Chapter 4

Sonochemical Decomposition of Phenol:
Evidence for a Synergistic Effect of Ozone and Ultrasound for the Elimination of Total Organic Carbon.

Abstract

The degradation of phenol (C_6H_5OH) was investigated under sonication, ozonation, and the combination of sonication and ozonation. The coupling of these two oxidation processes yielded phenol degradation kinetics that are similar to those predicted from the linear combination of the individual sonication and ozonation experiments. However, synergistic effects of sonolytic ozonation were observed for the reduction of the total organic carbon (TOC) in these systems. The rate of TOC decomposition was found to be proportional to both the aqueous steady-state ozone concentration and the ultrasonic power density. At 358 kHz, sonication combined with ozonation enhanced TOC loss rates by 43% over the sum of the rates obtained by the separate treatments. Intermediate species detected during the degradation of phenol indicate that while the primary degradation products are efficiently degraded by simple ozonolysis, the simultaneous addition of ultrasonic irradiation is necessary to degrade the more recalcitrant unsaturated daughter products.

Introduction

Phenol and related hydroxylated benzene and heterocyclic compounds are ubiquitous contaminants in the environment due to their numerous natural and anthropogenic sources. Ranked among the top 50 manufactured chemicals in the United States, phenol is currently used in the production of a wide-array of products that include synthetic resins, pesticides, and medications. Acute exposure to phenol and its quinone analogues is known to cause skin irritation, kidney damage, gastrointestinal discomfort, and headaches. Aesthetically these compounds also pose a nuisance with detectable taste and odors in water at concentrations as low as 1- 8 ppm.[1-3]

Degradation of phenolic compounds with conventional water treatment protocols typically produces an assortment of non-aromatic carboxylic acids and aldehydes. These degradation products are often quite refractory towards further oxidation and can decrease the overall oxidative efficiency of the system.[4-7] Investigations using combined oxidative processes (O_3/UV,[8] O_3/UV/Fe(II or III),[9] O_3/UV/Cu(I),[9] UV/H_2O_2/Fe(II)[10]) have demonstrated that in addition to enhancing the degradation rates of phenol, these combined systems achieve complete mineralization of the sample. These finding have been attributed to the enhanced *in situ* formation of ·OH and other free radicals.[8] While aromatics and unsaturated organics are commonly susceptible to direct ozone reactions, subsequent reactions with the saturated byproducts tend to be sluggish.[11,12] In contrast, ·OH is a non-selective oxidizer and reacts with a wide array of oxidizable components.[13]

Previous studies have investigated the ·OH-mediated degradation of phenol by ultrasound[4,14-17], and ultrasound in combination with UV,[18,19] O_3,[19] and UV/TiO_2.[20,21] These systems were found to be effective, with variable degrees of efficiency, for the degradation of phenol and its daughter products. However, only one previous study reported significant mineralization of the solute, as evidenced by a reduction of total organic carbon (TOC) in the sample.[18] Previous studies investigating the sonochemical oxidation of fulvic acid,[22] 4-nitrophenol,[23] pentachlorophenol,[24] azobenzene,[25] and methyl orange,[25] have all observed enhancement in the reduction of TOC when ozonation is combined with ultrasound. The focus of this investigation is to evaluate the potential of ultrasound and a combined ultrasound/ozone system to degrade and mineralize dilute samples of aqueous phenol.

Experimental Section

Ultrasonic Reactor and Ozone Generator

Experiments were performed in a 605 mL bench-scale sonochemical reactor (Allied Signal-ELAC Nautik USW). The ELAC reactor employs interchangeable bottom-mounted transducers (205, 358, 618, and 1078 kHz) operated at 100 Watts. The reactor is a glass vessel with an integrated water jacket for cooling. All runs were performed at 15 ^{o}C and were maintained at this temperature with a 1.5 kW thermostat (VWR 1157). The vessel is sealed with a hemispherical glass top with several sampling ports. A medium porosity glass frit was used to saturate the solution with various gases. One of the ports was left open to the atmosphere to allow for gas exchange. The emitting area of the ELAC transducer is 23.6 cm^2. The reported applied power for the small reactors has been previously determined using standard calorimetric procedures.[26]

Ozone was generated with a corona ozone generator (Orec V10-0). The O_2 feed gas was dried and purified with a molecular sieve and drierite cartridge (Alltech) prior to entering the instrument. The O_2/O_3 mixture was delivered to a solution in the reactor via a medium porosity glass frit and was sparged during sonication. Varying the voltage and flow rates of the of the ozone generator regulated ozone concentrations. Gas flow rates were monitored with a gas flow meter (Gilmont Instruments). Steady-state concentrations of ozone in the small reactor ranged from 0 to 400 μM.

Analytical Methods and Equipment

Aliquots were sampled with a glass syringe that was fitted with a stainless steel needle and were stored in amber glass vials and then analyzed to quantify the concentration of the substrates. Phenol (C_6H_5OH), hydroquinone (1,4-$C_6H_4(OH)_2$), catechol (1,2-$C_6H_4(OH)_2$), and p-benzoquionone (1,4-$C_6H_4O_2$) were quantified chromatographically with a Hewlett Packard 1090 Series II HPLC by UV detection, using a Restek Pinnacle IBD 5 μm, 250 x 3.2 mm column at 40 °C and an elution mixture of 40/60 methanol/water. Muconate ($^-O(O)C-(CH)_4-C(O)O^-$), maleate (cis - $^-O(O)C-(CH)_2-C(O)O^-$), fumarate (trans-$^-O(O)C-(CH)_2-C(O)O^-$), glyoxalate (OCC(O)OH), formate (HCO_2^-), and oxalate ($C_2O_4^{2-}$) concentrations were quantified using a Dionex Bio LC ion chromatograph. Separations were carried out on a 25 cm AS11 column with a 0.01 – 0.1 M NaOH eluent with a flow rate of 2 mL/min. Total organic carbon concentrations were measured with a Shimadzu TOC 5000 A organic carbon analyzer with a Shimadzu ASI 5000A autosampler. A heated course catalyst bed was heated to 680 °C . Samples were acidified with HCl to pH 1-2 and purged for 1 minute prior to injection with instrument grade air to remove any dissolved carbonate or bicarbonate. Samples were measured in triplicate.

Aqueous ozone concentrations were quantified in a 1 cm pathlength quartz cuvette with a Hewlett Packard 8452 A diode-array spectrophotometer at $\lambda = 260$ nm ($\varepsilon_{aq\ O3} = 3292\ M^{-1}cm^{-1}$). Steady-state concentrations were determined prior to the addition of the solute or the imposition of the acoustic field. In order to ensure that $[O_3]_{ss}$ remained constant during the course of an experiment, a separate vessel containing ultra-pure H_2O was sparged with the same ozone stream and the $[O_3]$ was determined. The maximum variation in $[O_3]_{ss}$ during the experiment was ± 10 μM. All pH measurements were made with a Beckman Altex 71 pH meter, and a Beckman glass pH electrode (model 39843).

Employed chemicals

Phenol (EM Science, > 99%), Hydroquinone (Adrich, >99%), 1,4 Benzoquinone (Aldrich, > 98%), Catechol (Sigma, >99%), Resorcinal (Sigma, >99%), Maleic Acid (EM Science, >98%), Malonic (Aldrich, >99%), Sodium Formate (Fluka, > 99%) and Oxalic Acid (Baker, >99.5%) were used without further purification. Water used for sample preparation was purified with a Millipore Milli-Q UV Plus system (R = 18.2 MΩ cm^{-1}).

Experimental Results and Discussion

Phenol Degradation Rates

Phenol Degradation Rates in the Presence of Ultrasound

The degradation of phenol in aqueous solution was performed using ultrasound at four separate frequencies: 205, 358, 618 and 1078 kHz (100 W applied power). Samples decayed quasi-exponentially over more than two half-lives and were modeled with first-order kinetics

$$-\left(\frac{d[C_6H_5OH]}{dt}\right)_{US} = {}^{US}k_{-Ph}[C_6H_5OH] \qquad (1)$$

Removal of the acoustic field halted further decomposition. Sonochemical degradation rates were found to be a maximum at 358 kHz with a corresponding pseudo first-order rate constant: ${}^{US}k_{-Ph}$ = 0.0154 min^{-1} ($[C_6H_5OH]_o$ = 1.0 mM (95 ppm)) (Fig. 1) This frequency dependence is in accordance with previous findings for the sonolytic degradation of similar semi-volatile organics[27-29] and complements previous investigations, which suggest that a maximum sonolytic phenol degradation rate exists between 20 and 500 kHz.[16,17] Rates measured at 358 kHz and 100 W were significantly accelerated at lower initial concentrations of the solute. The pseudo first-order constant, ${}^{US}k_{\text{-}Ph}$, measured as a function of initial phenol concentration (Fig. 2) leads to:

$$ {}^{US}k_{\text{-}Ph} \times 1000 = -6.09 \ln [C_6H_5OH]_o + 55.1 \tag{2} $$

This rate inhibition at higher solute concentrations is consistent with previous findings [15,30,31] and is attributed to competitive ·OH reactions with the *in situ* degradation by-products. The reported bimolecular rate constants for ·OH with the several of the species believed to be present in this system are shown in Table 1.

