EXHIBIT C

OZONE/UV OXIDATION OF CHLORINATED COMPOUNDS IN WATER*

By

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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.

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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_4Salt)	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 $\cong 8.2\times10^4$ (15°C)	1) $1.805\times10^{+3}$ (180-240 nm) 2) $0.543\times10^{+3}$ (240-290 nm)
2) Pentachlorophenol	C_6Cl_5OH	266.5 80.	1) 41.5×10^3 (200-236 nm) 2) 17.8×10^3 (236-275 nm) 3) 5.65×10^3 (275-355 nm)
3) O-dichlorobenzene	$C_6H_4Cl_2$	147	1) 1.70×10^3 (180-240 nm) 2) 0.0419×10^3 (240-285 nm)
4) Dichlorobutane	$Cl(CH_2)_4\ Cl$	127	1) 0.203×10^3 (180-220 nm) 2) 0.0165×10^3 (220-280 nm)
5) Chloroform	$CH\ Cl_3$	119.5 8.2×10^3 (20°C)	1) 0.058×10^3 (180-220 nm) 2) 0.0028×10^3 (220-270 nm) 3) 0.018×10^3 (270-350 nm)
6) Polychlorinated Biphenyls	$C_6H_aCl_5C_6H_cCl_d$	321 5.6×10^{-2} (20°C)	1) 58×10^3 (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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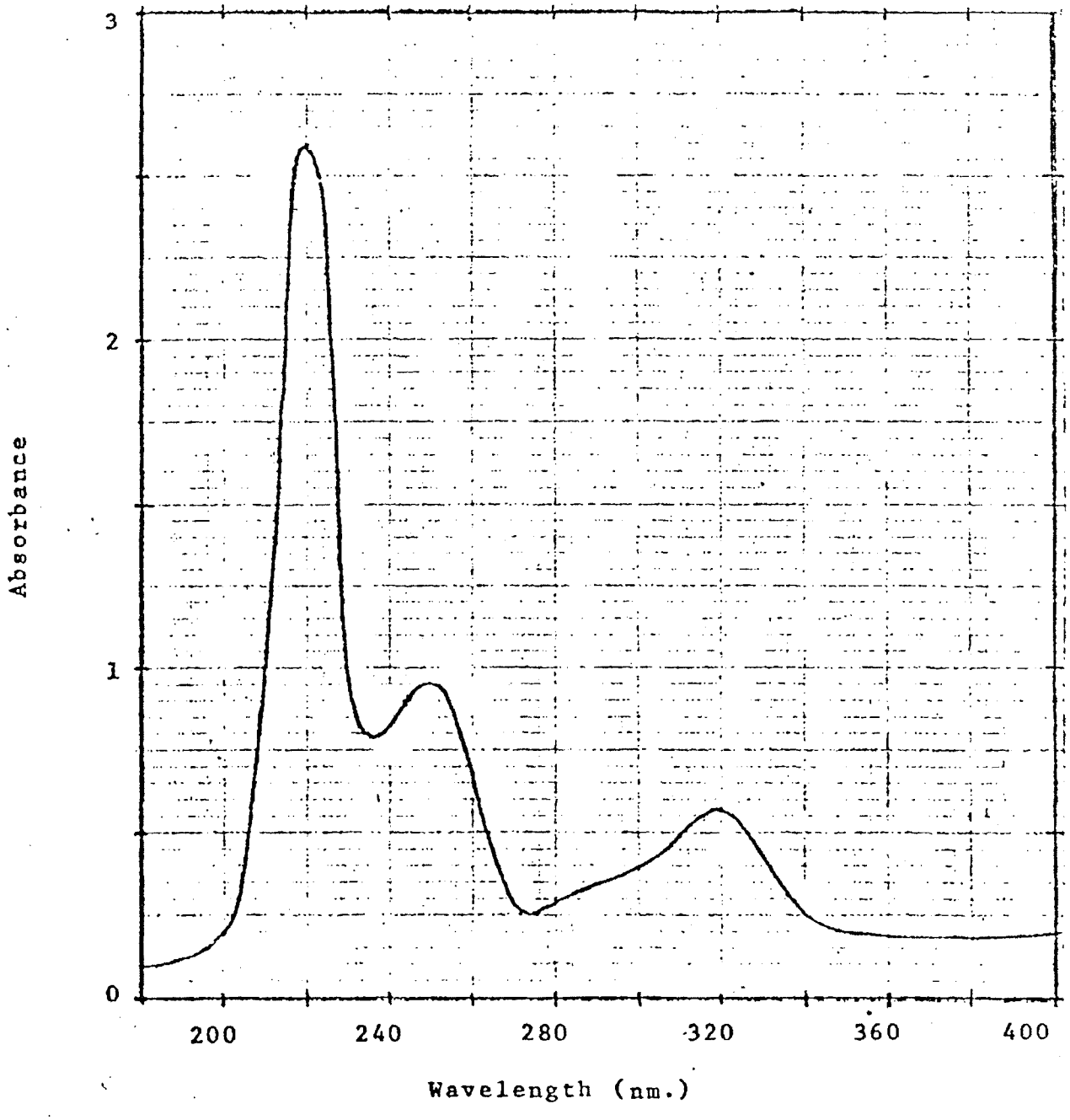


