

## Two-phase ozonation of chlorinated organics

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### Abstract

Although ozonation is an effective advanced oxidation process for the destruction of hazardous organic pollutants, a single-phase ozonation system is limited by low ozone solubility, low ozone stability, and a lack of selective oxidation potential. These problems may be overcome by mixing a non-polar fluorinated hydrocarbon solvent (FC40) with the aqueous solution. The primary advantages of the FC40 solvent are that it is non-toxic, reusable, has an ozone solubility 10 times that of water, and that 85% of the ozone remains in the solvent even after 2 h. This novel two-phase process has been utilized to study the rapid destruction of trichlorophenol (TCP), pentachlorophenol (PCP), 1,3-dichlorobenzene (DCB), and trichloroethylene (TCE). Our results show that 98% of a 50 mg/l solution of TCP can be degraded 30 s if a molar ratio of 12 moles ozone/mole TCP is utilized. Further studies have reported that the two-phase system is capable of degrading nearly 92% of a 10 mg/l solution of pentachlorophenol (PCP) within 1 min when a ratio of 4.3 moles ozone/mole PCP is used. Also, 80% of a 78 mg/l solution of 1,3 dichlorobenzene (1,3-DCB) is degraded within 5 min for a 21.2 molar ratio of ozone/1,3-DCB. Furthermore, these reaction rates are not altered significantly even if high concentrations of sodium bicarbonate, a free radical scavenger, are present in the aqueous phase.

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### 1. Introduction

Significant advances have been made to reduce environmental pollution problems caused by the discharge of hazardous compounds, and a variety of advanced oxidation processes have been developed for the destruction of hazardous organics from aqueous solutions. Chemical oxidation is an important hazardous waste treatment method since it destroys many organic compounds that are resistant to other treatment methods and it works well with dilute solutions. Some typical liquid-phase oxidation techniques include Fenton's reagent,  $H_2O_2$  and UV, ozone (with and without UV), and high temperature and pressure operations such as wet air oxidation (WAO) and supercritical water oxidation (SCWO) [1,2].

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In the last few years the amount of research being conducted in the field of single-phase ozonation has grown extensively [3–8]. As a powerful oxidizing agent, ozone is capable of oxidizing most organic as well as oxidizable inorganic compounds. However, aqueous-phase ozonation systems are limited by a lack of selective oxidation potential, low ozone solubility in water, and slow intermediate decomposition rates. Furthermore, ozone may decompose before it can be utilized for pollutant destruction since ozone is highly unstable in aqueous solutions. Naturally occurring compounds such as  $\text{NaHCO}_3$  also affect ozone reactions by inhibiting the formation of  $\text{OH}\cdot$  free radicals. To compensate for these factors, excess ozone is typically supplied to a reactor. Since ozone generation requires considerable electric power consumption (16–24 kWh/kg of  $\text{O}_3$ ) [8], attempts to enhance the ozone utilization rate and stability should lead to more efficient application of this process to hazardous waste treatment.

For these reasons, the ozonation process may be more efficiently carried out in a two-phase system consisting of an inert solvent (saturated with  $\text{O}_3$ ) contacted with an aqueous phase containing pollutants (Fig. 1). From practical considerations, the non-aqueous phase must meet the following criteria: non-toxic, very low vapor pressure, high density (for ease of separation), complete insolubility in water, reusability, selective pollutant extractability, high oxidant solubility, and extended  $\text{O}_3$  stability. Previously published studies [9, 10] have indicated that a number of fluorinated hydrocarbon compounds fit these criteria. For this project, FC40 (a product of 3M Co.) was chosen due to its low vapor pressure (3 mmHg). Two previous studies utilized a solvent (FC77) which had a vapor pressure of 42 mmHg. One of the studies utilized oxygen at elevated temperatures and pressures to destroy  $\beta$ -naphthol [10], while the second study utilized ozone to degrade phenol and  $\beta$ -naphthol [9]. Although both compounds are products of 3M Co., other industrially available fluorinated solvents could also be suitable for this purpose. The present project is a more in-depth study of two-phase ozonation with several priority pollutants.

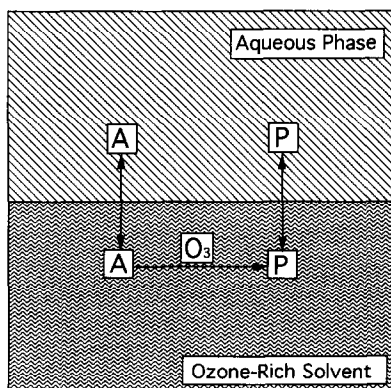


Fig. 1. Schematic of two-phase ozonation system.

Table 1  
Properties of FC40 at 25 °C [11]

Property	FC40	Water
Average molecular weight	650	18
Density	1.86	1.0
Boiling point	155 °C	100 °C
Vapor pressure (mmHg)	3	23.8
Ozone solubility <sup>a</sup>	~120 mg/l	~12 mg/l

<sup>a</sup> Our experimental data.

Not only do these fluorinated, reusable, solvents serve as both an ozone source (the solubility of O<sub>3</sub> is 10 times that of water), but also as a non-aqueous phase in which oxidation occurs. Studies have proven that the possibility of selective oxidation exists for solutions containing an organic pollutant and an ozone consuming inorganic, such as Na<sub>2</sub>SO<sub>3</sub> [9]. In these reactions, the selectivity results from the inability of the Na<sub>2</sub>SO<sub>3</sub> to partition to the non-polar solvent phase, and similar results would also be expected for aqueous solutions containing NaHCO<sub>3</sub>. In this way, the inorganics will remain and the ozone demand (and cost) for organic oxidation will be substantially lower. Some of the typical properties of FC40 are shown in Table 1.

For this project, the rapid degradation of 2,4,6-trichlorophenol (TCP), pentachlorophenol (PCP), 1,3-dichlorobenzene (DCB), and trichloroethylene (TCE) have been studied. The parameters measured for the reactions include pH drop, chloride concentration, and the initial and final pollutant concentration (by GC/MS and/or HPLC methods). In order to optimize the pollutant degradation, the molar ratio of ozone to pollutant (*M*), pH of the feed solution, and reaction time were varied. Also the effect of NaHCO<sub>3</sub> (a free radical scavenger) has been investigated, and some intermediates have been identified on selected ozonation reactions.

## 2. Literature review

A brief literature review is included in this section to provide some background information on ozonation studies. Recently, numerous studies on the ozonation of organic compounds in single-phase aqueous systems have been reported. These studies indicate that efficient destruction is possible for a wide variety of organic pollutants [4, 7, 12]. The research also indicates that ozonation may make several important pollutants, including herbicides, more amenable to biological degradation [13–15]. The kinetics of ozone reactions, ozone mass transfer, and ozone decomposition have also been investigated [16–19], and an excellent review of advanced oxidation processes (such as Fenton's reagent, H<sub>2</sub>O<sub>2</sub>/UV, and titanium dioxide-assisted photo-catalytic degradation) has been reported recently in the literature [1].

