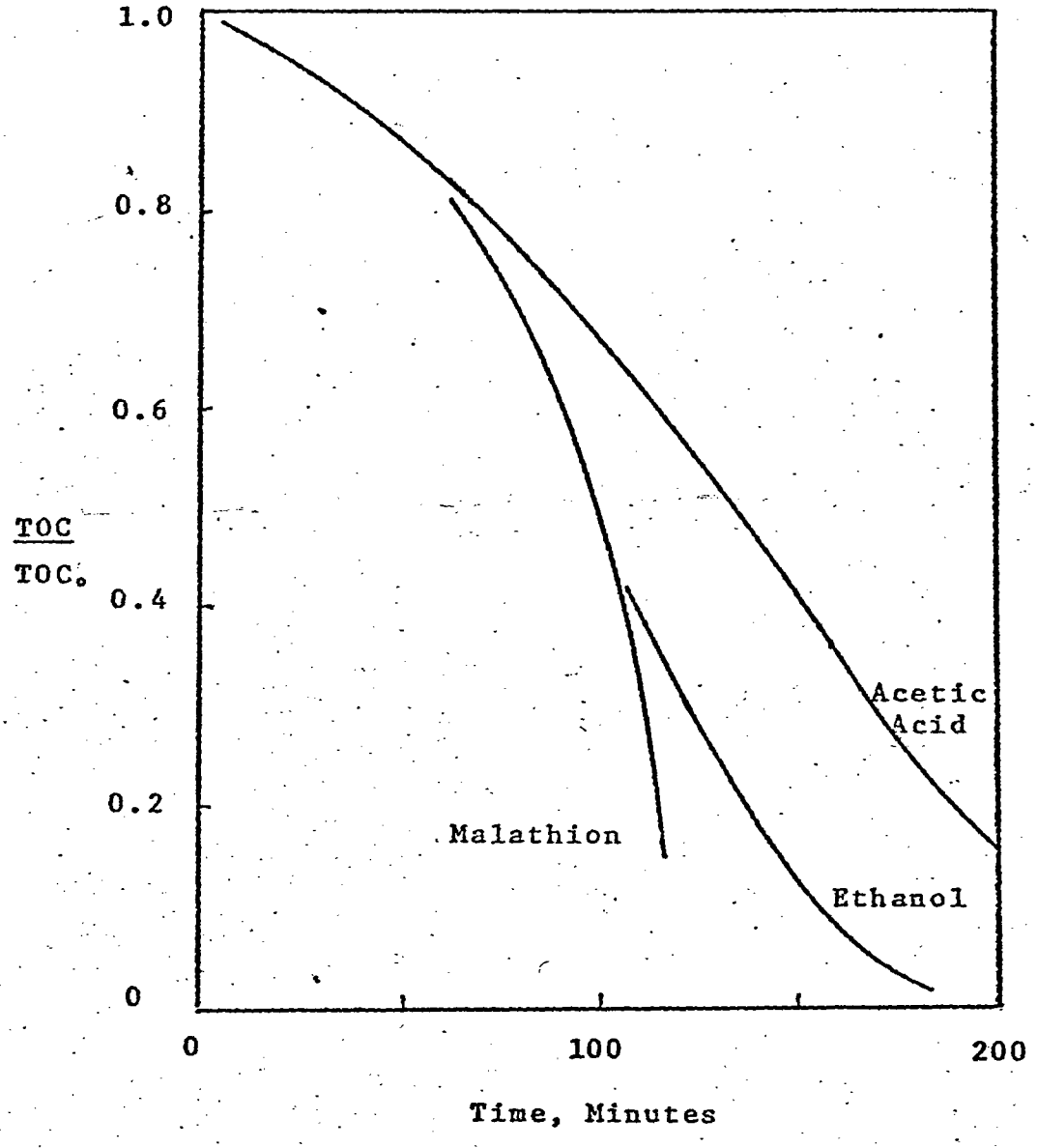


FIGURE 8. TOC Destruction for Malathion, Ethanol and Acetic Acid at 0.44 watts/liter UV and 50°C.



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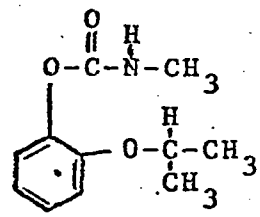
In summary, we can postulate several simultaneous reaction mechanisms for malathion, shown in Table XLV.

D. BAYGON

Baygon is o-isopropoxyphenyl methyl carbamate,



The material used for gas chromatographic standard was 98.7% purified by Chem Services, Inc. The same material was used for all runs except B1 for which was used Mobay Chemical Corporation's Baygon 1.5, which is 13.9% in unspecified solvent.

Tables XIII-XX present the data on the eight Baygon runs. The data show that ozone or ozone-UV quickly destroys the Baygon itself. UV alone slowly destroys the Baygon itself, but accomplishes almost no destruction of the Baygon oxidation products, as represented by TOC. Figures 9a and 9b show the destruction of TOC from Baygon and Baygon oxidation products. The stochiometric limiting line represents the theoretical rate at which TOC could be destroyed as ozone is added into the reactor, in accordance with the following chemical reaction,

$$2C_{11}H_{15}O_3N + 53O_3 \rightarrow 22CO_2 + 15H_2O + N_2 + 53O_2$$

This indicates that b=6.08 mg $O_3$/mg Baygon. It appears that destruction of TOC proceeds very satisfactorily at room temperature with ozone and 1.32 watts/liter UV or higher, and at 50°C with as little as 0.44 watts/liter UV.

The Baygon molecule contains an ester linkage, and when it hydrolyzes, a methyl amino acid is formed that is similar to glycine, $NH_2CH_2COOH$. Figure 10 compares the destruction by ozone-UV of TOC from Baygon and glycine (3,4), and shows similarity in the destruction of TOC from both molecules, but also shows that the Baygon destruction is enhanced more than is the glycine destruction by elevated temperature and UV.

Run B3, in Table XV, shows loss of TOC while treating with UV only. Extensive experimentation with the $O_3$-UV process has never shown any indication of oxidation other than by the ozone molecules, but for chloroform (6), vaporization loss has been confirmed. This



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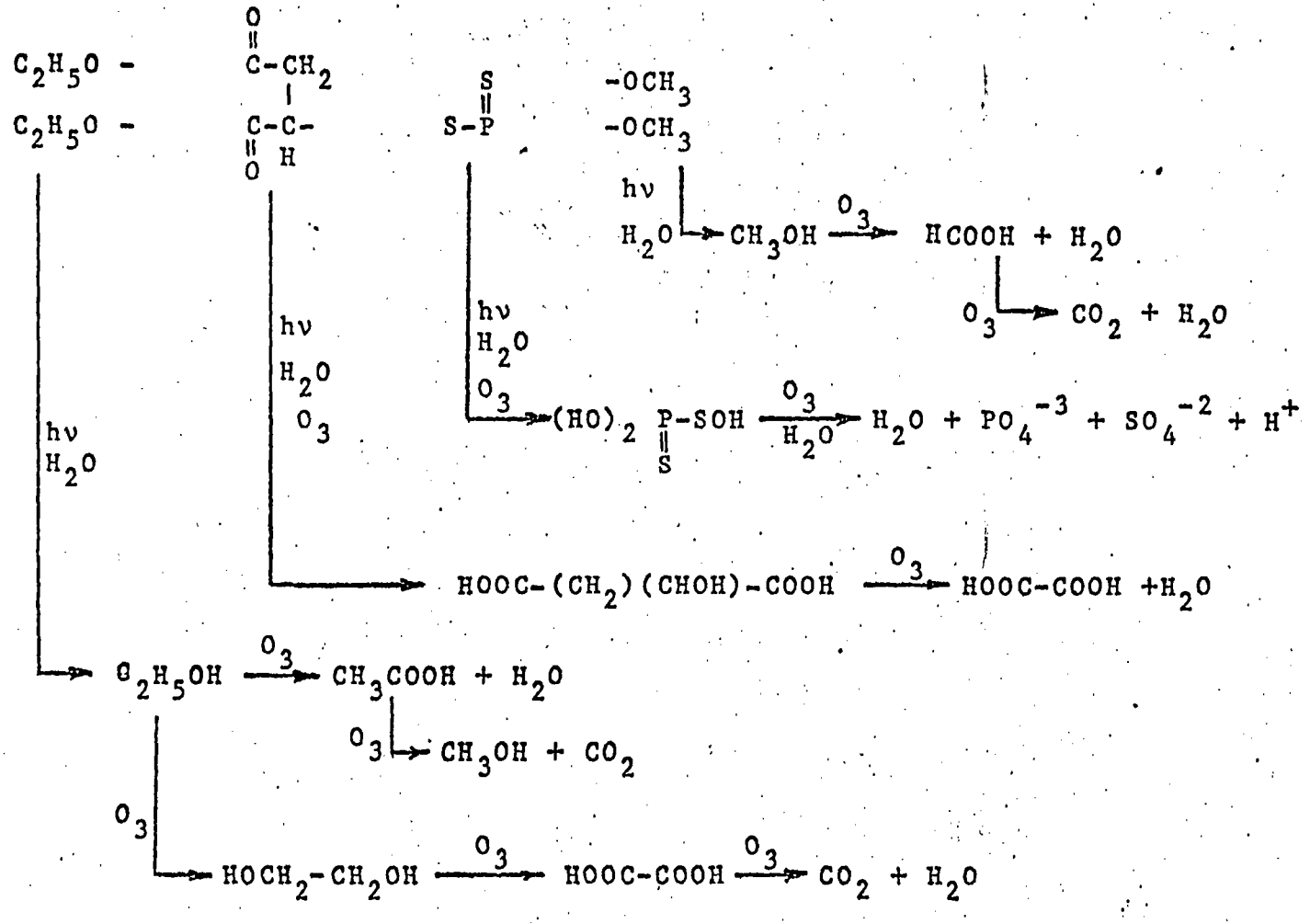
TABLE XLV