FIGURE 1. Pentachlorophenol UV-Spectrogram (7.0 mg/ℓ)

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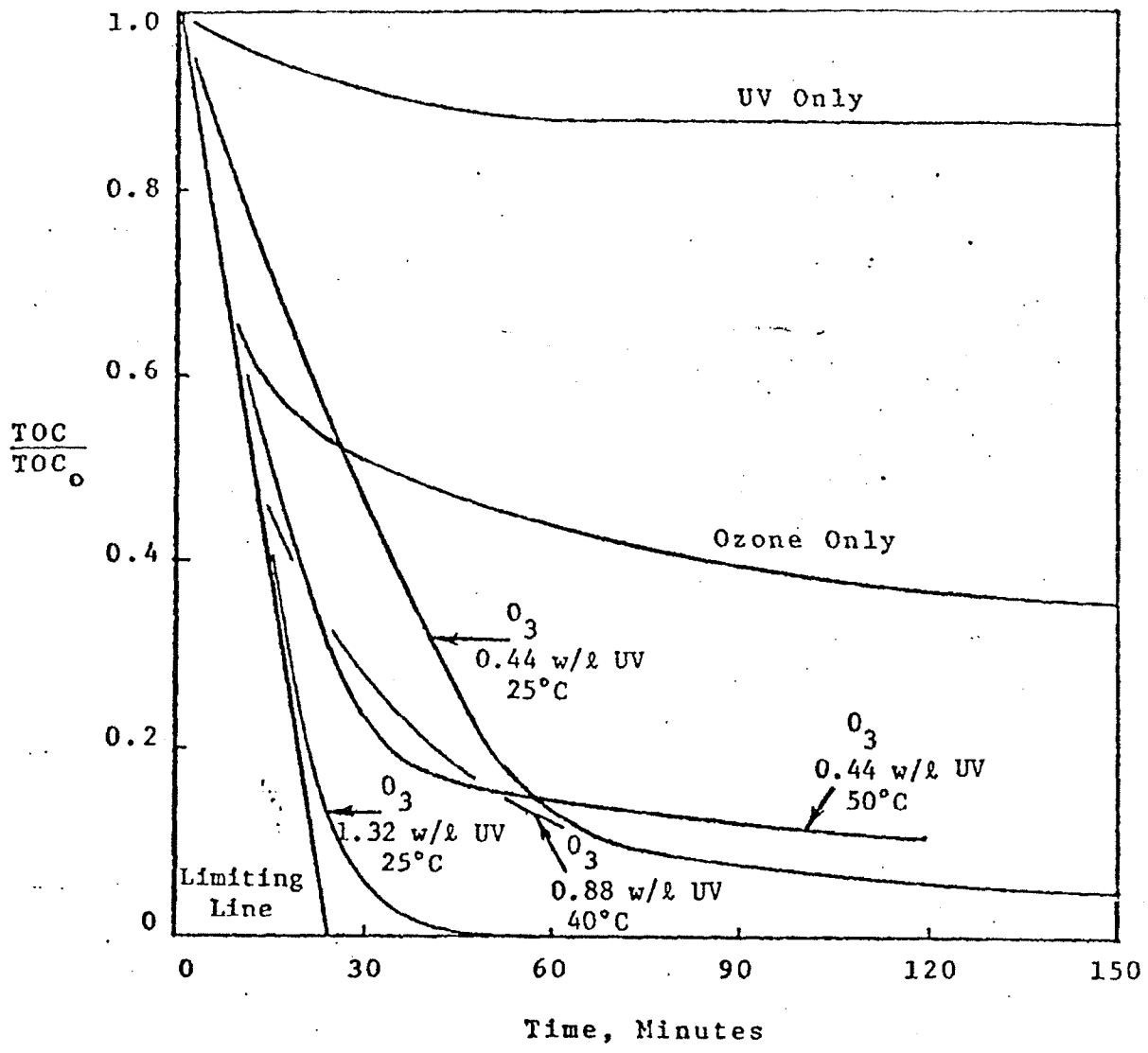
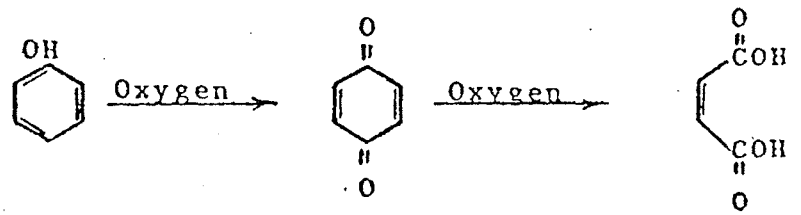


