Kinetics of the Aqueous-Phase Reaction Between Ozone and 2,4,6-Trichlorophenol

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A wetted-sphere absorber was used to measure absorption rates of ozone into aqueous-buffered solutions of 2,4,6-trichlorophenol (TCP). Gas consisting of approximately 2.5% ozone in oxygen was contacted with aqueous-buffered TCP solution flowing over a sphere in a laminar liquid film. Absorption data were obtained by measuring the change in the liquid-phase concentration of TCP from the inlet to the outlet of the absorber. A rigorous numerical model for this diffusion/reaction process was used to analyze the absorption data to determine the second-order rate constant of the reaction between ozone and TCP at 15−35°C and pH 2 and 7. The kinetic data indicate that the rate-limiting step for the reaction of aqueous TCP with ozone is the same at pH 2 and 7. Four reaction products that occur early in the reaction of ozone with aqueous TCP were identified by GCMS, including: 2,3,4,6-tetrachlorophenol (TRCP), 4,6-dichlorocatechol (DCC), 2,6-dichlorohydroquinone (DCHQ), and 2,6-dichloroquinone (DCQ). Only DCHQ and DCQ occurred in significant concentrations. Over the pH range of 2 to 5, both DCHQ and DCQ were detected in the reacted solutions, while for pH 6 and 7 only DCHQ was detected. Carbon-13 NMR analysis shows that over longer ozone exposure times short-chain carboxylic acids are the dominant species in the reacted TCP solutions.

Introduction

Treatment of industrial and municipal wastewater containing organic pollutants is of primary concern. Ozonation of these wastewaters has been effective in oxidizing organic pollutants into harmless compounds (CO_2 and H_2O) as well as breaking up refractory compounds into different compounds that are more easily treated with cheaper, more conventional methods such as biodegradation, ion exchange, and filtration.

In order to effectively treat wastewater with ozone and design appropriate treatment processes, reaction kinetics and reaction products must be determined. In addition, ozone solubilities and diffusivities must be known in order to model the diffusion/reaction process in this gas−liquid system.

There have been many studies of ozone reactions with aqueous organic compounds; however, very little kinetic data have been reported with the exception of the ozone reaction with phenol. The reaction of aqueous phenol with ozone has been extensively studied and the reaction kinetics and many of the reaction products have been determined (Eisenhauer, 1968; Gould and Weber, 1976; Augugliaro and Rizzuti, 1978; Li et al., 1979; and Hoigne and Bader, 1983). Hoigne and Bader (1983) report second-order rate constants for a large number of organic compounds at 20°C and for various pH values.

Of all the organic compounds found in wastewater, chlorinated aromatic compounds are among the most toxic and the most difficult to remove using conventional treatment techniques (such as biodegradation). Wegman and van den Broek (1983) reported that chlorinated phenolic compounds (including 2,4,6-trichlorophenol) were found in nearly all the rivers in The Netherlands that they studied. Chlorinated phenols are toxic and are suspected carcinogens. These compounds may be present in water as direct industrial pollution or as products of the chlorination of wastewater containing phenol or other aromatic compounds. Studies of ozonation of

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chlorinated phenolic compounds is of interest for wastewater treatment.

The objective of this work was to determine the second-order rate constant of the reaction of ozone with aqueous 2,4,6-trichlorophenol (2,4,6-TCP) as a function of temperature and solution pH. The kinetic rate constants are estimated from absorption data obtained in a wetted-sphere absorber at pH values of 2 and 7 and over the temperature range of 15 to 35°C. The reaction products and reaction sequence are determined by carrying out batch reactions and analyzing the solutions using gas chromatography and mass spectrometry. In addition, an estimate of the second-order rate constant of the reaction of 2,5-dichlorohydroquinone (2,5-DCHQ) with ozone is obtained at a pH of 2 and 25°C.

Experimental Studies

Reagents

The ozone used in this work was generated with a Model T-408 Welsbach Ozone Generator. Pure, dry oxygen was used as the feed gas to the generator, which was operated at 110 V, and a pressure of about 9 psig. Buffer solutions were prepared from sodium hydroxide pellets, concentrated phosphoric acid, and deionized water. All buffers were prepared with an ionic strength of 0.1 M. The 2,4,6-TCP was obtained from Aldrich Chemical Company with a minimum purity of 98%. The 2,5-DCHQ was obtained from Acros Organics with a purity of 97%. The toluene and ethyl ether used for extraction were obtained from Fisher Scientific with minimum purities of 99.9%.