Continuous sonolytic decomposition of aqueous phenol (~1 mM) yielded an array of degradation by-products that imparted a translucent brown hue and a pungent odor to the aqueous solution. This coloration was observed within the first hour of exposure and did not diminish with continued irradiation. Maximum coloration occurred at 358 kHz. Previous studies of the degradation of phenol with ultrasound[4,14-17,30,32] failed to report this phenomenon. After several hours of sonication the pH dropped from 5.3 to 3.0. In an effort to limit this depression in pH, due to HNO_3^- formation from air, separate experiments were performed under continuous gas sparging to prevent sonochemical fixation of atmospheric N_2 as NO_3^-. Control experiments determined that oxygen does not strip significant concentrations of phenol from aqueous solutions. O_2 and Ar/O_2 (80/20, v/v) gas mixtures were separately introduced to the solutions 30 min before and during sonication. A pH drop was still observed ($pH_{final} \sim 4$), however the color change was less intense and the solutions were clarified within 2 hours of continued treatment.

Previous studies evaluating the sonolysis of phenol have identified a complex array of reaction by-products[4], which are similar to those observed during the oxidation of phenol with ozone.[33] Our attempts to identify and quantify these byproducts were met with limited success. At 358 kHz in an air-saturated system, phenol and its quinone by-products were fully degraded within 4-5 hours of treatment. The formation of low-molecular weight aliphatic acids and aldehydes was also observed. The remainder of the unidentified by-products appears to be higher molecular-weight polymeric compounds arising from the reaction between two phenoxy radicals or between radical products and non-radical substrates. Previous investigations have identified wide array of phenoxy radical dimerization products produced during the oxidation of phenol.[34-36] The addition of an inert saturating gas (e.g., Ar or He) typically decreases the extent of sonopolymerization[37], which may explain why the O_2 and Ar/O_2 sparged systems showed little coloration.

Previous studies suggested that increasing dissolved Ar/O_2 concentrations can increase the collapse temperature of a cavitating bubble, thereby enhancing ·OH generation.[5,38,39] This increase in radical production could potentially improve observed sonochemical degradation rates of many organic solutes; however, results of this investigation indicate that the sonochemical degradation of phenol was inhibited at all frequencies compared to the air-saturated system. (Fig. 3) The optimal degradation rate in oxygenated solutions was obtained at 358 kHz: ${}^{US\text{-}O2}k_{\text{-}Ph} = 0.0108\ \text{min}^{-1}$ ($[C_6H_5OH]_o$ = 1 mM, O_2 = 25 mL/min, 100 W). The large ($R \geq 0.5$ mm) bubbles produced by the sintered glass frit were observed to be stable and buoyant and not subject to cavitation. The resonance radius, R_r, for a bubble exposed to ultrasound can be estimated as follows:

$$R_r = \frac{1}{2\pi f}\left[\frac{3KP_h}{\rho}\right]^{\frac{1}{2}} \qquad (3)$$

where f = frequency, K = polytropic index of saturating gas (K ≈ specific heat ratio), ρ = solution density, P_h = hydrostatic pressure.[37] Given equation 3 for f = 358 kHz, $R_r \cong 10$ μm is calculated. It can be inferred that the bubbles added during sparging of the system are not capable of producing significant cavitation effects. Gas sparges composed of millimeter-sized bubbles, though, can scatter sound or dissipate mechanical energy, thereby attenuating the intensity of the acoustic field within the reactor and reducing the observed degradation rates.[40]

Phenol Degradation with Ozone and O_3/US

Ozonated phenol solutions remained clear and colorless with no detectible odors. Degradation rates in the presence of steady state ozone concentrations, $^{O3}R_{-Ph}$, were assumed to follow pseudo first-order kinetics

$$-\left[\frac{d[Phenol]}{dt}\right] = {}^{O_3}R_{-Ph} = {}^{O_3}k'_{-Ph}[C_6H_5OH] = {}^{O_3}k_{-Ph}[O_3]_{ss}[C_6H_5OH] \qquad (4)$$

Phenol dissolved in an ozonated solution ($[O_3]_{ss}$ = 178 μm) decays exponentially with a pseudo first-order rate constant: $^{O3}k'_{-Ph} = -0.0159\ \mathrm{min}^{-1}$. (Fig. 4) Measurements of $^{O3}k'_{-Ph}$, as a function of ozone leads to $^{O3}k_{-Ph} = {}^{O3}k'_{-Ph}/[O_3]_{ss} = 72.7\ M^{-1}\mathrm{min}^{-1}$ or $1.2\ M^{-1}s^{-1}$ ($[C_6H_5OH]_o$ = 1 mM, pH ~ 5.3) (Fig. 5). Hoigne and Bader[41] reported that the bimolecular rate constant for ozone and $[C_6H_5OH]$ is $1.3 \times 10^3\ M^{-1}s^{-1}$ at pH = 2 – 6. This large discrepancy in rate constants suggests that ozone preferentially reacts with the degradation byproducts. As shown in Table 2, reported[41-43] bimolecular rate constants indicate much higher reaction rates for molecular ozone with a number of the aromatic and aliphatic byproducts as compared to phenol.

The simultaneous application of ozone and ultrasound at 358 kHz and 100 W of power enhanced the observed exponential rates. The linear dependence of the pseudo first-order rate constant, ${}^{O3\text{-}US}k'_{-Ph}$, on $[O_3]_{ss}$ is shown in Figure 5 where

$$ {}^{O3\text{-}US}k'_{-Ph}\ (\mathrm{min}^{-1}) \times 1000 = 1.04 \times 10^{-1}[O_3]_{ss} + 1.37 \times 10^{1} \qquad (5)$$

However, the overall phenol degradation rates are not significantly enhanced above the rate that would be achieved as a simple linear combination of the separate reaction processes.

$$ {}^{O3\text{-}US}R_{-Ph} = ({}^{O3}k'_{-Ph} + {}^{US}k_{-Ph})[C_6H_5OH] \qquad (6)$$

This finding is consistent with previous findings[24] which determined that the addition of ozone during sonication did not affect the first-order degradation rate for pentachlorophenol (C_6Cl_5OH). Degradation rates were also measured at a fixed ozone concentration of 350 μM and ultrasonic frequency of 358 kHz as a function of ultrasonic power density (PD). (Fig. 6) An increase in PD from 0-83.3 W/L doubled the degradation rates; however, a subsequent increase in PD from 83.3 W/L to 167 W/L did not result in further enhancements. Above 83.3 W/L we hypothesize the additional power resulted in enhanced degassing and pyrolytic decomposition of the aqueous ozone.

Elimination of Total Organic Carbon

TOC Degradation with Ultrasound or Ozone

The extent of phenol mineralization was determined by monitoring the concentration organic carbon remaining in solution as phenol was oxidized to CO_2 and H_2O

$$C_6H_5OH + 7\ O_2 \rightarrow 6\ CO_2 + 3\ H_2O \qquad (7)$$

The samples were acidified to pH ~ 1 and purged with instrument grade air to ensure all carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and H_2CO_3 are removed as CO_2 (g) from solution. Initial concentration vs. time profiles were fit to a normalized zero-order rate constant, k'_{-TOC}.

$$\frac{[TOC]}{[TOC]_o} = 1 - \left(\frac{k_{-TOC}}{[TOC]_o} \right) t = 1 - (k'_{-TOC})t \tag{8}$$

TOC degradation rates were determined to be independent of the nature of the saturating gas. A maximum rate was obtained at 358 kHz with a normalized pseudo zero-order rate constant of ${}^{US}k'_{-TOC} = 0.0002\ \text{min}^{-1}$ (100W, $[C_6H_5OH]_o$ ~1.0 mM). This represents a minimal reduction in TOC of only 10% after 400 minutes of sonolysis. (Fig. 7) This relatively small change in TOC with sonolytic degradation of phenol is consistent with previous studies.[18,19]

Simple ozonation was determined to be a far more effective technique for reducing TOC concentrations as shown in Figs. 7 and 8. The normalized rate constant, ${}^{O3}k'_{-TOC} = {}^{O3}k_{-TOC}/[TOC]_o$ as a function of $[O_3]_{ss}$ (Fig. 8), is given by

$${}^{O3}k'_{-TOC} \times 1000 = 6.4 \times 10^{-3}\ [O_3]_{ss} - 2.73 \times 10^{-1} \tag{9}$$

While similar phenol degradation rates are obtained using either $[O_3]_{ss} = 178\ \mu M$ or 358 kHz (100 W), the extent of mineralization obtained at this concentration of ozone is approximately five-fold greater. At $[O_3]_{ss} = 365\ \mu M$, the carbon content of a 1 mM phenol solution was reduced by 60% in 5 hours. (Fig. 7) When fit to zero-order kinetics, this yields a normalized rate constant, ${}^{O3}k'_{-TOC} = 0.0021\ \text{min}^{-1}$. After 300 minutes the degradation profile continues to follow zero-order kinetics, however at a much slower rate, ${}^{O3}k'_{-TOC} = 0.0006\ \text{min}^{-1}$ (Fig. 9). After 11 hours of continuous ozonation, ~ 15% of the original carbon remained in solution.

TOC Degradation with Combined Ozone and Ultrasound

The simultaneous application of ultrasound and ozone resulted in significantly enhanced phenol mineralization. (Figs. 7, 8, and 10) A maximum TOC degradation rate constant of ${}^{O3\text{-}US}k'_{-TOC} = 0.0033\ \text{min}^{-1}$ was obtained at 358 kHz (100 W) with $[O_3]_{ss}$ = 350 μM. This combination resulted in complete mineralization within 5 hours. The synergistic action of O_3 and US enhanced TOC degradation during the first 5 hours of treatment by 43% compared to the simple linear addition of the two independent systems and achieved complete mineralization of the sample.