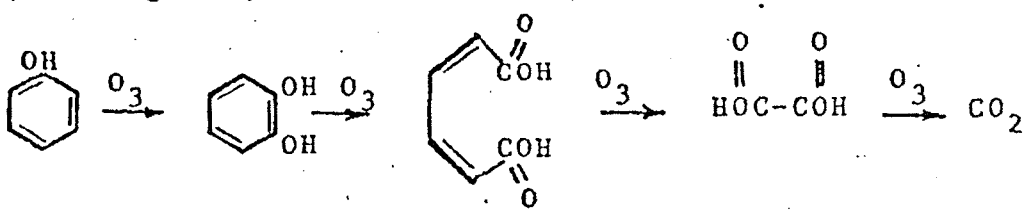
FIGURE 2. Destruction of Pentachlorophenol TOC (initial PCP, 70 mg/ℓ)

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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,



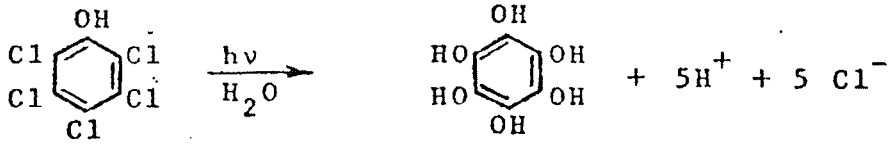
Bailey[7] has reviewed the ozone oxidation of phenol, and he concludes that the major pathway is through catechol to muconic acid. Since oxalic acid is found as an intermediate oxidation product, it appears that the ozone attacks muconic acid at the double bonds. Following the carbon structure only,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

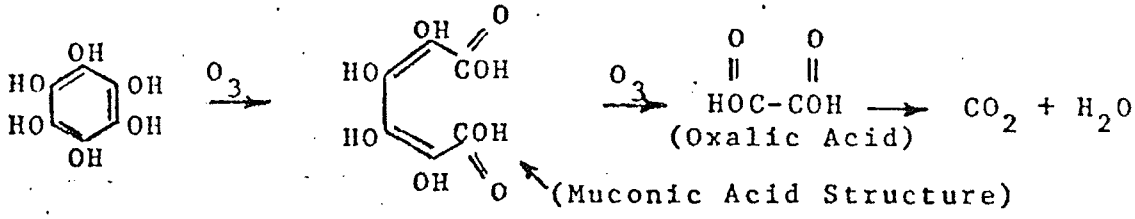
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TOC disappearance is small. This implies an initial chlorine loss caused by UV,