These studies have resulted in some general conclusions about the mechanisms of organic degradation by ozone. Ozone can react via two major pathways. The first pathway involves the reaction of the organic with molecular ozone. The rate constants for this pathway vary over 12 orders of magnitude. The second pathway involves reaction with free radicals formed during the decomposition of  $O_3$ , and this pathway is not as selective since the rate constants only vary 2–3 orders of magnitude [6]. Conditions that inhibit ozone decomposition favor direct ozone reactions while conditions which enhance ozone decomposition favor free radical reactions. Likewise, organic contaminants, such as aliphatic acids, aldehydes, and less highly activated aromatics, are more likely to react via the free radical pathway since they are slow to react with molecular ozone.

A free radical mechanism is the generally accepted method of ozone decomposition [20], and the hydroxyl radical is the important intermediate in ozone decomposition [21]. A steady-state hydroxyl radical concentration of  $10^{-10}$ – $10^{-12}$  M is sufficient to treat organic substrates [22]. As a result, several researchers have studied methods of enhancing the formation of free radicals within ozonation systems. Typically these methods include the addition of hydrogen peroxide [22–24], metallic catalysts [25–27], and UV [28–29].

Only a few studies have been conducted in non-aqueous systems. Pryor et al [30], conducted extensive studies in carbon tetrachloride to determine the reaction rate of biologically important compounds with ozone. Although carbon tetrachloride cannot be used in waste treatment due to its toxic nature, important information can be gathered from these studies since they were conducted in a non-polar solvent. The reactions appear to be quite selective since the reaction constant for styrene at 25 °C is approximately  $10^6$  times greater than the rate constant of tetrachloroethylene at the same temperature. The reaction conditions in these studies favored the direct ozonation pathway. In contrast, our previous studies contacted a non-polar solvent with an aqueous solution. Under these conditions, the indirect pathway is more prevalent since the presence of water promoted the decomposition of ozone and increased the concentration of hydroxyl radicals. As a consequence, the rapid destruction of phenol was achieved even in the presence of excess  $Na_2SO_3$  (an ozone scavenger) [9].

### 3. Materials and methods

Ozonation studies were conducted using pentachlorophenol (PCP), 2,4,6-trichlorophenol (TCP), trichloroethylene (TCE), and 1,3-dichlorobenzene (DCB) (Aldrich Chemical) as parent compounds. For all experiments, the non-aqueous solvent was FC40, obtained from 3M Co. The initial concentration ranges were varied for each compound: PCP at 10–100 mg/l for pH 3.5–11.7, TCP at 50 mg/l and 100 mg/l for pH 5–6, TCE at 440 mg/l for pH 4.4–10.0, and DCB at 26 mg/l and 78 mg/l for pH 2.1–11.2. The first stage of the study was to determine the partitioning coefficient for each compound studied. The next stage consisted of determining the effect of various variables on parent compound degradation (such as the ratio of  $O_3$  to pollutant, reaction time, and initial pH).

### 3.1. Experimental procedure

The ozonation process consisted of first saturating the FC40 with ozone for 30 min utilizing a Welsbach T-816 ozonator. Previous lab studies have proven that 20 min is a sufficient amount of time to completely saturate the FC40. The saturation concentration for ozone in FC40 is 120 mg/l at 25 °C. To ensure the quality, weekly checks were conducted on the ozone concentration in the solvent by the modified indigo dye method [31].

Next, a measured volume of HPLC grade water containing a known amount of pollutant was contacted with a measured volume of ozonated FC40, leaving only enough head space for intense mixing, and the batch reactor system was shaken by a mechanical shaker at a constant speed. After a specific amount of time, the phases were separated and the aqueous phase was quenched with NaHSO<sub>3</sub>. The aqueous phase was analyzed for pollutant concentration, chloride concentration, pH, and intermediates formed (in selected experiments). The FC40 phase was also analyzed for pollutant concentration.

After analysis, the solvent was purified and recycled. In order to ensure purity of the FC40, it was washed in between experiments by contacting 2 parts solvent with 1 part HPLC grade acetone. The system was shaken for 5 min and the phases were allowed to separate. Then the process was repeated using 1 part solvent with 1 part HPLC grade methanol, then twice using 1 part solvent with 1 part distilled water. This procedure was primarily used for the purpose of maintaining virgin quality FC40 for each batch experiment, but this procedure will not be necessary in actual practice. The final aqueous wash was tested on TOC (Beckman Model 915B) to ensure that no organics remained. Also the FC40 phase was analyzed periodically on GC/MS to ensure that no impurities or parent compounds were present.

### 3.2. Analytical procedures

Quantification of the pollutant concentrations was achieved by GC/MS and HPLC. For some cases, the distribution coefficient of parent compounds was also analyzed by UV. The analytical procedure is separated for parent compounds and selected intermediates and products.

#### 3.2.1. Parent compounds

Since the parent compounds may be present in both the aqueous and solvent phases, both phases must be analyzed to find the total amount of pollutant remaining after an ozonation. To determine the concentration of pollutant in the aqueous phase, the Prep-Sep C<sub>18</sub> disposable solid-phase extraction columns (Fisher Scientific) were utilized for PCP and DCB. The extraction procedure was as follows: wash column with 5 ml methanol; wash column with 5 ml distilled water; pass sample through column, 5–15 ml; elute sample twice with 1 ml methanol (methanol flow rate should be  $\leq 1$  ml/min). Percent recoveries were determined for each compound studied by extracting a known pollutant concentration. Results from experiments were corrected by the percent recoveries.

For PCP and DCB, the FC40 phase was analyzed for parent compound concentration. The pollutant was extracted by contacting a measured amount of the sample with a known amount of HPLC grade methanol. The system was shaken for 5 min and allowed to separate. The pollutant was extracted into the methanol, making it ready for GC/MS analysis. Once again, percent recoveries were determined for each compound studied by extracting a known pollutant concentration and experimental samples were adjusted accordingly.

Once the parent compounds were extracted, they were quantified by a Hewlett-Packard 5890 Series II gas chromatograph with an attached 5971A Quadrupole mass selective detector (GC/MS) equipped with NIST/EPA/MSDC 49K mass spectral database. PCP and DCB were analyzed by the procedure outlined by EPA Method 625 using a Supelco PTE-5 fused capillary column (30 m × 0.25 mm ID) under the following temperature program: 35 °C for 4 min, ramp 10 °C/min to 300 °C (Supelco GC Bulletin 872A). Helium at 30 cm/s was used as the carrier gas. Reproducibility for the GC/MS is ±4% for our compounds.