Wetted-sphere absorber

The kinetics of the reaction of ozone with aqueous 2,4,6-TCP were estimated from absorption data obtained in a wetted-sphere absorber. The apparatus is described in detail by Rinker et al. (1995). The wetted-sphere absorber is shown in Figure 1. The principle of the wetted-sphere absorber is to contact a gas (ozone) with a liquid (aqueous 2,4,6-TCP or 2,5-DCHQ) under conditions where the hydrodynamics and geometry are well defined so that the reaction/diffusion process can be modeled effectively and accurately. Since the wetted-sphere operates under steady-state conditions, the extent of reaction is monitored by simply measuring the liquid flow rate and the concentration of 2,4,6-TCP or 2,5-DCHQ at the inlet and outlet of the apparatus. The ozone−oxygen gas mixture from the ozone generator flowed at a rate of 275 mL/min continuously through the absorption chamber of the absorber for all experiments. The liquid flow rate over the sphere was approximately 50 to 60 mL/min.

Gas-phase ozone analysis

In order to model the absorption process, the bulk gas-phase partial pressure of ozone must be measured for each

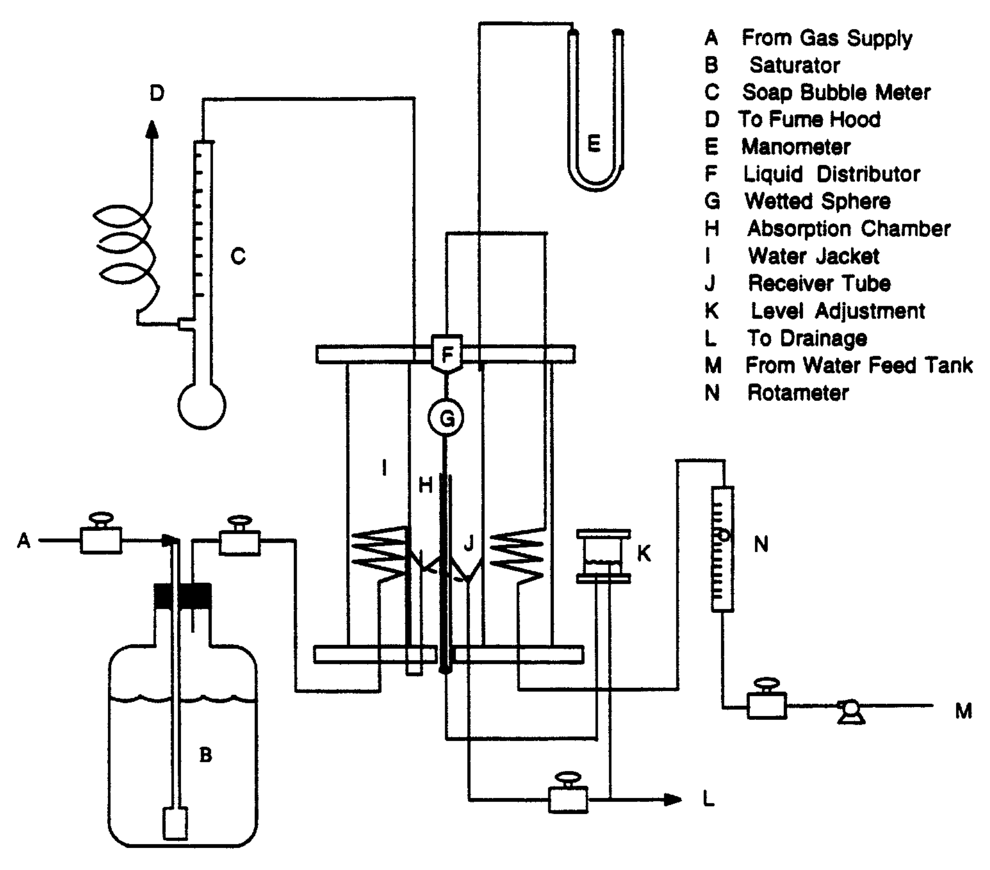

Figure 1. Wetted-sphere absorber.

experiment. The ozone partial pressure was determined by sparging the oxygen–ozone mixture of known flow rate through a 2 wt. % solution of potassium iodide in deionized water for a known length of time. The solution was acidified with 1.0-M sulfuric acid and titrated with 0.05-M sodium thiosulfate. Soluble starch was used as an indicator. The titration endpoint was designated by a brilliant blue-to-colorless color change.