(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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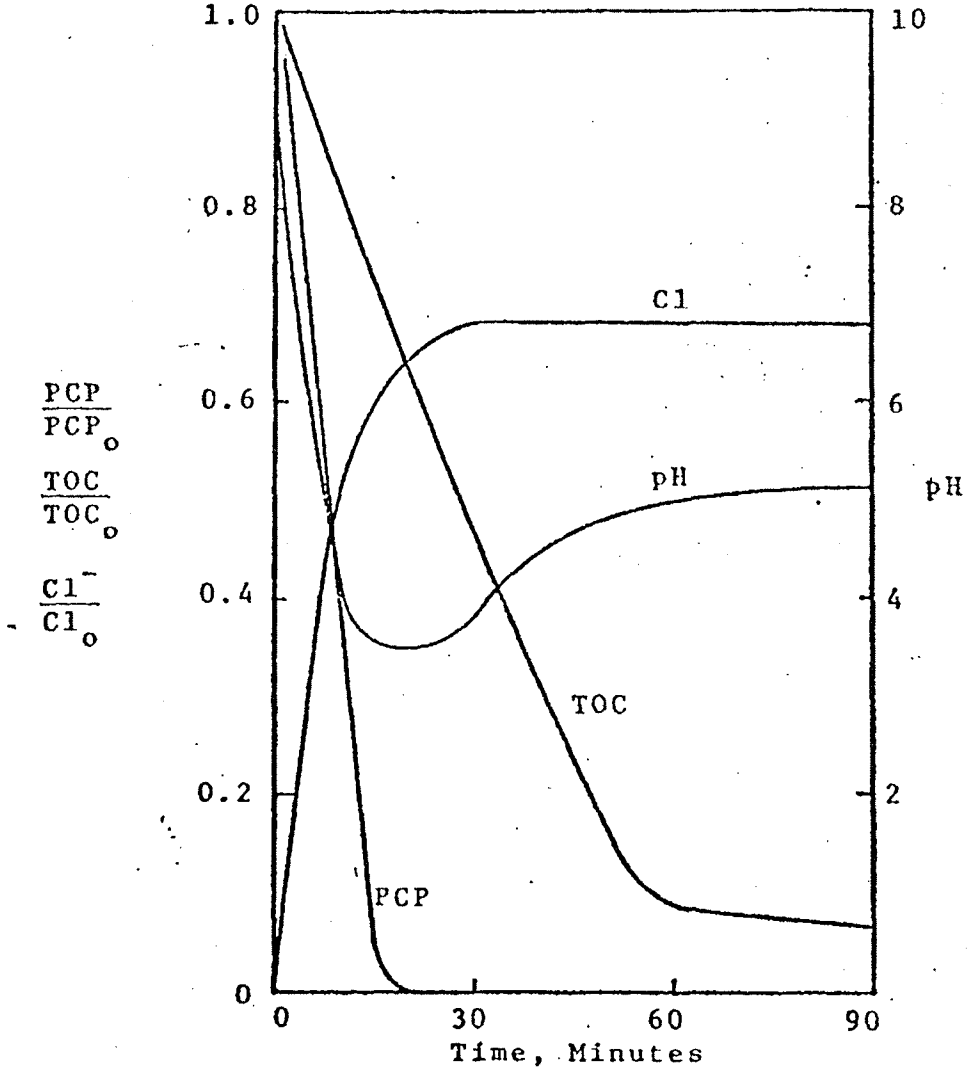
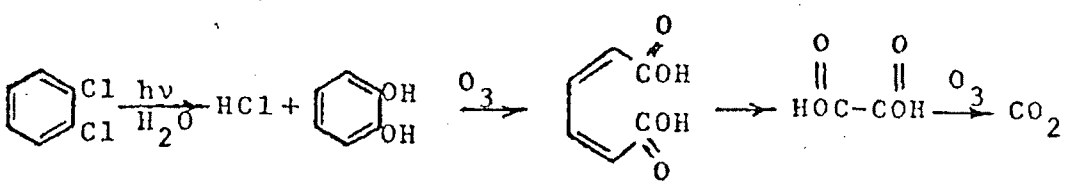