The data shown in Figure 7 indicates a lagtime of ~ 2 hours before the synergistic effect is observed. Gurol and Vatistas[8] observed a similar lag in enhancement in a O_3/UV reaction system. These findings suggest that the initial reduction in TOC was primarily the result of rapid reactions between molecular ozone and the aromatic and other unsaturated species within the solution; and that synergistic enhancement was only observed after the initial intermediates were oxidized into more refractory saturated organic species. Gurol and Vatistas[8] suggested that the application of ozone to a phenol sample immediately followed by an independent ·OH source (in the absence of O_3) might yield similar degradation kinetics. In Figure 11, [TOC] vs. time profiles for the independent and separate application of ozone and/or sonication are shown. The independent and successive application of each technique for 12 hours did not result in complete mineralization, regardless of the order of application. Thus, we conclude that a synergistic effect is responsible for the enhanced mineralization.

Separate experiments were performed using periodic sonication to verify that the enhanced TOC degradation was a result of the application of the combined system. An acoustic field was applied to an ozonated solution of phenol for 30 minutes, followed by 30 minutes of "silent" ozonation. This cycle was repeated for a total treatment time of ~ 6 hours until complete mineralization of the 1 mM phenol sample was achieved. Periodic pulsing of ultrasonic irradiation yielded a normalized pseudo zero-order rate constant of ${}^{\mathrm{O3\text{-}Pulsed\ US}}k_{\mathrm{-TOC}} = 0.0028\ \mathrm{min}^{-1}$ (Fig. 13). This represents a 15% reduction in the overall rate compared to continuous sonication and ozonation. Relative synergistic enhancements resulting from the simultaneous application of the two techniques were evident after ~ 150 minutes of reaction. Removal of the acoustic field decreased the observed rate of mineralization; however, this rate is re-established when ultrasonic irradiation is re-applied.

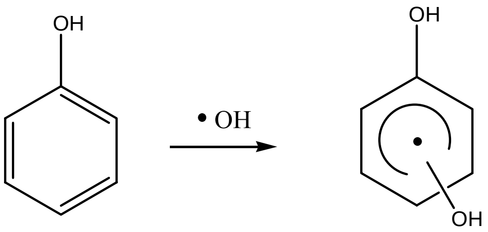
Identification of Refractory Organics

After partial mineralization ($[\mathrm{TOC}]/[\mathrm{TOC}]_o \sim 50\%$) with with ozone and ultrasound/ozone, the products remaining in solution were analyzed with HPLC-MS and IC. Approximately 40% of the detected TOC was determined to be oxalate ($H_2C_2O_2/HC_2O_2^-/C_2H_4O_2^-$) and 10% was found to be formate (H_2CO_2/HCO_2^-). Analyses of these solutions excluded the following compounds: phenol, hydroquinone, catechol, benzoquinone, resorcinol, mucconic acid, mucconic aldehyde, maleic, acetic, or fumaric acid. The remainder of the TOC was most likely glyoxylic acid or glyoxal. Upon further treatment, both glyoxylic acid and glyoxal should be oxidized to oxalate.[5]

Mechanisms of Phenol Mineralization

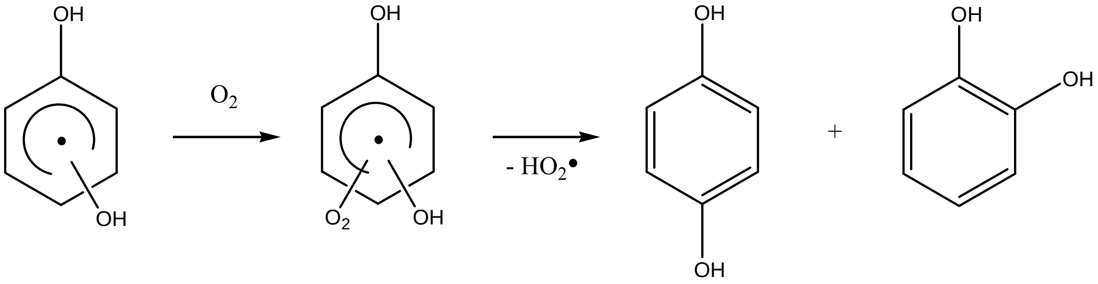
Phenol Mineralization with Ultrasonic Irradiation

Phenol is a moderately soluble compound in water ($C_w^{sat} = 0.63\,M$) with a relatively low vapor pressure (4.6×10^{-4} atm) and Henry's constant of phenol (4.0×10^{-4} L atm M^{-1}).[44] These physiochemical properties preclude significant concentrations of this species diffusing into the vapor phase of the acoustic cavitation bubbles. The lack of pyrolysis products (*e.g.*, acetylene and methane) during the sonolysis of aqueous phenol indicate that the sonochemical reactions primarily occur within the bulk solution rather than within the superheated regions of the interfacial zone surrounding the cavitation bubble.[30] Previous research[4,16-18,30] has shown that the sonochemical decomposition of phenol proceeds primarily through a free-radical mechanism in solution. Reaction with ·OH generate dihydroxyl cyclohexadienyl radicals



(10)

which upon further reaction with aqueous molecular oxygen yield hydroquinone and catechol.[18,45]



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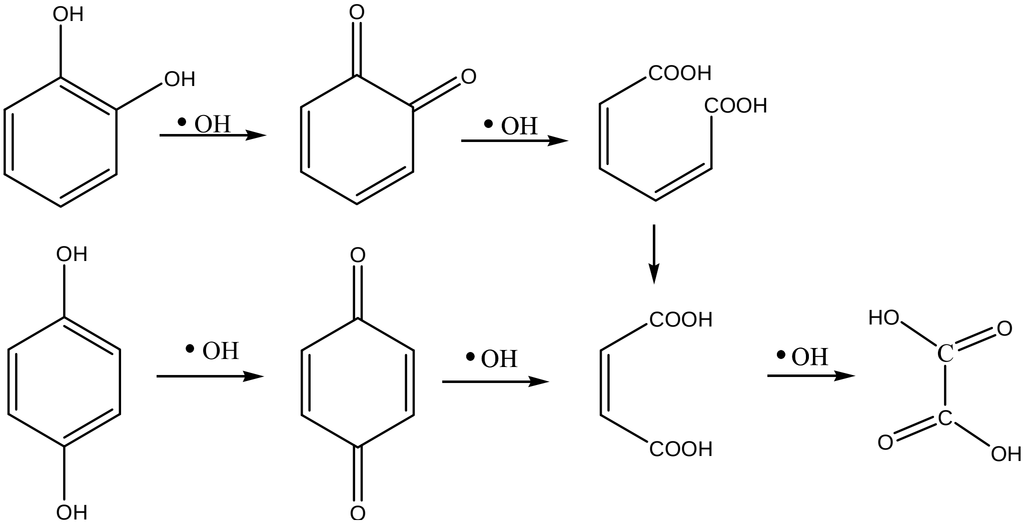
Subsequent radical reactions eventually yield ring cleavage products which undergo further oxidation to various unsaturated carboxylic acids including muconic and maleic acid, eventually generating oxalic acid.[17,18]



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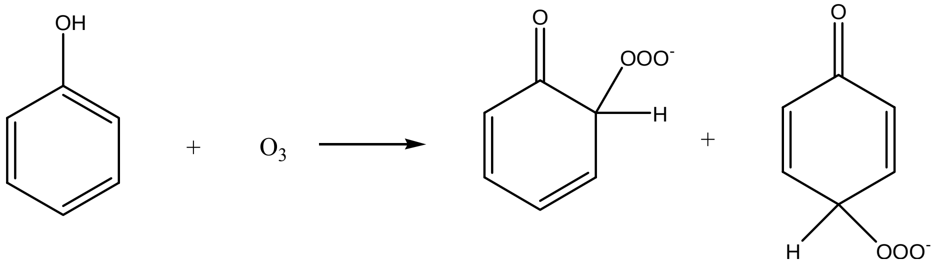
The reaction between oxalic acid (HO_2CCO_2H) and ·OH yields CO_2. The mechanism of the ·OH-mediated oxidation of oxalate is explained in further detail in Chapter 6.

While this mechanism suggests that sonochemical reactions should eventually degrade phenol to CO_2 and H_2O, the findings of this study (Figs. 7 and 11) were to the contrary. The recalcitrant nature of oxalate towards sonication has been observed previously.[5,19] Oxalate is known to react with the hydroxyl radical (Table 1); therefore the limited sonochemical mineralization of phenol and its degradation by-products suggests that oxalate and its precursors are moderately hydrophilic, limiting the accumulation of these species at the bubble interface where aqueous ·OH-radical concentrations are highest.