MALATHION REACTION MECHANISMS



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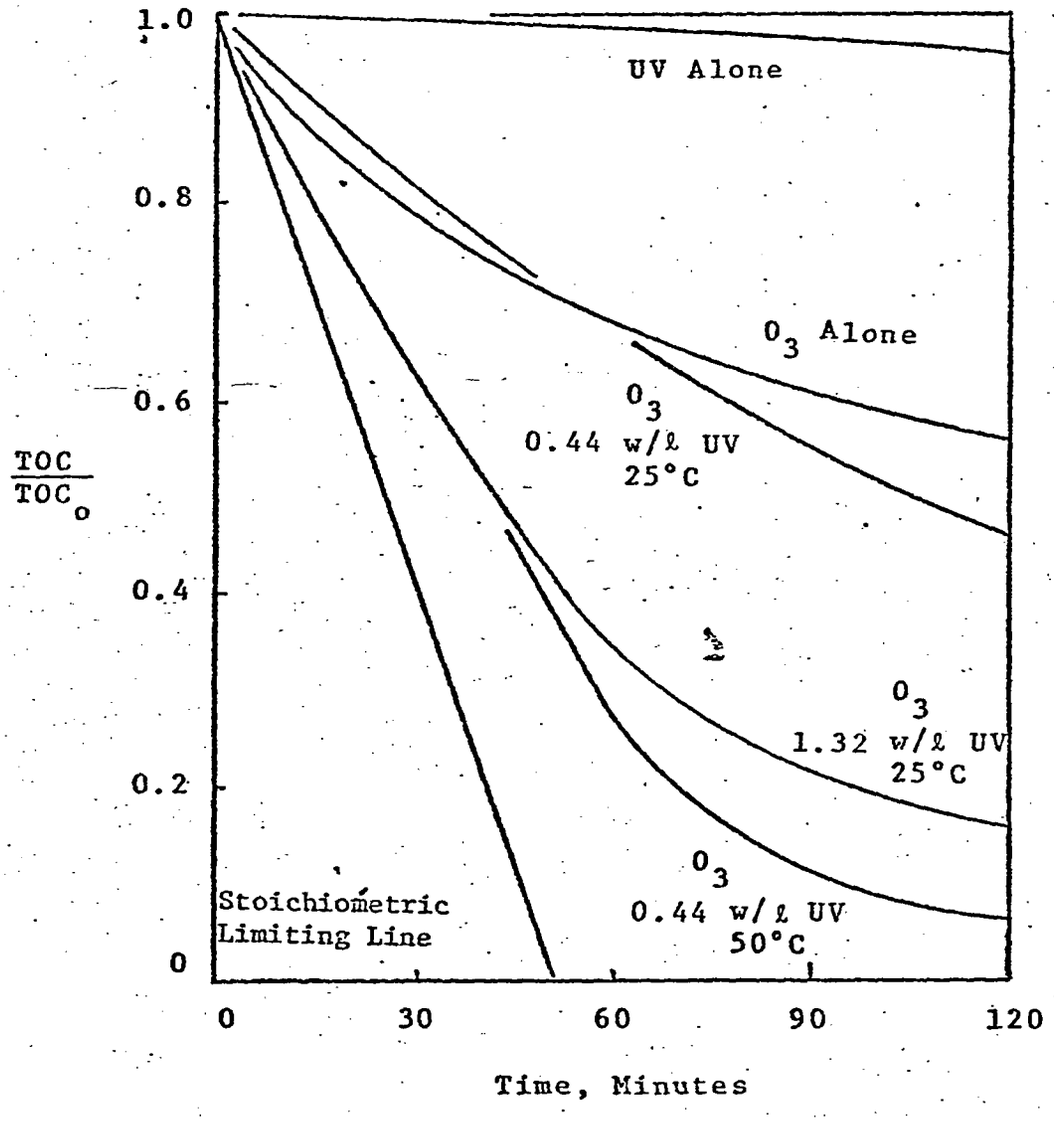


FIGURE 9a. Destruction of Baygon TOC



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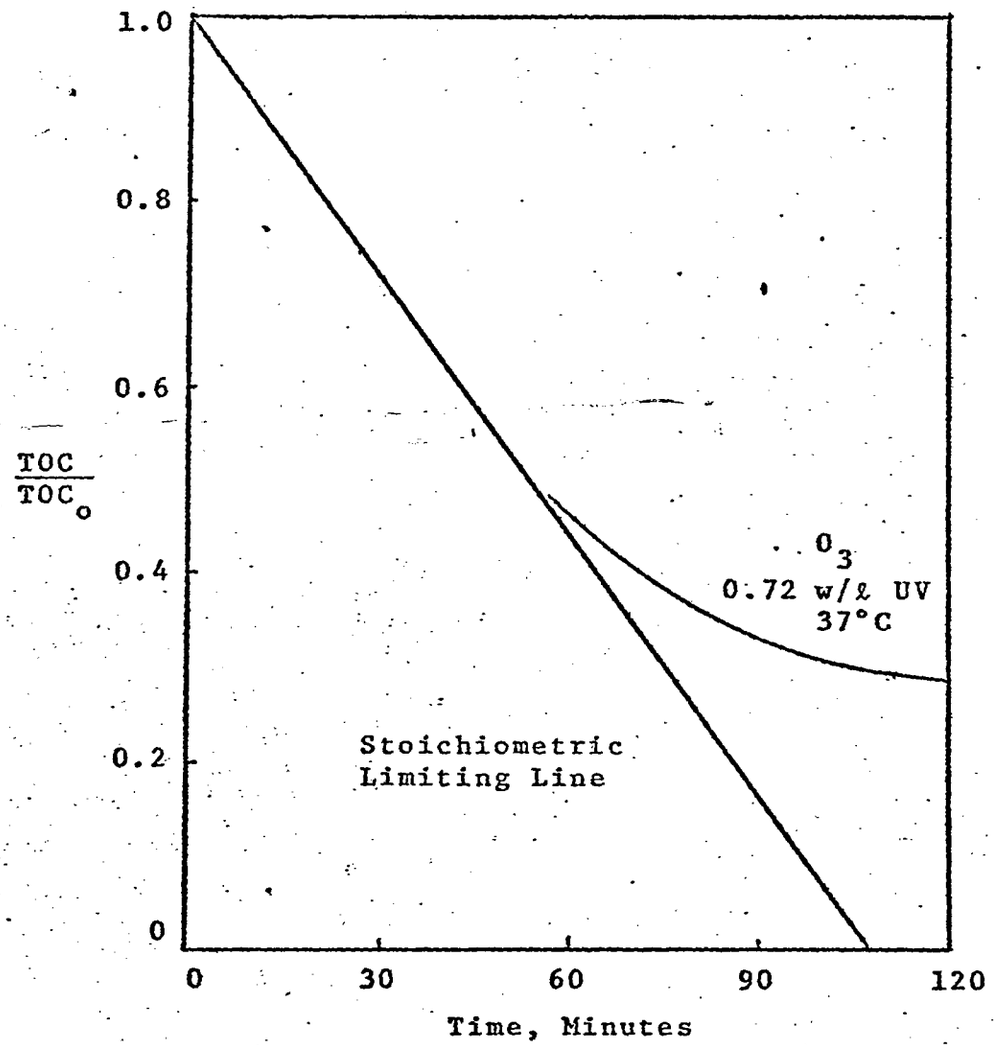


