

2-Chlorophenol Oxidation in Supercritical Water: Global Kinetics and Reaction Products

Ruokang Li, Phillip E. Savage, and David Szmukler

Dept. of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109

2-Chlorophenol (2CP) was oxidized in near-critical and supercritical water in a high-pressure plug-flow reactor. The global kinetics for 2CP disappearance were described by a rate law that was 0.88 ± 0.06 order in 2CP, 0.41 ± 0.12 order in O_2 , and 0.34 ± 0.17 order in water. The activation energy was 11.0 ± 3.8 kcal/mol, and the Arrhenius pre-exponential factor was $10^{2.0 \pm 1.2} M^{-0.63} s^{-1}$. The uncertainties represent 95% confidence intervals. The products of 2CP oxidation included CO , CO_2 , HCl , other chlorophenols, chlorohydroxybenzaldehydes, dichlorophenoxyphenols, dichlorobiphenols, and chlorinated dibenzodioxins and dibenzofuran. The molar yields of the organic products were determined for a set of experiments at $380^\circ C$ and 278 atm. The most abundant products were 2CP dimers such as dichlorophenoxyphenols and dichlorobiphenols, and the highest yield observed for any individual product was 0.6%. Although the yields of these products were low, their selectivities were high. For example, at 3.6 s, the shortest residence time studied under these conditions, about 50% of the carbon in the 2CP that reacted appeared in 2CP dimers, 18% appeared as CO_2 , and the balance (32%) was presumably in single-ring and ring-opening products. A reaction pathway analysis using the Delplot methodology revealed that the evolution of products from 2CP oxidation in supercritical water was consistent with a reaction network comprising two parallel primary reactions. One primary reaction path led to dichlorophenoxyphenols and dichlorobiphenols whereas the second primary reaction led to single-ring and ring-opening products. The 2CP dimers were converted to single-ring and ring-opening products, which were, in turn, ultimately oxidized to CO_2 .

Introduction

Supercritical water oxidation (SCWO) is a technology being advanced for the ultimate destruction of organic compounds. Organic carbon can be rapidly converted to CO_2 , hydrogen to H_2O , and chlorine to HCl . Proposed reaction conditions include temperatures between 400 and $650^\circ C$ and pressures around 250 atm. These values are typically selected because water above its critical point ($T_c = 374^\circ C$, $P_c = 218$ atm) possesses a high solubility for both organics and oxygen. Thus, a single phase containing oxygen, organic, and water can exist at reaction conditions, and the rate of interphase mass transfer need not limit the reaction rate as it typically does at subcritical

conditions. Furthermore, the temperatures employed in SCWO oxidation result in intrinsic reaction rates sufficiently high that the oxidation of organics goes essentially to completion on the order of a few minutes. Modell (1989) provides a more complete discussion of SCWO technology, and he delineates additional advantages of SCWO over more conventional waste treatment technologies.

One of the SCWO research frontiers that has been attracting attention in recent years is the reaction pathways, kinetics, and mechanisms. Tester and his colleagues (for example, Helling and Tester, 1987, 1988; Webley and Tester, 1989, 1991; Webley et al., 1991) have determined global reaction rate laws for the oxidation of several simple compounds such as CO , CH_4 , and NH_3 at a single pressure of 250 bar. These rate laws were then

Correspondence concerning this article should be addressed to P. E. Savage.

used to test the predictions of detailed chemical kinetics models. Yang and Eckert (1988) oxidized 4-chlorophenol in SCW and examined the effects of different homogeneous catalysts, the organic and oxygen concentrations, and temperature on the reaction rate. They detected CO_2 and CO as the major gaseous products and 1,4-benzoquinone as the major liquid product. Wightman (1981) performed limited SCWO experiments with a large number of compounds and reported data that permitted a qualitative assessment of their relative reactivities. Finally, Savage and his colleagues (Thornton and Savage, 1990, 1992a,b; Li et al., 1992; Thornton et al., 1991) have recently provided the global kinetics, identified many of the reaction products, and investigated the reaction pathways for the oxidation of phenol in near-critical and supercritical water. Thornton and Savage (1992a) also provide a more thorough review of previous SCWO kinetics studies.

This article reports the results of an investigation into the global kinetics of and reaction products from 2-chlorophenol (2CP) oxidation in SCW. 2CP was selected as the reactant for this research because it is frequently found in industrial waste waters. It is generally considered to be resistant to biodegradation, and the literature provides only very limited data for the oxidation of 2CP in near-critical and supercritical water (Baillod et al., 1982; Dietrich et al., 1985; Levec, 1990; Staszak et al., 1987).

Experimental

The oxidation reactions were conducted in a plug-flow reactor. The reactor feed streams were prepared by dissolving high-pressure oxygen in deaerated, deionized, and distilled water at about 15°C in one feed tank, and loading an aqueous solution of 2CP into a second feed tank. This second vessel was blanketed with helium so that no oxygen would be present in the 2CP feed stream. The feed stream from each vessel was then brought to the desired operating pressure using individual Eldex model AA-100-S metering pumps, each with a nominal 0.1–10 mL/min flow rate range and a maximum operating pressure of 340 atm.

Each feed stream was then preheated by flowing through a 2-m length of 0.0625-in. (1.59-mm) OD $\times$ 0.010-in. (0.25-mm) thickness Hastelloy C-276 tubing coiled within a Techne model SBL-2 fluidized sand bath. This split feed arrangement ensured that no oxygen contacted 2CP before the reaction temperature and pressure had been achieved. The two feed streams were then mixed at the entrance to the reactor, which was fashioned from a length of 0.125-in. (3.18-mm) OD $\times$ 0.035-in. (0.89-mm) wall thickness Hastelloy C-276 tubing and coiled within the sand bath. The oxidation reactions were then conducted in this isothermal, isobaric, plug-flow reactor.

We performed 2CP pyrolysis experiments in the flow reactor, and the highest conversion achieved was less than 3%, which occurred at 380°C and 278 atm and a residence time of about 120 s. It was not possible to exclude all oxygen from the 2CP solution used in the pyrolysis experiments so a portion of this conversion is attributable to oxidation reactions. The residence times of the 2CP feed stream in the preheater line were always less than 120 s so the influence of pyrolytic reactions on the measured global kinetics is expected to be small.

The reactor effluent was cooled, depressurized, and then separated into liquid and vapor phases. The flow rates of each phase were measured, and these values were used along with

the density of the reaction mixture at the reaction conditions to calculate the residence time in the reactor. The density of the reaction mixture was assumed to be the same as the density of water because the mixture was always over 99.8 mol % water.

Products in the gas phase were analyzed using a dedicated Hewlett-Packard model 5890 Series II gas chromatograph equipped with a 1/8-in. OD Supelco Carboseive S-II permanent gas column and a thermal conductivity detector. The amount of 2CP that remained unreacted was determined by analyzing the liquid product samples using reverse-phase, high performance liquid chromatography. A mixture of 72 vol % deionized water and 28 vol % acetonitrile served as the mobile phase, and a Superco octadecyl-dimethylsilyl column served as the stationary phase. The variable wavelength uv-vis detector was set at 210 nm. Quantitative results were obtained by comparing the integrated 2-chlorophenol peak areas with those of standard solutions. The concentration of chloride ion (Cl^-) in the liquid product samples was measured using a Dionex ion chromatography system. A 0.025 M Na_2CO_3 and 0.025 M NaHCO_3 aqueous solution served as the mobile phase. It flowed at 2 mL/min through a Dionex AS4A column, and the chloride ion concentration was monitored using a conductivity detector.