Direct GC/MS analysis was used for TCP in the FC40 phase. The set up consisted of a HP-5 column (cross linked 5% diphenyl- and 95% dimethyl-polysiloxane column, 25 m × 0.2 mm × 0.5 µm film thickness) with the following temperature program: 70 °C for 2 min, ramp 20 °C/min to 210 °C.

TCP in the aqueous phase was quantified directly using a Varian 5040 LC (VISTA 54 system) with a Varian UV-50 variable wavelength ultraviolet detector (HPLC). The system is equipped with a VISTA 401 CDS Intelligent Terminal to control the LC and integrate and manipulate data from the UV detector. For detection of TCP, a Varian Micropack MCH-5 (reverse phase octyldecylsilane on silica) column, 30 cm × 4 mm, was used under the following conditions: isocratic, 60% acetonitrile/40% water, flow rate 1.2 ml/min; sample injection volume 50 µl; detector wavelength 280 nm. The reproducibility for TCP was ±5% with a detection limit of 1 mg/l.

### 3.2.2. Selected intermediates and products

Besides parent compound analysis, select intermediates and products were also analyzed. Preliminary identification, and in some cases quantification, of intermediates were established from the ozonation process for TCP and PCP. For all parent compounds, the extent of dehalogenation and pH change were also examined.

Intermediates from the degradation of TCP were extracted with Prep-Sep C<sub>18</sub> columns and analyzed on GC/MS utilizing the following temperature program: 70 °C for 1 min, ramp 15 °C/min to 210 °C.

Organic acids from PCP ozonation were monitored on HPLC using a SUPELCOGEL™ C-610H column, 30 cm × 7.8 mm under the following conditions: mobile phase, 0.1% H<sub>3</sub>PO<sub>4</sub>, flow rate 0.5 ml/min; sample injection volume 50 µl; detector wavelength 210 nm. The detection limit for oxalic acid on HPLC was 3 mg/l with ±3% reproducibility. The aqueous phase from ozonation experiments was separated from the FC40 phase and centrifuged to ensure that there was no FC40 present during HPLC analysis.

Chloride concentration in the aqueous solution was measured by an Orion combination chloride electrode (Model 96-17B) with a reproducibility of ±4%. For

calibration, at least 5 data points were taken in the linear range (molar concentration range  $10^{-1}$ – $10^{-4}$ ) using NaCl standards. Standards were spiked with the pollutant of interest and the  $\text{Cl}^-$  concentration was compared to the standard  $\text{Cl}^-$  concentration to ensure that there was no interference caused by the pollutant. To determine if there was any interference caused by an intermediate from the ozonation reactions, an ozonation sample was spiked with a  $\text{Cl}^-$  standard and the theoretical concentration was compared to the experimental concentration.

### 3.2.3. Ozone analysis

Before ozonation studies were conducted, ozone concentration in the solvent phase was measured to determine  $\text{O}_3$  saturation concentrations and  $\text{O}_3$  stability. The standard indigo dye method is recommended by *Standard Methods for the Examination of Water and Wastewater*, 17th edition [32] for determining ozone concentration in the aqueous phase. However, this method must be modified in order to accurately measure the ozone concentration in the FC40 phase. A detailed procedure is outlined by Van Dierdonck [31] for the analysis of ozone in the FC40 phase. The difference between the absorbances of the reagent blank and the sample represents the quantity of ozone utilized in the decolorization of the indigo dye solution. The ozone concentration is then calculated by the following equation:

$$\text{mg O}_3/\text{LFC40 solvent} = \frac{\Delta A \text{ MW}_{\text{O}_3} V_{\text{reagent}}}{\Delta \epsilon b V_{\text{FC40}}}$$

where  $\Delta A$  = (absorbance of reagent blank) – (absorbance of the reagent + sample),  $\text{MW}_{\text{O}_3}$  = molecular weight of ozone, 48 000 mg/mole,  $V_{\text{reagent}}$  = volume of reagent (l),  $\Delta \epsilon$  = change in absorption coefficient per mole ozone added (20 000 l/(mole cm)),  $b$  = cell path length (cm), and  $V_{\text{FC40}}$  = volume of ozone saturated sample added to the reagent (l). The results of separate analysis of four different ozone saturation experiments in FC40 indicate that ozone concentration can be established within  $\pm 2.7$  mg/l.

For quick analysis of ozone concentration, absorbance of ozone in FC40 was measured at  $\lambda = 290$  nm on a Bausch and Lomb Spectronic 1001 spectrophotometer (reproducibility  $\pm 5\%$ ) and concentrations were obtained by a comparison to the modified indigo dye method. The UV method correlated extremely well ( $R^2 = 0.99$ ) with the modified indigo dye method when no interferences were present at 290 nm.

## 4. Results and discussion

The major focus of this research was to quantitatively establish the feasibility of degrading chlorinated organics in a short reaction time. The major variables studied were  $\text{O}_3$  dosage, feed pH, and reaction time. The experiments were characterized in terms of parent compound degradation, pH drop, free chloride formation, and selected intermediate identification. The only source of ozone is the solvent (FC40) phase. Feed ozone dosage is reported in terms of molar ratio of ozone to parent

compound ( $M$ ). The molar ratio was changed by varying the aqueous and solvent volumes while maintaining a constant parent compound concentration. Percent chloride formation is the amount of chloride measured in the aqueous phase after an ozonation run compared to the maximum amount of chloride that can be released by the parent compound. For 100% chloride formation, the compound has achieved complete dehalogenation.

A distribution coefficient,  $K_D$ , describes the extent that a compound partitions between the FC40 phase and the aqueous phase.  $K_D$  is determined for each pollutant studied by the following equation:

$$K_D = \frac{(C_A)_s}{C_A} \quad (2)$$

where  $(C_A)_s$  is the concentration of parent compound in the solvent (FC40) phase and  $C_A$  is its concentration in the water phase. The concentration for the aqueous phase was measured by GC/MS and by UV at 210 nm for TCE. The FC40 phase concentration can be determined by material balance.