FIGURE 9b. Destruction of Baygon TOC



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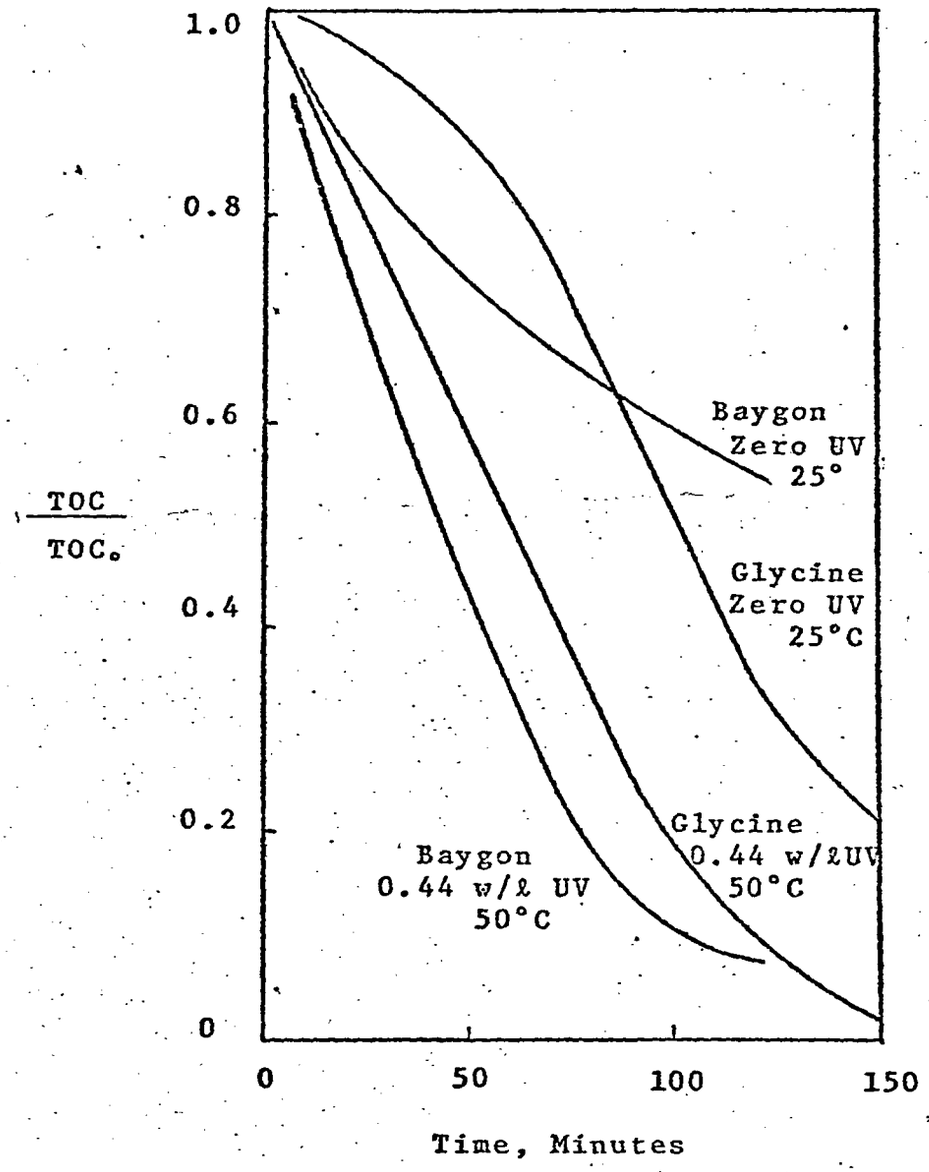


FIGURE 10. TOC Destruction for Baygon and Glycine



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implies a hydrolysis of the structure ring-$OCH(CH_3)_2$ to form isopropyl alcohol, a small portion of which is lost because of its relatively high volatility.

The summary of simultaneous mechanisms for Baygon is shown in Table XLVI.

E. VAPAM

Vapam is sodium N-methyldithiocarbamate dihydrate,

$$CH_3-\overset{H}{\underset{|}{N}}-\overset{S}{\overset{\|}{C}}-S-Na\cdot 2H_2O$$

The material used for gas chromatographic standard and for runs was 98% purified by Chem Services, Inc.

Tables XXI-XXVII present the data on the seven Vapam runs. The Vapam analyses show that Vapam itself is destroyed by ozone alone or ozone-UV very quickly; essentially none is left by the time the first treated sample is taken at 15 minutes into the run. UV alone will very slowly decompose Vapam itself, but the ozone-UV combination is required for substantial destruction of the intermediate oxidation products, as represented by TOC. The sulfate found in the samples increases as the extent of TOC destruction increases, and for Run V2, ozone with 1.32 watts/liter UV, the sulfate found in the final sample corresponds closely to the total sulfur in the Vapam charged to the reactor.

Figure 11 shows the destruction of TOC from Vapam and Vapam oxidation products. The stochiometric limiting line represents the theoretical rate at which TOC could be destroyed as ozone is added into the reactor, in accordance with the following chemical reaction,

$$2C_2H_4NS_2Na\cdot 2H_2O + 25O_3 \rightarrow 4CO_2 + 7H_2O + 4SO_3 + N_2 + 2NaOH + 25O_2$$

This indicates that b=3.63 mg $O_3$/mg Vapam. UV alone causes no destruction of TOC. Ozone alone destroys only about 70% of the TOC. Ozone with UV is required for substantial destruction of TOC.

Figure 12 shows time profiles for Vapam, pH, TOC and sulfate for a typical $O_3$-UV run. The rapid drop in pH implies that oxidation of the sulfur in the molecule is an early step in the mechanism. This leads to the postulated mechanism,

$$CH_3NH(CS)SNa \xrightarrow[H_2O]{O_3,h\nu} CH_3NHCOOH + 2SO_4^{=} + 3H^{+} + Na^{+}$$



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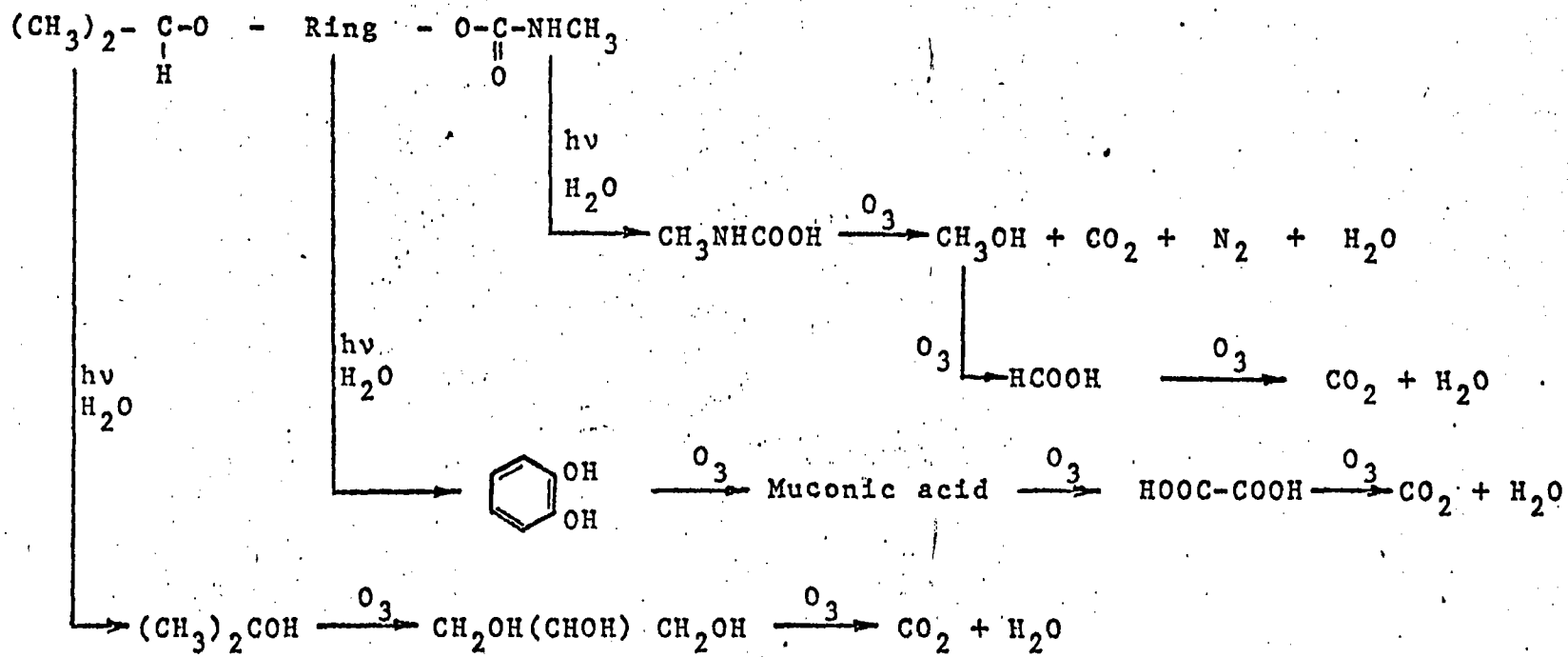
TABLE XLVI