The aqueous reactor effluent samples were also subjected to a liquid-liquid extraction protocol, which was similar to EPA Method 604 for phenols (Federal Register, 1984), in order to concentrate, identify, and quantify the reaction products. Ten mL of dichloromethane was used to extract the organic products from a 20 mL aqueous sample. The extraction was repeated three times so that 30 mL of dichloromethane was finally obtained. This dichloromethane solution was then placed in a Kuderna-Danish concentrator, which was immersed in a water bath. The bath temperature was gradually increased until only 1 mL of extract remained. A Hewlett-Packard model 5890 gas chromatograph with a model 5970 mass selective detector (GC/MS) was then used to identify these extracted reaction products. Quantification of the product concentrations was accomplished using a Hewlett-Packard 5890 gas chromatograph with a flame ionization detector. The sample constituents were separated on a 12 m $\times$ 0.2 mm OD HP-1 capillary column using helium as the carrier gas. Detector response factors relative to the standard, 2,2'-biphenol, were determined experimentally for each product commercially available. The response factors for most of the compounds were around 1.0 except for a dichlorodibenzodioxin, which was 3.4, and a dichlorobiphenol, which was 0.4. The response factors for products that were not commercially available were assumed to be equal to those for an isomer of some other related compound. The uncertainty in these estimated response factors is about $\pm 20\%$ for all of the products except dichlorophenoxyphenols, which had a much higher uncertainty. The reason for this higher uncertainty will be discussed in the section where quantitative data for the product yields are reported. Additional details about the reactor, experimental procedure, and analytical methods have been reported previously (Thornton, 1991; Thornton and Savage, 1990; Thornton et al., 1991).

Global Kinetics of 2-Chlorophenol Disappearance

Table 1 provides a complete listing of the results from 62 2CP oxidation experiments. These experiments were accom-

Table 1. Summary of 2-Chlorophenol Oxidation Experiments

T °C	P atm.	τ s	2CP Conc. M	O ₂ Conc. M	H ₂ O Conc. M	X %
300	278	14.6	5.99×10^{-4}	4.12×10^{-2}	41.51	24.3
330	278	13.6	5.51×10^{-4}	3.79×10^{-2}	38.20	29.5
360	278	11.8	4.85×10^{-4}	3.33×10^{-2}	33.61	31.0
380	185	13.2	8.03×10^{-5}	5.49×10^{-3}	5.71	8.6
380	205	17.7	1.04×10^{-4}	7.12×10^{-3}	7.40	16.7
380	219	19.0	1.32×10^{-4}	8.99×10^{-3}	9.28	23.6
380	225	22.9	1.56×10^{-4}	1.06×10^{-2}	10.97	41.1
380	225	26.8	1.54×10^{-4}	1.05×10^{-2}	10.97	60.6
380	232	34.5	2.28×10^{-4}	1.55×10^{-2}	15.97	72.1
380	246	24.1	3.42×10^{-4}	2.57×10^{-2}	24.22	65.2
380	260	27.1	3.77×10^{-4}	2.89×10^{-2}	26.96	67.5
380	278	20.4	3.19×10^{-4}	1.07×10^{-2}	28.42	45.7
380	278	35.1	3.28×10^{-4}	9.63×10^{-3}	28.42	62.0
380	278	49.2	3.70×10^{-4}	1.01×10^{-2}	28.42	76.0
380	278	69.8	3.26×10^{-4}	9.76×10^{-3}	28.42	85.2
380	278	5.9	3.86×10^{-4}	2.97×10^{-2}	28.42	17.2
380	278	10.2	4.00×10^{-4}	2.87×10^{-2}	28.42	23.4
380	278	21.1	4.02×10^{-4}	3.02×10^{-2}	28.42	59.0
380	278	32.8	3.76×10^{-4}	3.22×10^{-2}	28.42	76.4
380	278	44.4	3.84×10^{-4}	3.02×10^{-2}	28.42	88.9
380	278	59.1	3.95×10^{-4}	3.08×10^{-2}	28.42	98.6
380	278	19.9	9.90×10^{-4}	3.76×10^{-2}	28.42	57.5
380	278	34.0	1.03×10^{-3}	3.50×10^{-2}	28.42	74.1
380	278	47.3	1.04×10^{-3}	3.47×10^{-2}	28.42	93.2
380	278	59.6	1.04×10^{-3}	3.65×10^{-2}	28.42	98.5
380	278	7.2	1.41×10^{-3}	3.60×10^{-2}	28.42	19.1
380	278	29.6	1.55×10^{-3}	3.64×10^{-2}	28.42	68.9
380	278	40.2	1.60×10^{-3}	3.58×10^{-2}	28.42	82.4
380	278	50.1	1.48×10^{-3}	3.74×10^{-2}	28.42	93.6
380	278	58.6	1.57×10^{-3}	3.61×10^{-2}	28.42	99.0
380	278	69.5	1.64×10^{-3}	3.53×10^{-2}	28.42	98.6
380	278	3.6	1.95×10^{-3}	4.09×10^{-2}	28.42	9.2
380	278	5.2	1.98×10^{-3}	4.29×10^{-2}	28.42	11.4
380	278	7.3	2.05×10^{-3}	4.19×10^{-2}	28.42	13.2
380	278	10.1	2.03×10^{-3}	3.97×10^{-2}	28.42	18.9
380	278	13.9	2.04×10^{-3}	4.20×10^{-2}	28.42	34.7
380	278	18.6	2.13×10^{-3}	3.80×10^{-2}	28.42	46.7
380	278	24.7	2.07×10^{-3}	3.88×10^{-2}	28.42	54.7
380	278	29.5	2.04×10^{-3}	4.07×10^{-2}	28.42	67.2
380	278	33.9	2.15×10^{-3}	3.77×10^{-2}	28.42	69.1
380	278	40.0	2.09×10^{-3}	3.99×10^{-2}	28.42	78.7
380	278	49.5	1.97×10^{-3}	4.14×10^{-2}	28.42	82.1
380	278	57.4	2.12×10^{-3}	3.95×10^{-2}	28.42	97.1
380	278	67.5	2.05×10^{-3}	4.03×10^{-2}	28.42	99.7
380	278	29.4	1.82×10^{-3}	1.94×10^{-2}	28.42	75.4
380	278	39.7	1.98×10^{-4}	1.47×10^{-2}	28.42	79.5
380	278	41.0	2.32×10^{-4}	1.21×10^{-2}	28.42	70.9
380	278	27.9	2.52×10^{-4}	1.42×10^{-2}	28.42	61.0
380	278	40.5	3.02×10^{-4}	7.01×10^{-3}	28.42	58.3
380	278	38.4	4.41×10^{-4}	4.44×10^{-2}	28.42	92.2
380	278	40.9	5.79×10^{-4}	3.63×10^{-2}	28.42	83.5
380	278	11.4	6.27×10^{-4}	3.47×10^{-2}	28.42	28.4
380	278	5.8	6.46×10^{-4}	3.41×10^{-2}	28.42	20.7
380	278	40.5	8.17×10^{-4}	2.21×10^{-2}	28.42	66.4
380	278	14.7	1.13×10^{-3}	3.73×10^{-2}	28.42	30.4
380	294	29.9	4.06×10^{-4}	3.19×10^{-2}	29.37	76.0
390	278	45.2	3.15×10^{-4}	2.58×10^{-2}	23.09	89.1
400	278	28.1	1.98×10^{-4}	1.62×10^{-2}	14.50	69.7
410	278	21.6	1.50×10^{-4}	1.22×10^{-2}	10.96	54.4
420	278	10.0	5.04×10^{-4}	1.27×10^{-2}	9.40	25.4
420	278	16.9	5.08×10^{-4}	1.26×10^{-2}	9.40	40.7
420	278	24.0	5.43×10^{-4}	1.22×10^{-2}	9.40	58.1