FIGURE 3. Related Time Profiles, Oxidation of Pentachlorophenol. (Re: Figure 2.)

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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,

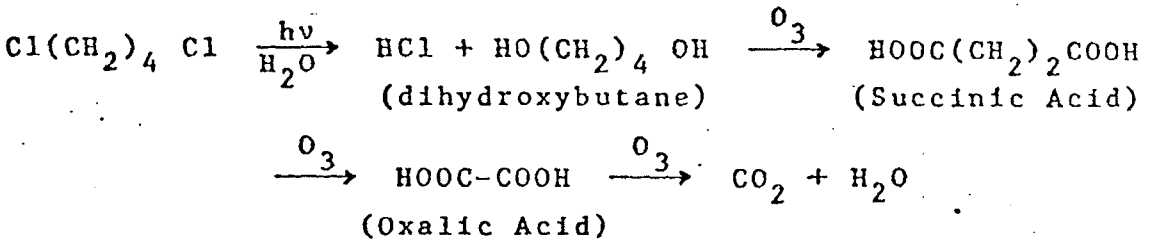


DCBZ was charged to the reactor at the 100 mg/ℓ level, and by GC analysis was 95% destroyed in the first 15 minutes; destruction was complete by 30 minutes.

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,



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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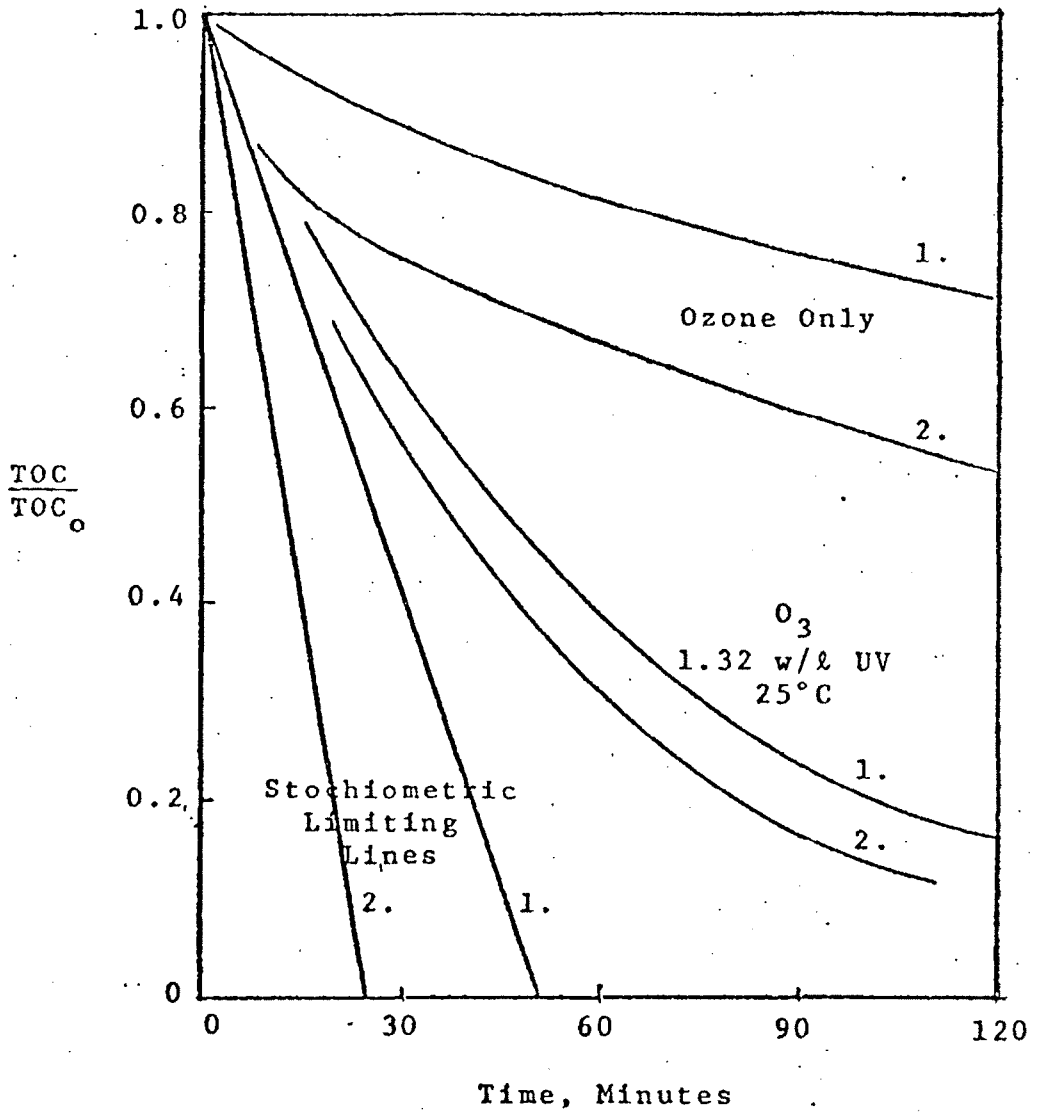