BAYGON REACTION MECHANISMS



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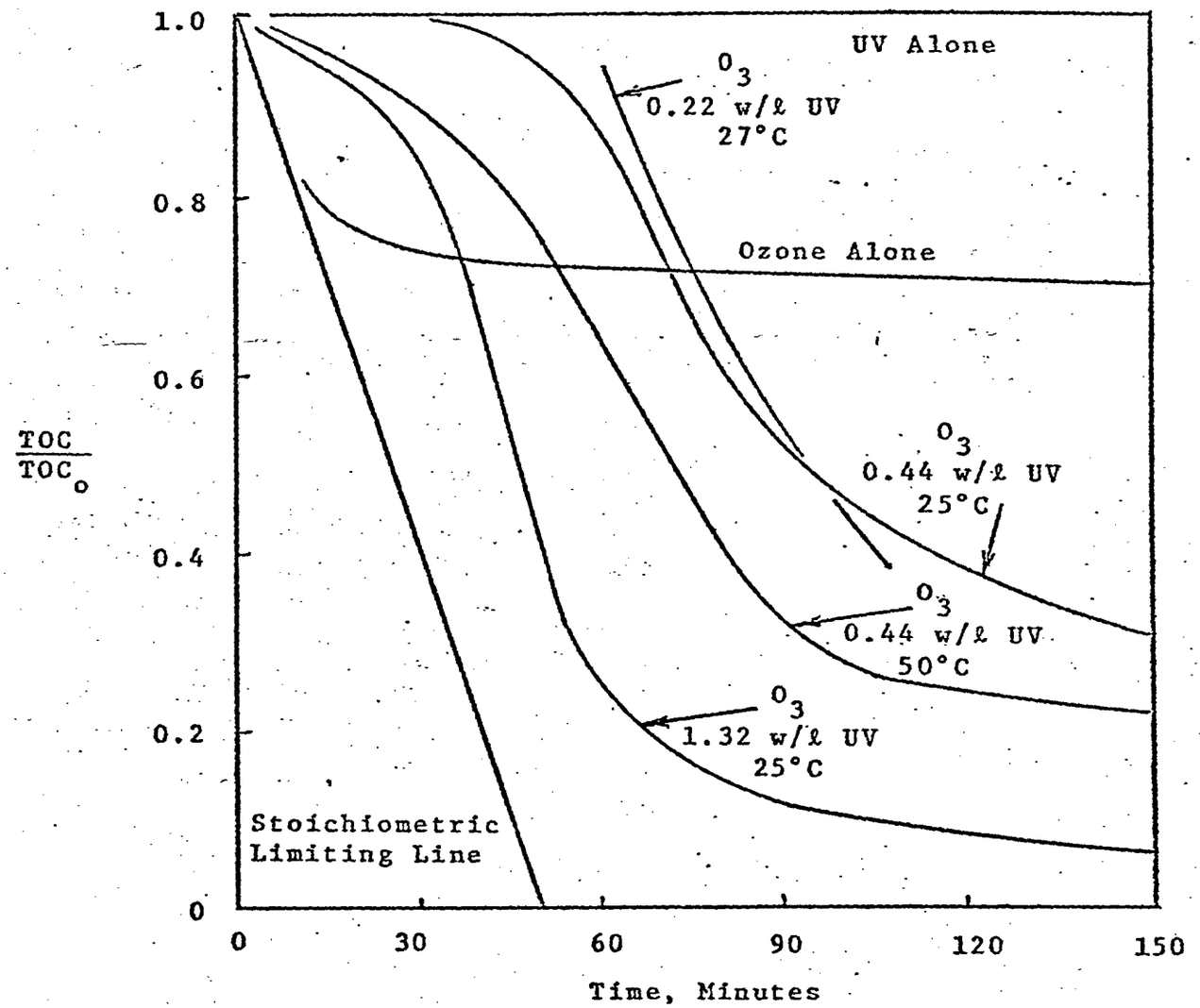


FIGURE 11. Destruction of Vapam TOC



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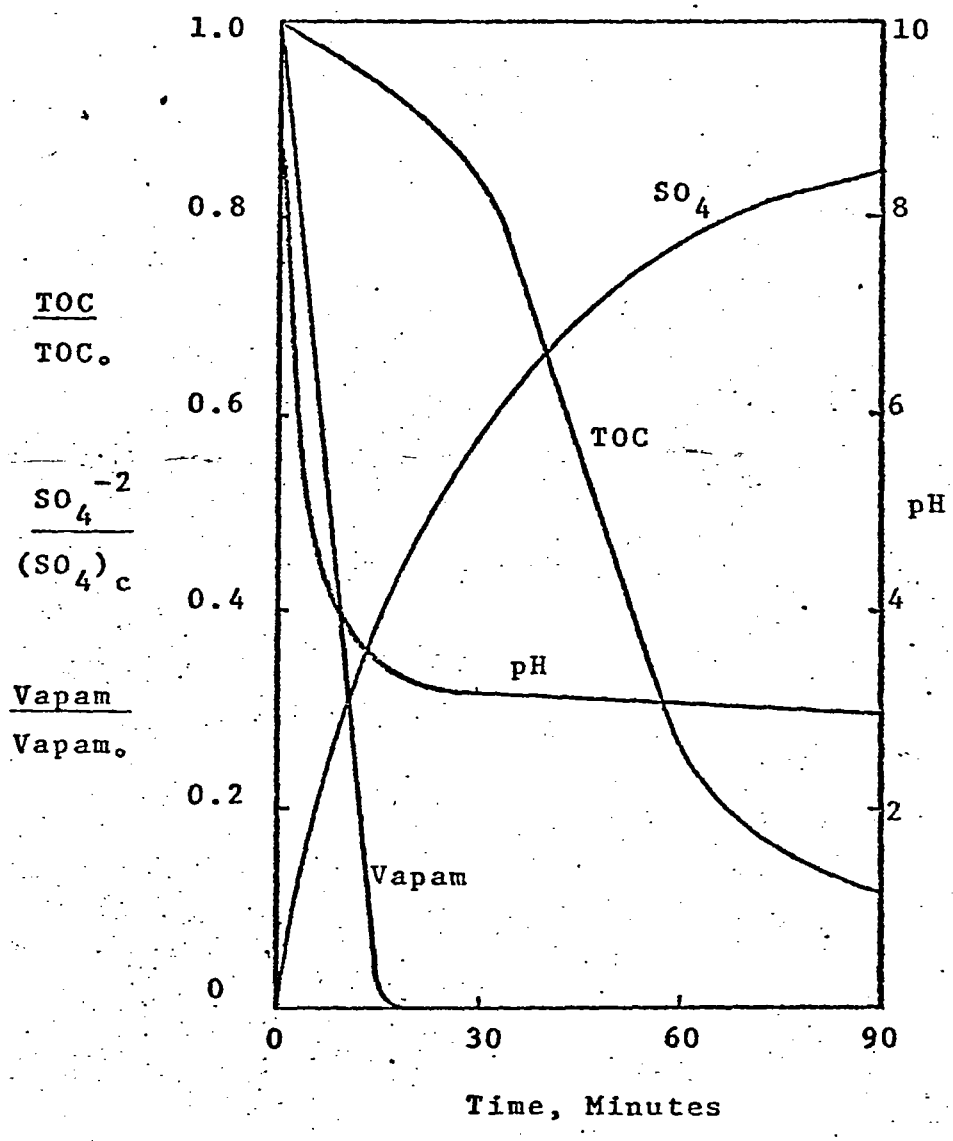


FIGURE 12. Related Time Profiles, Oxidation of Vapam (Re: Figure 11)



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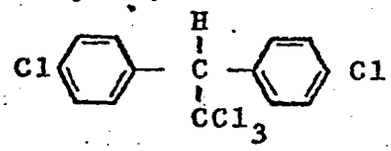
followed by

$$CH_3NHCOOH \xrightarrow{O_3} CH_3OH + CO_2 + N_2 + H_2O$$

$$O_3 \longrightarrow HCOOH \xrightarrow{O_3} CO_2 + H_2O$$

F. DDT

DDT is dichlorodiphenyltrichloroethane,



The material used for gas chromatographic standard and for runs is 30% o,p and 70% p,p' from Chem Services, Inc. For the runs, DDT was added to the reactor in a solution of 1.0 gm DDT per 1.0 liter reagent grade methanol.