plished at temperatures between 300 and 420°C and pressures from 185 to 294 atm. These conditions included oxidation in both near-critical and supercritical water. Reactor residence times ranged from 3.6 to 69.8 s. The initial 2CP concentrations were between 8.0×10^{-5} and 2.2×10^{-3} M, and 2CP was always the limiting reactant. The excess oxygen was between 192% and 1,680%, which resulted in oxygen concentrations between 5.49×10^{-3} and 4.44×10^{-2} M. The final column in Table 1 provides the 2CP conversion, X , which was calculated as $X = 1 - [2CP]/[2CP]_0$, where $[2CP]_0$ is the 2CP concentration at the reactor entrance.

The objectives of our global kinetics analysis were to determine the Arrhenius parameters (A and E_a) and the reaction orders (a , b , and c) for 2CP, O₂, and H₂O for the rate expression for 2CP disappearance during SCW oxidation given in Eq. 1. Similar power-law expressions have been used frequently to correlate SCW oxidation kinetics, so our use of the same type of expression here will provide a basis for comparison with previous work. These rate laws typically capture the general trends in the data, but they cannot be expected to capture the details of the complex oxidation chemistry.

$$\text{Rate} = A \exp\left(-\frac{E_a}{RT}\right) [2CP]^a [O_2]^b [H_2O]^c \quad (1)$$

The rate constant was taken to be independent of pressure (that is, $\Delta V^\ddagger = 0$). Thus, all pressure effects were manifested in the variation of the reactant concentrations since SCW is a compressible fluid.

Combining the rate law of Eq. 1 with the definition of conversion and the design equation (Fogler, 1992) for a constant-volume, plug-flow reactor leads to

$$\frac{dX}{d\tau} = A \exp\left(-\frac{E_a}{RT}\right) [2CP]_0^{a-1} (1-X)^a [O_2]^b [H_2O]^c \quad (2)$$

The reactor operated isobarically and isothermally, and oxygen and water were always present in large excess. Therefore, the concentrations of O₂ and H₂O can be taken to be conversion invariant and approximately equal to their initial concentrations. Equation 2 can then be separated and integrated analytically. Using the initial condition of $X=0$ at $\tau=0$ yields

$$[(1-X)^{1-a} - 1] = (a-1)A \exp\left(-\frac{E_a}{RT}\right) [2CP]_0^{a-1} [O_2]^b [H_2O]^c \tau \quad \text{if } a \neq 1 \quad (3)$$

$$\ln(1-X) = -A \exp\left(-\frac{E_a}{RT}\right) [O_2]^b [H_2O]^c \tau \quad \text{if } a = 1 \quad (4)$$

Optimized values for the parameters a , b , c , A , and E_a in Eq. 3 were obtained by applying a nonlinear regression method to the data in Table 1. The objective function minimized in the regression method was the sum of the squares of the differences between the values of X calculated from Eq. 3 and those measured experimentally. The optimal values of the kinetics parameters lead to the global rate law of Eq. 5 to describe 2CP oxidation.

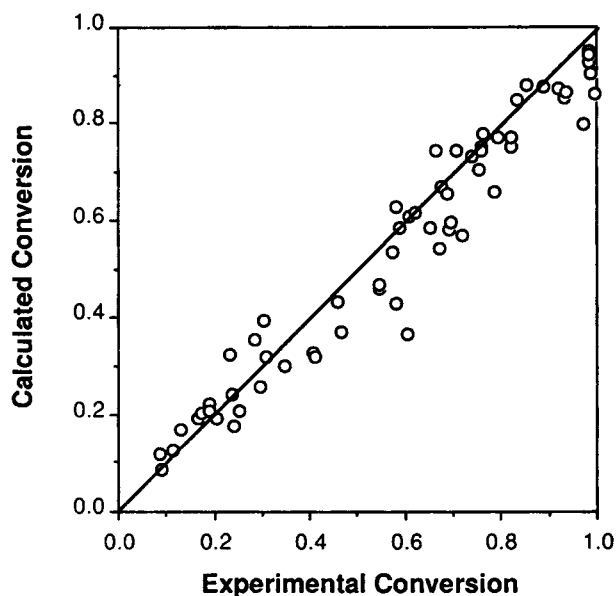


Figure 1. Comparison of experimental and calculated 2-chlorophenol conversions.

Calculated conversions are based on rate law of Eq. 5.

$$\text{Rate} = 10^{2.0 \pm 1.2} \exp\left(-\frac{11,000 \pm 3,800}{RT}\right) \times [\text{2CP}]^{0.88 \pm 0.06} [\text{O}_2]^{0.41 \pm 0.12} [\text{H}_2\text{O}]^{0.34 \pm 0.17} \quad (5)$$

The rate is in mol/L·s, all concentrations are in mol/L, and the activation energy is in cal/mol. The uncertainties expressed in Eq. 5 are the 95% confidence intervals.

Figure 1 shows the parity plot of the experimental 2CP conversions and those calculated from Eq. 3 with the optimized rate law parameters. This plot verifies that the estimated parameters provide a good description of the experimental data.

Examining the parameter values in Eq. 5, one observes that the reaction order with respect to O_2 is greater than zero. That oxygen has an effect on the global kinetics of SCW oxidation is consistent with recent work with phenol (Thornton and Savage, 1992a) and methane (Webley and Tester, 1991). Most earlier SCWO research (for example, Helling and Tester, 1987; Yang and Eckert, 1988) had found that the reaction rate did not depend on the O_2 concentration. The rate law in Eq. 5 also shows that increasing the pressure at constant temperature and constant 2CP and O_2 concentrations increases the reaction rate. This acceleration is accounted for by including the water concentration in the rate law. Higher pressures result in higher water densities. Finally, temperature has two competing effects on the reaction rate. Increasing the temperature at constant pressure increases the rate constant, but it decreases the reaction density and, hence, the concentrations. The relative importance of these competing effects has been explored in more detail in a previous report on phenol oxidation in SCW (Thornton and Savage, 1992a).