#### 4.1. Ozone stability in a fluorinated hydrocarbon

To demonstrate ozone stability in the fluorinated hydrocarbon, the solvent (in this case, FC40) was saturated with ozone and removed from the ozone source. No significant change in  $O_3$  concentration was observed after the first 5 min, and after 2 h in a closed container with no head space, the  $O_3$  concentration remained steady at

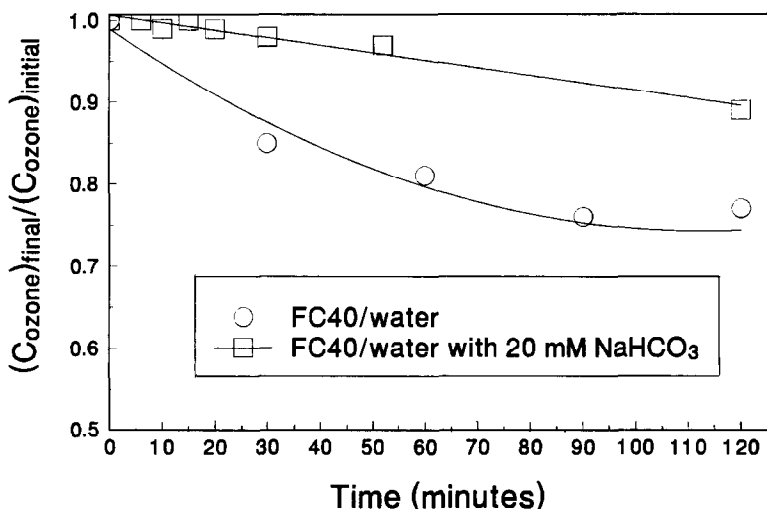


Fig. 2. Ozone decomposition in a two-phase FC40/water system (conditions: equal volumes FC40 and water, no mixing).



85%  $\pm$  2% of the initial concentration. The effect of water on ozone decomposition was also established. An experiment was conducted in which equal volumes of ozonated FC40 and distilled water (pH = 6) were contacted in a closed container with no head space. The ozone concentration in the solvent phase was measured over time by the modified indigo dye method. At least 77% of the initial O<sub>3</sub> concentration remained even after 2 h (92 mg/l O<sub>3</sub>) as shown in Fig. 2. It should be noted that the solvent used in this experiment had been used repeatedly in ozonation experiments (washed between experiments by the method described earlier) for over a year, proving its reusability and capacity for long-term ozone stability.

Free radical scavengers, for example bicarbonate, are compounds which compete with other hazardous organics for the OH $\cdot$  during single phase ozonation. Since free radical scavengers exist naturally in water systems, it is imperative to explore their effect on the new two-phase ozonation system. It is expected that the presence of a free radical scavenger in the aqueous phase will cause the ozone to be more stable in the solvent phase. An experiment following the previous conditions was performed with the addition of 20 mM NaHCO<sub>3</sub> to the aqueous phase to prove this theory. Fig. 2 shows the results obtained from the ozone decomposition experiment with the presence of NaHCO<sub>3</sub> compared to that without a free radical scavenger. As can be seen, the addition of sodium bicarbonate increased the ozone stability, with an ozone decomposition of only 10% after 2 h.

#### 4.2. Ozonation of trichlorophenol

The determination of the partitioning coefficient ( $K_D$ ) is important for predicting the degradation of the parent compound in a two-phase system. The experimentally determined  $K_D$  value (FC40/water, water at pH 6) at pH < pK<sub>a</sub>, was 0.60. The ozonation kinetics were studied for  $M = 1.5$ –12 at an initial pH of 5–6. With  $M = 12$  for 50 mg/l TCP, the trichlorophenol concentration in the water phase dropped below the HPLC detection limit ( $\sim$ 1 mg/l) within 30 s. GC/MS analysis of the FC solvent phase proved that destruction of TCP, and not extraction, was occurring. The TCP concentration in the FC40 phase of the system described above fell below the detection limit of the GC/MS (0.2 mg/l) in less than 30 s.

At a lower molar ratio ( $M = 6$ ), the concentration of TCP in the aqueous phase was approximately 2 mg/l at 1 min and it dropped to below 1 mg/l by 10 min (Fig. 3). The TCP concentration in the solvent phase was below 0.2 mg/l by 1 min (Fig. 4).

Within 1 min, the majority of the bound chloride in both two-phase systems ( $M = 6$  and  $M = 12$ ) was converted to free chloride (Fig. 5). All of the free chloride (Cl<sup>-</sup>) remained in the aqueous phase, since Cl<sup>-</sup> has no affinity for the FC40 phase. Approximately 70% of the bound chloride in the system was converted to free chloride for both the high and low molar ratios. The remaining 20–30% of the chloride may have been bound within intermediate compounds instead of being converted to free chloride.

Trichlorophenol destruction efficiency increased with increasing ozone dosages. This relationship is illustrated in Fig. 6, which compares the concentration of TCP remaining in the aqueous phase at 1 min. A molar ratio of 3 moles of ozone/mole of

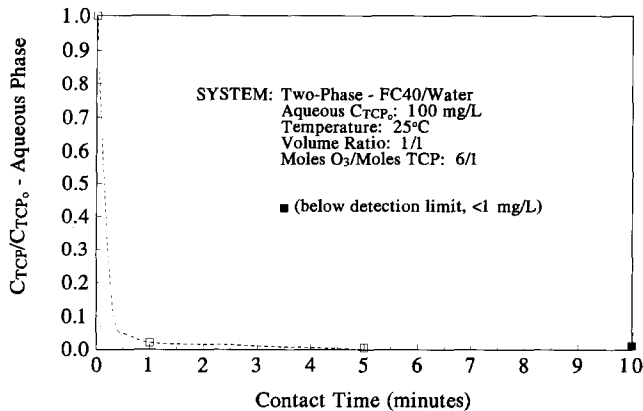


Fig. 3. Trichlorophenol (TCP) concentration in the aqueous phase vs. reaction time for a two-phase FC40/water system at  $O_3$ /TCP molar ratio = 6.

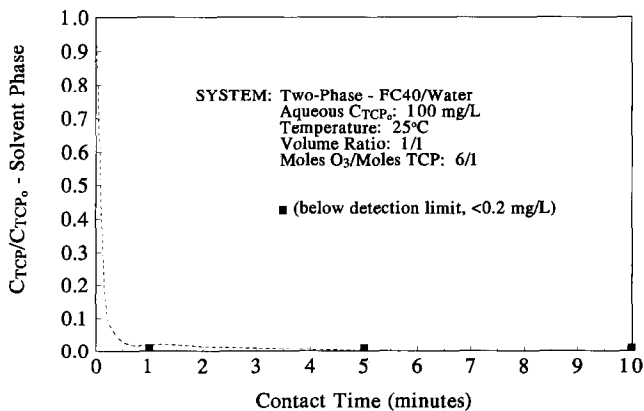


Fig. 4. Trichlorophenol (TCP) concentration in the FC40 solvent phase of a two-phase FC40/water system at  $O_3$ /TCP molar ratio = 6.

TCP was sufficient to degrade >95% of the TCP initially present ( $C_{TCP_0} = 100$  mg/l). At a contact time of 5 min, the same molar ratio was capable of >99% destruction of TCP.