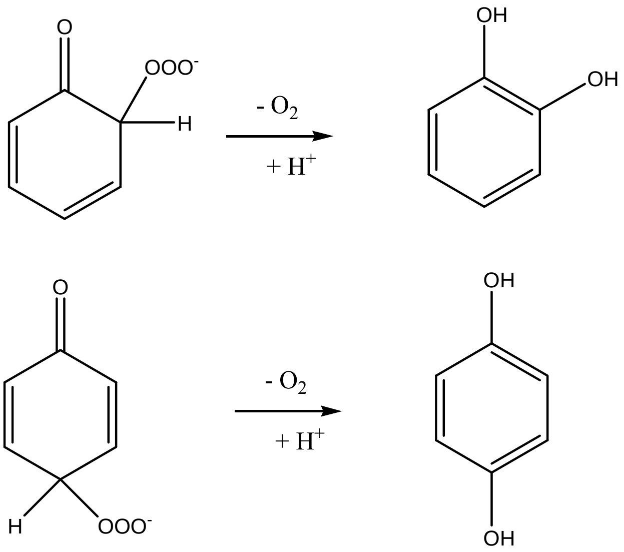
Phenol Mineralization with Ozonolysis

The ozonolysis of phenol produces a collection of degradation by-products which are quite similar to those produced using ultrasonic irradiation.[4] Due to resonance stabilization, electrophilic addition of O_3 occurs at the *ortho* and *para* positions, producing a trioxide anion



(13)

This intermediate can subsequently lose molecular oxygen to generate the dihydroxy benzene products, catechol and hydroquinone, respectively.[33,45]



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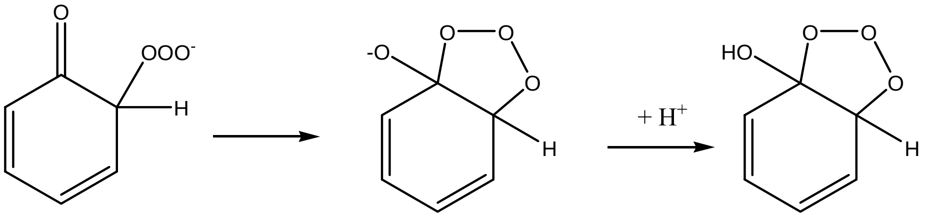
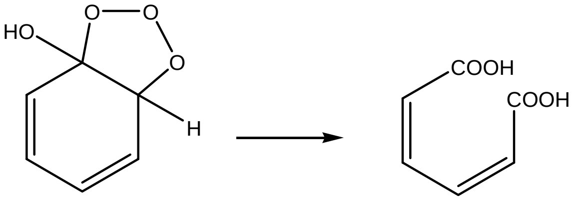
In addition to Reaction 14, the ozone adduct may also close to form the Criegee intermediate



(15)

which upon further rearrangement results in ring-cleavage to produce muconic acid[33,45]



(16)

Catechol and hydroquinone also undergo further ring-opening reactions according to the Criegee mechanism to generate muconic, maleic, and other linear olefinic carboxylic acids.[33] Continued ozonation of these intermediate products leads to decarboxylation and the formation of glyoxal, and glyoxylic acid, which are then oxidized oxalic acid.[33,46,47] As indicated by its minimal bimolecular rate constant with ozone (Table 2), oxalic acid is a stable end product that is not efficiently oxidized with molecular ozone. The sharp transition in TOC degradation rates in Figure 9 suggests that after ~ 5 hours of ozonation, all unsaturated organics susceptible to ozonation have been eliminated.

Phenol Mineralization with US/O_3

As shown in Figures 7, 8, and 11, the reduction of TOC in the combined ultrasound/ozone system is significantly enhanced compared to the predicted rates obtained by the linear addition of these independent oxidative treatments. As compared to simple ozonolysis, the synergism of combined system was most pronounced during the later half of the TOC loss experiments, indicating that while the primary products are efficiently oxidized by O_3, later generation daughter products (*e.g.*, glyoxal, glyoxylic acid, oxalic acid) require simultaneous treatment. TOC loss rates were found to be dependent on both the aqueous O_3 concentration and the ultrasonic power density, shown in Figures 8 and 10, respectively.

These findings clearly indicate that that concurrent application of the two techniques is necessary to improve the overall TOC removal efficiency. The pulsed ultrasound experiments shown in Figure 12 suggest that the combination of the two treatment agents generates a short-lived reaction oxidizing species, most likely ·OH, which is capable of enhancing the TOC loss rates within our system. The two proposed[24,37,48] mechanisms for the enhanced production of ·OH are

I. the thermolytic decomposition of ozone in the acoustic cavitation bubble
II. the chemical degradation of ozone

As mentioned previously, the inability of phenol and its refractory by-products to efficiently partition into the interfacial regions of the cavitation bubble limits efficient oxidation via mechanism I. Rather than reacting directly with the substrates present in the bulk solution, the additional OH-radicals produced within the cavitation bubbles are expected self-react within the bubble and the interfacial region to generate H_2O_2.

It was initially hypothesized that the enhancement observed in our system could be the result of chemical reactions in the bulk solution between aqueous ozone and sonically generated H_2O_2. While O_3 does not react directly with H_2O_2, O_3 decomposition in the bulk solution is accelerated by reaction with HO_2^-

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \qquad pKa = 11.8 \qquad (17)$$

$$O_3 + HO_2^- \rightarrow \text{products} \qquad (18)$$

While the products of rxn 18 have been shown to enhance the reactivity of solutions undergoing simple ozonolysis, the identity of these products and the mechanism of this enhancement are somewhat obscure. Staehelin and Hoigne[49] have proposed that reaction 18 initiates a free-radical chain which enhances the bulk-phase OH-radical production. However, in Chapter 5 we provide compelling evidence in opposition to a free-radical mechanism and in support of a reaction which produces HO_3^- via a hydride transfer. In Chapter 6 we found evidence that in the absence of sonochemically generated ·OH, this trioxide anion may oxidize oxalate and other refractory organics, but only at high steady-state H_2O_2 concentrations that are not typically observed during sonolytic ozonation.[50,51] Therefore, the chemical degradation of aqueous O_3 by sonochemically generated H_2O_2 is not expected to significantly enhance the mineralization rates in our system.

Instead, we propose synergism in our system likely involves the rapid oxidation by ozone of free-radical species generated by OH-radical attack on otherwise refractory products. The details of this mechanism for bioxalate, one of the refractory compounds present in our system, are discussed in Chapter 6. A schematic of the general oxidiation mechanism of phenol with ultrasonic irradiation combined with ozonation is shown in Figure 13. According to this mechanism, the oxidation of phenol (A) and its initial degradation by-products (B, C, D, …) occurs rapidly within solution via the independent action of ozonation. Direct attack by molecular ozone eventually yields saturated species

(X) which are resistant to further oxidation by O_3, but can be oxidized via OH-radical attack to produce ·X. These radical intermediates are then susceptible to oxidation by O_3. This reaction has the capacity to regenerate OH, thereby propagating a free-radical mechanism and enhancing the mineralization of the more recalcitrant products generated within our system.

Conclusions

This study demonstrates that the combination of ozonation and sonication is able to decompose aqueous phenol to CO_2 and H_2O more efficiently than predicted by the simple linear addition of two independent systems. TOC loss profiles and the evolution of intermediate species detected during the degradation of phenol indicated that while the primary products are efficiently oxidized by simple ozonolysis, later generation species require simultaneous ultrasonic treatment. A free-radical mechanism within the bulk solution is provided to explain this phenomenon.

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Table 1

Reported[13] Bimolecular Rate Constants with ·OH

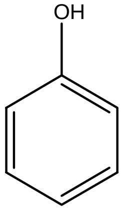
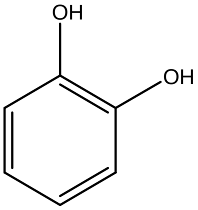
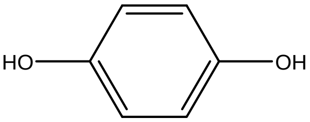
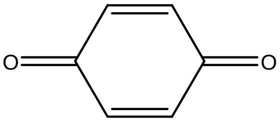
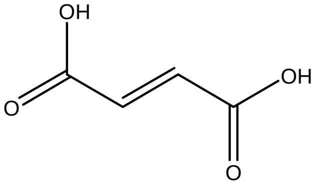
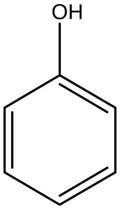
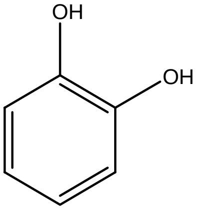
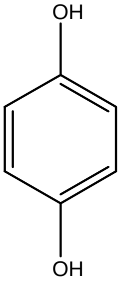
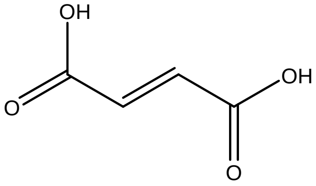
Compound		Rate Constant ($M^{-1}s^{-1}$)
Phenol		6.6×10^9
Catechol		1.1×10^{10}
Hydroquinone		5.2×10^9
Benzoquinone		1.2×10^9
Maleic acid		6.0×10^9
Formate	HCO_2^-	4.3×10^9
Glyoxal	HCOCHO	6.6×10^7
Oxalic Acid	$HOOCCOO^-$	4.7×10^7

Table 2

Bimolecular Rate Constants with Molecular Ozone

Compound		Rate Constant $(M^{-1}s^{-1})$	Reference
Phenol		1.3×10^3	41
Catechol		3.1×10^5	43
Hydroquinone		1.5×10^6	43
Maleic acid		2.4×10^4	43
		5.0×10^3	52
Formate	HCO_2^-	1.0×10^2	41
Glyoxylate	$HCOCO_2^-$	1.9	41
Oxalate	$HC_2O_4^-$	≤ 0.04	41