Comparing the reaction orders and activation energy for 2CP given in Eq. 5 with those reported previously for phenol oxidation in SCW (Thornton and Savage, 1992a) reveals that the reaction order for water differed the most for these two

compounds. It was 0.34 ± 0.17 for 2CP but 0.7 for phenol. The reaction orders for the organic compound were 0.88 ± 0.06 and 1.0 for 2CP and phenol, respectively, and those for oxygen were 0.41 ± 0.12 and 0.5, respectively. The activation energies were 11.0 ± 3.8 kcal/mol and 12.4 kcal/mol, respectively. The Arrhenius pre-exponential factors for both 2CP and phenol were on the order of 10^2 , a value that is much lower than the pre-exponential factors for most elementary reactions. This result indicates that the oxidation mechanism is complex and undoubtedly comprises a large number of elementary steps.

Further comparison of the present rate law with previous kinetics studies can be made by considering rate data reported by Yang (1988) and Yang and Eckert (1988) for the uncatalyzed oxidation of 4-chlorophenol. These investigators provide average rates for 4-chlorophenol oxidation at 400°C and 240 atm and at 340°C and 140 atm. The first set of conditions is within the temperature and pressure range used in the present investigation whereas the second set is not. Further, Yang and Eckert (1988) frequently used much higher organic and oxygen concentrations than those used in the present work. Thus, a comparison of the present rate law for 2-chlorophenol oxidation with the data of Yang and Eckert (1988) for 4-chlorophenol requires some extrapolation.

Figure 2 summarizes this comparison. Figure 2a provides the average 4-chlorophenol oxidation rates reported by Yang (1988) for the two different reaction conditions as a function of the 4-chlorophenol concentration. The oxygen concentration was ten times the stoichiometric amount. The discrete points are experimental data (Yang and Eckert, 1988), and the solid curves in Figure 2a are the predicted rates based on the rate law of Eq. 5. Inspection of Figure 2a reveals that the rate law reported here for 2-chlorophenol quantitatively predicts the rates of 4-chlorophenol oxidation at 400°C and 240 atm reported by Yang and Eckert (1988). This quantitative agreement is probably fortuitous given that the rate law is being extrapolated to concentrations nearly an order of magnitude higher than those used to determine its parameters and that the data and the rate law are for two different chlorophenol isomers. Further inspection of this figure shows that the rate law consistently underpredicted the rate of 4-chlorophenol oxidation at 340°C and 140 atm. Nevertheless, the trend in the data for 4-chlorophenol oxidation at these milder conditions is predicted by the present global rate law for 2-chlorophenol.

Figure 2b provides Yang's (1988) data for the oxidation of stoichiometric mixtures of 4-chlorophenol and oxygen. The solid lines are the rates calculated from Eq. 5. Once again, we observe good agreement between the data and rate law predictions at 400°C and 240 atm, but a consistent underprediction of the rates at 340°C and 140 atm. The rate law does capture the linear trend in the data at these milder conditions, however, and it possesses approximately the same slope as the data.

Yang and Eckert (1988) interpreted the data in Figure 2 as indicating that the global rate law was zero-order in oxygen, first-order in chlorophenol at low concentrations, and second-order in chlorophenol at high concentrations. We show here that the trends in these data are consistent with the form of the rate law in Eq. 5, which has a nonzero reaction order for oxygen, a constant reaction order for chlorophenol, and the sum of the chlorophenol and oxygen orders exceeding unity.

To summarize this comparison, it appears that the rate law in Eq. 5, which was developed for 2-chlorophenol oxidation,

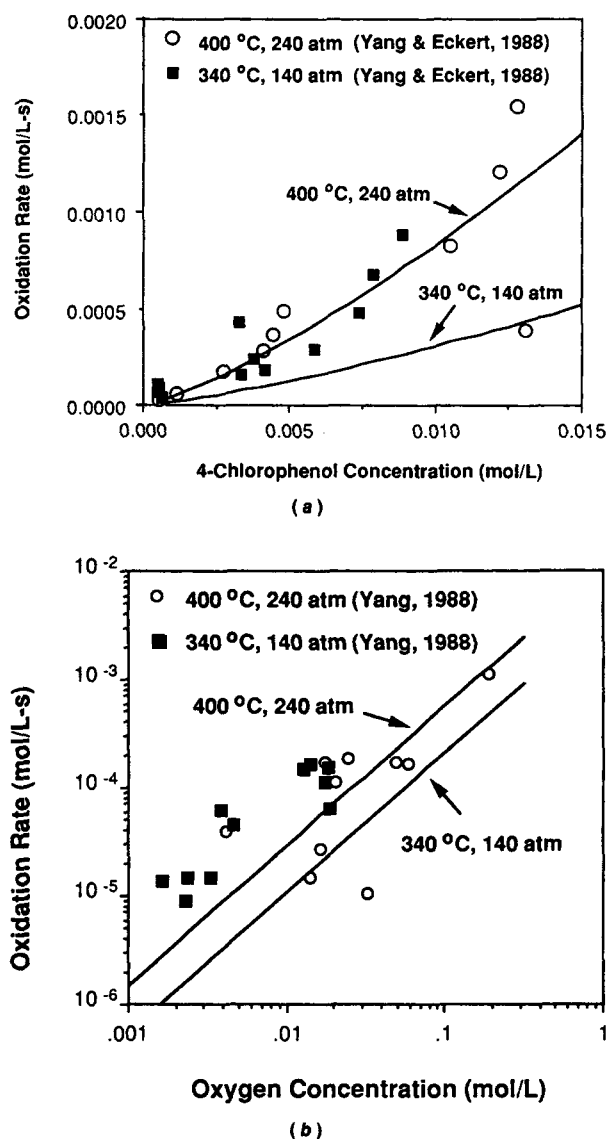


Figure 2. Comparison of rate data for 4-chlorophenol oxidation (Yang, 1988) and predictions based on 2-chlorophenol rate law in Eq. 5.

a. 900% excess oxygen; b. Stoichiometric oxygen.

can be extrapolated to predict the trends in, and at times quantitative values of, the rates of 4-chlorophenol disappearance reported by Yang (1988). This observation suggests that the key features of the SCW oxidation chemistry for these two chlorophenol isomers may be similar.

Reaction Products

One of the focal points of our work with 2CP has been the identification and quantification of the yields of the products from incomplete oxidation in SCW. Earlier research into phenol oxidation in SCW showed that dimers such as phenoxyphenols and biphenol were major primary products (Thornton et al., 1991; Thornton and Savage, 1992b). Thus, we were particularly interested in determining whether analogous products arose from 2CP oxidation in SCW. In this section of the article, we first present the identities of different 2CP oxidation products,

and then we present quantitative information about the products' molar yields and selectivities. These quantitative data were obtained from a set of experiments accomplished at nominal reaction conditions of 380 °C, 278 atm, $[2CP]_0 = 0.0020$ M, and 180% excess oxygen.

Product identities

CO_2 and CO were the only gas-phase products consistently detected in appreciable yields. Ion chromatography revealed the presence of chloride ion (presumably from dissociation of HCl) in the aqueous phase of the reactor effluent. GC/MS analysis of the aqueous-phase products extracted in dichloromethane revealed a very large number of reaction products. Figure 3 displays a representative total ion chromatogram, which corresponds to an oxidation experiment at 380 °C, 278 atm, and 24.7 s using a feed stream containing 0.0020 M 2CP and 0.0388 M ($\approx 180\%$ excess) oxygen at reaction conditions. The identities of many of the compounds are given in Figure 3, and an assessment of the reliability of these identifications is summarized in Table 2. Methods of product identification included inspection of the mass spectra, searching the GC-MS computer library for compounds with similar mass spectra, comparing the mass spectra of products with mass spectra of authentic compounds acquired on the same GC-MS, and comparing the GC retention times of products and authentic compounds.