Extraction of aqueous samples

In order to do gas-chromatography (GC) analysis on the aqueous samples from the wetted-sphere absorber, the unreacted organic must be removed from the buffered aqueous solution, because the ions in the buffer can cause irreparable damage to the GC column. The 2,4,6-TCP was extracted from 30-g samples of aqueous buffered solution with 3 g of toluene in a 40-mL sample vial capped with a screw top fitted with a removable Teflon-coated septum. Extractions of standard solutions of aqueous 2,4,6-TCP were used to correlate the GC areas with the aqueous concentration of 2,4,6-TCP. For the 2,5-DCHQ samples, the unreacted 2,5-DCHQ was extracted from 100 g of aqueous sample with 100 mL of ethyl ether twice. The ether was then completely evaporated at room temperature, and 1.0 mL of ethyl ether was added. Samples of the extract in ether were then analyzed by GC.

Gas chromatography analysis

A Perkin-Elmer (Model 8500) gas chromatograph was used to analyze the extracted samples. The GC was equipped with a 30-m-long, 0.54-mm-ID Alltech capillary column. The stationary phase of the column was SE-54, with a film thickness of 1.2 μm. The GC was equipped with a FID detector. The operating conditions of the GC method used to analyze the 2,4,6-TCP/toluene samples are as follows:

Carrier Gas: Helium
Flow rate: 16 mL/min
Oven T: 90°C for 0.5 min ramped to 240°C at 30°C/min, hold at 240°C for 1.5 min
Injector T: 300°C
Detector T: 300°C
Sample size: 1.0 μL

A minimum of three injections were done for each sample with a maximum average deviation of 2%. The GC method used to analyze the 2,5-DCHQ/ether samples is as follows:

Carrier Gas: Helium
Flow rate: 10 mL/min
Oven T: 40°C for 0.5 min ramped to 240°C at 15°C/min hold at 240°C for 6.2 min
Injector T: 300°C
Detector T: 300°C
Sample size: 1.0 μL

Batch-reactor studies and product identification

While the wetted-sphere absorber works well for obtaining absorption data for estimating kinetic rate constants, it does not lend itself to product identification, because so little 2,4,6-TCP is consumed during the short exposure times of about 0.5 s. A batch reactor was used to carry out product identification experiments and to observe product distributions as a function of time. The reactor consisted of a 250-mL flask fitted with a sparging stone. The ozone was sparged through 200 mL of aqueous buffered 2,4,6-TCP solution that was stirred with a magnetic stir-bar. The 2,4,6-TCP solutions were sparged with ozone for times ranging from 0.5 min to 16 min. The solutions were extracted with 100 mL of ethyl ether. The ether was then evaporated at room temperature until about 1 mL of extract remained to concentrate the 2,4,6-TCP and reaction products. Samples of the concentrated extract were injected into the Perkin-Elmer GC, which gave several peaks corresponding to reaction products. The GC operating conditions for the analysis of the ether extracts was the same as that used to analyze the 2,5-DCHQ/ether samples just described.

Several samples of concentrated extract were analyzed using gas chromatography with mass spectrometry (GCMS) in order to identify the reaction products. The GCMS system consisted of a Hewlett-Packard Model 5890 Series II gas chromatograph and a Hewlett-Packard Model 5971A mass spectrometer. The column was a 50-m-long, 0.2-mm-ID Pona column with a stationary phase of methyl silicone gum with a thickness of 0.5 μm. The mass spectra of the reaction products were compared with spectra from the NIST/EPA/NIH 75K Mass Spectra Database in order to identify the products.

Data Analysis and Modeling

In order to estimate the second-order constant of the reaction of ozone with aqueous 2,4,6-TCP or 2,5-DCHQ from the data obtained in the wetted-sphere absorber, the hydrodynamics and mass-transfer processes occurring in the liquid film on the sphere must be modeled. The development of the model used to interpret the data from this study is discussed below.