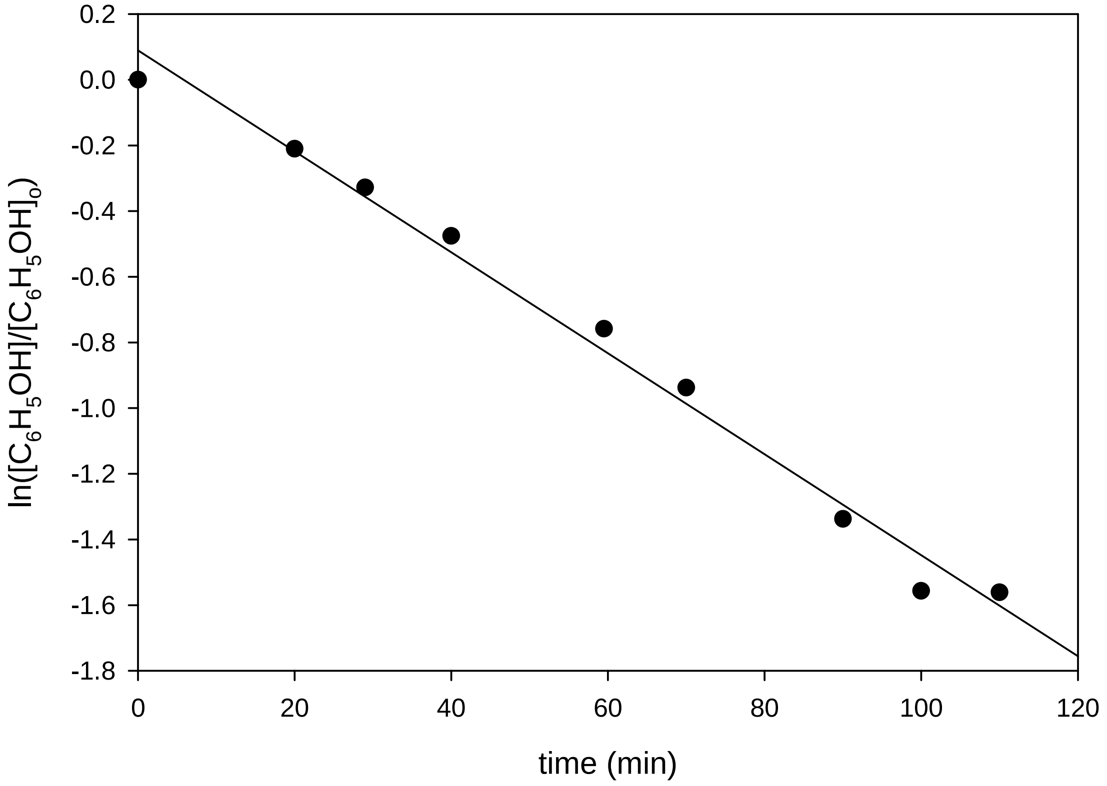


Figure 1: Degradation of phenol with ultrasound ($[C_6H_5OH]_o$ = 1 mM, 358 kHz, 100 W, 0.605L, 15 °C)

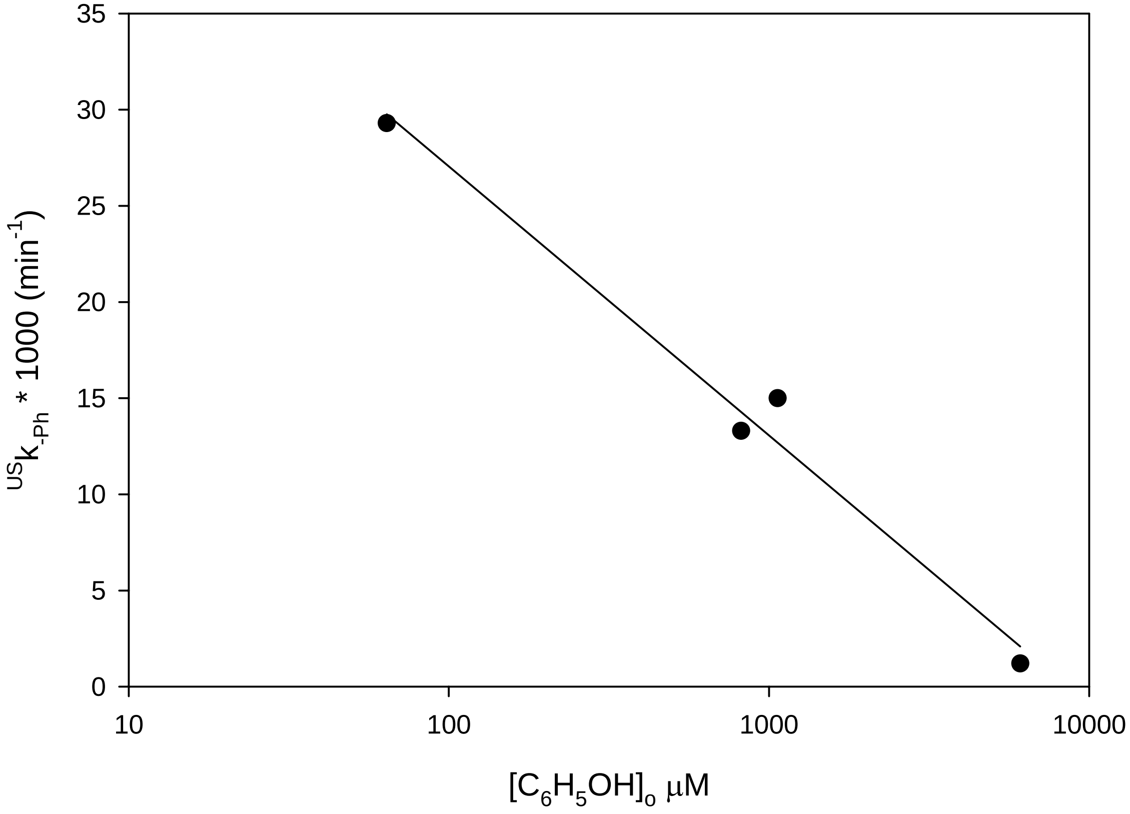


Figure 2: Phenol sonolytic pseudo first-order degradation constants as a function of $[C_6H_5OH]_o$ (358 kHz, 100 W, 0.605 L, 15 °C)

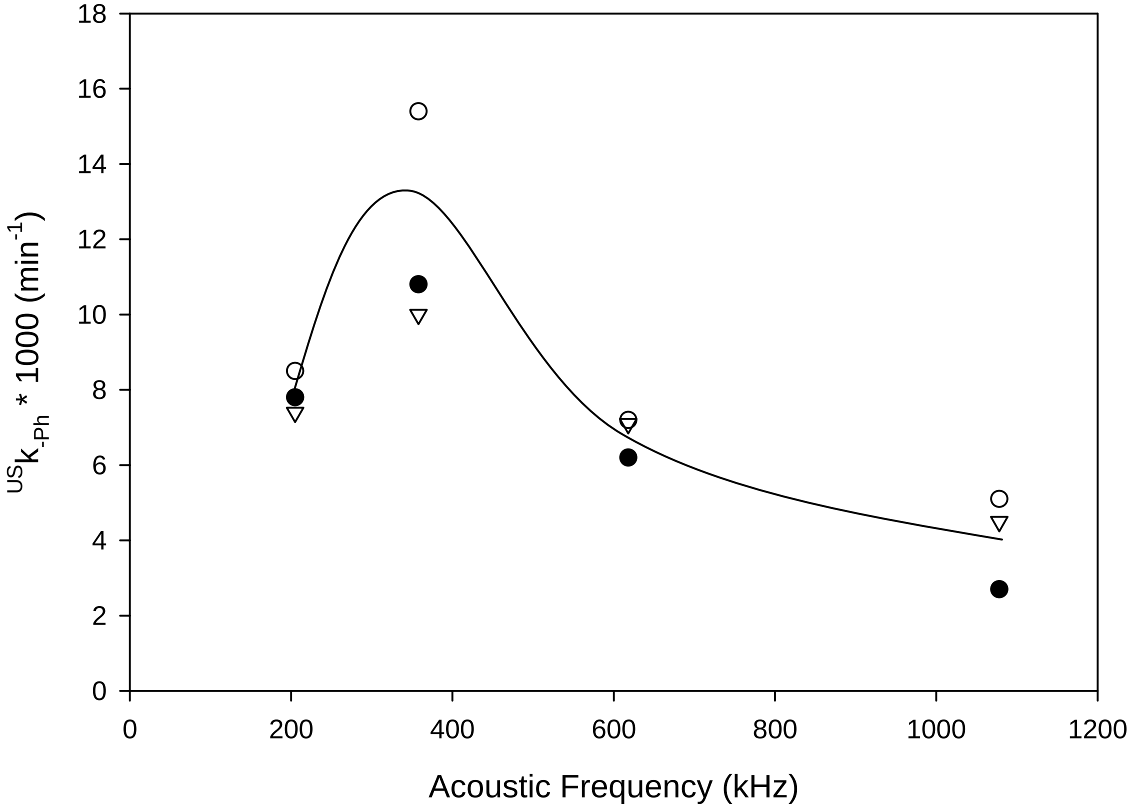


Figure 3: Phenol sonolytic pseudo first-order degradation constants as a function of frequency and gas sparge ($[C_6H_5OH]_o$ = 1 mM, 100W, 0.605L, 15 °C). ○: no gas sparge; ●: 25 mL/min Ar/O_2 (80/20, v/v); ∇: 25 mL/min O_2