Peak 2 in Figure 3 is the reactant, 2CP, and peak 12 is the standard, 2,2'-biphenol, which was used to quantify the reaction products. Background experiments revealed that 2,2'-biphenol was not one of the reaction products. Nine of the reaction products (peaks 1, 3-6, 9, 13, and 22 in Figure 3) were positively identified. The chromatographic analysis did not completely resolve 3- and 4-chlorophenol so they appeared as the single peak numbered 6 in Figure 3. The positive identifications given in Figure 3 and Table 2 were obtained by matching both the mass spectrum and GC retention time for each compound with those of the authentic compound. This method could not be used to positively identify all of the remaining products because authentic standards were not commercially available. In these cases we relied on an inspection of the products' mass spectra and a comparison of these spectra with spectra stored in the computer workstation library. For example, consider the compounds corresponding to peaks 7, 8, and 11, which we identified as chlorohydroxybenzaldehyde isomers. The mass spectra for these products had a molecular ion peak at $m/z = 156$, which provided the molecular weight. Additionally, the intensity of the peak at $m/z = 158$ was about $1/3$ of the intensity of the molecular ion peak, which indicated that the molecule contained a single chlorine atom because the ratio of the natural abundance of ^{37}Cl to ^{35}Cl is 0.325 (Silverstein et al., 1991). Thus, the molecular formula for these products was $C_7H_5O_2Cl$. A large number of organic compounds have this molecular formula, but a much smaller number will also be consistent with the fragmentation pattern apparent in the mass spectra. The fragmentation patterns for these products all showed a peak at $m/z = 155$ that had an abundance greater than the molecular ion peak. The presence of an M-1 peak that is larger than the molecular ion peak can be indicative of an aromatic aldehyde, and it arises from loss of the aldehydic hydrogen. The M-1 ion can then eliminate CO to give a peak

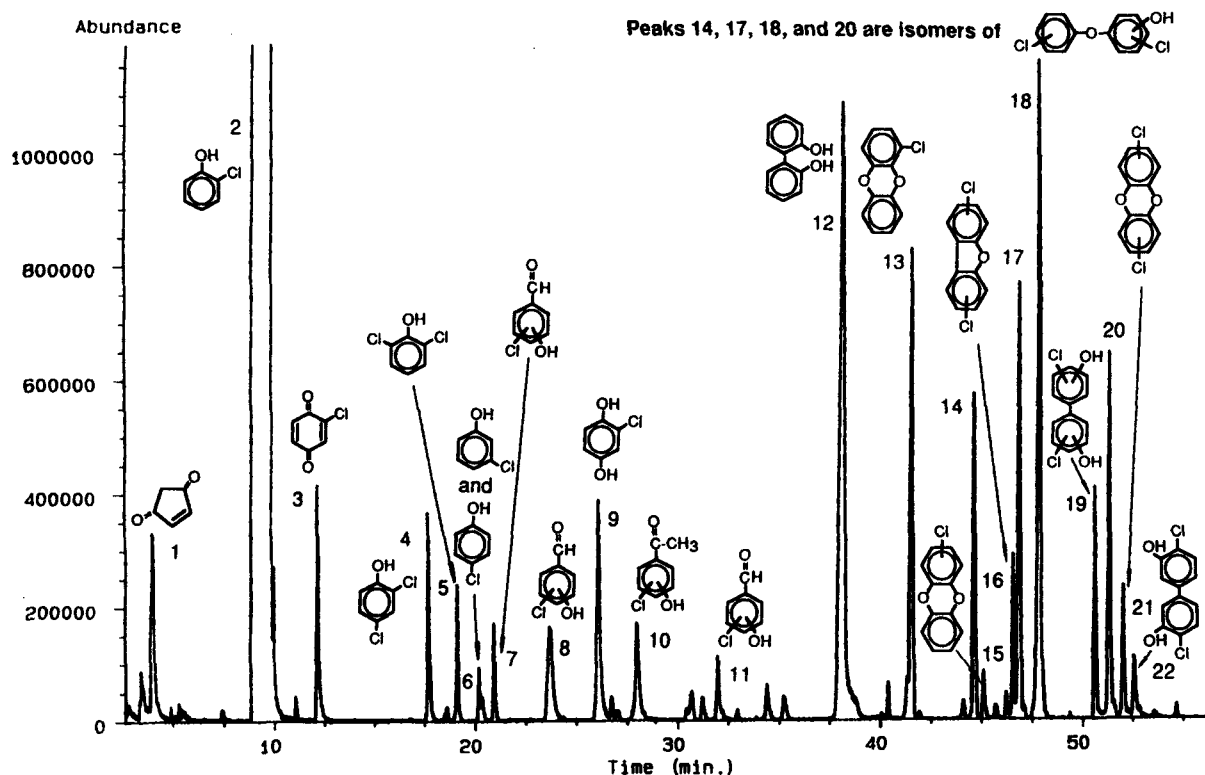


Figure 3. Total ion chromatogram of 2-chlorophenol oxidation products (nominal reaction conditions were 380°C, 278 atm, 0.0020 M 2CP, 180% excess oxygen, and 24.7 s residence time).

at 127, which was also present in the mass spectrum of each of these products. Thus, synthesizing all of the available information from the mass spectrum led to the identification of these three peaks as chlorohydroxybenzaldehyde isomers. Corroboration of this product identification was obtained by ob-

serving a very good match between the mass spectra of these products and that of 5-chloro-2-hydroxybenzaldehyde, which was available in the computer library. Products such as the chlorohydroxybenzaldehydes, whose identities depended upon inspection of their mass fragmentation patterns and a match

Table 2. Summary of Product Identification

Peak No. in Fig. 3	Identity	Comments
1	cyclopent-2-en-1,4-dione	Positive identification*
2	2-chlorophenol	Reactant
3	2-chloro-1,4-benzoquinone	Positive identification
4	2,4-dichlorophenol	Positive identification
5	2,6-dichlorophenol	Positive identification
6	4 (& 3)-chlorophenol	Positive identification
7	chlorohydroxybenzaldehyde	MW = 156, 1 Cl atom, library match
8	chlorohydroxybenzaldehyde	MW = 156, 1 Cl atom, library match
9	chloro-hydroquinone	Positive identification
10	(chlorohydroxyphenyl)-ethanone	MW = 170, 1 Cl atom, library match
11	chlorohydroxybenzaldehyde	MW = 156, 1 Cl atom, library match
12	2,2'-biphenol	Standard
13	1-chlorodibenzodioxin	Positive identification
14	dichlorophenoxyphenol	MW = 254, 2 Cl atoms
15	chlorodibenzodioxin	MW = 218, 1 Cl atom, library match
16	dichlorodibenzofuran	MW = 236, 2 Cl atoms, library match
17	dichlorophenoxyphenol	MW = 254, 2 Cl atoms
18	dichlorophenoxyphenol	MW = 254, 2 Cl atoms
19	dichlorobiphenol	MW = 254, 2 Cl atoms
20	dichlorophenoxyphenol	MW = 254, 2 Cl atoms
21	dichlorodibenzodioxin	MW = 252, 2 Cl atoms, library match
22	4,4'-dichloro-3,3'-biphenol	Positive identification