GC/MS analysis was used for intermediate identification of the compounds in the aqueous phase at a low ozone concentration ( $M = 1.5$ ) and a short contact time (30 s). The system studied had less  $O_3$  than required for complete TCP oxidation. In this way, the decomposition of the intermediates was reduced, and thus allowed us to isolate some of the intermediate compounds. As shown in Fig. 7, several peaks appeared in the chromatogram of the extracted aqueous phase.

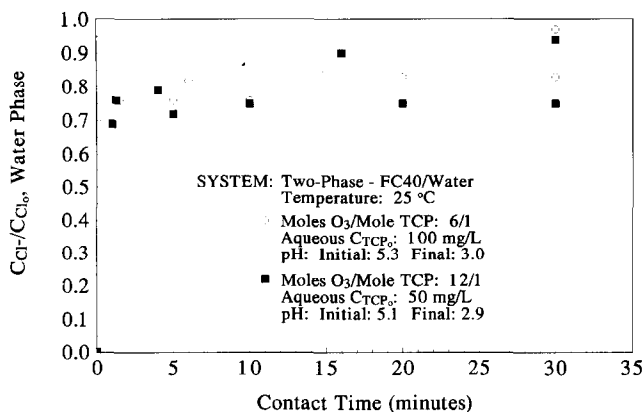


Fig. 5. Free chloride formation during ozonation of trichlorophenol (TCP).

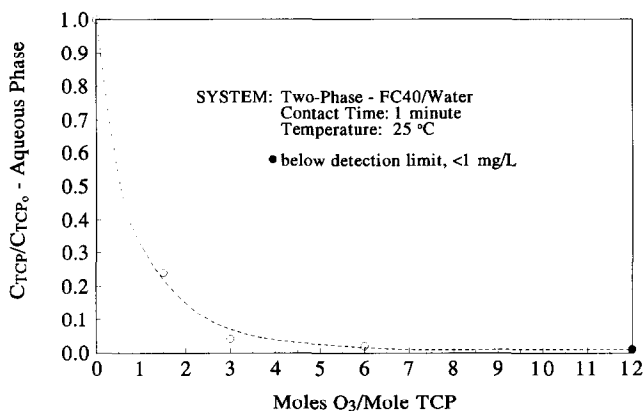


Fig. 6. Trichlorophenol (TCP) concentration vs. ozone/TCP molar ratio at a contact time of 1 min.

A search was conducted on the NIST/EPA/MSDC 49K mass spectral database to see if any of these intermediates were recognized by the database. Most of the peaks were not recognized; however, two peaks were tentatively identified. The first unknown intermediate (retention time: 9.861 min) was matched (matched quality: 97%) with 2,6-dichloro-2,5-cyclohexadiene-1,4-dione. Unknown intermediate B (retention time: 13.530 min) was matched (match quality: 98%) with 2,5-dichloro-1,4-benzenediol. Although these are only tentative identification, they are reasonable when compared to the intermediates reported in the literature. It is imperative to note that these are transitory intermediates that are not present at higher ozone concentrations and/or longer contact times, even if some of the TCP has not been consumed yet.

The next series of experiments were conducted to establish the effect of free radical scavengers in the aqueous phase. Bicarbonate is a hydroxyl radical scavenger and it

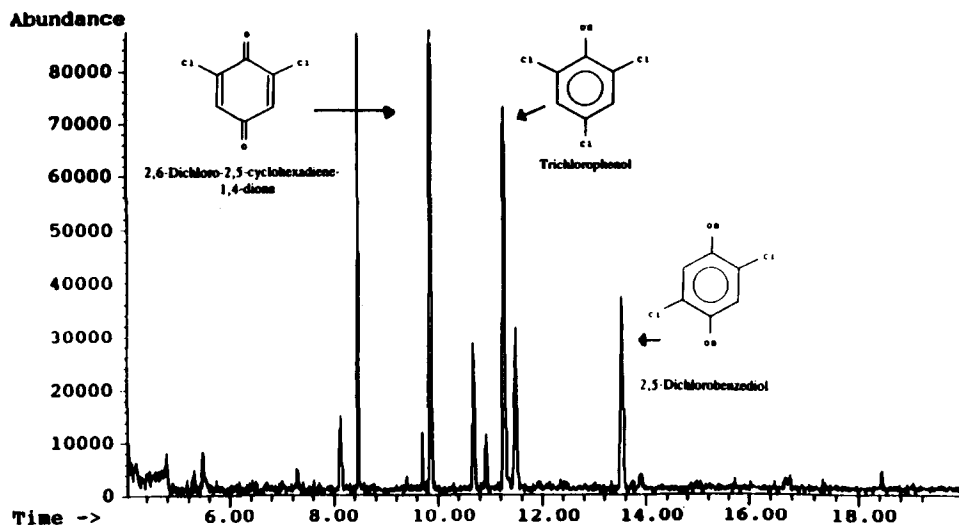


Fig. 7. Gas chromatogram of trichlorophenol and decomposition products in the aqueous phase of a two-phase FC40/water system at an ozonation time of 30 s. (Experimental conditions:  $C_{TCP_0} = 100$  mg/l,  $O_3/TCP$  molar ratio = 1.5, extraction concentration factor = 7.5.)

has been shown that it can alter pollutant decomposition in a single-phase aqueous system [33]. In our two-phase system; however, there is no reduction in TCP destruction at  $M = 12$ . In an ozone-limited system ( $M = 1.5$ ), a 0.008 M sodium bicarbonate ( $NaHCO_3$ ) concentration caused no significant reduction in TCP destruction. After 2 min, 69% destruction occurred in the system without bicarbonate and 65% destruction occurred in the system with bicarbonate. This is in strong contrast to the results shown by Stowell and Jensen [34]. In their study of a single-phase aqueous system, a  $NaHCO_3$  concentration of 0.01 M was shown to significantly decrease the extent of chlorendic acid destruction. Free chloride release was used to measure chlorendic acid decomposition. Reduction in free chloride formation indicated that chlorendic acid destruction was reduced approximately 40% at an ozonation time of 30 min.

#### 4.3. Ozonation of pentachlorophenol

A distribution coefficient,  $K_D$ , was first established for pentachlorophenol. The experimental  $K_D$  was determined to be  $10.2 \pm 0.6$  at pH 3.5. Direct analysis of both phases showed material balance closure within  $\pm 6\%$ . It is hypothesized that at  $pH > pK_a$  (4.7) [18] where PCP is ionized, the partitioning coefficient should decrease. The  $K_D$  value at pH 10.2 is 0.03, proving that  $K_D$  is lower at higher pH's.