Model development

Higbie's penetration model (Higbie, 1935; Danckwerts, 1970) was used to set up the diffusion/reaction partial differential equations that describe the absorption of O_3 into aqueous solutions of 2,4,6-TCP or 2,5-DCHQ in a wetted-sphere absorber. The following irreversible, second-order, overall reaction was assumed to take place:

$$O_3 + \text{Organic} \xrightarrow{k_2} \text{products}, \tag{1}$$

with the rate of reaction given by

$$r_{O_3} = k_2 [O_3][\text{organic}]. \tag{2}$$

For laminar liquid flow over a sphere, the velocity results of Lynn et al. (1955) are used to describe the liquid-film hydrodynamics. The partial differential equations describing the diffusion and irreversible second-order reaction of both O_3 and 2,4,6-TCP (or 2,5-DCHQ) in the aqueous phase for flow over a sphere were solved in the same manner as described by Rinker et al. (1995). Since the concentration boundary layer is very thin, the velocity variation in the radial direction is neglected and the interfacial velocity (which varies in the

Table 1. Absorption of Ozone into Aqueous 2,4,6-TCP in a Wetted-Sphere Absorber

pH	T °C	10^3 [TCP]$_{\text{in}}$ (kmol/m^3)	10^3 [TCP]$_f$ (kmol/m^3)	10^9 D_{O_3} (m^2/s)	10^9 D_{TCP} (m^2/s)	10^6 Q (m^3/s)	10^6 υ (m^2/s)	P_{O_3} atm	H_{O_3} (atm·m^3)/kmol	10^{10} G_{O_3} (kmol/s)	k_2 m^3/(kmol·s)
2	15	1.695	1.410	1.51	0.609	0.851	1.139	0.0263	57.6	2.425	7,500
2	20	1.632	1.324	1.74	0.690	0.984	1.009	0.0289	66.6	3.031	14,400
2	25	1.616	1.330	1.99	0.782	1.024	0.898	0.0252	76.6	2.929	21,500
2	30	1.518	1.185	2.20	0.864	0.995	0.824	0.0267	87.7	3.313	39,000
2	35	1.713	1.310	2.48	0.977	0.882	0.744	0.0265	100.1	3.554	49,000
7	15	1.462	1.286	1.51	0.609	1.036	1.139	0.0235	86.2	1.823	13,700
7	20	1.455	1.250	1.74	0.690	1.027	1.009	0.0271	99.2	2.105	16,900
7	25	1.462	1.225	1.99	0.782	1.078	0.898	0.0259	114.2	2.555	40,000
7	30	1.385	1.107	2.20	0.864	0.951	0.824	0.0272	131.3	2.644	55,000
7	35	1.451	1.124	2.48	0.977	0.928	0.744	0.0255	149.7	3.034	113,000

θ-direction) is used in the equations. The boundary condition for O_3 at gas–liquid interface is

$$-D_{\text{O}_3}\frac{\partial[\text{O}_3]}{\partial x}\bigg|_{x=0}=k_g\left(P_{\text{O}_3}-[\text{O}_3]|_{x=0}H_{\text{O}_3}\right), \qquad (3)$$

where H_{O_3} is the physical equilibrium constant (Henry's law constant) of O_3, which is defined as the interfacial partial pressure of O_3 in the gas, P_{O_3}, divided by the interfacial concentration of O_3 in the liquid, $[O_3]$; and k_g is the gas-phase mass-transfer coefficient with a value of 2.65×10^{-5} kmol/(atm·m^2·s) for all of the experiments. This value was estimated from experiments in which H_2S was absorbed from a N_2 carrier gas into aqueous methyldiethanolamine.

The method-of-lines was used to transform each partial differential equation into a system of ordinary differential equations by discretizing the spatial variable x (Hanna and Sandall, 1995). The finite difference expressions that were used to approximate the spatial derivatives are similar to those that were used elsewhere (Rinker et al., 1995). Typical values for the initial nodal spacing h_0 at the gas–liquid interface are of the order of 10^{-11}, and for the total number of interior nodes used are about 35 nodes. The nodal spacings were successively doubled as the integration moved from the gas–liquid interface toward the sphere surface. Additional details regarding the numerical implementation are given in the article by Rinker et al. (1995).

The system of partial differential equations was transformed into a larger system of ordinary differential equations that were then integrated by using the code DDEBDF (which is due to L.F. Shampine and H.A. Watts) from the SLATEC subroutine library in double-precision FORTRAN on an HP-735 workstation. The numerical method presented here was checked for first-order kinetics against the results presented by Wild and Potter (1968).