*Both retention time and mass spectrum of product match those of authentic compound.

with library mass spectra, are so denoted in Table 2. We believe these identifications are correct, but they remain tentative because we could not verify the retention times and mass spectra with authentic compounds. Using the approach illustrated above, we also identified peaks 15, 16, and 21 as a chlorodibenzodioxin, a dichlorodibenzofuran, and a dichlorodibenzodioxin, respectively, because of the good match between the products' mass spectra and those of reference spectra stored in the computer library. Finally, there existed a group of peaks for which the computer library provided no good matches with reference spectra. These compounds (peak numbers 14, 17, 18, and 20) showed a strong molecular ion peak at $m/z=254$ and contained 2 chlorine atoms. They also exhibited strong peaks at $m/z=219$ and 184, which resulted from the loss of 1 and 2 Cl atoms, respectively. Thus, the molecular formula of these compounds is $C_{12}H_8O_2Cl_2$. Probable reaction products consistent with this formula include dichlorophenoxyphenols and dichlorobiphenols. [The nonchlorinated analogs of these compounds were major products from phenol oxidation in SCW (Thornton et al., 1991).] The mass fragmentation patterns for peaks 14, 17, 18, and 20 did not resemble the computer library spectrum for a dichlorobiphenol. Thus, we concluded that peaks 14, 17, 18, and 20 were due to dichlorophenoxyphenol isomers.

The discussion above shows that the reaction products extracted from the aqueous reactor effluent into dichloromethane can be roughly categorized into five groups: chlorinated and nonchlorinated cyclodiones (peaks 1 and 3), chlorinated phenols (peaks 4, 5, 6, and 9), chlorinated hydroxybenzaldehydes and hydroxyphenylethanone (peaks 7, 8, 10, and 11), chlorinated dibenzodioxins and dibenzofuran (peaks 13, 15, 16, and 21), and chlorinated phenoxyphenols and biphenols (peaks 14, 17–20, and 22). In Yang's report on 4-chlorophenol oxidation in SCW, only benzoquinone, which belongs to the first group was found in the uncatalyzed reactions (Yang, 1988). Metal-catalyzed homogeneous reactions, however, led to products that would fall within both the first and second groups. Yang reported no products from the third, fourth or fifth groups.

Product yields

Having identified a large number of the 2CP oxidation products, we next quantified these products' molar yields. Here we define molar yield as the molar concentration of the product in the reactor effluent divided by the molar concentration of 2CP at the reactor entrance. Table 3 provides the molar yields of the 20 identified organic reaction products at 13 different residence times for SCWO of 2CP at nominal reaction conditions of 380°C, 278 atm, $[2CP]_0 = 0.0020$ M, and 180% excess oxygen. We note here that the uncertainty in most of the yields is $\pm 20\%$, but the uncertainty in the dichlorophenoxyphenol yields is much larger because the lack of authentic standards prevented us from determining detector response factors experimentally. The mean response factor for related compounds (for example, a set of dichlorophenols and 2CP dimers) was 1.5, but the range of response factors was from 0.4 for a dichlorodibenzodioxin to 3.4 for a dichlorobiphenol. This large variation in detector response was obtained from thermal conductivity, flame ionization, and mass spectrometric detectors. We used the mean response factor of 1.5 to calculate the dichlorophenoxyphenol yields reported in Table 3.

The yields of each of the individual products were always low. No product ever possessed a yield of greater than 0.01 (1%). The most abundant products at short reaction times (less than 10 sec) were the dichlorophenoxyphenols (peaks 14, 17, 18, and 20) and dichlorobiphenols (peaks 19 and 22). The yields of these products decreased with increasing residence time, however, and they were less than 0.1% after about 55 s. At intermediate reaction times (20–30 sec) the cyclodiones (peaks 1 and 3), 2-chlorohydroquinone (peak 9), and 1-chlorodibenzodioxin (peak 13) were among the most abundant products. The temporal variation of the molar yields for each of these products reveals a maximum between 30 and 50 s, which suggests that these products underwent further oxidative degradation. Finally, at 67.5 s, the longest residence time studied at these conditions, the only products present in concentrations above the detection limits included the cyclodiones, the dichlorophenoxyphenols, 1-chlorodibenzodioxin (peak 13) and a dichlorodibenzofuran (peak 16). The persistence of these latter two compounds is consistent with previous work with phenol oxidation in SCW (Thornton et al., 1991; Thornton and Savage, 1992b), which showed that dibenzofuran and dibenzodioxin were among the last of the phenol dimers to be degraded.

Figure 4 displays the carbon yield (moles of carbon atoms in product/moles of carbon atoms fed to reactor) for the identified organic products, CO plus CO₂, and 2CP as a function of residence time. At short residence times, where the 2CP conversion was low, the carbon yield in the extracted organic products was about three times as high as the yield in the carbon oxides. As the residence time increased, however, the carbon oxide yield increased steadily whereas the carbon yield in the extracted products decreased. At 67.5 s the CO + CO₂ yield was 58.1% while the carbon yield in the extracted organic products was 0.5%. The total amount of carbon contained in the identified products (both gas and liquid) is also plotted in Figure 4. The total carbon recovery decreased from about 98% at 3.6 s where the 2CP conversion was 9.2% to about 60% at 67.5 s, where the conversion of 2CP was 99.7%. Presumably, the balance of the carbon resides in ring-opening products such as low-molecular-weight carboxylic acids. Our GC-MS analyses and extraction protocol did not include identification or quantification of such products, but previous work revealed that such products are formed from phenol oxidation in SCW (Thornton and Savage, 1990).

Figure 5, which displays the temporal variation of the Cl yield for 2CP oxidation, reveals that very little of the chlorine in the reaction products was associated with organic compounds. Most of it appeared as Cl⁻ in the cooled and depressurized reactor effluent. The Cl⁻ presumably arose from the dissociation of HCl. The total Cl yield was always around 100% indicating essentially complete recovery of Cl. At times, however, experimental uncertainty in the ion chromatography led to total Cl yields exceeding 100%.