Studies were conducted to determine an optimum molar ratio of ozone to pollutant for a solution of 10 mg/l PCP. Several experiments were conducted for which the molar ratios were varied from 3 to 6 for a reaction time of 1 h in a 250 ml reactor

vessel. Analysis included extracting and concentrating up to 10 times both the aqueous and FC40 phases separately, and finding their individual PCP concentrations by GC/MS. Knowing the volumes for each phase, the mass of PCP remaining per phase was determined, leading to an overall mass of PCP remaining. A percentage degraded was determined by dividing the final total PCP mass by the initial PCP mass. At  $M = 4.3$  and  $M = 6$ , the percent PCP degraded in the system was greater than 95%, however there was still approximately 25% PCP remaining for  $M = 3$ . Therefore, a molar ratio of 4.3 was used to do a kinetic study of PCP degradation.

To obtain kinetic data, the initial pH was maintained between 3.5 and 4.5 since  $K_D$  is independent of pH in this range. The reaction time was the only variable changed. Once again, the results were obtained by analyzing both the solvent and aqueous phases. The aqueous-phase concentrations are plotted in Fig. 8. The PCP concentration drops quickly (within 30 s) from 10 mg/l to  $\sim 22$  mg/l and there is  $< 1$  mg/l remaining after only 1 min. The overall PCP degraded by the two-phase system is shown in Fig. 9. The experiments indicate that a total of 79% degradation of PCP occurs within 30 s and nearly 92% total degradation occurs after 1 min.

To study the effect of initial pH on the degradation of PCP, experiments were also conducted at  $\text{pH} > 10$  at an ozonation contact time of 5 min. Using a 10 mg/l solution of PCP, it was found that there was  $\sim 95\%$  PCP degradation at initial pH 10.5 for  $M = 4.3$ , compared to  $\sim 89\%$  PCP degradation at pH around 4. Since the partitioning coefficient is significantly lower at a higher pH, this result indicates that mass transfer is not a limiting factor in the degradation of PCP in the two-phase system, and that a higher pH is preferred for better PCP destruction. The enhanced reaction rate at a high pH is consistent with single aqueous-phase ozonation results reported in the literature [18].

Since the parent compound degradation was rapid, the order of the reaction at high pH was determined by varying the feed PCP concentration. The feed was varied from 10–100 mg/l while the initial pH, ozone dosage, and reaction time were held constant.

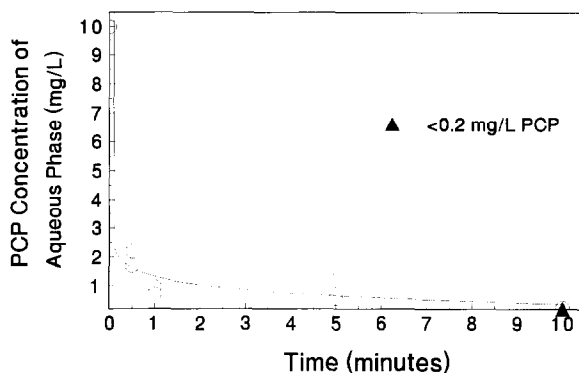


Fig. 8. Pentachlorophenol (PCP) concentration in the aqueous phase vs. reaction time for a two-phase FC40/water system,  $\text{O}_3/\text{PCP}$  molar ratio = 4.3.

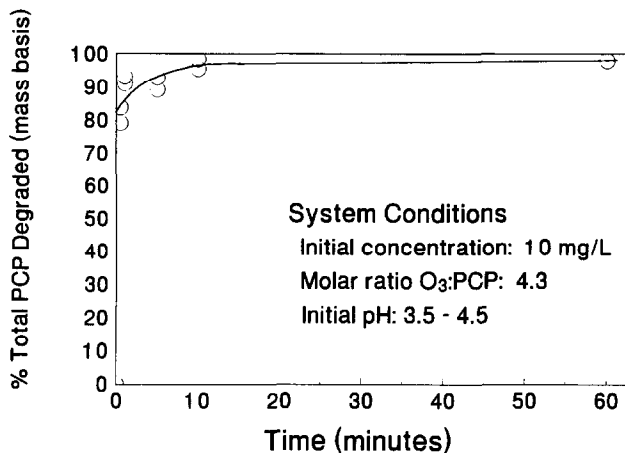


Fig. 9. Total pentachlorophenol (PCP) degradation with respect to reaction time in a two-phase FC40/water system.

Table 2  
Effect of feed concentration on PCP degradation

$C_{A0}$ (mg/l)	$C_A$ (mg/l)
100	7.0
50	3.2
25	1.0
10	0.5

$M = 4.3$ ;  $\text{pH} = 10.3$ ; reaction time = 0.5 min.

The data in Table 2 report the aqueous phase concentrations of the feed ( $C_A$ ) and residual ( $C_{A0}$ ) solutions. Calculations (shown in the Kinetic Model section) prove the reaction to be first order.

In an attempt to identify some intermediate organic acids formed during ozonation, HPLC analysis was used on the ozonated products. For a 100 mg/l PCP solution at an initial pH 11.7, 5 min ozonations were conducted for  $M = 6$ . Two significant peaks were detected by the HPLC organic acid column. Fig. 10(A) shows the HPLC result of the aqueous phase from the 5 min ozonation experiment. The peak at time 9.4 min is not yet identified, however, the peak at 10.3 min was shown to coincide exactly with oxalic acid as shown in Fig. 10(B). Fig. 10(B) shows the same ozonated sample spiked with oxalic acid, and the peak concentration was found to increase within 5% of the expected result. Studies by Stowell showed that oxalic acid is a product formed from single-phase ozonation of 2-chlorophenol [35]. From a calibration of oxalic acid on the HPLC, the maximum concentration of acid produced by ozonation of a 100 mg/l