FIGURE 4. Destruction of 1. Dichlorobenzene (initial, 100 mg/ℓ). 2. Dichlorobutane (initial, 50 mg/ℓ).

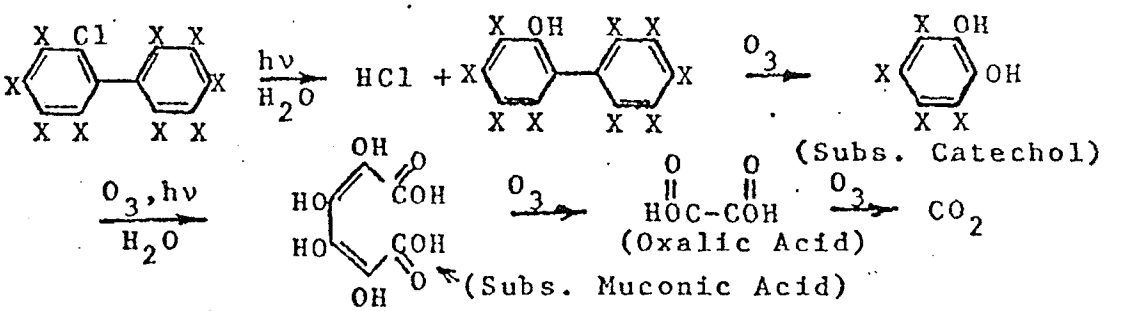
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minutes for complete destruction is required. Destruction of TOC from dichlorobutane and intermediate oxidation products proceeds less rapidly, as shown in Figure 4.