Implications to SCW oxidation pathways

The data in Table 3 showed that the products identified as dichlorophenoxyphenol and dichlorobiphenol isomers were the most abundant reaction products at short residence times and that their yields decreased with increasing residence time. These observations suggest that these products form directly from

Table 3. Molar Yield of Oxidation Products

Peak No. in Fig. 3	Residence Time(s)						
	3.6	5.2	7.3	10.1	13.9	18.6	24.7
1	9.20×10^{-4}	1.53×10^{-3}	2.57×10^{-3}	4.31×10^{-3}	3.96×10^{-3}	2.65×10^{-3}	3.19×10^{-3}
3	3.27×10^{-5}	1.10×10^{-4}	1.02×10^{-4}	8.13×10^{-4}	8.17×10^{-4}	2.36×10^{-3}	2.09×10^{-3}
4	1.91×10^{-3}	1.77×10^{-3}	1.73×10^{-3}	1.68×10^{-3}	1.18×10^{-3}	1.25×10^{-3}	9.52×10^{-4}
5	6.24×10^{-5}	1.27×10^{-4}	1.55×10^{-4}	1.84×10^{-4}	9.87×10^{-5}	5.95×10^{-4}	5.24×10^{-4}
6	1.39×10^{-4}	2.08×10^{-4}	3.20×10^{-4}	2.33×10^{-4}	2.40×10^{-4}	3.40×10^{-4}	5.71×10^{-4}
7	0	0	0	0	2.57×10^{-4}	5.47×10^{-4}	5.45×10^{-4}
8	0	0	0	0	6.87×10^{-5}	1.43×10^{-3}	1.56×10^{-3}
9	0	0	1.79×10^{-3}	3.11×10^{-3}	2.82×10^{-3}	4.18×10^{-3}	3.64×10^{-3}
10	0	0	0	0	8.94×10^{-5}	5.65×10^{-4}	1.35×10^{-3}
11	0	0	2.60×10^{-5}	1.46×10^{-4}	1.50×10^{-4}	5.03×10^{-4}	6.10×10^{-4}
13	6.49×10^{-4}	7.27×10^{-4}	6.24×10^{-4}	6.81×10^{-4}	5.70×10^{-4}	2.48×10^{-3}	1.92×10^{-3}
14	1.05×10^{-3}	1.15×10^{-3}	9.93×10^{-4}	9.93×10^{-4}	8.09×10^{-4}	1.23×10^{-3}	7.92×10^{-4}
15	4.07×10^{-4}	4.67×10^{-4}	4.46×10^{-4}	4.03×10^{-4}	4.01×10^{-4}	2.58×10^{-4}	1.58×10^{-4}
16	1.57×10^{-4}	1.73×10^{-4}	3.05×10^{-4}	2.39×10^{-4}	2.58×10^{-4}	6.35×10^{-4}	6.40×10^{-4}
17	3.81×10^{-3}	3.52×10^{-3}	2.40×10^{-3}	2.05×10^{-3}	1.65×10^{-3}	2.00×10^{-3}	1.13×10^{-3}
18	5.95×10^{-3}	5.61×10^{-3}	4.00×10^{-3}	3.31×10^{-3}	2.78×10^{-3}	3.42×10^{-3}	2.11×10^{-3}
19	5.17×10^{-3}	5.24×10^{-3}	4.03×10^{-3}	3.60×10^{-3}	3.16×10^{-3}	3.14×10^{-3}	1.85×10^{-3}
20	3.15×10^{-3}	3.00×10^{-3}	2.28×10^{-3}	1.97×10^{-3}	1.80×10^{-3}	1.21×10^{-3}	7.37×10^{-4}
21	1.54×10^{-4}	1.39×10^{-4}	7.89×10^{-5}	6.81×10^{-5}	1.18×10^{-4}	1.96×10^{-4}	1.17×10^{-4}
22	2.48×10^{-3}	1.66×10^{-3}	1.38×10^{-3}	1.05×10^{-3}	1.46×10^{-3}	1.31×10^{-3}	8.16×10^{-4}

Peak No. in Fig. 3	Residence Time(s)					
	29.5	33.9	40.0	49.5	57.4	67.5
1	4.83×10^{-3}	5.05×10^{-3}	8.37×10^{-3}	8.76×10^{-3}	4.39×10^{-3}	2.41×10^{-3}
3	3.26×10^{-3}	3.28×10^{-3}	5.03×10^{-3}	4.26×10^{-3}	3.01×10^{-3}	1.60×10^{-3}
4	9.85×10^{-4}	1.11×10^{-3}	1.15×10^{-3}	9.04×10^{-4}	2.01×10^{-4}	0
5	6.13×10^{-4}	7.92×10^{-4}	7.72×10^{-4}	7.48×10^{-4}	1.41×10^{-4}	0
6	6.65×10^{-4}	8.05×10^{-4}	1.13×10^{-3}	1.26×10^{-3}	3.41×10^{-4}	0
7	7.18×10^{-4}	7.34×10^{-4}	9.47×10^{-4}	8.76×10^{-4}	2.40×10^{-4}	0
8	1.70×10^{-3}	1.91×10^{-3}	2.28×10^{-3}	2.45×10^{-3}	1.23×10^{-3}	0
9	4.53×10^{-3}	4.19×10^{-3}	4.39×10^{-3}	3.98×10^{-3}	1.83×10^{-3}	0
10	7.97×10^{-4}	8.12×10^{-4}	1.43×10^{-3}	1.44×10^{-3}	8.97×10^{-4}	0
11	7.27×10^{-4}	6.61×10^{-4}	6.89×10^{-4}	7.74×10^{-4}	2.94×10^{-4}	0
13	2.00×10^{-3}	2.47×10^{-3}	2.01×10^{-3}	2.61×10^{-3}	8.92×10^{-4}	4.44×10^{-4}
14	6.03×10^{-4}	6.73×10^{-4}	4.73×10^{-4}	3.84×10^{-4}	7.74×10^{-5}	8.12×10^{-5}
15	9.38×10^{-5}	1.21×10^{-4}	1.22×10^{-4}	1.03×10^{-4}	0	0
16	9.04×10^{-4}	9.17×10^{-4}	1.17×10^{-3}	1.53×10^{-3}	8.33×10^{-4}	2.90×10^{-4}
17	8.83×10^{-4}	1.11×10^{-3}	7.50×10^{-4}	9.38×10^{-4}	2.22×10^{-4}	2.66×10^{-4}
18	1.67×10^{-3}	1.89×10^{-3}	1.27×10^{-3}	1.44×10^{-3}	3.03×10^{-4}	4.59×10^{-4}
19	1.50×10^{-3}	1.51×10^{-3}	5.88×10^{-4}	2.63×10^{-4}	0	0
20	6.98×10^{-4}	7.41×10^{-4}	6.51×10^{-4}	4.17×10^{-4}	1.16×10^{-5}	0
21	8.75×10^{-5}	1.20×10^{-4}	1.08×10^{-4}	1.80×10^{-4}	4.34×10^{-5}	0
22	6.04×10^{-4}	4.57×10^{-4}	4.66×10^{-4}	0	0	0

2CP and then undergo reactions to form other products. Verification of this postulated scenario can be obtained by using the Delplot method for reaction pathway resolution (Bhore et al., 1990). This method, in its simplest form, requires plots of selectivity (moles product formed/moles reactant reacted) as a function of conversion. These plots are termed first rank Delplots. Primary products, those that form directly from the reactant, possess positive y-intercepts on a first rank Delplot. Products that appear later in the reaction network possess y-intercepts equal to zero. Figure 6 displays a first rank Delplot for the four dichlorophenoxyphenol isomers. It is clear that extrapolation of the data in Figure 6 to zero conversion leads to a positive y-intercept for each of the products. Thus, each of these products forms directly from 2CP. The decrease in selectivity with conversion is consistent with these products participating in secondary reactions. The Delplots for the dichlorobiphenols were similar.