The model just developed was used to estimate the forward rate coefficient, k_2, of the overall reaction between ozone and 2,4,6-TCP or 2,5-DCHQ by adjusting the value of k_2 until the theoretically predicted rate of absorption of O_3 was within 1% of the experimentally measured rate of absorption.

In order to implement the model just described, several physicochemical properties must be known. The solubility of ozone in the aqueous buffered TCP solutions was estimated using the correlation reported by Roth and Sullivan (1981) for the solubility of ozone in water as a function of pH and temperature. That correlation is

$$H_{\text{O}_3}=\frac{6.91\times10^8}{\rho_{\text{water}}}[\text{OH}^-]^{0.035}\exp\left(\frac{-2{,}428}{T}\right), \qquad (4)$$

where H_{O_3} is Henry's constant for ozone in water (atm·m^3/kmol); T is the temperature (K); and ρ_{water} is the density of water (g/L). H_{O_3} is also a function of the ionic strength of the solutions. The buffer solutions used in this work had a concentration of about 0.1 molar. At this level the effect of ionic strength on the gas solubility should be small and was neglected in this work. The diffusion coefficients of ozone, 2,4,6-TCP, and 2,5-DCHQ in water at 25°C were estimated from the Wilke-Chang equation to be 1.99×10^{-9} m^2/s, 7.82×10^{-10} m^2/s, and 2.45×10^{-9} m^2/s, respectively. The viscosities used in this work are those of water reported by Al-Ghawas et al. (1989).

Results and Discussion

Absorption experiments with ozone and aqueous 2,4,6-TCP were carried out at pH values of 2 and 7 over the temperature range of 15 to 35°C in the wetted-sphere absorber. The absorption data as well as the physicochemical property estimates are listed in Table 1. The numerical model was used to analyze the absorption data to obtain estimates for the second-order rate constant (k_2) of the reaction of 2,4,6-TCP with ozone. The estimates of k_2 are listed in Table 1 and are plotted in Figure 2 as functions of temperature. The reaction rate of ozone with 2,4,6-TCP is clearly faster at a pH of 7 than at a pH of 2, which is in agreement with the observations of several authors who have studied the reaction between ozone and aqueous phenol (Li et al., 1979; Hoigne and Bader, 1983; Gould and Weber, 1976). Hoigne and Bader (1983) report a second-order rate constant for the reaction of 2,4,6-TCP with ozone at a pH of about 1.4 and a temperature of about 20°C as approximately 1.2×10^4 m^3/(kmol·s), which is in good agreement with the value of 1.44×10^4 m^3/(kmol·s) at a pH of 2 and 20°C from this study. Arrhenius correlations for k_2, along with the 95% confidence limits for the activation energies, were obtained by least-squares and are given by

$$k_2=4.46\times10^{16}\exp\left(\frac{-8{,}450\pm1{,}980}{T}\right)\qquad \text{at pH}=2 \quad (18)$$

$$k_2=3.20\times10^{18}\exp\left(\frac{-9{,}570\pm3{,}220}{T}\right)\qquad \text{at pH}=7. \quad (19)$$

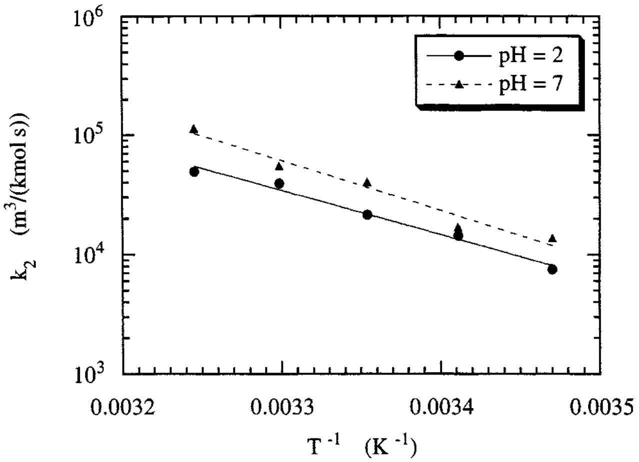

Figure 2. Arrhenius plot of the second-order rate constant of the reaction of ozone with aqueous 2,4,6-trichlorophenol at pH 2 and 7 and 15–35°C.