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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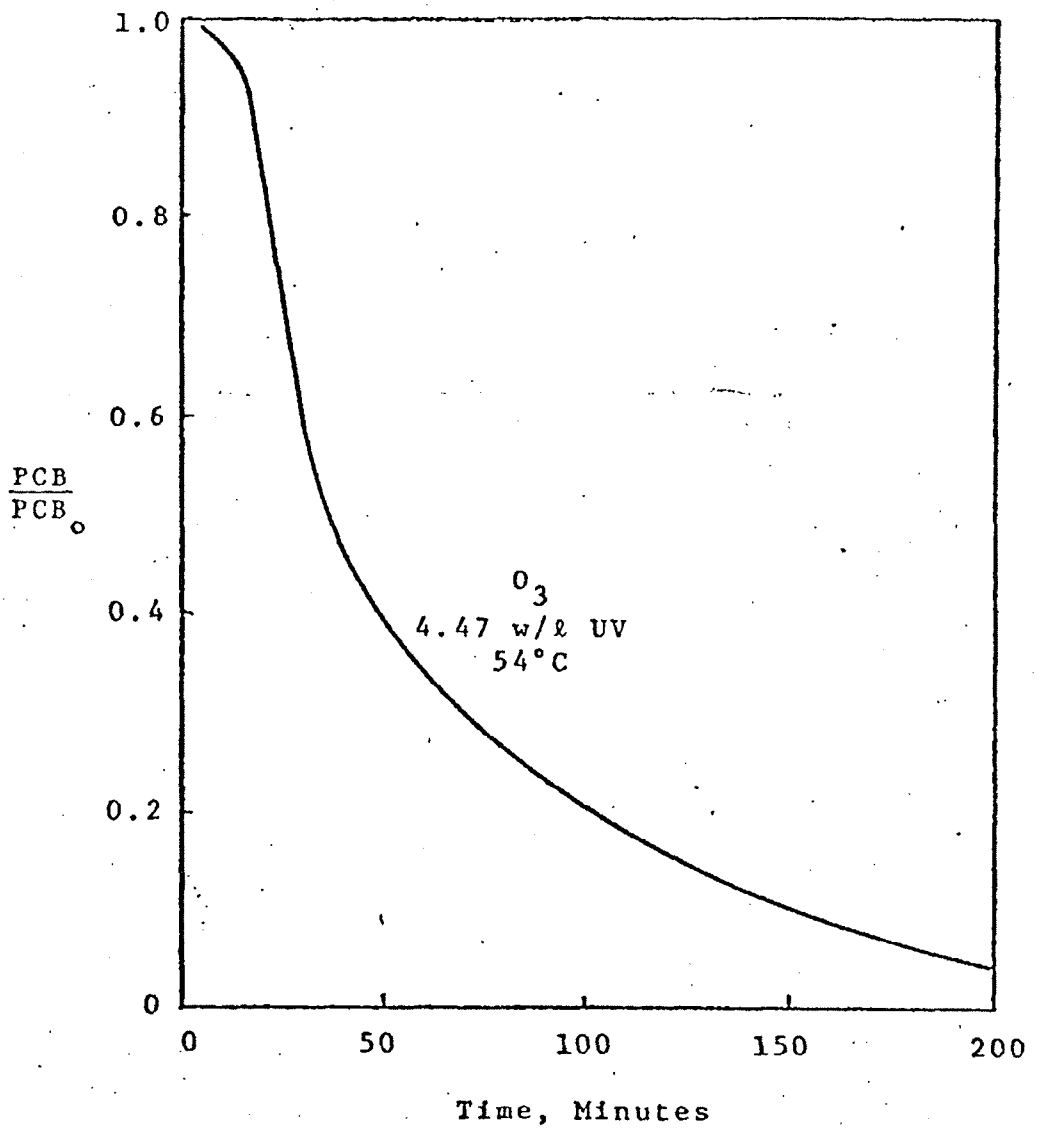


FIGURE 5. Destruction of Polychlorinated Biphenyls (PCB) (initial, 0.5 mg/ℓ)

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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]:

$$HCCl_3 \xrightarrow[\text{Oxidizer}]{\text{Strong}} HCO_2Cl_3 \xrightarrow{H_2O} Cl_3CHO + H_2O_2$$
$$\downarrow$$
$$COCl_2 + HCl$$