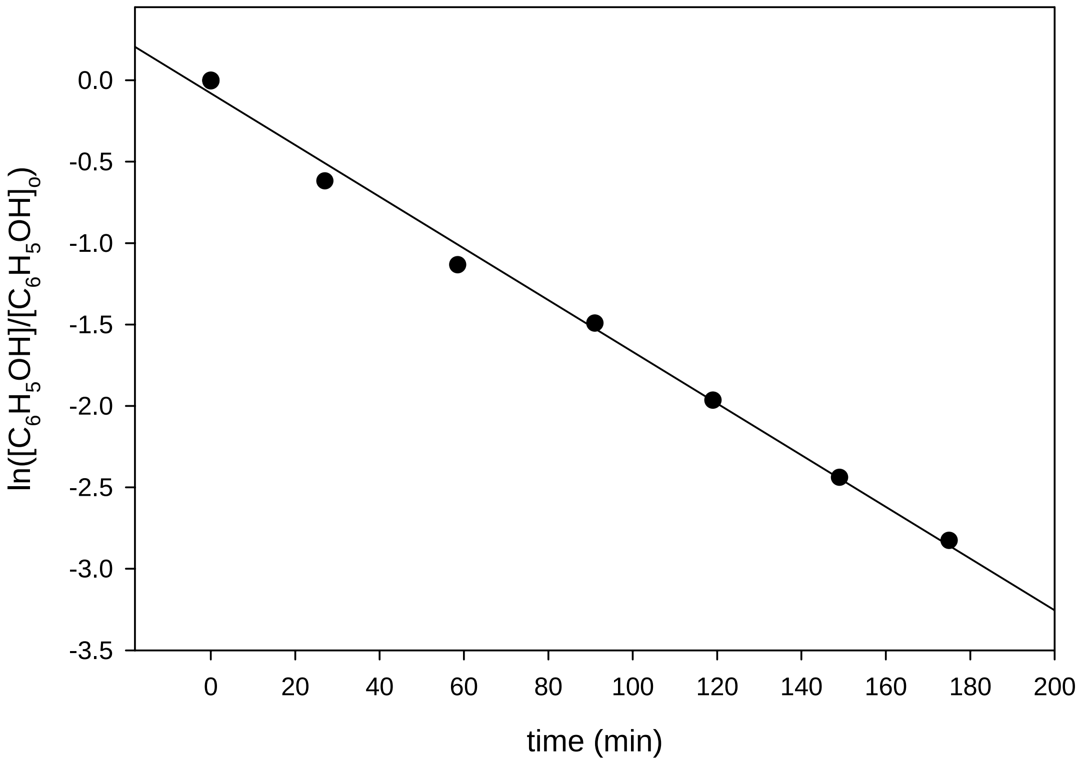


Figure 4: Degradation of phenol with ozone ($[O_3]_{ss}$ = 178 μM, $[C_6H_5OH]_o$ = 1 mM, 0.605 L, 15 ^oC).

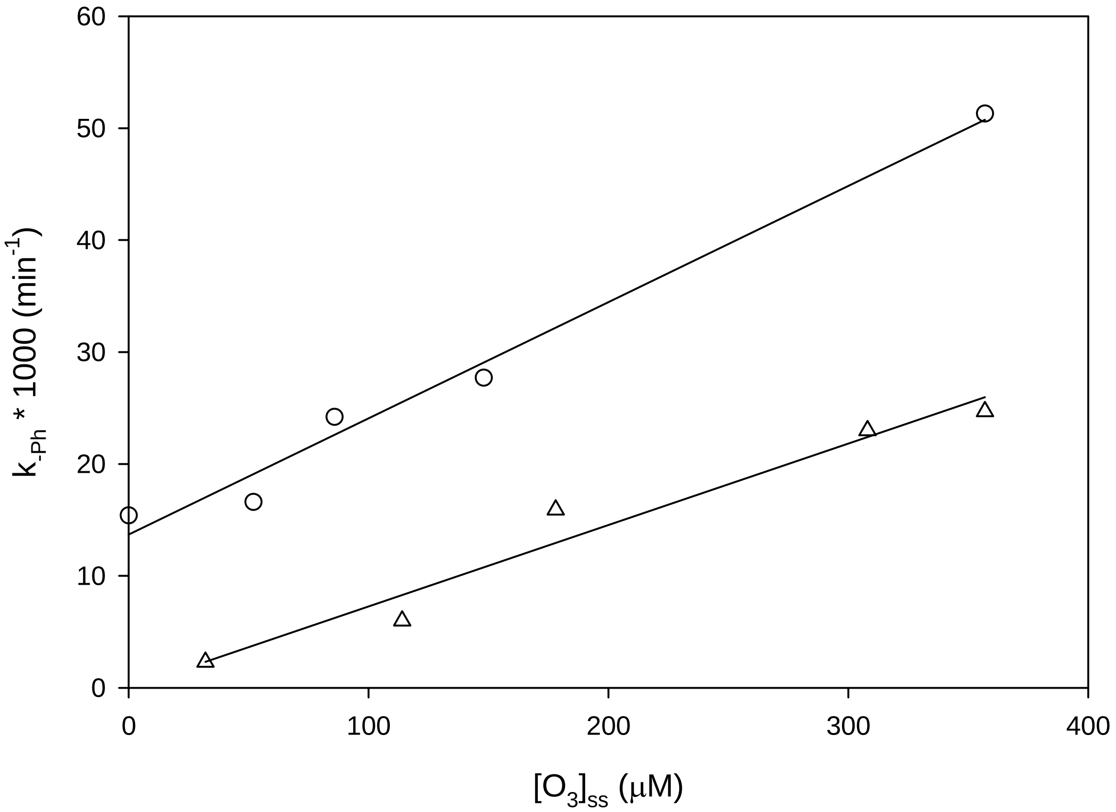


Figure 5 : Phenol pseudo-first order degradation constants versus steady state ozone concentration (0.605 L, 15 °C, $[C_6H_5OH]_o$ =1 mM). Δ: O_3 only; O: US/O_3 (358 kHz, 100W).

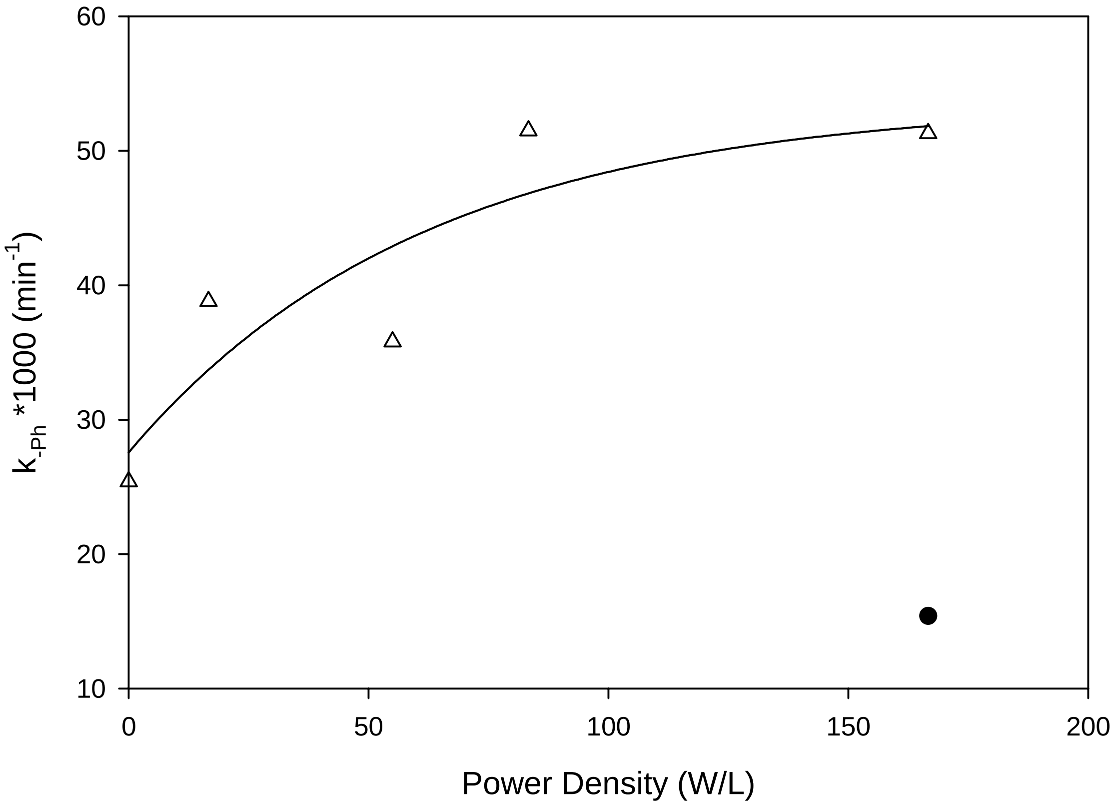


Figure 6: Phenol pseudo first-order degradation constants versus applied ultrasound power (358 kHz, $[C_6H_5OH]_o$ = 1 mM, 0.605 L, 15 °C). Δ: $[O_3]_{ss}$ ~350 μM; •: US only