The ozone demand of DDT was calculated from,

$$2\ C_{14}H_9Cl_5 + 65O_3 \longrightarrow 28CO_2 + 9H_2O + 5Cl_2 + 65\ O_2$$

which corresponds to b= 4.4 mg $O_3$/mg DDT.

Figure 13 shows selected data for the destruction of DDT as followed by GC analysis. The expanded scale is for ease in labeling the lines, rather than pointing up any significance in the shape of the curves. As observed previously for other compounds, $O_3$-UV is more effective than either ozone or ultraviolet applied separately, and 1.32 watts UV per liter appears to be the highest intensity from which benefit can be derived.

Refering to Tables XXXVI-LXII, the TOC values are contributed almost entirely by the methanol used as the solvent for DDT, and the TOC values therefore have no significance to DDT destruction. Just as with pentachlorophenol, DDT by GC analysis disappears very quickly when treated with ozone-UV and less quickly when treated with UV alone. The chlorinated ring structure leads to the postulation that as with pentachlorophenol, UV light causes the chlorine atoms on the rings to go to HCl while replacing them with hydroxyls. The hydroxyls strongly activate the ring for removal of side chains (the trichloroethane bridge)



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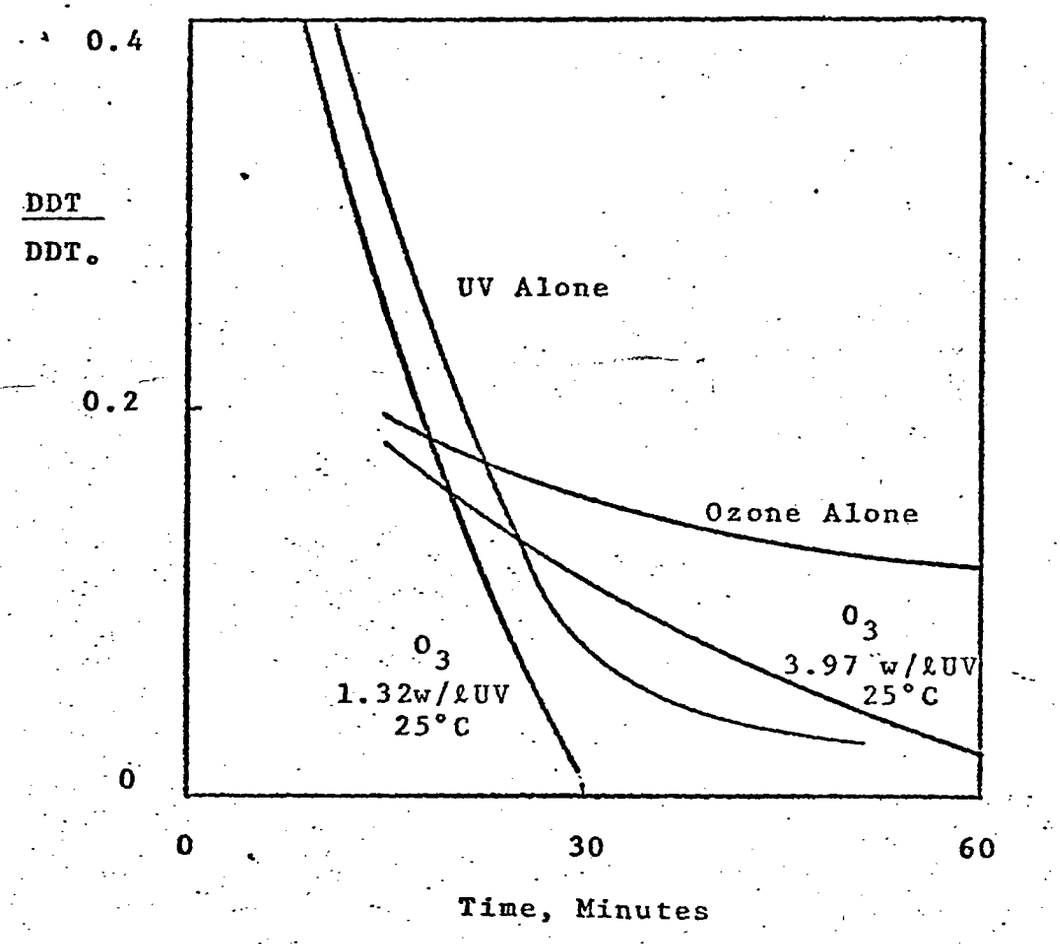


FIGURE 13. Destruction of DDT



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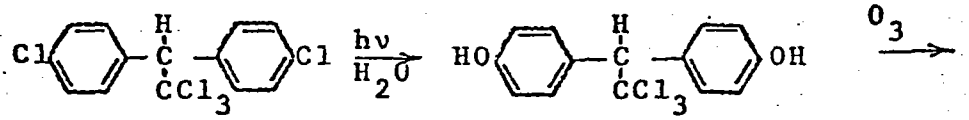
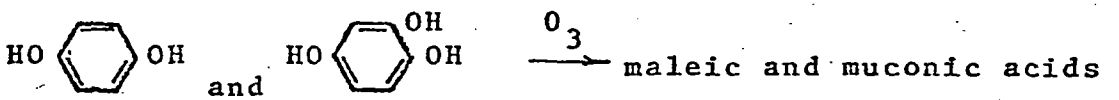
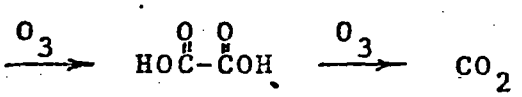
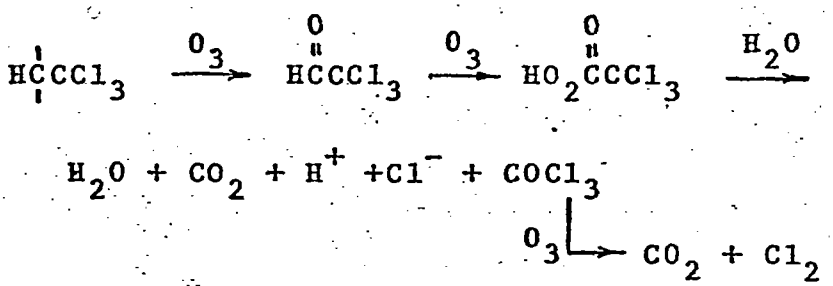
and for oxidation at the ortho position. This mechanism is shown for the ring structure carbons by,







The extremely low concentration of DDT being treated can make no detectable contribution to TOC, pH, or chloride ion, and these parameters can contribute nothing to the elucidation of reaction mechanism. However, the structure of the trichloroethane bridge, similar to chloroform (6), implies a similar mechanism,



Because the DDT is present in such low concentration, any phosgene formed can not be present in hazardous concentration.



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## IV. CONCLUSIONS

1. The ozone-ultraviolet process has been demonstrated extremely effective in the oxidation destruction of pesticides in water, and all their intermediate oxidation products, with all carbon in the molecules going to carbon dioxide.

2. The performance of $O_3$-UV is unequaled by any other process with the pesticide itself being destroyed in only a few minutes of contact time with the process.

3. In general, elevated temperature enhances the reaction rate, but not as dramatically as using additional ultraviolet light.

4. Rapid assessment of other pesticides in water is made possible by mathematical models and laboratory techniques already developed.

5. A properly designed multitaged reactor system, with ozone and ultraviolet light, can accomplish complete removal of pesticides from water, and based on these results, designs can now be developed for prototype units to treat potable water or effluents in the field.

6. The low pressure and medium pressure mercury vapor lamps appear to have an equivalent effect based on the actual ultraviolet light intensity per liter of solution.



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## V. RECOMMENDATIONS

1. Compromise conditions should be selected on the basis of the data so that all of the pesticides studied are effectively (although not necessarily optimally) destroyed.

2. Based on the compromise conditions, a design should be executed for a staged, flow pilot scale system which should be effective for the destruction of any aqueous pesticide solution.