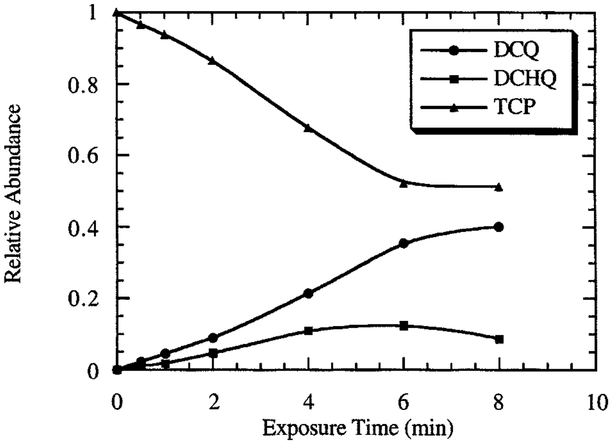

Figure 3. Relative abundance of reaction products as a function of ozone exposure time.

It can be seen in Figure 2 and from the Arrhenius correlations that the activation energies for the pH 2 and pH 7 kinetics are nearly the same (well within the accuracy of the least-squares fits), which indicates that the rate-limiting step in the reaction of 2,4,6-TCP with ozone is the same at pH 2 and 7.

In addition to determining the kinetics of the reaction of ozone with aqueous 2,4,6-TCP, several products were identified from batch-reactor experiments and GCMS analysis. Four products were identified: 2,6-dichlorohydroquinone (2,6-DCHQ); 2,6-dichloroquinone (2,6-DCQ); 4,6-dichlorocatechol (4,6-DCC); and 2,3,4,6-tetrachlorophenol (TRCP). The concentrations of 4,6-DCC and TRCP were observed to be relatively small compared to 2,4,6-TCP, 2,6-DCHQ, and 2,6-DCQ, and therefore do not seem to be major products of the reaction of 2,4,6-TCP with ozone. Obviously, TRCP cannot be formed from a direct reaction of 2,4,6-TCP with ozone, but from a reaction of some chlorine species that was produced from the reaction of 2,4,6-TCP with ozone. Since TRCP is a side product and was only observed in trace amounts, it does not seem likely that the kinetics were significantly affected by the side reaction(s) that formed TRCP. Because of the resonance structure of 2,4,6-TCP, it is possible for an −OH group to be substituted in both the ortho and para positions, and therefore it is not surprising that both 2,6-DCC and 2,6-DCHQ were detected in the reacted samples. However, the formation of 2,6-DCHQ seems to be favored over the formation of 4,6-DCC in this system. The concentrations of 2,6-DCHQ and 2,6-DCQ were significant, which indicates that these are the main products of the reaction of ozone with 2,4,6-TCP, at least in the early stages of ozonation.

Batch-reactor experiments were carried out with 2,4,6-TCP and ozone at pH values of 2, 3, 4, 5, 6 and 7. Both 2,6-DCHQ and 2,6-DCQ were detected in significant concentrations over the pH range of 2 to 5, while only 2,6-DCHQ was detected for pH's of 6 and 7. Since 2,6-DCHQ is the only product observed at both pH 2 and 7 and the activation energies of the second-order reaction rates are similar within experimental error, it is reasonable to conclude that the rate of 2,4,6-TCP consumption is controlled by a reaction leading to 2,6-DCHQ.

The relative abundances of 2,4,6-TCP, 2,6-DCHQ, and 2,6-DCQ were determined as functions of time from batch-reactor experiments with ozone exposure times of 0.5 min to 8 min. A representative graph of the results from these experiments is shown in Figure 3 for a pH of 2. This graph clearly shows that the concentration of 2,6-DCHQ grows initially and then reaches a maximum, while the concentration of 2,6-DCQ grows continuously. This type of behavior indicates that 2,6-DCQ is formed from the oxidation of 2,6-DCHQ either by ozone or by some other reactive oxidizer in solution. However, a parallel reaction scheme cannot be ruled out based on the results shown on Figure 3. If the reaction rate is controlled by the formation of a reaction intermediate that can then react with other species in solution to form both 2,6-DCQ and 2,6-DCHQ, then a parallel reaction scheme is possible. Li et al. (1979) proposed a reaction mechanism in which ozone initiates a set of free-radical chain reactions for the ozone/aqueous phenol system in which the initial formation of the two free radicals from one molecule of ozone and one molecule of phenol is the rate-limiting step. A similar mechanism may exist for the reaction of aqueous 2,4,6-TCP with ozone.