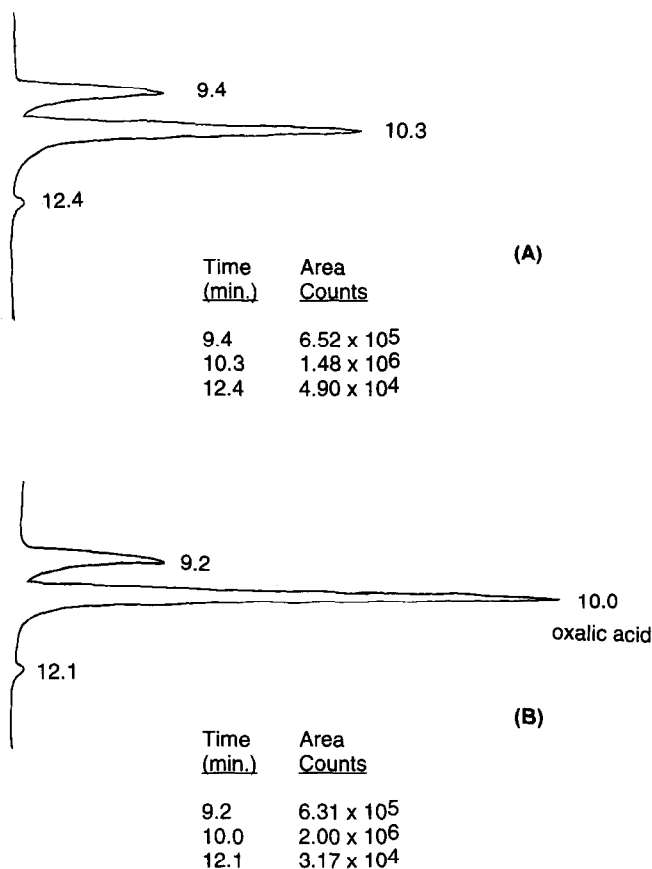


Fig. 10. Aqueous phase HPLC results from a 5 min ozonation of pentachlorophenol (PCP) in the two-phase FC40/water system (A), previous sample spiked with oxalic acid (B) (conditions:  $O_3/PCP$  molar ratio = 6, C-610H organic acid column,  $\lambda = 210$  nm).

solution of PCP ( $M = 6$ , 5 min) was determined to be 70 mg/l. Assuming that all the PCP is degraded to oxalic acid only (no  $CO_2$ ), it would theoretically yield 101 mg/l acid.

The maximum amount of chloride that can be released from 100 mg/l PCP is 66.6 mg/l ( $1.88 \times 10^{-3}$  M). Chloride analysis of the previous ozonated samples showed approximately 90% chloride formation after 5 min ozonation for  $M = 6$ , initial pH = 11.7. It is suspected that some of the chloride may be tied up in intermediates not yet identified. An experiment was also conducted to determine the effect of  $NaHCO_3$  on dehalogenation. Once again, using 100 mg/l PCP at  $M = 6$  (pH 10.7), a 5 min ozonation was performed with the addition of 20 mM  $NaHCO_3$  in the aqueous phase. Chloride analysis showed complete dehalogenation, proving that  $NaHCO_3$  does not adversely effect the degradation of PCP.

In order to simulate a continuous reaction system, one study was conducted by continuously bubbling  $O_3$  into the reactor. For this case, the extent of dehalogenation and oxalic acid formation was established. Since ozone was supplied continuously (still in the solvent phase), we were able to maintain high  $O_3$  concentrations in the FC40 phase. The ozonation of 100 mg/l PCP (pH 11.7) yielded complete dehalogenation for a 5 min ozonation (100% chloride formation) and 70 mg/l oxalic acid formation.

Final pH values after ozonating for all time intervals studied at  $M = 4.3$  were found to range from 3.2 to 3.6, dropping from the initial pH between 3.5–4.5. For the case where initial pH was 11.7, the final pH dropped to 7.0 in 5 min at  $M = 6$ . These results support the theory that acids are being formed as intermediates.

#### 4.4. Ozonation of other chlorinated organics

Not only were chlorinated phenols studied, but preliminary experiments were conducted on other chlorinated organics as well. Both trichloroethylene (TCE) and 1,3-dichlorobenzene (DCB) were studied to determine if they could be degraded efficiently in a two-phase system. Before experiments were conducted, the partitioning coefficients for both compounds were established. For TCE, the  $K_D$  was  $18.5 \pm 1.3$  and the  $K_D$  for DCB was  $22 \pm 2.2$ . After ozonation, aqueous-phase samples were collected and the amount of chloride released was determined. The maximum chloride which could be released from a 440 mg/l TCE solution was 356.6 mg/l, while 37.7 mg/l could be released from a 78 mg/l DCB solution. For selective DCB reactions, both phases were analyzed for the parent compound on GC/MS.

The effect of pH on the reactions was determined for both compounds by varying the pH of the feed solution between 2.1 and 10.0. The TCE reactions were conducted in a 35 ml reactor vessel with  $M = 0.6$ . The pH of the feed solution was 4.4, 6.6, and 10.0, but the chloride concentration remained near 78 mg/l, signifying that  $22 \pm 3\%$  of the chloride was released. From these results, it may be concluded that a feed pH in the range of 4.4–10.0 does not have a significant effect on the chloride formation in a TCE/FC40 system. Similar conclusions were recorded for single-phase systems [21]. The results were quite different for DCB, though. As seen in Table 3, negligible amounts of chloride were released at pH values below 5.4. However, when the feed pH was near 10, 3.9 mg/l was released, which corresponded to 10.3% of the total.

Next the effect of ozone dosage was established by varying the molar ratio of ozone to the pollutant ( $M$ ). Two sets of experiments were conducted for TCE. One set was conducted at  $M = 0.6$  and the other at  $M = 1.0$ . As shown in Table 4, both experiments resulted in a release of approximately 25% of the chloride ions. It should be noted that the theoretical ozone dosage for complete destruction of TCE to  $CO_2$ ,  $H_2O$ ,  $HCl$ , and  $O_2$  is  $M = 4.5$ , so both of these conditions were conducted in an ozone-limited situation. Even though only 13% and 22% of the theoretical ozone was supplied for these reactions, 25% of the chloride was released. For  $M = 0.6$  and a reaction time of only 1 min, it was also observed that approximately 90% of the TCE was degraded from the aqueous phase. Further research is being conducted to



Table 3  
pH dependence for the reaction of 78 mg/l 1,3-dichlorobenzene

Initial pH	Final pH	% Chloride formed
9.8	5.6	10.3%
5.4	3.4	< 0.1%
2.1	2.1	< 0.1%

$M = 6.4$ .

Table 4  
Effect of ozone dosage on chloride formation for TCE

Ozone dosage	Final pH	% Chloride released
$M = 0.6$	2.7	$28.6 \pm 5.6\%$
$M = 1.0$	2.7	$23.6 \pm 0.7\%$

Ozonation time = 30 min; initial pH = 6; feed concentration = 440 mg/l TCE.

Table 5  
Effect of ozone dosage for 1,3-dichlorobenzene degradation

$M$	Initial mass (mg)	Final mass in FC40 phase (mg)	Final mass in aqueous phase (mg)	Percent destroyed
21.2	0.390	0.072	< 0.020	76.5 %
6.4	0.650	$0.183 \pm 0.004$	< 0.014	69.7 %

Initial pH = 9.8.

optimize the TCE degradation in the two-phase system, and the results signify that the two-phase system is efficient for the dehalogenation of TCE.