3. The pilot scale system should be operated to demonstrate effective destruction of the design pesticides, and any others of interest, to determine a capacity rating of the system for each pesticide.

4. A full scale design and cost estimate should be developed.

DSW 361242



STLCOPCB4097853

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13. ABSTRACT

This work was undertaken to establish the feasibility of the oxidation destruction in water of five pesticides: malathion, Baygon, Vapam, pentachlorophenol, and DDT, by ozone with ultraviolet light. Each separate pesticide was treated by ozone with various combinations of ultraviolet intensities and temperatures in a sparged stirred tank reactor. Not only was the pesticide destroyed, as indicated by gas chromatographic analysis, but also the total organic content of the water, with contributions from the pesticide and from intermediate oxidation products, was reduced to the limit of detectability. A mathematical model was developed, and constants were calculated from the data to characterize the reactions. Data resulted which will permit the design of prototype treatment equipment to remove pesticide from potable water or from effluent.

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| 14 KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Wastewater Treatment | 8 | 3 | | | | |
| Potable Water Treatment | 8 | 3 | | | | |
| Oxidation of Pesticides | 2 | 3 | | | | |
| Ultraviolet Light | 5 | 3 | | | | |
| Ozonation | 6 | 3 | | | | |
| Total Organic Carbon | 10 | 3 | | | | |