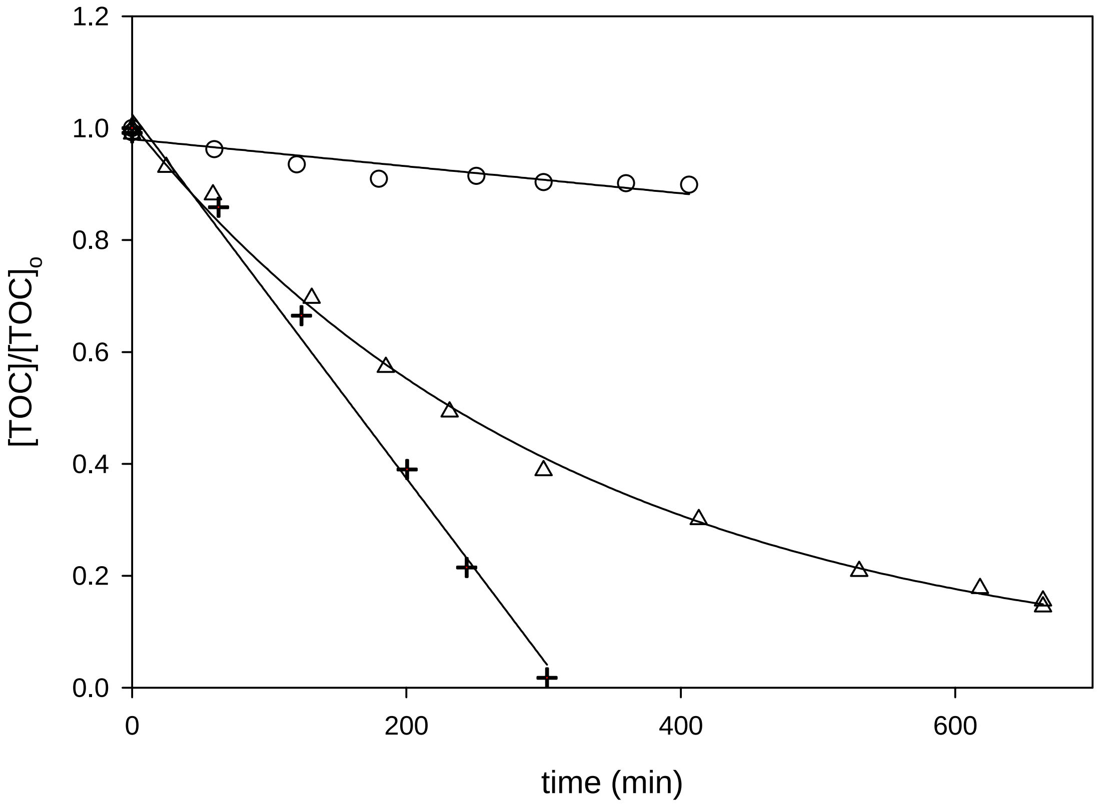


Figure 7: TOC degradation of phenol (0.605 L, 15 ^{o}C, $[C_6H_5OH]_o$ ~ 1 mM). O: US only (358 kHz, 100 W); Δ: O_3 only ($[O_3]_{ss}$ = 365 μM); +: US + O_3 ($[O_3]_{ss}$ = 350 μM, 358 kHz, 100 W)

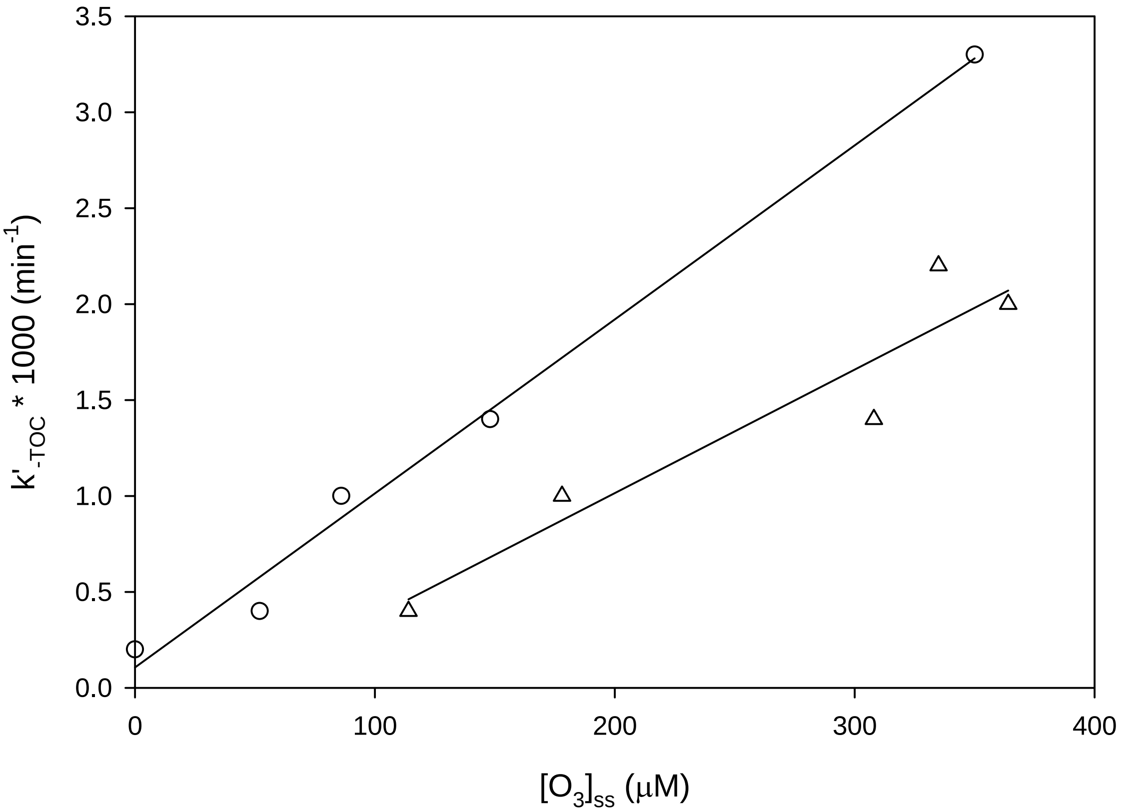


Figure 8: Normalized TOC degradation rates for phenol versus steady-state ozone concentrations. ($[C_6H_5OH]_o$ = 1 mM, 0.605 L, 15 °C) Δ: O_3 only; ○: US + O_3 (358 kHz, 100 W)

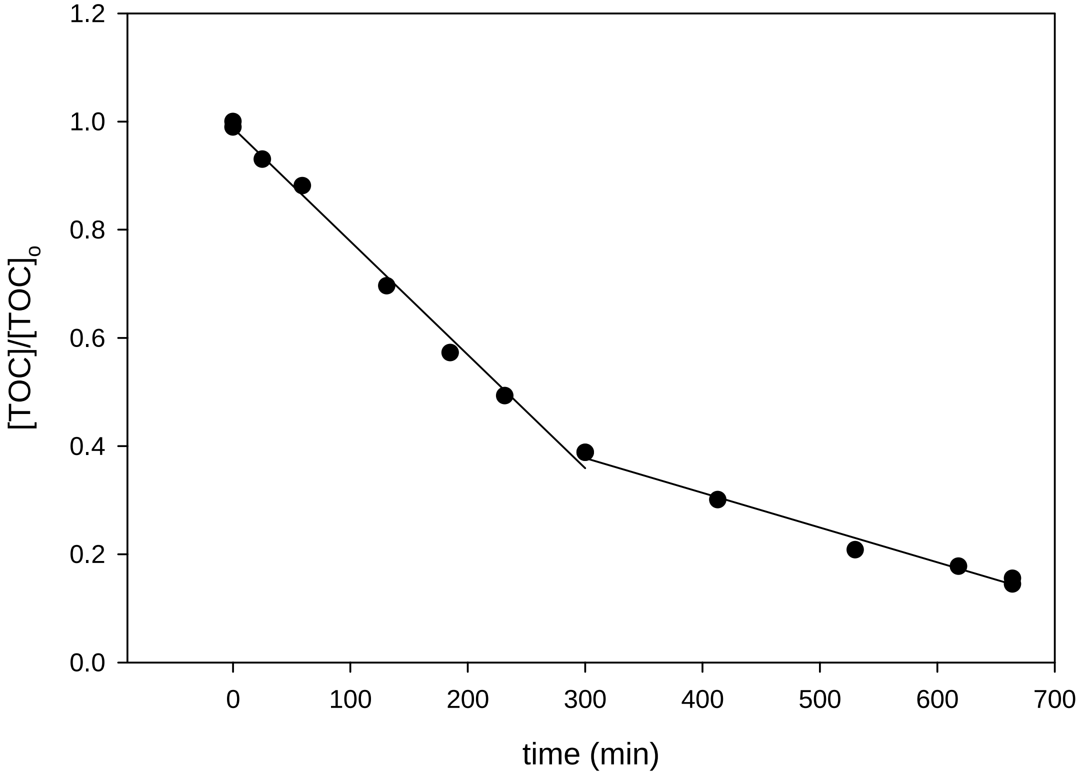


Figure 9 : TOC degradation for phenol with ozone ($[O_3]_{ss}$ = 365 μM, $[C_6H_5OH]_o$ ~ 1 mM, 0.605 L, 15 °C)