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

$$HCCl_3 \xrightarrow{O_2} HCO_2Cl_3 \longrightarrow Cl_2 + CO_2 + HCl$$
$$\downarrow$$
$$COCl_2 + HCl + 1/2\ O_2$$

the carbonyl chloride (phosgene) decomposing thermally by,

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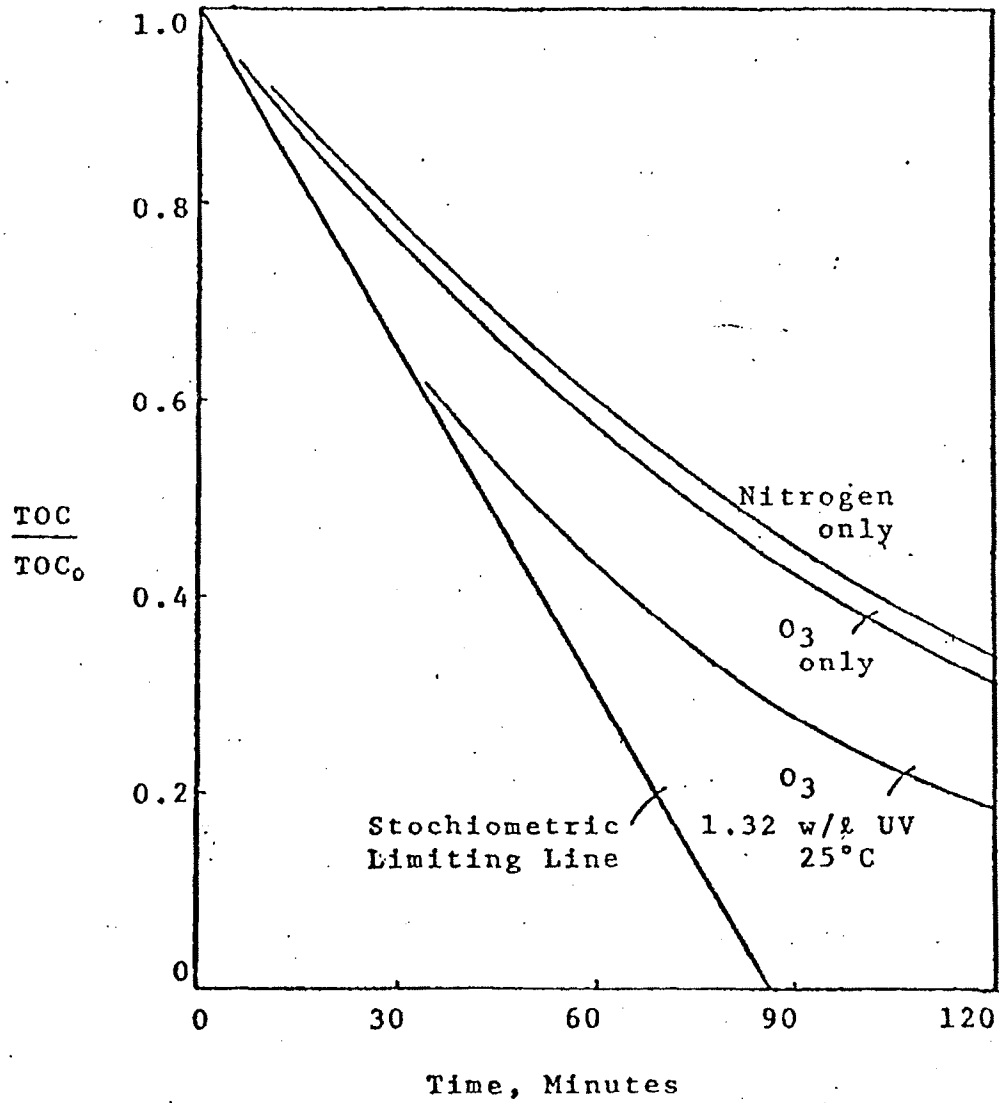


FIGURE 6. Destruction of Chloroform TOC (initial chlororm, 600 mg/ℓ)

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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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3. Jack E. Payne, Manager of Technical Services of Houston Research, Inc., has 15 years of industrial experience in technical and analytical services in chemical production, research in chemical and photochemical reactions, environmental monitoring and control, and industrial hygiene. He received a BS Chemistry degree from University of Texas, and did graduate work at Texas A&I and University of Texas. He is a member of Alpha Chi Sigma and the ASTM Committee on Standards for Dissolved Ozone.

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