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Exhibit F

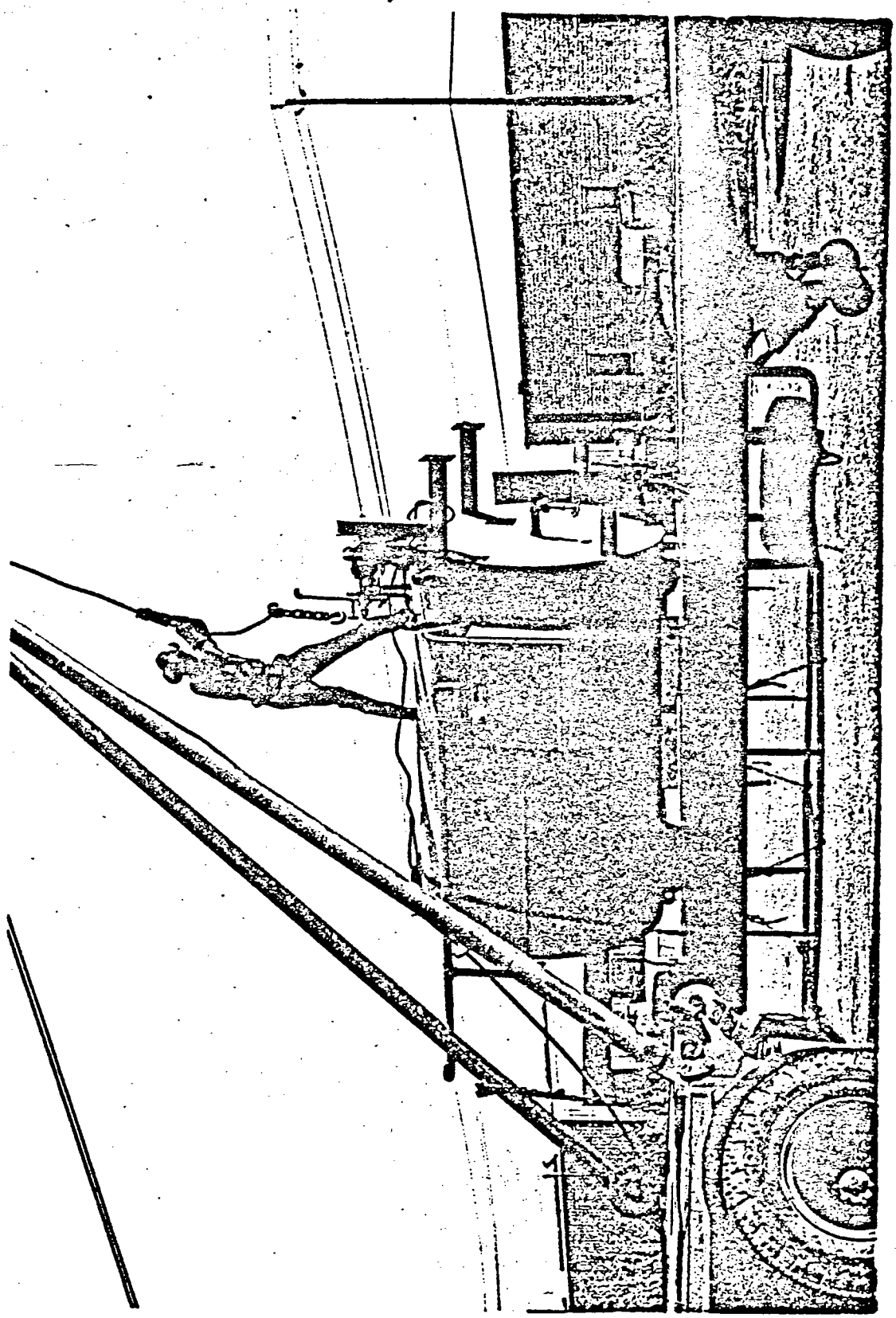

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Exhibit G

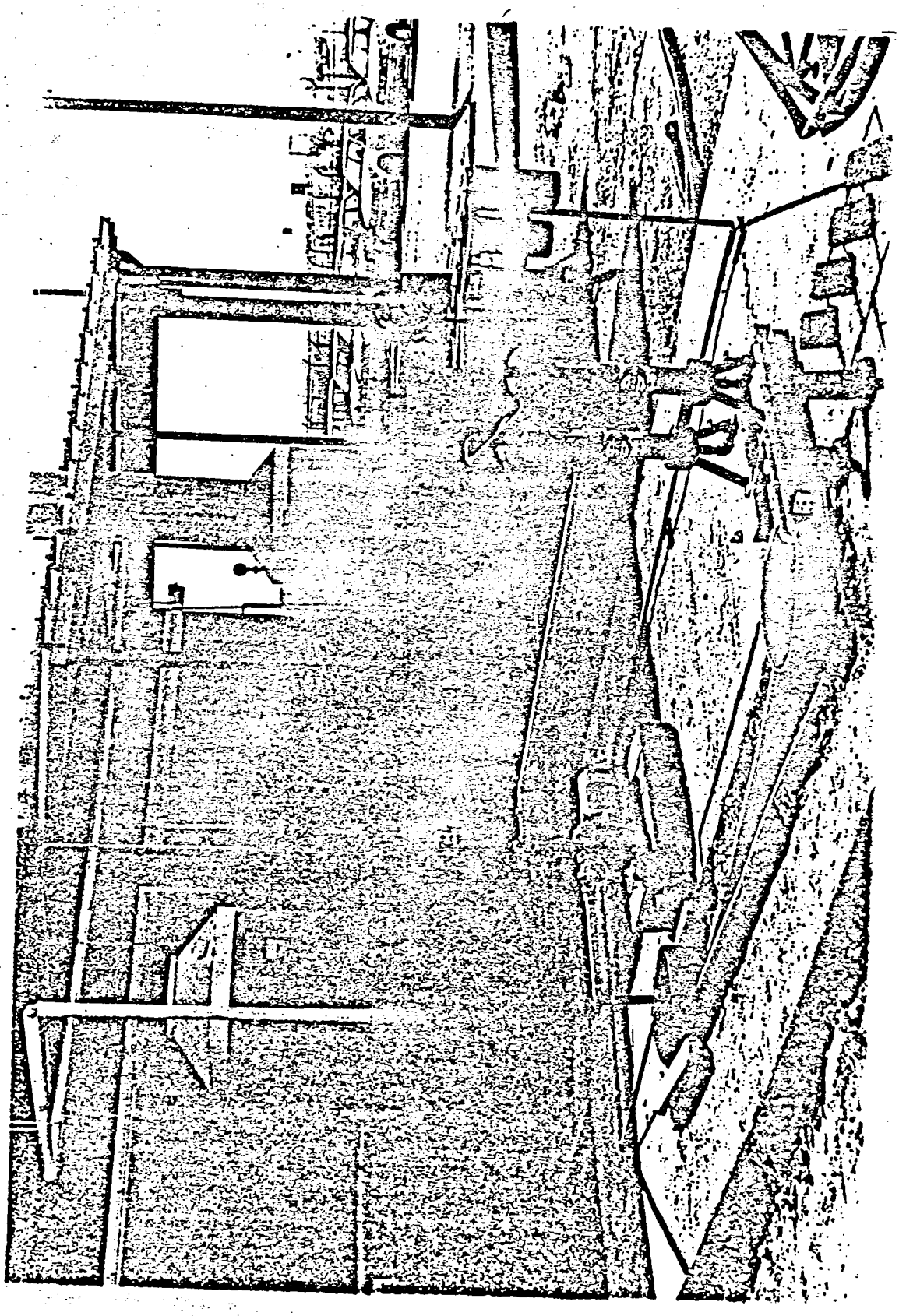

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Exhibit H

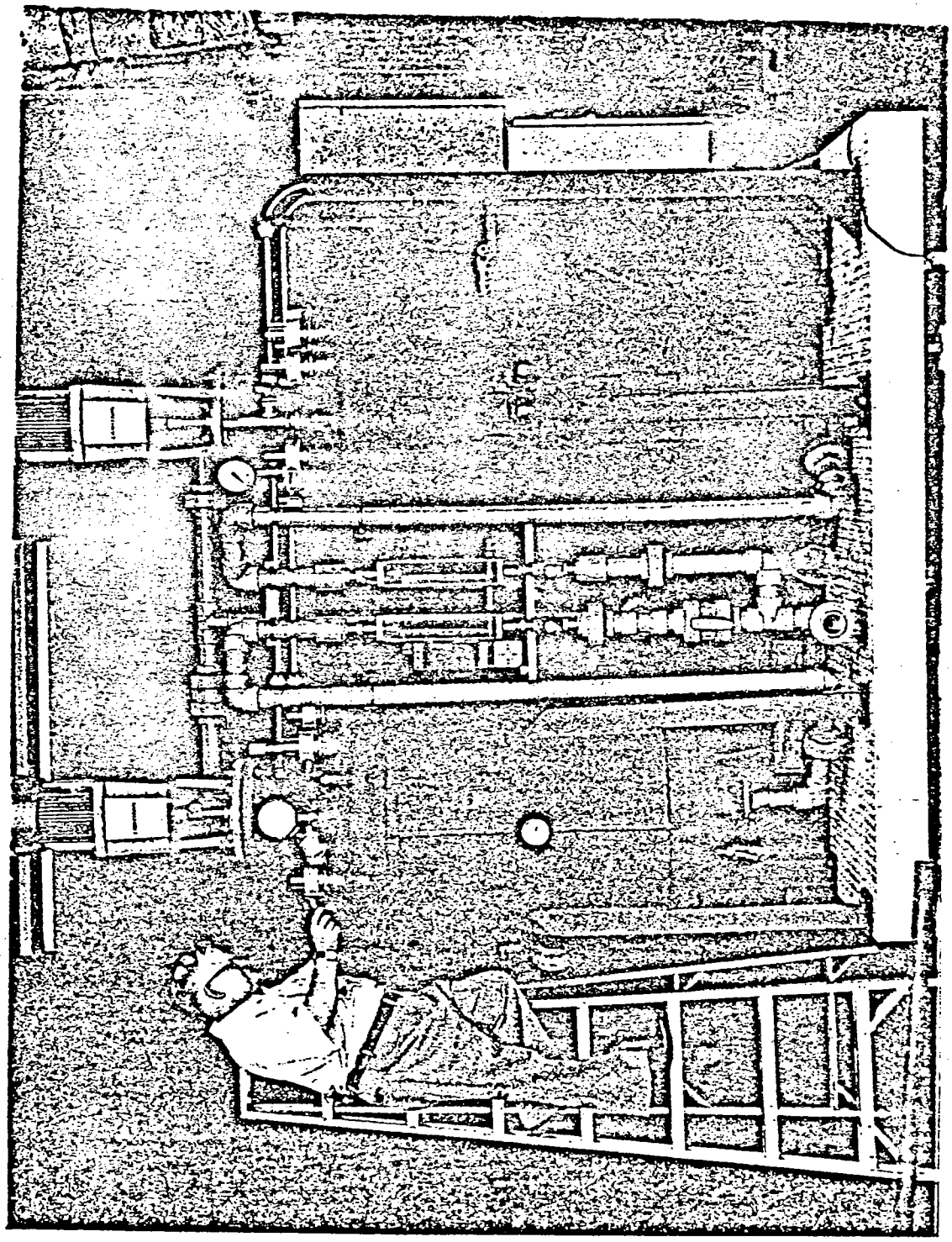

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Exhibit I

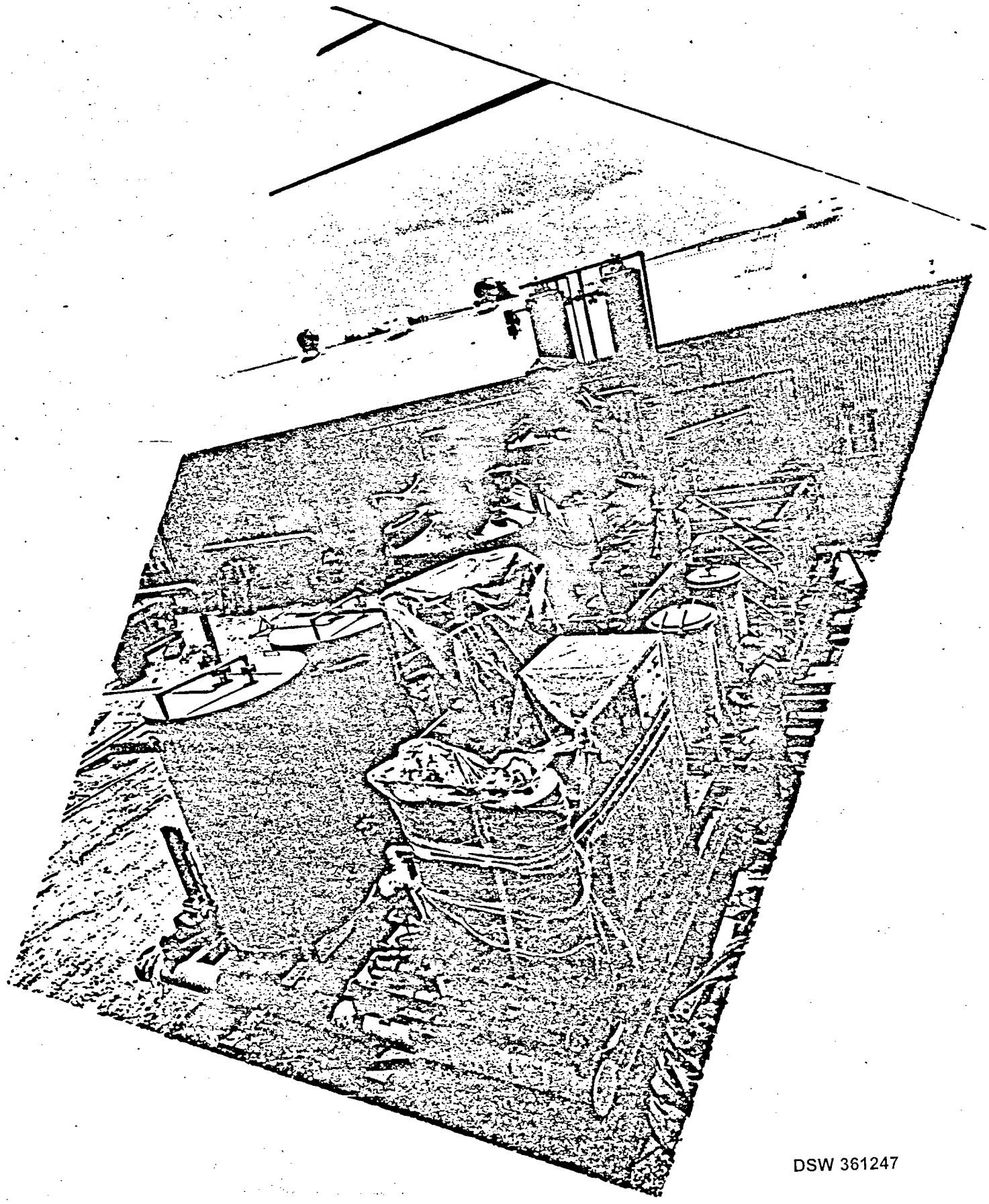

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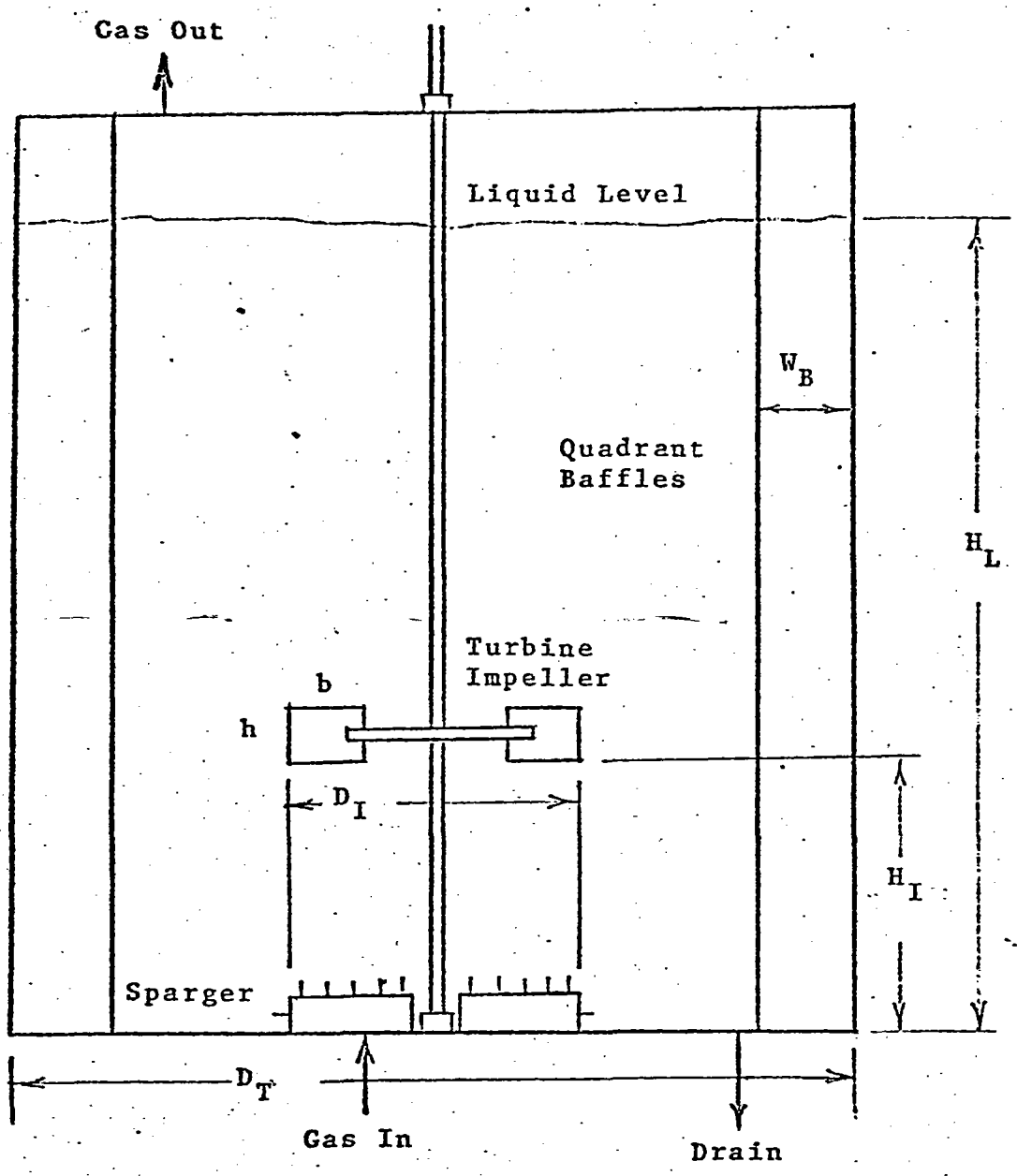
Exhibit J




Reactor Configuration

Dimensions: $H_L = D_T$, $W_B = D_T/10$, $D_I = D_T/3$, $H_I = D_I$

Sparger Holes: Three 1/16" holes/in$^2$

Impeller: Six blades, $b = D_I/4$, $h = D_I/5$