In order to determine whether 2,6-DCHQ and 2,6-DCQ are formed in parallel or in series from the reaction of 2,4,6-TCP with ozone, aqueous 2,6-DCHQ can be exposed to ozone and the products can be identified by GCMS. However, 2,6-DCHQ could not be obtained from the usual supply houses. On the other hand, it was possible to obtain 2,5-DCHQ from Acros Organics. The latter would be a product of the reaction of ozone with aqueous 2,4,5-TCP. Batch-reactor experiments were carried out with aqueous 2,5-DCHQ and ozone at a pH of 2, and the products were identified using GCMS. The only observable product identified by GCMS was 2,5-dichloroquinone (2,5-DCQ). From this, it was concluded that 2,6-DCQ is formed by further oxidation of 2,6-DCHQ by ozone.

Absorption experiments in the wetted-sphere absorber were carried out with aqueous 2,5-DCHQ at a pH of 2 and 25°C, and the results are listed in Table 2. The second-order

Table 2. Absorption of Ozone into Aqueous 2,5-DCHQ in a Wetted-Sphere Absorber

pH	T °C	10^3 [DCHQ]$_{in}$ (kmol/m^3)	10^3 [DCHQ]$_f$ (kmol/m^3)	10^9 D_{O_3} (m^2/s)	10^9 D_{DCHQ} (m^2/s)	10^6 Q (m^3/s)	10^6 υ (m^2/s)	P_{O_3} atm	H_{O_3} (atm·m^3)/kmol	10^{10} G_{O_3} (kmol/s)	k_2 m^3/(kmol·s)
2	25	5.10	3.80	1.98	2.45	0.764	0.902	0.0251	114.7	9.93	232000
2	25	5.12	3.82	1.98	2.45	0.788	0.902	0.0312	114.7	10.2	160000
2	25	5.10	3.98	1.98	2.45	0.787	0.902	0.0305	114.7	8.84	1050000

rate constant was determined to be $(1.7 \pm 0.6) \times 10^5$ m^3/kmol·s at a pH of 2 and 25°C, which is approximately one order of magnitude larger than the rate constant for the reaction of 2,4,6-TCP with ozone (2.15×10^4 m^3/kmol·s). This explains why the relative abundance of 2,6-DCHQ in Figure 3 is smaller than that of 2,6-DCQ. While we do not expect the reaction of 2,6-DCHQ with ozone to have the same rate constant as 2,5-DCHQ with ozone, we do expect the order of magnitude of the rate constants to be the same.

After ozonation times of roughly 16 min in the batch reactor, no peaks (besides the solvent peak) were observed in the chromatograms of the extracts. It is reasonable to expect that eventually the products just discussed degrade into organic acids, ketones, and aldehydes that cannot be detected by the GC system used in this work. In order to confirm this, several samples of the concentrated ether extracts from the 16-min runs were combined and all the ether was evaporated at room temperature. The remaining residue was then dissolved in D_2O in preparation for C-13 NMR. The spectrum obtained from the C-13 NMR revealed a very strong signal in the 160- to 180-ppm region. The results are by no means conclusive, but the fact that the largest signal was in the 160- to 180-ppm region indicates the presence of a significant number of carboxyl carbons in the solution mixture. This is not surprising, since Gould and Weber (1976) found that several two-carbon acids and aldehydes (oxalic acid, glyoxalic acid, and glyoxal) are products formed from the long-term exposure of aqueous phenol to ozone. These compounds probably do not affect the rate of TCP consumption, but knowledge of their presence in the ozonated solutions is important in the design of downstream treatment processes and in determining ozone demand.

Acknowledgment

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Notation

D_{O_3} = diffusion coefficient of O_3 in the aqueous solution, m^2/s
k_2 = second-order rate coefficient of reaction (Eq. 1), m^3/(kmol·s)
P_{O_3} = partial pressure of O_3 in the gas phase, atm
r = independent spatial variable measured from the center of the sphere in the positive radial direction, m
R = radius of the sphere, m
Δ = thickness of the liquid film on the sphere, m
θ = angular coordinate measured from the top of the sphere, rad

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