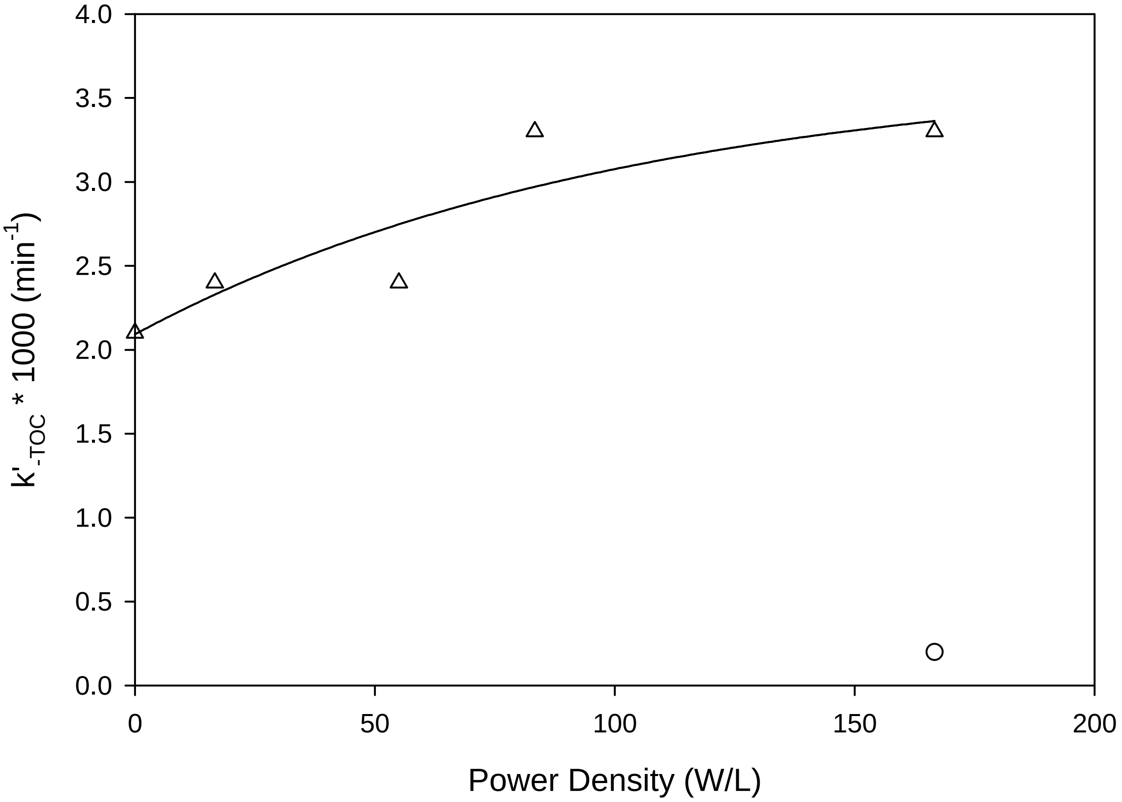


Figure 10: Phenol TOC normalized zero-order degradation constant versus applied ultrasound power (358 kHz, $[C_6H_5OH]_o$ ~ 1 mM, 0.605 L, 15 °C). Δ: $[O_3]_{ss}$ ~ 350 μM; ○: US only

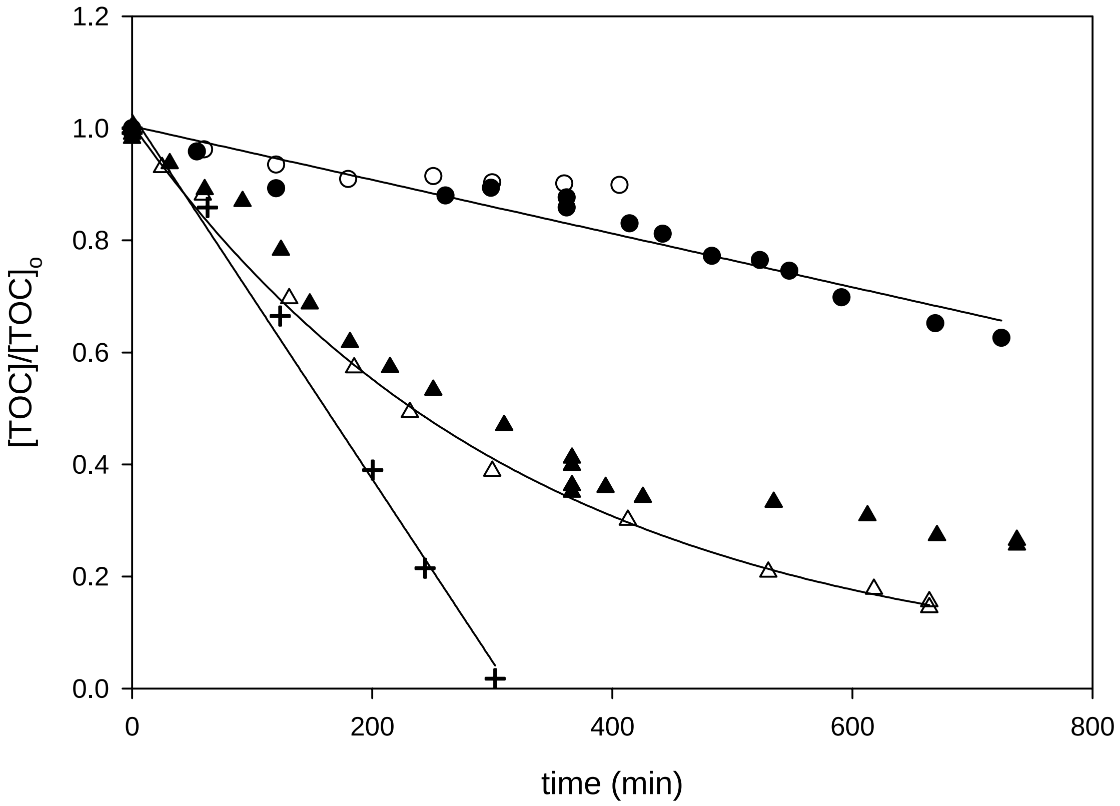


Figure 11: TOC degradation of phenol (0.605 L, 15 °C, $[C_6H_5OH]_o$ ~ 1 mM) ○: US alone (358 kHz, 100 W); ●: US (358 kHz, 100 W) then O_3 ($[O_3]_{ss}$ = 340μM); Δ: O_3 alone ($[O_3]_{ss}$ ~365 μM); ▲: O_3 ($[O_3]_{ss}$ = 338 μM) then US (358 kHz, 100 W); +: O_3 concurrently with US ($[O_3]ss$ = 350 μM, 358 kHz, 100 W)

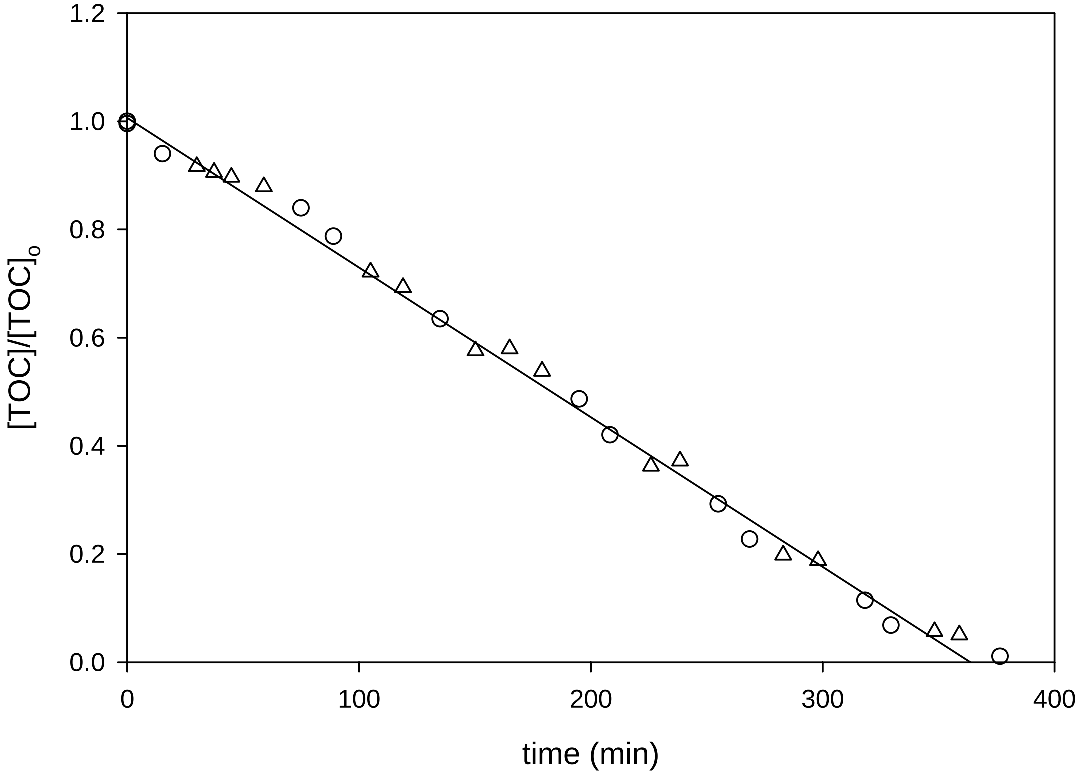


Figure 12: TOC degradation of phenol using ozone and pulsed ultrasound ($[C_6H_5OH]_o$ = 1 mM, 15 °C, 0.605 L). Δ: O_3 alone ($[O_3]_{ss}$ = 300 μM); ○: US + O_3 (358 kHz, 100 W, $[O_3]_{ss}$ = 300 μM)

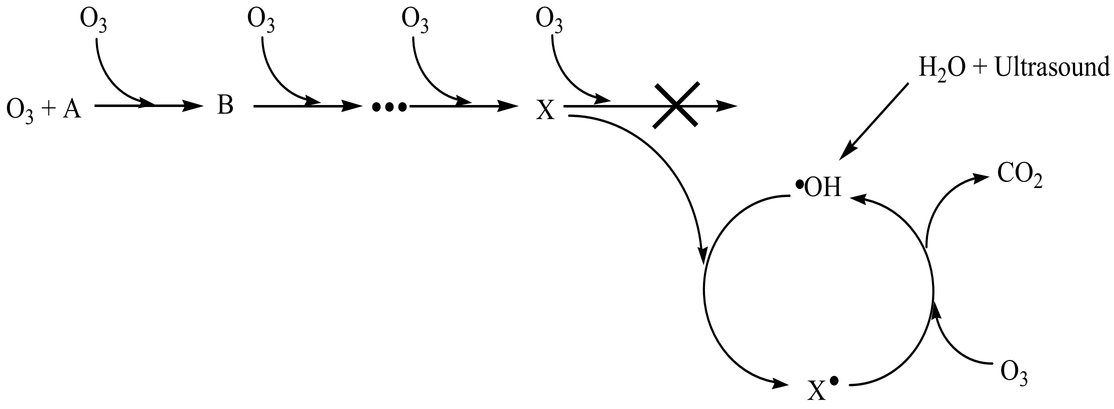


Figure 13. Proposed reaction mechanism for the oxidation of phenol with ultrasonic irradiation combined with ozonolysis.