Applying the Delplot methodology to the other 14 reaction products in Table 3 revealed only one additional compound that was a major primary product. This compound was 2,4-dichlorophenol. Here we define a major product as one that possessed a selectivity greater than 0.02 at at least one residence time. Thus, the major primary products from 2CP oxidation in SCW were 2CP dimers and a dichlorophenol. This observation is consistent with earlier work with the SCWO of phenol, which showed that phenol dimers such as phenoxyphenols and biphenol were major primary products (Thornton and Savage, 1992b).

A simplified global reaction network consistent with the foregoing discussion is displayed in Figure 7. Two parallel primary pathways are shown. One leads to phenol dimers, and the second leads directly to single-ring products such as dichlorophenols and, possibly, ring-opening products. The dimers can undergo secondary oxidation reactions to form ring-

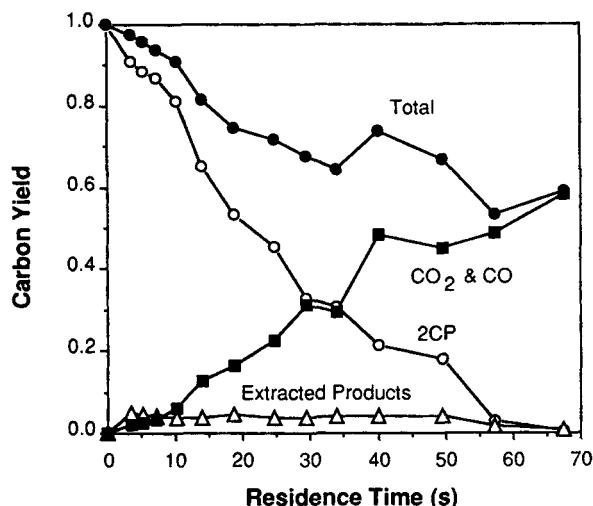


Figure 4. Temporal variations of yields of carbon-containing products (nominal reaction conditions were 380°C, 278 atm, 0.0020 M 2CP, 180% excess oxygen).

opening products and single-ring compounds, which are eventually oxidized to CO₂.

Summary and Conclusions

- The disappearance of 2-chlorophenol during oxidation in near-critical and supercritical water proceeds with a global rate law that is 0.88 ± 0.06 order in 2-chlorophenol, 0.41 ± 0.12 order in oxygen, and 0.34 ± 0.17 order in water. The activation energy is 11.0 ± 3.8 kcal/mol, and the Arrhenius pre-exponential factor is $10^{2.0 \pm 1.2} \text{ M}^{-0.63} \cdot \text{s}^{-1}$. The uncertainties in the parameter estimates represent 95% confidence intervals.

- The 2CP oxidation products include CO, CO₂, HCl, cy-

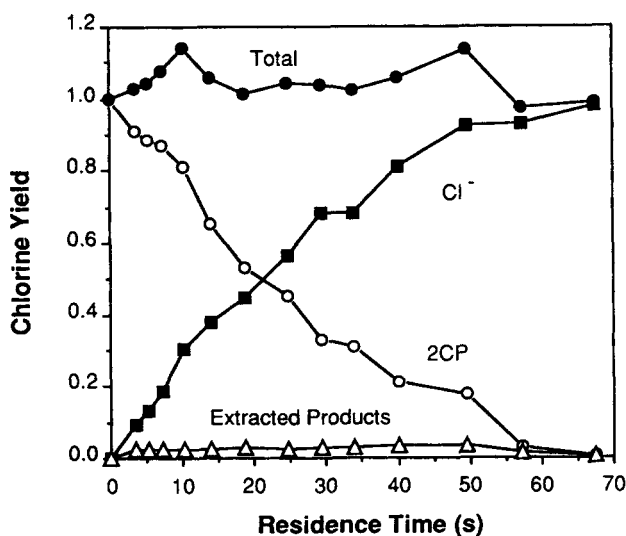


Figure 5. Temporal variations of yields of chlorine-containing products (nominal reaction conditions were 380°C, 278 atm, 0.0020 M 2CP, 180% excess oxygen).

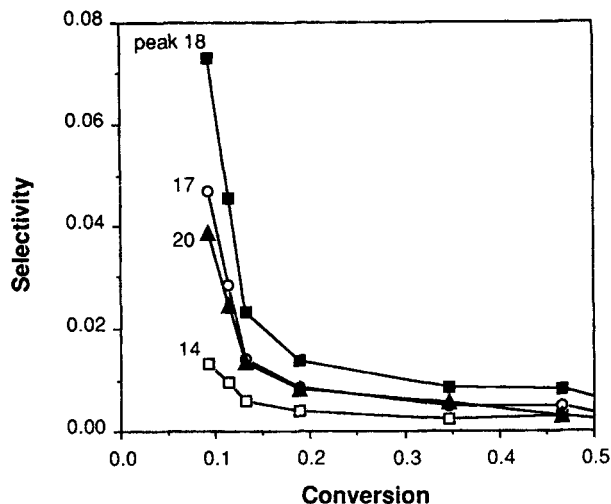


Figure 6. First rank Delplot for dichlorophenoxyphenols (nominal reaction conditions were 380°C, 278 atm, 0.0020 M 2CP, 180% excess oxygen).

clodiones, chlorinated phenols, chlorinated hydroxybenzaldehydes and hydroxyphenylethanone, chlorinated dibenzodioxins and dibenzofuran, dichlorophenoxyphenols, and dichlorobiphenols.

- The temporal variation of the yields of the carbon containing products was consistent with a global reaction network comprising two parallel primary steps. The first pathway leads to 2CP dimers, and the second pathway leads to single-ring and ring-opening products. The dimers can be converted to ring-opening products, and these are ultimately oxidized to CO₂.

- The primary organic products with the highest selectivities were dichlorophenoxyphenols, dichlorobiphenols, and dichlorophenol. Roughly 50% of the carbon in the 2CP fed to the reactor was converted to 2CP dimers at 380°C, 278 atm, 3.6 s, [2CP]₀ = 0.002 M, and 180% excess oxygen. Thus, the primary pathway to 2CP dimers is clearly important in the overall reaction network.

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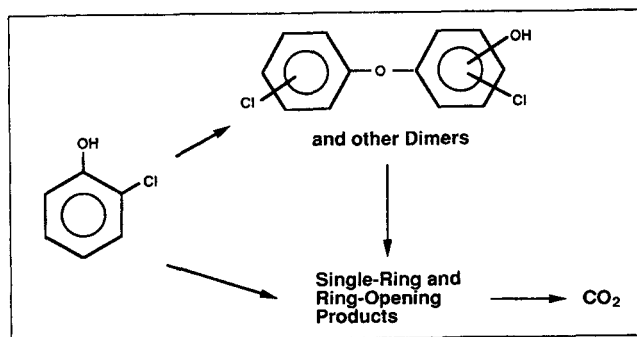


Figure 7. Global reaction network for 2CP oxidation in SCW.

Notation

- A = Arrhenius pre-exponential factor
 a = reaction order for 2-chlorophenol
 b = reaction order for oxygen
 c = reaction order for water
 E_a = activation energy
 M = moles per liter
 R = gas constant
 T = temperature
 $\Delta V^\ddagger$ = activation volume
 X = 2-chlorophenol conversion

Greek letters

- τ = residence time

Subscripts

- o = inlet
 c = critical

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