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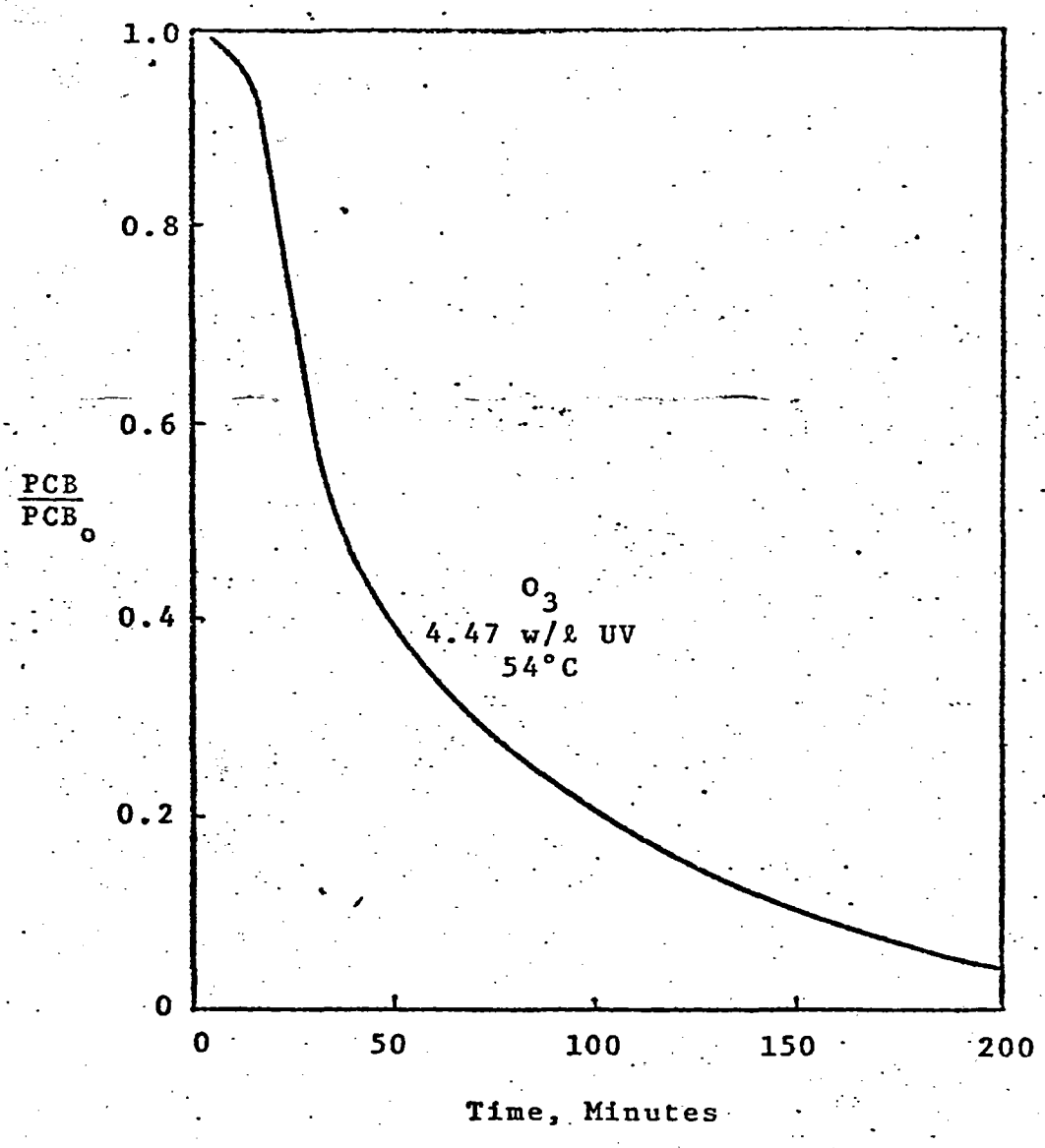
Exhibit K




Destruction of Polychlorinated Biphenyls (PCB)
(initial, 0.5 mg/ℓ)

DSW 361252

Exhibit L

## Capital and Operating Cost

| | 20 gpm | 160 gpm | 1700 gpm |
|---|---|---|---|
| **Capital Cost, $1000** | | | |
| Carbon plus pretreatment | 174 | 570 | 3407 |
| Ozone-Ultraviolet (Including ozone generator) | 152 | 422 | 1380 |
| **Annual treatment cost, $1000/year (Including amoritization, 8%-10 years)** | | | |
| Carbon plus pretreatment | 43.8 | 145.9 | 992 |
| Ozone-Ultraviolet | 36.7 | 145.1 | 974 |
| **Treatment Cost, $/1000 gal** | | | |
| Carbon plus pretreatment | 4.17 | 1.73 | 1.11 |
| Ozone-Ultraviolet | 3.49 | 1.72 | 1.09 |

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