For the ozone dosage experiments with DCB, a feed solution of 26 mg/l was utilized and  $M$  values of 6.4 and 21.2 were studied. Since the theoretical dosage of ozone for this compound is  $M = 14$ , the first experiment had 46% of the required ozone and the second experiment had 151%. The data in Table 5 shows that ~70% of the DCB was degraded in both experiments, signifying that increasing  $M > 6$  does not have a significant effect on the disappearance of the parent compound. Further experiments must be conducted to determine the effect of ozone dosage on the by-products in DCB degradation.

#### 4.5. Preliminary kinetic model

A kinetic model was developed for a comparative study of rate constants. The model assumes the reaction occurs in the FC phase only and that the mass transfer

effects are negligible. The overall material balance of the parent compound for a two-phase ozonation reaction has been derived utilizing the definition of  $K_D$  [36–38]:

$$-(K_D V_s + V_w) \frac{dC_A}{dt} = V_s K_D k (C_{O_3})_s C_A, \quad (3)$$

where  $V_s$  = solvent (FC40) volume,  $V_w$  = water volume,  $C_A$  = aqueous phase concentration of parent compound,  $k$  = rate constant, and  $(C_{O_3})_s$  = ozone concentration in the FC40 phase. Many literature results on aqueous-phase ozonation reported first-order behavior, so for the case of a first-order reaction and  $(C_{O_3})_s / C_A \gg 1$ , Eq. (3) can be integrated from time 0 to  $t$  to obtain

$$\ln \frac{C_{A0}}{C_A} = \frac{k'}{(1 + V_w / V_s K_D)} t, \quad (4)$$

where  $k' = k(C_{O_3})_s$ . Eq. (4) can be simplified to

$$\ln \frac{C_{A0}}{C_A} = k_{app} t, \quad (5)$$

$$k_{app} = \frac{k'}{(1 + V_w / V_s K_D)}; \quad (6)$$

$k_{app}$  can easily be computed from Eq. (5) if the reaction is first order. By correlating  $\ln(C_{A0}/C_A)$  vs.  $t$  for the initial data in Fig. 8 (from 0 to 1 min), the reaction of PCP at a low pH was indeed first order with  $k_{app} = 2.64$  and a correlation coefficient ( $r^2$ ) = 0.93 and the standard error of the regression line = 0.30. For PCP data at a high pH (Table 2), the first-order kinetics were verified by computing  $k_{app}$  for each of the feed concentrations, and  $k_{app}$  was found to be independent of  $C_{A0}$  ( $k_{app} = 5.8 \pm 0.5$ ). For TCP,  $k_{app}$  was calculated by using the data point at 1 min from Fig. 3 and Eq. (5).

Using Eq. (6) with our experimental values of  $V_w$ ,  $V_s$ , and  $K_D$ ,  $k'$  can easily be calculated. Table 6 shows the  $K_D$  and rate constant values for the studied pollutants. For PCP at a high pH, the apparent rate constant is twice the value obtained at the lower pH. This behavior is consistent with trends reported in the literature [18]. A comparison was made between single-phase, aqueous ozonation of TCP (Fig. 11)

Table 6  
Kinetic rate constants for chlorinated organics in a two-phase ozonation system

Compound	Feed pH	$K_D$	$k_{app}$ ( $\text{min}^{-1}$ )	$k'$ ( $\text{min}^{-1}$ )
Trichlorophenol	6	0.60	> 3.9	> 6.5
Pentachlorophenol	4	10.2	2.64	6.7
Pentachlorophenol	10	0.03	$5.8 \pm 0.5$	$200 \pm 17$

Temperature = 25°C.

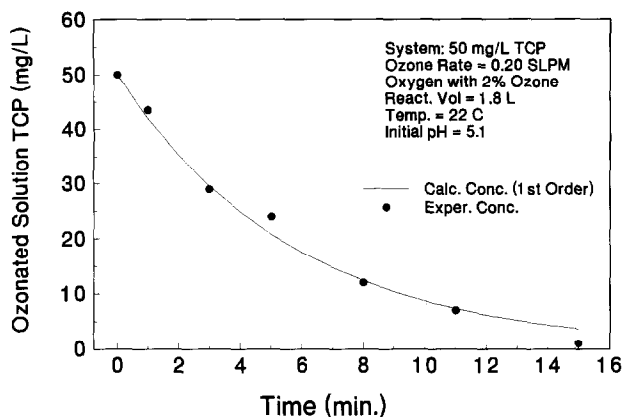


Fig. 11. Trichlorophenol (TCP) decomposition in a traditional single-phase aqueous ozonation process [39].

with the two-phase system. The single-phase ozonation achieved 90% destruction of TCP in 10 min, whereas the FC40/water system was able to achieve 99% destruction in 1 min. The calculated first-order rate constant for single-phase ozonation was only  $0.18 \text{ min}^{-1}$ , compared to  $6.5 \text{ min}^{-1}$  for the two-phase system (Table 6) [39].

## 5. Conclusions

The two-phase ozonation system has outperformed traditional aqueous-phase systems in three key areas: (1) higher ozone solubility and stability, (2) fast pollutant degradation, and (3) selective oxidation. Not only was the solubility of  $\text{O}_3$  in FC40 ten times greater than in water, but  $85 \pm 2\%$  of the  $\text{O}_3$  (102 mg/l) remained in the solvent even after 2 h. It should be noted that these results were obtained from a volume of FC40 which had been utilized repeatedly for the previous one year, proving its reusability.

In terms of pollutant degradation, 99% of a 50 mg/l TCP feed solution could be degraded in 5 min in the novel system, whereas only 90% could be degraded in 10 min for a single-phase system. Even for more highly substituted chlorinated phenols, such as PCP, the two-phase system could destroy 90% of the parent compound in 1 min. With TCP under ozone-limiting conditions ( $M = 1.5$ , reaction time = 0.5 min), two distinct intermediates (2,6-dichloro-2,5-cyclohexadiene-1,4-dione and 2,5-dichloro-1,4-benzenediol) were observed. With PCP, significant oxalic acid formation occurred. The extent of dehalogenation was lower for the non-phenolic compounds (DCB and TCE).

The presence of sodium bicarbonate ( $\text{NaHCO}_3$ ), a free radical scavenger, did not decrease the efficiency of the two-phase system. In fact the presence of  $\text{NaCO}_3$  improved the stability of  $\text{O}_3$  in the FC40 phase. Also 98% of the TCP solution could

still be degraded within 1 min, and complete dehalogenation of PCP could be achieved within 5 min.

The first-order rate constant for TCP was 37 times higher than the value for the single aqueous-phase system. For PCP, the enhancement of free radical formation at high pH values resulted in a 30-fold increase in the reaction rate constant as compared to the low pH.

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